COMPARATIVE INVESTIGATION OF THE CATALYTIC PROPERTIES OF CRYSTALLINE ALUMINOSILICATES OF VARIOUS TYPES.

COMMUNICATION 3. SELECTIVITY OF THE CONVERSION OF METHANOL ON ZEOLITES OF VARIOUS TYPES

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Zeolites of types A, X, and Y are used as catalysts for the dehydration of alcohols to olefins [1, 2]. In view of the interest in the synthesis of fuel from nonpetroleum raw material, the process of high-temperature conversion of alcohol is considered as a promising method for obtaining gasolines [3]. In particular, a method has been developed for obtaining high-octane fuels from methanol using silica-rich zeolites of the ZSM type [4].

According to the literature [5, 6], the conversion of alcohols on zeolites ZSM takes place in the sequence: methanol→dimethyl ether→ethanol→carbonium ion. The subsequent conversions may take place by two pathways: 1) the interaction of the carbonium ion with methanol with the formation of higher isoolefins; or 2) the alkylation of the carbonium ion with olefins to form aromatic and cycloaliphatic hydrocarbons [5].

It appeared of interest to study the features of the conversion of methanol into hydrocarbons on zeolites of various types. In the present investigation we have made a comparative study of the selectivity of the action of zeolites of the type of mordenite and erionite and of silica-rich zeolites (TsVK) in reactions of methanol at various contact times (τ).

EXPERIMENTAL

The zeolites were decationized by being treated with ammonia buffer solution with intermediate calcination between treatments at 450-500°C (Table 1).

Catalytic activity was determined by two methods: 1) using a pulsed microcatalytic gradientless apparatus with a vibrofluidized bed of catalyst and dilutions of methanol vapors with helium to a concentration of 3-6 mmole/liter. The microreactor with a volume of 1.5-2 cm^3 was charged with 0.01-0.05 g of catalyst. The activation of the type Y zeolites was carried out at 450°C for 2 h in a current of He. The TsVK was activated at 530°C with oxygen. The reaction temperature was 380°C and the space velocity of the feed of the gaseous mixture 10^4-10^6 h^{-1}; 2) using a flow-through apparatus with a stationary catalyst bed; the degree of conversion of the methanol was close to 100% and the space velocity calculated to gaseous methanol was 10^2-10^3 h^{-1}. The reaction temperature was 380-460°C.

The amount of undesorbable organic compounds that deposited on the catalyst during an experiment was determined from the difference between the amount of methanol converted and the sum of the products isolated, calculated as carbon. The solid deposits were extracted from the catalyst, and the extract was then analyzed chromatographically.

TABLE 1. Chemical Compositions of the Zeolites, %

Catalyst	Na	K	Cl	SiO_2/Al_2O_3, mol.%
HE (erionite)	0,03	1,96	0,3	6,4
HM (mordenite)	0,13	–	–	15,4
HY	0,9	–	0,2	4,69
TsVK	0,1	–	–	62,8

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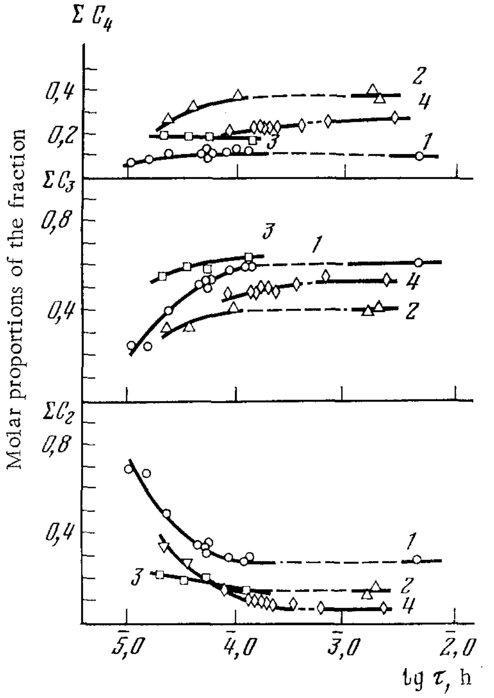


