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Study of Stability and Selectivity of Catalytic Action of ZSM-Type Zeolites in Methanol Transformation

The duration of stable catalytic action (DSA) in methanol transformation on ZSM-type zeolites with the ratio of SiO_2/Al_2O_3 from 24 to 280, synthesized in the presence of quaternary ammonium bases, has been determined. The DSA is shown to decrease with increasing aluminum content of zeolites, while the yield of aromatic hydrocarbons products increases. From NMR ^{27}Al and ^{29}Si data it was concluded that the formation of nondesorbed compounds proceeds on the centers of multipointed adsorption, including more than one aluminum atom. And probably one of them is in extraframework (cation) position.

It is well known that in synthesis and transformation of hydrocarbons highly silicious ZSM zeolites, in contrast to other types of zeolites, do not loose their activity for a long time. The stability of these zeolites to coke formation is accounted for (*1, 2*) by steric factors, due to which the synthesis of coke precursors is prevented by a small size of zeolite channels. This conclusion is in contradiction with the data which show that zeolites of this type are loosing their activity as a result of coke poisoning. It appears that coke formation does take place on ZSM zeolites, although with considerably lower rate than that on low silicious zeolites in the same conditions.

It has been proposed (*3, 4*) that chemical factors—formation of strong catalytic centers—are responsible for the instability of zeolite action. This supposition has been developed on the base of NMR ^{27}Al and ^{29}Si data for Y and ZSM zeolites (*5, 6*). Like in (*7, 8*), $Si(OAl)_n$-groups, where $n = 0 \rightarrow 4$, were found in zeolites of type Y, and mordenite, which is in good agreement with the model of aluminum atoms distribution, developed by Dempsey (*9*) and later by Mikovsky and Marschall (*10*).

It was found by ^{29}Si-NMR, that upon decationation of zeolites, the intensity of ^{29}Si-NMR signals from $Si(OAl)_3$ and $Si(OAl)_4$ groups decreased, whereas that from $Si(OAl)_2$, $Si(OAl)_1$, and $Si(OSi)_0$ groups increased. Simultaneously, the intensity of ^{27}Al-NMR signal with a chemical shift of 0–3 pp, referred to aluminum atoms outside the framework, increased (*4*).

It was concluded (*5, 6*) that upon thermochemical treatments $[Si(OAl)_n]^{n-} \rightarrow [Si(OAl)_{n-1}]^{(n-1)^-} \cdot Al^{3+} \cdot (n-1)/3$ transfer took place which resulted in the formation of centers of multicenter interaction with a reagent molecule, and which are capable of producing a superacid effect. The probability of such formation should increase with increasing the total content of aluminum in zeolites or at a nonuniform distribution of aluminum atoms over zeolite crystal. This is in agreement with the results reported in (*11*), where for ZSM-5 zeolites, mordenite, and offretite interrelation between aluminum content in zeolites and the rate of coke formation was found, and in (*12*), where the formation of superacid centers was assumed resulting from the existence of polymer oxo-aluminum groups $(AlO)_n^+$. It might be expected then, that in ZSM zeolites an increase of aluminum content or some peculiarity of zeolite synthesis will result in inhomogeneity of aluminum distribution in zeolite framework. The latter will influence zeolite stability of catalytic action. In this article the duration of stable catalytic action of zeolites as a function of their alumina content and the method of synthesis was determined.

PROCEDURE

1. Catalyst preparation. ZSM zeolites were synthesized by the known procedure (*13*) using silicasol, sodium aluminate, and organic substances, such as tetrabutylammonium bromide (Table 1, samples N P1-P9) and butyl alcohol (sample N P-10). The

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synthesized zeolites had the ratio SiO_2/Al_2O_3 ranging from 24 to 280. The samples of a high phase frequency and a high degree of crystallization were used in experiments. Table 1 gives the chemical composition of the samples examined.

