CATALYTIC ACTIVITY AND ACID PROPERTIES OF Al-PENTASILS AND ISOMORPHICALLY SUBSTITUTED (Fe, B) SILICATES

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The catalytic activity of Al-containing pentasils and their isomorphically substituted analogs (ferri- and borosilicates) in transformations of n-alkanes are directly dependent on their acidity. Elemental silicates have a lower acidity and are significantly less active in cracking and aromatization of n-alkanes of C_6-C_{10} composition than Al-pentasils. The degree of conversion of alkanes decreases and the aromatizing capacity of zeolites decreases strongly with a decrease in the concentration of acid sites on pentasils with a different composition of the framework (SiO_2/Al_2O_3 35-1000). Ferri- and borosilicates are close in activity in cracking and aromatization of n-alkanes but differ significantly in their acid characteristics. In particular, NH_3 is adsorbed on ferrisilicate with high heats both on acid sites active in these reactions and in the Fe_2O_3 phase present in the ferrisilicate and inactive in catalysis.

The catalytic properties of zeolites are determined by their acidity to a significant degree. The effect of Bronsted (B) and Lewis (L) acidity on the mechanism of transformation of hydrocarbons for zeolites of type X, Y, and mordenite is discussed in detail in [1]. However, the information on the correlation of the catalytic and acid properties of pentasils and especially isomorphically substituted silicates is very limited and is basically only partial [2-7]. The goal of the present study was to establish a correlation between the acid properties (number and strength of sites) and catalytic properties of a series of Al-pentasils and elementary silicates in reactions of transformation of aliphatic hydrocarbons.

EXPERIMENTAL

Aluminosilicate pentasils: TsVM ($SiO_2/Al_2O_3(M) = 35$); pentasil-280 (M = 280), silicalite,* and elementary silicates: ferrisilicate* FS (M = 234) and borosilicate* BS (M = 179) were used in the study. They all have a structure of the pentasil type. The study was conducted on H forms ($Na_2O < 0.1\%$). n-Hexane, n-octane, and n-decane with a purity of ≥98% were used as the starting hydrocarbons. The catalytic experiments were conducted at 350 and 450°C in a flow-type setup; the amount of catalyst was 2.5 cm^3 (1.65 g), and the volume flow rate of the reactant was 0.9 h^{-1}. The samples were first activated in an air current for 5 h at 550°C; regeneration was conducted between experiments for 2 h in the same conditions. The initial activity of the catalysts virtually did not change during the entire series of experiments. The duration of the experiment was 3 h. The products of the reaction were analyzed by GLC.

The heats of adsorption (q) of NH_3 at 30°C were measured to study the acidity of the zeolites. The measurements were performed in a Calvet microcalorimeter connected to a vacuum setup. Before the measurements began, all of the samples were evacuated at 480°C to ~10^{-4} torr. The cavities of the zeolites were filled with small portions of NH_3, and this permitted obtaining the dependences of q on the degree of filling, which indicates the type

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*They contain Al_2O_3 impurity from the raw material: $SiO_2/Al_2O_3 = 800$-1000 on conversion to the contaminant aluminum; the modulus of FS and BS was calculated in consideration of the total concentration of Fe and B in the zeolite.

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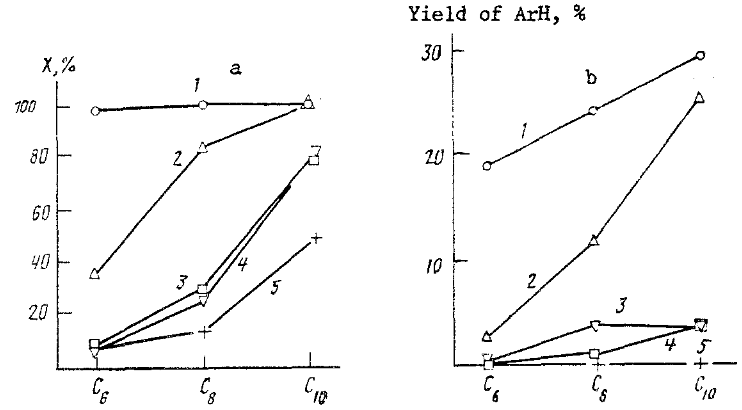

Fig. 1. Conversion (a) and yield of aromatic hydrocarbons (b) in transformations of n-alkanes on pentasils: 1) TsVM; 2) pentasil-280; 3) FS; 4) BS; 5) silicalite (350°C, $v = 0.9\ h^{-1}$).

of distribution of the adsorption sites. The values of q were used as the strength of the acid sites, and all sites adsorbing NH_3 with $q > 80$ kJ/mole were considered acid sites. The number of acid sites corresponded to the number of adsorbed molecules.