Fig. 1

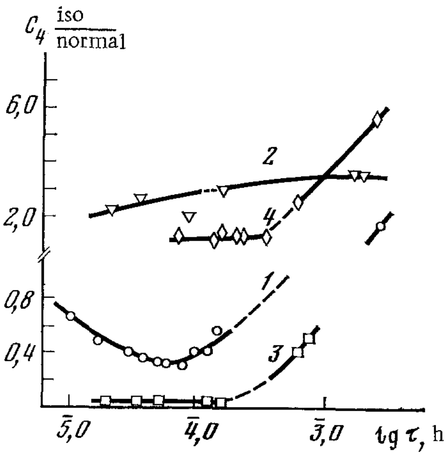


Fig. 2

Fig. 1. Dependence of the amounts of C_2, C_3, and C_4 hydrocarbons in the methanol conversion products on the time of contact on the following zeolites: 1) mordenite; 2) zeolite Y; 3) erionite; 4) TsVK.

Fig. 2. Dependence of the amount of isoparaffins in the methanol conversion products on the time of contact on the following zeolites: 1) mordenite; 2) zeolite Y; 3) erionite; 4) TsVK.

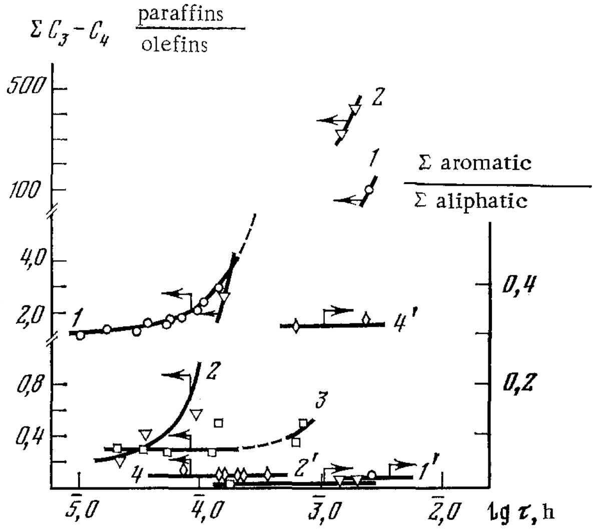


Fig. 3. Change in the amounts of olefins and aromatic hydrocarbons in the reaction products as a function of the time of contact. Composition of the reaction mixture: 5% methanol, remainder helium (1-4), and 100% methanol (1'-4'); 1) mordenite; 2) zeolite Y; 3) erionite; 4) TsVK.

TABLE 2. Composition (mole %) of the Hydrocarbon Products of the Conversion of Methanol on Zeolites of Different Natures (reaction temperature 380°C, diluent gas He, P_{tot} 1 atm, $\tau 9\cdot 10^{-5}$ h)

Product	Zeolite			
	HE	HM	HY	TsVK
Methane	0,3	0,4	0,1	0,1
Ethane and ethylene	16,9	41,8	12,1	13,4
Propane	12,4	34,9	7,9	1,7
Propylene	46,5	14,4	32,8	58,4
Isobutane	0,6	1,4	15,9	4,0
n-Butane	3,8	3,4	0,9	0,1
n-Butene	3,3	0,5	3,0	2,3
Isobutene	–	0,6	7,5	5,0
trans-But-2-ene	7,0	1,5	5,8	2,5
cis-But-2-ene	3,8	0,6	2,7	3,1
Isopentanes	0,1	0,2	5,2	1,7
n-Pentane	1,1	0,3	0,4	–
Pentenes	3,4	–	2,6	2,7
Isohexanes	0,2	–	2,2	4,6
n-Hexane	0,6	–	0,9	0,4
Including:				
C_2-C_6 olefins	77	28	65	84
i-C_4-C_6	0,9	2,2	30,8	15,3
Aromatic hydrocarbons	Absent			

CO and CH_4 were separated in a column containing zeolite NaA, and the other reaction products in columns containing 25% of diglycerol on Chromosorb P, 15% of polyethylene glycol-1000 on Chromosorb W, or 7% of paraffin oil on Zikeev quarry tripoli.