All zeolites were calcined in flowing air at 530–550°C. Ion exchange was carried out upon 1–2 h heating at 60–70°C in ammonia buffer solution. Zeolites with a low content of Na were prepared by repeating the ion exchange 2–3 times with an intermediate calcination of samples between treatments at 400–450°C. The residual content of sodium was determined by the flame photometer, silicon content by the gravimetric method, aluminum for samples with high aluminum content by complexometric titration, and for samples with low Al content by atomic adsorption method using a spectrophotometer of type "Spectrum." The degree of zeolites crystallization was characterized by the intensity of lines on diffractograms in the region of reflection angles θ = 3.8–4.5 and 11.5–12.5. Diffractometers JPC-50 and DRON-1 were used.

2. *Catalytic activity and stability.* The activity and stability of catalysts were studied using flow type reactors. Catalysts were activated in the reactor in O_2 flow during 2 h at 530–540°C and then cooled to the reaction temperature (380°C) in the helium flow. The system was then tested for leak tightness to avoid oxygen penetration onto the catalyst during the run. Liquid methanol was conducted to the reactor by a fluid-flow pump at a space velocity of 1–1.1 h^{-1}.

TABLE 1

Chemical Composition of Zeolites

Catalyst	Chemical composition (%)		Adsorption capacity (cm^3/g)	
	Na_2O	SiO_2/Al_2O_3	H_2O	C_7H_{16}
P-1	2.25	38	0.08	0.18
P-2	0.4	38	—	—
P-3	1.34	51	0.09	0.17
P-4	0.43	51	—	—
P-5	1.19	135	0.08	0.18
P-6	0.38	135	—	—
P-7	1.87	202	0.03	0.17
P-8	0.38	202	—	—
P-9	0.04	280	0.05	0.20
P-10	0.04	48	—	—
P-11	0.1	50[a]	—	—

[a] Synthesized without addition of an organic compound.

The catalytic activity (A_τ) was characterized by the ratio W_h/W_m, where W_h is the weight of hydrocarbons with the initial boiling temperature 35°C and W_m the weight of methanol converted during 3 h after τ-experiment duration. The test was terminated as soon as A_τ decreased to 0.03 A_0, where A_0 is the initial catalytic activity of zeolite. Chromatographic analysis of the reaction products was performed by chromatographs of LCH-8 type equipped with catarometer and flame-ionization detectors. Products were separated on columns with polyphenyl ether on shemalite (column length 4.5 m and ϕ 3 mm), and with dinonylphtalate on Chromosorb (column length 3 m and ϕ 3 mm).

Two indeces were used to characterize the stability of catalyst operation:

τ_0—time of catalyst operation without diminishing of initial activity, A_0, in hours.

τ_1 and τ—time of catalyst operation up to reaching A_τ = 0.5 A_0 and 0.03 A_0, respectively.

The selectivity of zeolite action was characterized by the values of S, i.e., the ratio of weight of aromatic or aliphatic hydrocarbons to the overall weight of hydrocarbon C_{5+} produced.

EXPERIMENTAL RESULTS

X-Ray diffraction patterns obtained for all samples given in Table 1, do not show any principal differences.

The most intensive lines in X-ray patterns for samples 3–8, 10, and 11 are in the range of d/n = 11, 12; 10.0; 3.85; 3.80; 3.75; 3.71; 3.64 Å.

For samples 1, 2, and 9 two lines in the range d/n 3.85 and 3.80 are converging to form one line with d/n = 3.82–3.84 with the intensity 100. X-Ray patterns for samples are identified in a rhombic configuration with parameters $a = 20.0$ Å, $c = 13.42$ Å, and the P_{nma} type symmetry.

On the basis of these data all zeolites synthesized were classified as ZSM-5 type.

Figure 1 shows the dependence of the catalytic activity of zeolites on the duration of catalyst operation. One may observe a period of time, during which the yield of liquid hydrocarbons is constant, and a period when the yield of hydrocarbons rapidly diminishes, and the amount of dimethyl ether and converted methanol at the outlet of the reactor increases. The time of a stable action (τ_0) of the catalysts studied differs considerably. The value of τ_0 depends on the SiO_2/Al_2O_3 ratio and on sodium content.

