STABILITY OF CATALYTIC ACTIVITY AND SELECTIVITY OF ZEOLITES

DIFFERING IN CHEMICAL COMPOSITION

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High-silica zeolites of the ZSM type, in contrast to other types of zeolites, will operate for prolonged periods without losing activity in reactions of hydrocarbon synthesis and conversion. In [1, 2], the stability of these zeolites with respect to coke formation processes was explained on the basis that, because of the small dimensions of the zeolite channels, it is impossible to synthesize in these channels the hydrocarbons that are predecessors of coke. However, after a certain period of operation, even zeolites of this type will lose activity as a result of poisoning by coke.

According to [3, 4], rapid poisoning of zeolites is caused by the appearance of Al atoms in cationic positions. These enter into the composition of centers that accelerate reactions of hydrogen redistribution, with the formation of highly degraded compounds. In later studies, this hypothesis was expanded by comparing the ²⁷Al and ²⁹Si NMR spectra for Y and ZSM-5 zeolites. It was established in [5, 7] that in the Y zeolites, in the second coordination sphere of the Si atoms, there may be two or three Al atoms entering into the zeolite skeleton, and also in the form of Al³⁺ cations. Groups of this type may be centers for multipoint adsorption, which is responsible for the superacidity effect. It should be expected that in ZSM zeolites, as the Al content is increased, the degree of nonuniformity of Al distribution in the zeolite skeleton will increase, and hence the stability of their catalytic action in hydrocarbon synthesis and conversion will be poorer. In the present work, as a test of this hypothesis, we have determined the operating time limits for a number of ZSM zeolites in relation to the contents of Al and Na cations.

EXPERIMENTAL

<u>Preparation of Catalysts.</u> The ZSM zeolites were obtained from a silica sol, Na aluminate, and Bu_4NBr , following procedures given in [8]. The SiO_2/Al_2O_3 ratio in the zeolites was varied from 24 to 280. Samples with a high phase purity and a high degree of crystallinity were selected for use in these studies (see Table 1).

All of the zeolites were calcined in flowing O_2 at $530-550^{\circ}C$. The ion exchange was performed after the heat-treating, using an ammonia buffer solution (pH 9.5); the zeolites were stirred with this solution for 1-2 h at 60-70°. Zeolites with low Na contents were prepared by two or three such ion-exchange treatments, with calcination at 400-450° between treatments. The residual Na content was determined by flame photometry, the Si content by gravimetric analysis, the Al in the high-Al samples by complexometric titration, and the Al in the low-Al samples by atomic absorption in a Spektr type spectrophotometer. The degree of crystallinity of the zeolites was characterized by the intensities of the lines in the diffractograms in the reflection anlge intervals $\theta = 3.8-4.5^{\circ}$ and 11.5-12.5°, as determined in URS-50 and DRON-1 diffractometers.

The catalytic activity and the stable operating time of the catalysts at 0.1 MPa and 380° were investigated in continuous-flow reactors. Liquid methanol was fed to the reactor by means of a liquid pump at a space velocity of $1.0-1.1 \ h^{-1}$. Analogous experiments, under pressure, were performed in an experimental continuous-flow unit with recycle in a two-stage process of methanol conversion to hydrocarbons under pressures of $1.0-2.0 \ MPa$. As the catalyst for the first stage (methanol $\ddagger DME$) we used γ -Al₂O₃. The equilibrium conversion of methanol to dimethyl ether (DME) in the first stage of the process was 80%.

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Fig. 1. Time of stable operation τ_0 (1), time for 50% drop in activity τ_1 (2), and time for complete poisoning of catalyst τ_2 (3), as functions of SiO₂/Al₂O₃ mole ratio.

Fig. 2. Variation of composition of liquid reaction products with operating time on catalysts P-1 and P-4 at 0.1 MPa (a) and P-10 catalyst at 2.0 MPa (b): 1, 3, 5) C_{5+} aliphatic hydrocarbons; 2, 4, 6) C_{6+} aromatic hydrocarbons.

	TABLE	1.	Chemical	Composition	of	Zeolites
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Tupo of optoluct	Chemical composition		Degree of crystal-
Type of catalyst	Na₂O, %	SiO ₂ /Al ₂ O ₃	linity, %
P-1 P-2 P-3 P-4 P-5 P-6 (granulated, 30% Al ₂ O ₃)	0,4 0,43 0,38 0,38 0,04 0,08	38 51 135 202 280 90	$ \begin{array}{r} 90 \\ 70 \\ 90-100 \\ 100 \\ 100 \\ 95-100 \end{array} $

The activity of the catalysts was characterized by the ratio of the weight of hydrocarbons with initial boiling point $\geq 35^{\circ}$ to the weight of methanol passed through the reactor; this ratio was designated as A. The composition of the reaction products was analyzed by GLC in an LKhM-8 chromatograph with a katharometer and flame ionization sensors. The products were separated in columns with polyphenyl ether on shimalite (4.5 m × 3 mm) and dinonyl phthalate on Chromosorb (3 m × 3 mm).