DISCUSSION OF RESULTS

Figures 1-3 show the compositions of the hydrocarbon products of the conversion of methanol on zeolites of various types as functions of the time of contact. The results obtained on the pulsed ($\tau = 10^{-5}$-10^{-4} h) and the flow-through ($\tau = 10^{-3}$-10^{-2} h) apparatuses are plotted on common graphs. With an increase in τ, the yield of dimethyl ether decreased and the proportion of hydrocarbons in the reaction product increased on all the catalysts studied. In the hydrocarbon part of the reaction products the yield of the ethane–ethylene fraction decreased and the amount of C_3-C_4 hydrocarbons increased (see Fig. 1). The proportion of isobutene and isobutane in the latter rose sharply (Fig. 2). The proportion of saturated hydrocarbons in the reaction products also rose and the amount of olefins fell (see Fig. 3). At $p/p_S = 1$ and $\tau > 10^{-3}$ h aromatic hydrocarbons appeared in the reaction products on zeolites HY, HM, and TsVK.

It follows from Tables 2 and 3 that on all the zeolites studied practically the same set of hydrocarbons was formed. However, the amounts of the individual hydrocarbons in the reactions products obtained at the same time of contact differed considerably for the various types of zeolites. Thus, at $\tau \leqslant 2\cdot 10^{-5}$ h the products of the conversion of methanol on mordenite contained mainly the ethylene–ethane fraction (about 70%), and C_4 hydrocarbons amounted to less than 10%. On erionite in the same range of τ, the propane–propylene fraction predominated, on the type Y zeolite the C_4 fraction, and on TsVK the main reaction product consisted of C_3 hydrocarbons (see Table 2).

At the same time of contact and low partial pressures of methanol, the highest yield of isohydrocarbons was obtained on zeolite HY (60-70%) and TsVK (70-80%), and the lowest (∿5%) on H-erionite. At $\tau \leqslant 2\cdot 10^{-5}$ h, the amount of C_3-C_4 olefins in the products of the conversion of methanol on TsVK was ∿90%, on mordenite 40%, and on type Y zeolite ⩽ 10%. Finally, in the region of high partial pressures of methanol and $\tau > 10^{-3}$ H, the yield of aromatic hydrocarbons on TsVK amounted to 30 mole%, while on H-mordenite it was only 3% and on HY ⩽ 1 mole%. No formation of cyclic compounds was observed on erionite (see Table 3).

The compositions of the products of the cracking of n-octane and the conversion of methanol at the same contact times and partial pressures of the reactants were practically identical (Table 4).

TABLE 3. Composition (mole%) of the Hydrocarbon Products of the Conversion of Methanol on Zeolites of Different Types (reaction temperature 380°C, $\tau 3 \cdot 10^{-3}$ h)

Product	Zeolite			
	HE	HM	HY	H-TsVK
Methane	0,1	0,3	1,0	0,1
Ethane and ethylene	57,6	37,3	15,7	4,9
Propane	11,3	35,6	40,0	34,4
Propylene	23,8	9,5	1,7	5,1
Isobutane	1,9	3,8	28.2	17,9
n-Butane	1,3	4,3	8,1	2,7
n-Butylene	0,8	0,5	–	–
Isobutylene	0,4	1,4	0.1	0,6
trans-But-2-ene	1,8	0,8	Traces	0,3
cis-But-2-ene	0.7	0,3	»	0,2
Isopentanes	–	1,4	3,5	4,8
n-Pentane	0,1	0,4	0.9	0,6
Pentenes	0,2	1,6	–	0.5
Isohexanes	–	2,8	0,1	2,9
n-Hexane	–	–	0.3	0,2
Benzene	–	Traces	Traces	1,9
Toluene	–	»	»	8.2
Xylenes	–	»	0.4	11,3
Propylbenzene	–	–	Traces	3,5
Including:				
C_2- C_6 olefins	67	22	2,5	7,5
i-C_4-C_6	2,3	9,4	31,9	26.2
Aromatic hydrocarbons	None	Traces	0,4	24,9

TABLE 4. Compositions of the Liquid Fractions of the Products of the Conversion of Methanol and of the Cracking of n-Octane on Zeolite TsVK (space velocity 1 h^{-1})

Hydrocarbon	From methanol, % (380°C)	From octane, % (450°C)
C_4	0,20	0,04
C_5	1,60	0,24
C_6	5,30	0,93
C_7	2,80	0,61
C_8	1,20	8,04
Isopropylcyclohexane	–	1,34
Benzene	2,80	–
Toluene	29,00	26,60
Xylenes	30,60	36,00
Propylbenzene	7,80	13,60
C_{10} and higher aromatics	18,70	12,60