For zeolites with Na_2O content 1–2%, the time of stable operation increases from 24 to 220 h when SiO_2/Al_2O_3 ratio grows from 24 to 200 (Fig. 2, curve 1′). For the same samples with lower content of Na_2O (0.4%) τ_0 changes from 120 to 360, respectively (Fig. 2, curve 1). In the latter case the overall operation time of catalysts increases up to 600 h (curve 3′). Further decrease of aluminum content in zeolite and increase of SiO_2/Al_2O_3 ratio up to 280 results in a decrease of a stable operation time, as well as τ_1 and τ. Thus, for the above conditions the time of catalyst activity (i) increases with decreasing of the sodium content, and (ii) varies extremely with aluminum content.

In the series of experiments described, the longest periods of stable action was stated for zeolites with $SiO_2/Al_2O_3 = 120$–150. Under other experimental conditions the maximum on curves 1′–3′ will probably shift.

1. *Selectivity of Zeolite Action as a Function of Catalyst Operation*

The composition of liquid hydrocarbon products of methanol transformation substantially varies with increasing the time of zeolite operation (Figs. 3–5), that is, the overall content of aliphatic hydrocarbons in the reaction products increases, whereas that of aromatic hydrocarbons decreases.

Such a tendency manifested itself most strongly for zeolites with a lower SiO_2/Al_2O_3 ratio (40–50, Figs. 3–4) and more weakly for zeolites with a higher SiO_2/Al_2O_3 ratio (130 and more) (Fig. 5).

2. *Selectivity of Zeolite Action as a Function of Chemical Composition*

Figure 6 shows the data on the composition of liquid hydrocarbon products of methanol transformation for catalysts containing different amounts of Al_2O_3.

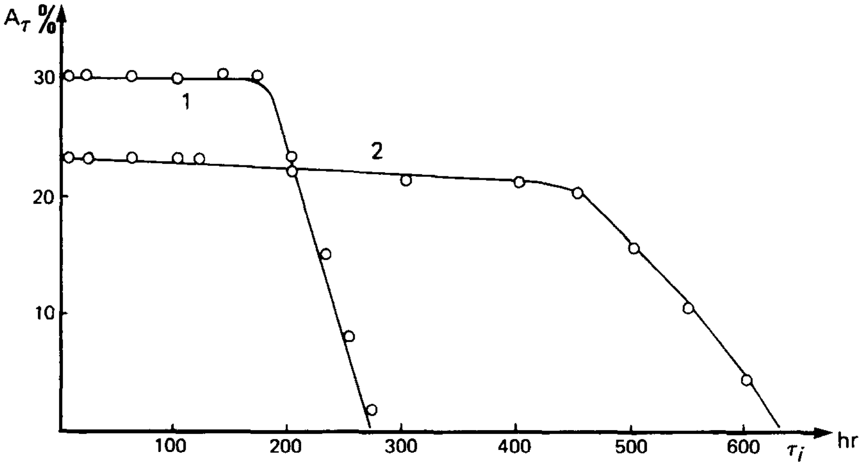

FIG. 1. Variation of methanol transformation to liquid hydrocarbons as a function of the period of catalyst operation: (1) P-4, (2) P-6.