The stability of catalyst operation was characterized by two indexes: τ_0 is the catalyst operating time (h) without any drop from the initial activity A_0 ; τ_1 and τ_2 are the respective catalyst operating times (h) until the catalyst activity has dropped to the levels A = 0.5 A₀ and 0.03 A₀.

The zeolite selectivity was characterized by the values of S_{ar} and S_{al} , the ratios of the weights of aromatic and aliphatic hydrocarbons to the total weight of liquid hydrocarbon reaction products.

The time of stable operation of these catalysts τ_0 depends on the SiO₂/Al₂O₃ ratio (Fig. 1). The greatest values of τ_0 were found for the zeolites with SiO₂/Al₂O₃ = 120-150. It is possible that the maxima on curves 1 and 2 would be shifted if the conditions of the experiments were changed.

<u>Selectivity of Zeolites in Relation to Catalyst Operating Time.</u> The composition of the liquid hydrocarbon products from the conversion of methanol changes markedly with increasing time of operation of the zeolite catalysts (Fig. 2). The total content of aliphatic hydrocarbons in the reaction products increases, and the total content of aromatic hydrocar-



Fig. 3. Composition of liquid hydrocarbons on P-10 catalyst as a function of pressure: 1) C_{5+} aliphates; 2) C_{6+} aromatics; 3) C_{9+} aromatics; 4) durene.

Fig. 4. Composition of liquid products in first 5-10 h of operation as a function of SiO_2/Al_2O_3 mole ratio. Hydrocarbon contents: 1) C_{5+} aliphatics; 2) C_{6+} aromatics; 3) C_{7+} aliphatics; 4) C_{9+} aromatics.

bons decreases; these trends are observed in the runs at 0.1 MPa and also in those at 2.0 MPa. The trends are the most pronounced for the zeolites with low modulus (SiO_2/Al_2O_3) .

Selectivity of Zeolites in Relation to Pressure. An increase in pressure leads to a decrease in the content of aliphatic hydrocarbons in the reaction products and an increase in the content of aromatic hydrocarbons, mainly in the content of heavy, highly alkylated and aromatic (including durene) (Fig. 3). The value of τ_0 drops from 550 h at 0.1 MPa to 350 h at 2.0 MPa. The increase in content of aromatic hydrocarbons with increasing pressure is most likely related to the increase in the partial pressures of methanol and intermediate products, which should favor secondary conversion reactions (alkylation of monomethyl- and dimethylaromatic compounds).

<u>Selectivity of Zeolites in Relation to SiO_2/AI_2O_3 Ratio.</u> Data on the composition of the liquid hydrocarbon products from methanol conversion in the first 5-10 h of catalyst operation, for catalysts with identical Na₂O content (0.35-0.4%) but with different contents of Al (Fig. 4), show that an increase in the silicate modulus from 38 to 280 leads to an increase in the content of aliphatic hydrocarbons in the reaction products from 35% to 67%, with a corresponding drop in the content of aromatic compounds from 65% to 33%.

DISCUSSION OF RESULTS

If the stability of ZSM catalytic activity with respect to coke formation were governed solely by the geometry of the zeolite channels [1, 2], we should expect that zeolites of this type would operate indefinitely. In the work reported here, we have established that the zeolites operate stably for a limited time, and that the zeolite operating time for a given crystal structure decreases with increase content of Al. After the period of stable operation, the activity drops off rapidly.