The activity of the type Y zeolites and of the mordenites fell with time, mainly through a decrease in the yield of hydrocarbons. For the type Y zeolite (0.9% Na), during the first 30 min of working the degree of conversion of the methanol fell from 100 to 10%. The amount of undesorbed deposits on the catalyst by the end of the second hour of working was 6-8%. The erionite and TsVK showed a considerably greater stability in their action. Thus, no fall in the activity of the TsVK during the first 15 h of its working was observed. The amount of undesorbed deposits by the end of this period was 2%, i.e., considerably less than in the case of zeolite Y. According to the results of chromatographic analysis, the extract of the coke deposits obtained on TsVK consisted mainly of naphthalene and alkylnaphthalenes.

For all the zeolites studied, the same tendency to change in the selectivity in the conversion of methanol with an increase in the time of contact and in the p/p_s ratio of the methanol was observed. Thus, at short times of contact a decrease in the yield of dimethyl ether in all cases was accompanied by an increase in the yield of olefins, mainly C_2. With an increase in τ, the yield of C_2-C_3 olefins fell and the yield of saturated and aromatic hydrocarbons rose. It may therefore be assumed that for all the zeolites studied the scheme of conversion by Chang and Silvestry [5] applies: 1) dehydration of methanol to dimethyl ether; 2) elimination of water from the latter with the formation of olefins. The composition of the reaction products is determined by the nature of the secondary transformation of the olefins, including those resulting from the reactions: 3) alkylation of the alcohols by the olefins; and 4) redistribution of hydrogen in the olefins with the formation of compounds more unsaturated than the initial olefins. Chromatographic analysis of the reaction products showed that this leads to the formation of aromatic compounds and isoparaffins. No dienes and trienes are found in the reaction products; and 5) desorption of the monoaromatic compounds into the gas phase or their alkylation by their olefins with the subsequent closure of a second ring, the further redistribution of hydrogen, and the formation of polycyclic undesorbed reaction products by the scheme

$$\text{Olefins} \longrightarrow \begin{matrix}\text{Paraffins}\\ + \\ \text{Monoaromatic hydrocarbons}\end{matrix} \begin{matrix}\nearrow \text{Desorption into the gas phase} & (1)\\ \\ \searrow \text{Polycyclic hydrocarbons (coke)} & (2)\end{matrix}$$

The same tendency to a change in the composition of the reaction products with an increase in τ indicates that the sequence of the stages of conversion is also the same on all the zeolites studied. The differences in the compositions of the reaction products formed at the same time of contact indicate that the rates of the individual stages differ.

Since the rates of the individual stages were not determined, their ratio can be judged qualitatively from the change in the composition of the reaction products with a variation in the time of contact. In this connection, we may note the following facts: 1) under identical reaction conditions and at the same time of contact, higher yields of saturated and lower yields of unsaturated hydrocarbons were observed on type Y zeolites and mordenite. On TsVK and erionite there were more olefins than paraffins in the reaction products over a wide range of times of contact. All this permits us to consider that the rate of secondary transformations of the olefins in the hydrogen redistribution reactions on zeolite Y is much greater than of TsVK and erionite.

2. Isoparaffins and coke are formed predominantly on zeolite Y at large values of τ. Apparently, the aromatic compounds obtained as the result of the redistribution of hydrogen in the olefins undergo further rapid and irreversible conversions on type Y zeolites.

On TsVK, in addition to the slow process of coke formation, an evolution of monoaromatic compounds into the gas phase is observed. In this case, the rate of desorption of the monoaromatic compounds is apparently greater than the rate of their alkylation by the olefins and subsequent transformation into the polycyclic hydrocarbons. On the whole, it may be concluded that on zeolite Y the conversion of the olefins takes place at a considerably higher rate and predominantly by pathway (2), while on TsVK these reactions take place at a lower rate and predominantly by pathway (1) (see scheme).

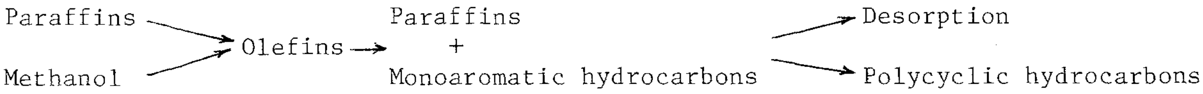
On erionite, the main reaction products over a wide range of values of τ were olefins. Apparently, the chain of conversions of methanol on these zeolites is mainly interrupted at the second stage, and the subsequent stages take place at a lower rate than on TsVK zeolite.