RESULTS AND DISCUSSION

As the data in Table 1 and Fig. 1 show, the catalysts studied in transformations of C_6, C_8, and C_{10} n-alkanes differ strongly in effect. The aluminosilicate systems: TsVM-35 and pentasil-280, exhibited the highest activity in the overall transformation of the hydrocarbons. The elementary silicates and silicalite are significantly less active (Fig. 1a).

On TsVM, all three alkanes almost totally undergo cracking with subsequent partial aromatization of the unsaturated fragments formed. Pentasil-280 exhibited significantly lower catalytic activity than TsVM in these reactions. These differences are especially clearly observed in transformations of C_6 and C_8 hydrocarbons; for example, conversion (X) of C_6 was 98% on TsVM at 350°C and 35% on pentasil-280. We note that the aromatizing capacity of TsVM is also significantly higher: the yield of aromatic hydrocarbons (ArH) attains 20% on it, while it is ≤3% on pentasil-280. Silicalite has the lowest activity among the zeolites investigated: conversion of C_6 and C_8 is 7 and 13%, respectively; conversion of C_{10} is 45% in the same conditions. The higher X of the latter is observed on all zeolites studied and is apparently due to the relatively lower stability of this hydrocarbon in comparison to n-alkanes of lower molecular weight [8].

FS and BS are similar in catalytic activity in the reactions studied and occupy an intermediate position between Al-pentasils and silicalite. The zeolites studied in cracking and aromatization of n-alkanes can thus arbitrarily be placed in the following order with respect to the activity: TsVM > pentasil-280 > FS ≈ BS > silicalite. It should be noted that the aromatizing capacity of these zeolites changes symbatically with their catalytic activity in cracking of C_6-C_{10} hydrocarbons. This finding is in agreement with the previously obtained results on preliminary fragmentation of the molecules of saturated hydrocarbons (alkanes, cyclanes) in the presence of high-silicon zeolites with subsequent aromatization of unsaturated particles [9, 10].

On the whole, the data obtained suggest that acid sites of similar strength and distribution can be responsible for cracking and aromatization of n-alkanes. Bridge OH groups bound with the lattice Al of pentasil which are strong acid sites of the B type are probably such sites [11, 12]. It should be emphasized that the zeolites studied differ significantly with respect to the framework composition and should naturally differ with respect to the acid properties. In this respect, determining the number and strength of the acid sites of these zeolites is an important problem.

The heats of adsorption of NH_3 (Fig. 2) were measured on all of the zeolites by adsorption calorimetry and compared with the results of catalysis (Fig. 1). Note that TsVM zeolite has the highest concentration of acid sites with q = 100-120 kJ/mole; it is also the most active in cracking and aromatization of n-alkanes. There is a small number of strong acid sites which absorb NH_3 with high initial heats in pentasil-280, and it consequently exhibits significantly less catalytic activity than TsVM. There is only a very small number of acid sites on silicalite, apparently due to contaminant Al. Although the concentration of $Al_2O_3 <$ 0.2%, this amount is apparently sufficient to give the zeolite marked catalytic activity, especially in the case of cracking of the less stable n-decane.

TABLE 1. Transformations of C_6-C_{10} n-Alkanes ($v = 0.9\ h^{-1}$)

Reactant	T, °C	Composition of products, %								
		liquid hydrocarbons			gaseous hydrocarbons					
		init. hydrocarbons	Σ ArH C_5 — C_{11}	Σ ArH C_6 — C_{10}	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	Σ C_4
TsVM										
C_6	350	8,3	21,0	70,7	–	0,4	1,5	0,4	65,0	32,7
C_8	350	0,2	24,8	75,0	–	0,2	1,3	3,9	65,7	28,9
	450	4,9	5,2	89,9	3,6	1,4	8,4	1,8	69,9	14,9
C_{10}	350	–	34,4	65,6	–	0,5	0,7	1,4	57,8	39,6
Pentasil-280										
C_6	350	80,4	16,7	2,9	–	2,0	2,0	6,8	52,7	36,5
	450	78,1	11,2	10,7	–	4,9	10,1	13,4	53,4	18,2
C_8	350	26,7	53,2	20,1	–	1,4	0,9	4,5	48,0	45,2
	450	35,4	22,9	41,7	1,3	3,9	4,6	11,4	44,7	34,1
C_{10}	350	1,4	57,6	41,0	–	1,8	1,0	5,4	45,6	46,2
	450	сл.	31,5	68,5	1,3	4,3	2,9	11,3	40,5	39,7
FS										
C_6	350	98,8	1,2	–	–	–	–	–	–	–
	450	87,5	12,5	–	3,8	6,2	11,9	28,2	37,6	12,3
C_8	350	81,9	16,5	1,6	–	14,8	1,3	14,1	34,8	35,0
	450	74,6	16.9	8,5	4,2	5,6	9,9	25,7	33,0	21,6
C_{10}	350	37,1	58,6	4,3	–	1,9	0,3	16,9	28,7	52,2
	450	43,1	39,8	17,1	2,1	4,5	5,4	24,3	31,2	32,5
BS										
C_6	350	97,9	2,1	–	–	–	–	–	–	–
	450	92,1	7,9	–	3,4	9,6	14,0	27,6	36,8	8,6
C_8	350	80,1	16,6	3,3	–	2,0	0,6	21,4	33,1	42,9
	450	61,9	30,9	7,2	–	7,6	5,8	25,8	37,5	23,3
C_{10}	350	29,8	65,8	4,4	–	2,2	0,5	18,2	29,5	49,6
	450	46,0	42,2	11,8	–	5,7	2,1	24,3	30,9	37,0
Silicalite										
C_6	350	99,0	1,0	–	–	–	–	–	–	–
	450	95,1	4,9	–	–	9,9	15,5	39,1	35,5	–
C_8	350	88,6	11,4	–	–	1,6	1,2	26,5	34,7	36,0
	450	84,5	15,5	–	–	7,5	5,9	33,7	32,0	20,9
C_{10}	350	61,7	38,3	–	–	2,1	0,4	24,9	27,7	44,8
	450	60,8	34,5	4,7	0,7	7,5	4,7	36,1	29,2	21,8