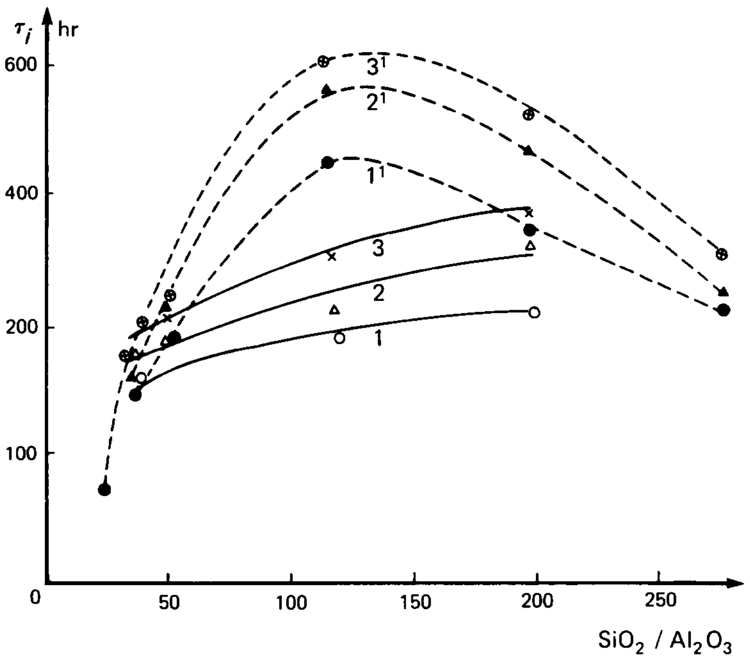

FIG. 2. Stable operation time (τ_0—curves 1 and 1′), time of a half-decrease of activity (τ_1—curves 2 and 2′), and total catalyst operation time (τ—curves 3 and 3′) vs the mole SiO_2/Al_2O_3 ratio in the samples. Curves 1, 2, 3 correspond to zeolites having 1–2% Na_2O. Curves 1′, 2′, 3′ correspond to zeolites having 0.4% Na_2O.

The increase of silicate modulus in zeolites from 38 to 280 involves an increase in the content of aliphatic hydrocarbons in liquid reaction products, obtained on these zeolites, from 35 to 67%, the content of aromatic compounds being decreased from 65 to 33%.

The composition of hydrocarbon products is given in Table 2. The liquid fraction of hydrocarbons, synthesized during the first 5 h of operation on zeolites with $SiO_2/Al_2O_3 = 38$, contains 69–50% of aromatic hydrocarbons (mainly toluenes and xylenes) and only 43–31% of aliphatic ones, mainly C_5–C_7.

Quite an opposite ratio of aromatic and aliphatic hydrocarbons is observed for more silicious zeolites (P-6 and P-8): 35–36% for the first and 61–65% for the second.

Samples P-10 and P-11 were synthesized in hydrothermal conditions at 170°C in the presence of butyl alcohol (P-10) or in the absence of organic compounds (P-11). Though the total degree of crystallization of these samples was very high and X-ray diffraction patterns were the same, the samples showed a low stability of catalytic action in the same conditions, under which samples 1–9 were tested. The degree of methanol conversion began to fall from the very beginning of the catalytic experiment and became zero in 22 h for sample 10, and in 15 h for sample 11. As shown by ESCA study the SiO_2/Al_2O_3 ratio ranges from 125 to 130 (average value 48–50) in the surface crystal layers of these samples which points to the nonuniform distribution of aluminum, with a greater part of aluminum atoms being located in the inner volume of crystals.

DISCUSSION

If the assumption that the stability of ZSM zeolites to coke formation is due to the geometry of their channels (*1*, *2*) is correct, these zeolites might operate during unlimited period of time. We have determined that the catalytic action of zeolites is stable during a limited period of time, and

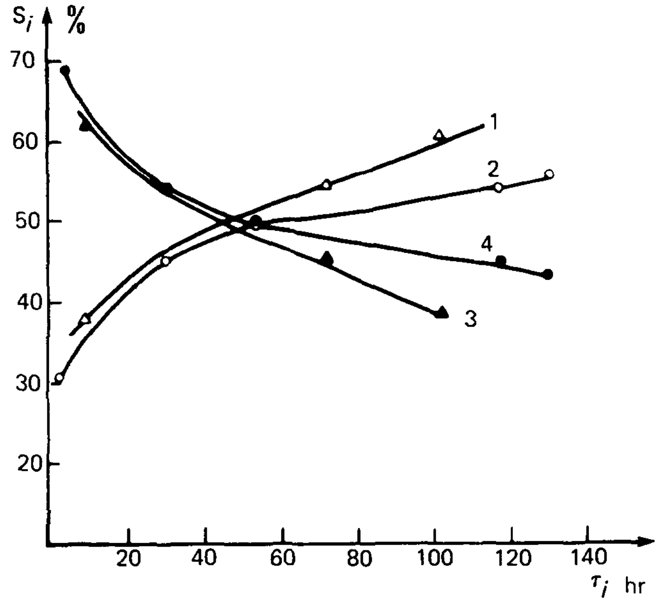

FIG. 3. Content (in % mass) of aliphatic C_{5+} (1 and 2) and aromatic C_{6+} (3 and 4) in liquid products of methanol transformation vs the time of operation of P-1 (1 and 3) and P-2 (2 and 4) catalysts.