The fact of the formation of monoaromatic compounds on type ZSM zeolites is connected by Rollman and Walsh [7] with steric hindrance for the synthesis of polycyclic hydrocarbons (coke). It is assumed that this is due to the small dimensions of the zeolitic cavities and features of their configuration. This hypothesis may be valid for erionites, in which the kinetic diameter of the inlet windows does not exceed 4.0 Å [8]. The size of the cavities in these zeolites is so small that the formation of isoparaffins and aromatic compounds in them is impossible because of geometric limitations. The characteristics of the selectivity of the action of the type ZSM (TsVK) zeolites are difficult to explain from this point of view. In actual fact, on zeolites ZSM (TsVK), just as on zeolite Y, isoparaffins and alkylaromatic hydrocarbons are formed, while according to Shepelev and Jone [9] the formation of naphthalenes has been observed on zeolites of this type. In the present investigation it was also established that polycyclic compounds (coke) are formed on TsVK. These facts do not permit all the features in the selectivity of the action of zeolites of types Y and TsVK to be referred solely to steric hindrance. It must be assumed that a substantial influence on the selectivity of these catalysts is exerted by physicochemical factors and, namely, differences in the concentrations of centers accelerating the secondary conversions of the olefins.

The Al content of Y zeolites is 1.5-2 orders of magnitude higher than of TsVK. We have shown previously [10, 11] by ^{27}Al NMR spectroscopy that the states of the Al atoms in the zeolites of both types likewise differ substantially. Thus, in the highly decationized zeolites of type Y, $\sim$20% of the total number of Al atoms acquire octahedral coordination on hydration. On the basis of this fact, it was concluded [10, 11] that the Al atoms in zeolites Y after decationization depart from the framework into cationic positions. In the decationized and hydrated TsVK zeolites, the Al atoms present in an octahedral environment were not detected by the NMR method. Their concentration is apparently so low that the possibility of their detection is beyond the limits of sensitivity of the method used. On the basis of the results of IR and ^{27}Al NMR spectroscopy and catalytic experiments, it was concluded that the centers of acid–base action in Y zeolites in C–H bond cleavage, alkylation, and hydrogen redistribution reactions are $[\mathrm{Al{-}O{-}Si}]_3^- \cdot \mathrm{Al}^{3+}(\mathrm{OH}^-)\ldots\mathrm{H}^+$.

The poisoning of zeolite Y with coke leads to a decrease in the yield of hydrocarbons but does not affect the rate of conversion of methanol into dimethyl ether. This permits the assumption that the methanol → dimethyl ether stage and the subsequent dimethyl ether → hydrocarbons stages take place on centers of different natures. This, in its turn, permits all the conversions taken together to be assigned to the type of processes taking place by the mechanism of polyfunctional catalysis in which the yields of all intermediate products are not limited by the position of the thermodynamic equilibrium. In Weisz's classification [13], processes of this type are called "trivial polyfunctional catalysis." In this respect, there is a definite similarity between the conversion of methanol and the cracking of paraffins on zeolites. Results indicating identical compositions of the products of the two reactions (see Table 4) confirm this conclusion.

The conversion of methanol and the cracking of paraffins on zeolites can be described by a single scheme of transformations:



In both cases, the selectivity of the action is determined by the depth of the secondary transformations of the olefinic intermediate reaction products.

CONCLUSIONS

1. On zeolites HY, mordenite, and erionite and on a silica-rich zeolite (TsVK), the conversion of methanol takes place by a single pathway: methanol → dimethyl ether → olefins → → paraffins and monoaromatic hydrocarbons → polyaromatic hydrocarbons.

2. The selectivity of conversion on zeolites Y, mordenite, and TsVK at the same times of contact and the same partial pressures of methanol depends not only on geometric factors but also on the concentration of aluminium atoms in the cationic positions of the zeolite.

3. The conversion of methanol into hydrocarbons on zeolites, just like the cracking of paraffins, can take place by a mechanism of "trivial" bifunctional catalysis.

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