Incorporation of boron into its lattice in the stage of crystallization of the zeolite does not increase the concentration of strong acid sites in comparison to silicalite. Nevertheless, the increased catalytic activity of BS in cracking of n-alkanes in comparison to silicalite could be caused by the appearance of a small number of acid sites which absorb NH_3 with $q \approx 80$ kJ/mole in BS.

In turn, isomorphic substitution of Al by Fe introduces its own specific features both in the catalytic properties and in the acidity spectrum of the zeolite. Actually, FS has significantly more sites which adsorb NH_3 with high heats than BS and silicalite (Fig. 2). However, the catalytic activity of FS in reactions of cracking and aromatization of n-alkanes is close to BS (Fig. 1). On the other hand, it was shown in [13] that FS is an efficient catalyst of transformation of ethylene into hydrocarbons of higher molecular weight; its oligomerizing activity in transformations of ethylene is significantly higher than on aluminum-containing pentasils.

At first glance, the apparent contradiction between the acid and catalytic properties of elementary silicates is in fact due to the specific features of the isomorphically substituted silicates. Actually, there is a relatively large number of sites which adsorb NH_3 with relatively high heats ($q > 100$ kJ/mole) in the case of FS (see Fig. 2), and they are apparently inactive in cracking and aromatization of n-alkanes. It was shown in [14] that in addition to $>\mathrm{Si(OH)}-\mathrm{Fe}<$ structural groups, Fe ions not entering the framework of the zeolite but existing in the form of an independent Fe_2O_3 phase are present in FS. The appearance of an absorption band at 3675 cm^{-1}, which should be assigned to vibrations of FeOH groups similar to the hydroxyl groups on the surface of Fe_2O_3, in the diffuse light scattering IR spectrum indicate their presence. These OH groups are also perhaps an additional source of adsorption of NH_3 with high q.

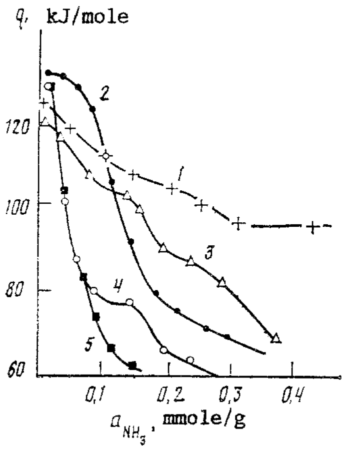

Fig. 2. Heat of adsorption of NH_3 on zeolites at 30°C (see Fig. 1 for legend; a – adsorption).

The data obtained thus indicate that the catalytic activity of FS is primarily due to acid OH groups of the >Si(OH)Fe< bridge type. Due to the difference in the ionic radii of Fe^{+3} (0.67 Å) and Al^{+3} (0.55 Å) and the electron affinity [15], these groups in FS have a lower acidity in comparison to the analogous >Si(OH)Al< bridge groups in pentasils [16, 17]. For this reason, cracking and aromatization in the presence of FS take place to an insignificant degree. At the same time, not only oligomerization of lower olefins, but also side reactions of cracking and aromatization take place successfully in the case of pentasils [12].

On the whole, the results obtained indicate the undoubted dependence of the catalytic properties of Al-pentasils and elementary silicates on the acid properties of the samples studied.

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