the duration of stable action for zeolites of the same crystalline structure depends on aluminum content. After a period of stable operation activity rapidly falls. All the above facts point to that the reactions of coke formation do take place on ZSM zeolites, though at different rates, and permit one to consider three alternative suppositions:

(1) Catalytically active centers of hydrocarbon synthesis and those of coke formation are located in different areas, which is in agreement with the supposition made in (*1*, *2*). If the former centers are inside the

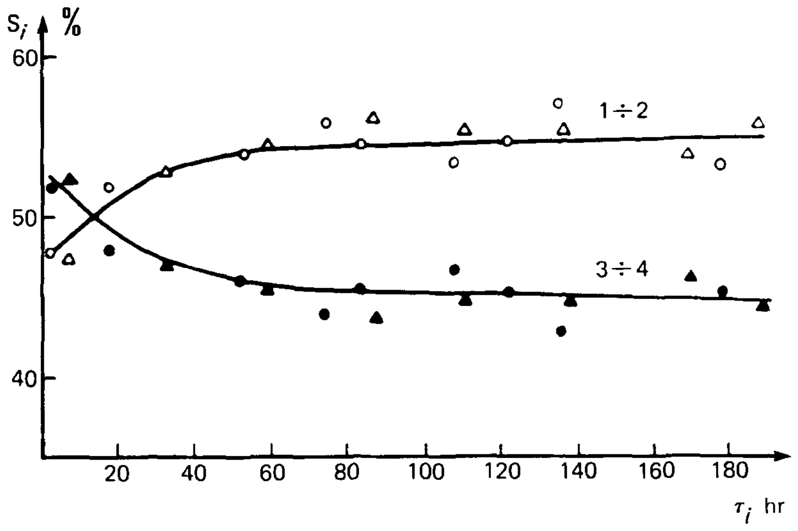

FIG. 4. Content (in % mass) of aromatic hydrocarbons C_{6+} (3 and 4), and aliphatic hydrocarbons C_{5+} (1 and 2) in liquid products of methanol transformation vs the time of operation of P-3 (1 and 3) and P-4 (2 and 4) catalysts.

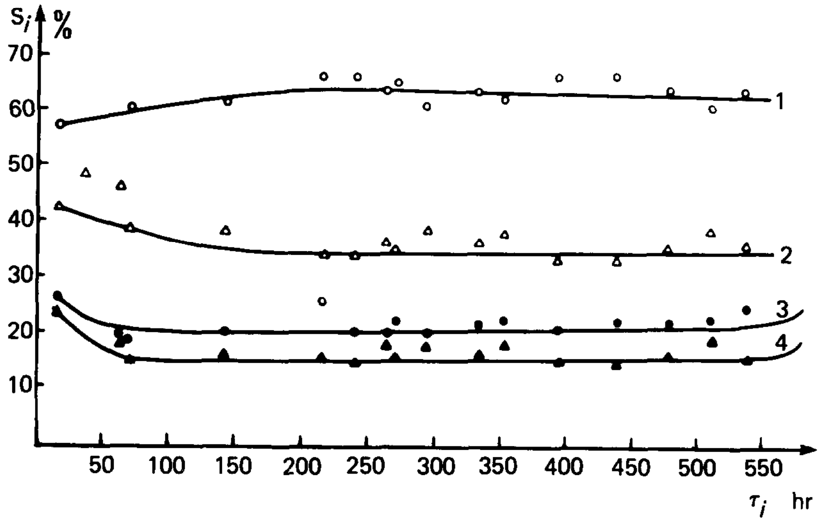

FIG. 5. Content (in % mass) of (1) aliphatic hydrocarbons C_{5+}, (2) aromatic hydrocarbons C_{6+}, (3) aliphatic hydrocarbons C_{7+}, (4) aromatic hydrocarbons C_{9+}. in liquid products in methanol transformation vs the time of operation of P-8 catalyst.

zeolite crystal, and the latter ones are on outside, the catalyst activity should not be changed until coke depositions on the crystal surface prevent the access of molecules to the inside of zeolites. If this supposition is valid, there is no reason to expect the selectivity of the process to change in time or with increasing the content of aluminum in zeolite. However, the dependence of selectivity of zeolite action on its chemical composition and time of operation has been experimentally proved. Hence, the supposition of coke formation on the surface of zeolite particles does not account for the regularities observed.