In order to explain the fact that coke formation reactions do not take place in the ZSM zeolites, even though at a low rate, let us examine three alternative hypotheses: 1) The centers catalyzing reactions of hydrocarbon synthesis and the centers catalyzing reactions of coke formation are spatially separated; this is consistent with the hypothesis advanced in [1, 2]. If the first group of centers is located within the zeolite crystals and the second group on its outer surface, the catalyst activity should not change until coke deposits on the crystal surface block the access of molecules to the interior void spaces of the zeolite. If this hypothesis were valid, there would be no grounds for considering that the process selectivity should change with the passage of time or with increasing content of Al in the zeolites. And the experiments do demonstrate that the zeolite selectivity is dependent on the chemical composition and on the operating time. This means that the hypothesis of coke formation on the surface of the zeolite particles cannot provide an explanation for all of the relationships actually observed. 2) Nondesorbable compounds are formed on all of the Al atoms throughout the entire volume of the crystal, and they grow continuously; in this case, they are the centers of catalytic action. A similar hypothesis was advanced in [9]. In this case, the zeolite activity should remain unchanged until the instant at which, as a result of blockage of the channels by carbonium ion chains, the process begins to be retarded by mass transfer limitations. The length of the stable operating period of the zeolite should be inversely proportional to the Al content. In this case also, the selectivity of methanol conversion should not depend on the catalyst operating time or on the Al content. These predictions are not supported by the experimental data. 3) Cyclic and nondesorbable compounds are formed on centers that manifest the properties of superacids. Previously [5], on the basis of ²⁷Al NMR data [3-5] and ²⁹Si NMR data [6, 7], it was concluded that the distribution of Al in zeolites is nonuniform. In low-silica zeolites, groups including two or three Al atoms in the outer coordination sphere of the silicon have been found [6, 7], and also Al atoms in cationic positions [3-5]. This suggested that such centers are centers of multipoint interaction with the adsorbed molecule, centers on which hydride ion shift reactions will proceed at a high rate, with the formation of highly dehydrogenated and condensed products. The distribution of $Si(OA1)_n$ groups among those with n = 0, 1, 2, 3, and 4 may be subject to some sort of statistical law, and the probability of formation of groups with a greater value of n should increase with increasing total content of Al. If this model of the distribution of Al in zeolites is correct, there should be differences in the strength of the active centers.

The higher the concentration of the $Si(OA1)_{n>1}$ groups, the higher will be the rates of formation of aromatic, polyalkylaromatic, and difficultly desorbed compounds, and the higher will be the process selectivity with respect to aromatic hydrocarbons. Moreover, as operating time is accumulated on the catalyst, the first result from poisoning will be deactivation of the centers of multipoint adsorption that catalyze the formation of alkylaromatic compounds. This should lead to a timewise change in the process selectivity.

The best explanation of our experimental data is based on the hypothesis that the concentration and composition of centers of multipoint interaction with the reactant have a decisive influence on the selectivity and stability of zeolite catalysts. After poisoning and disengagement of these centers from the catalytic process, uniform-strength active centers remain in the zeolite, and hence a section of stable selectivity may be observed, related to a conversion in accordance with model No. 2, gradual filling of the zeolite void space volume by catalytically active, nondesorbable organic compounds.

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CONCLUSIONS

l. The stable operating time of high-silica zeolites in the synthesis of hydrocarbons from methanol depends on the content of aluminum in the zeolite. The selectivity of methanol conversion to aromatic hydrocarbons increases with increasing SiO_2/Al_2O_3 ratio and with increasing pressure.

The increase in selectivity of methanol conversion to aromatic and polyalkylaromatic hydrocarbons with decreasing $\rm SiO_2/Al_2O_3$ ratio may be related to the presence of $\rm Si(OAl)_{n>1}$ groups in the zeolites.

LITERATURE CITED

- 1. P. Weisz, Proceedings of 7th International Congress on Catalysis (1980), p. 1.
- 2. L. D. Rollman and D. E. Walsh, J. Catal., <u>56</u>, 139 (1979).
- 3. K. G. Ione, V. G. Stepanov, V. M. Mastikhin, and E. A. Paukshtis, Proceedings of 5th International Conference on Zeolites, Naples (1980), p. 223.
- 4. K. G. Ione, E. A. Paukshtis, V. G. Stepanov, V. M. Mastikhin, and E. N. Yurchenko, Izv. Akad. Nauk SSSR. Ser. Khim., p. 1717 (1981).
- 5. K. G. Ione, V. G. Stepanov, G. V. Echevskii, A. A. Shubin, and E. A. Paukshtis, Zeolites, <u>4</u>, 114 (1984).
- 6. E. Lippmaa, M. Magi, A. Samoson, G. Engelhardt, and A.-R. Grimmer, J. Am. Chem. Soc., <u>102</u>, 4889 (1980).
- 7. G. Engelhardt, E. Lippmaa, and M. Magi, J. Chem. Soc., Chem. Commun., p. 712 (1981).
- 8. US Pat. 3,804,746 (1974).
- 9. D. J. Bartomouf, J. Phys. Chem., <u>83</u>, 249 (1979).