(2) Nondesorbed compounds (carbonium-ion chains) are formed over the whole crystal volume in complex with aluminum

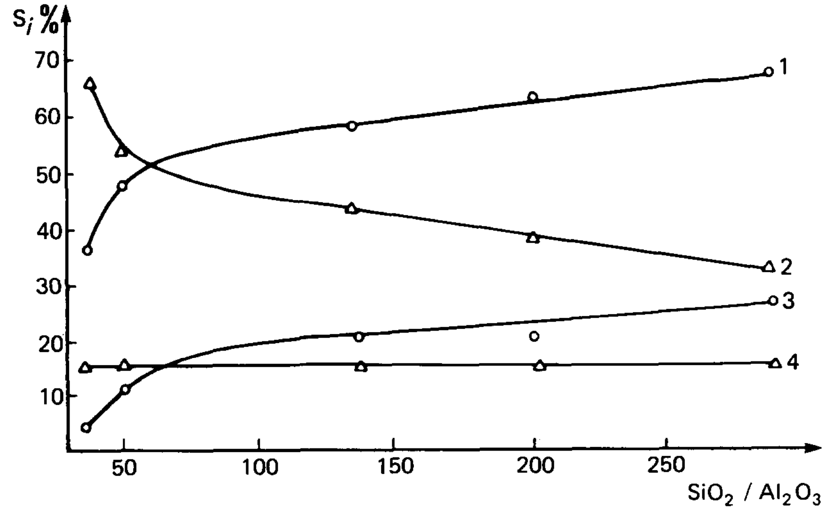

FIG. 6. Content (in % mass) of (1) aliphatic hydrocarbons C_{5+}, (2) aromatic hydrocarbons C_{6+}, (3) aliphatic hydrocarbons C_{7+}, (4) aromatic hydrocarbons C_{9+}. in liquid products of methanol transformation vs the mole ratio of SiO_2/Al_2O_3 in samples during the first 10 h of operation.

TABLE 2

Composition of Liquid Hydrocarbon Products of Methanol Transformation for Various Zeolite Species

Liquid fraction components	P-2		P-6		P-8	
	Time from the beginning of operation (h)					
	5	100	5	100	5	100
Aliphatic						
C_5	20.7	24.3	17.7	16.7	28.5	20.7
C_6	6.8	15.5	27.9	24.4	29.4	23.9
C_7	2.1	4.9	11.3	11.1	10.5	9.5
C_8	0.9	3.9	5.5	7.0	5.5	6.9
C_9	0.2	0.9	1.8	2.0	1.0	2.5
C_{10+}	—	—	0.6	0.4	—	0.5
Total	30.7	49.5	64.8	61.6	64.9	64.0
Aromatic						
Benzene	4.6	1.7	1.8	1.9	2.3	2.4
Toluene	18.6	5.2	4.2	3.4	4.9	3.7
Xylene	30.8	20.3	15.0	16.8	15.6	14.5
Ethyl toluene	4.2	6.3	3.1	3.9	5.4	6.1
Pseudocumene	6.7	10.5	7.7	8.9	4.2	5.4
Durene	2.2	2.6	2.0	2.4	1.0	1.9
C_{10+}	2.2	3.5	1.3	1.1	1.7	2.0
Total	69.3	50.0	35.1	38.4	35.1	36.0

atoms; they are constantly growing and provide centers of catalytic action. Such a supposition was made in (*14*). In this case zeolite activity should remain unchanged until the process is hindered by mass transfer, due to the blocking of channels by long carbonium-ion chains. The length of zeolite stable operation should be inversely proportional to Al content. In this case selectivity of methanol transformation should not depend on the length of catalyst operation and aluminum content. These suppositions do not permit one to explain all phenomena observed.

(3) The coke precursors and nondesorbed compounds are formed on centers which show properties of superacids. It was concluded from ^{27}Al- (*3–6*) and ^{29}Si- (*7, 8*) NMR data (*15*) that aluminum distribution in zeolites does not coincide completely with the model of active site $[Si—O—Al]^-$ proposed earlier. In low silicious zeolites $[Si(OAl)_n]^{n-}$ groups were detected having 2, 3, and 4 Al atoms in the external coordination sphere of silicon atoms (*7, 8*), as well as aluminum atoms in cation positions (*3–6*). We may, therefore, suggest the presence of the $[Si(OAl)_n]^{n-}\cdot Al^{3+}_{n/3}$ type centers which may provide a multipoint interaction with an adsorbed molecule. These groups may show superacid properties and accelerate the hydride-ion shift reactions with the formation of deeply dehydrogenated and condensed products. The probability of formation of groups with a higher value of "*n*," including aluminum atoms in the cation position, will grow with increasing of the total content of aluminum in zeolites. If such a model of aluminum distribution in zeolite is valid, the strength of its active centers with acid–base properties should be different.

The higher the concentration of $Si(OAl)_{n>1}$ groups, the higher is the rate of formation of aromatic, polyaromatic, nondesorbed compounds, and the higher is the process selectivity with respect to aromatic hydrocarbons. Centers of multipoint absorption catalyzing the formation of alkylaromatic compounds will be poisoned first, during catalyst operation, which results in variation of the process selectivity in time. This phenomenon has been observed experimentally. A time of stable action of zeolites observed may be accounted for by an assumption of a gradual filling of zeolite cavities with catalytically active organic additives.

An idea on acid activity of zeolites as a collective property, dependent on the total content of aluminum atoms in the zeolite framework, and its electronegativity has been developed in a number of works (*15–17*). Data on the nonuniformity of aluminum distribution in zeolites permit one to conclude that catalytic properties are dependent on the local distortions in zeolite framework, which, in turn, leads to the nonuniformity of the structure and properties of acid centers. That ZSM-5 zeolites, synthesized in the presence of butyl alcohol or without organic additives, show no stable catalytic activity leads us to the conclusion that the distribution of aluminum atoms over crystals in this case is less uniform than upon synthesis in the presence of quaternary ammonium salt and their bases. A nonuniform distribution may be due to the deviation of the number of $Si(OAl)_{n>1}$ or $Al(OSi)_{n>1}$ groups in the zeolite framework from the average statistical value assumed in (*9, 10*). This, in turn, must lead to the increase in the number of the $[Si(OAl)_{n-1}]^{n-1} \cdot Al^{3+} \cdot (n - 1)/3$ type centers, which we consider as the centers of the multipoint interaction with reagent molecule and formation of coke precursors.

CONCLUSION

The period of stable catalytic operation and selectivity of highly silicious zeolites for hydrocarbons synthesis from methanol depends on the content of aluminum. The selectivity of methanol transformation to aromatic hydrocarbons increases with decreasing the SiO_2/Al_2O_3 ratio. Previously obtained ^{27}Al- and ^{29}Si-NMR data point to the presence of the groups including more than one aluminum atom in the second coordination sphere of silicon atoms (among these aluminum atoms in cation positions) in zeolites. Such groups may be the centers of multipoint interaction with the reagent molecule which have the superacid properties.

Hydrogen redistribution on such centers accompanied by the formation of alkylaromatic, polyaromatic nondesorbed compounds, and other coke precursors should proceed at a high rate. Increasing of aluminum content in zeolites will increase the probability of formation of such centers. This, in turn, leads to an increase in the concentration of aromatic hydrocarbons in reaction products and to a decrease of time of catalyst stable operation.

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K. G. IONE
G. V. ECHEVSKII
G. N. NOSYREVA

Institute of Catalysis
Novosibirsk, USSR

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