mixture. The H^+ concentration in the solution was maintained by adding an appropriate amount of CH_3COOH. Agitation of the reactor with a frequency of 500-700 min^{-1} ensured occurrence of the reaction in the kinetic region. The reaction products were analyzed for quinone and H_2O_2 contents iodometrically in the presence and in the absence of catalase according to [9].

The reaction rate was measured in the initial steps of the process, when the conversion of hydroquinone did not exceed 5%, with the amount of the absorbed O_2 depending linearly on the duration of the reaction. The oxidation of Q_9H_2 was studied spectrophotometrically in an isooctane—ethanol mixture (1:1) according to the increase of the quinone from Q_9 (λ 275 nm).

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CONCLUSIONS

Palladium clusters catalyze the oxidation of models of coenzyme Q_{10}, hydroquinone and ubiquinone Q_9H_2, by molecular oxygen.

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COMPARATIVE STUDY OF TRANSFORMATIONS OF C_3H_6 AND $i\text{-}C_4H_8$ ON ZEOLITES OF THE PENTASIL AND MORDENITE TYPE

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The transformations of lower olefins on high-silicon (HS) zeolites of the pentasil family were studied in [1, 2], but the correlation between the catalytic activity of these zeolites, the concentration of Al in them, and their acid properties have not been studied. The behavior of HS zeolites of other structural types, for example, dealuminated mordenites (DM), has been insufficiently studied in these reactions [3, 4], in contrast to isomerization of xylenes on HS zeolites with a different backbone composition and of different structural types [5-7].

The transformations of C_3H_6 and $i\text{-}C_4H_8$ on HSZ pentasils with a different concentration of Al in the backbone and on samples of DM of approximately the same composition were studied to compare the activity, stability, and selectivity of action of HSZ and DM zeolites in oligomerization and aromatization of these olefins and to determine the causes of the differences in the catalytic properties of zeolites of these structural types.

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EXPERIMENTAL

The H forms of HS zeolites (HHSZ) with a SiO_2/Al_2O_3 ratio of (x) = 37, 60, 104, and 280, the starting mordenite (HM, x = 10), and DM (x = 18, 32, 68, 240, and 300) were used in the study. The samples of DM were prepared by treating the Na form of mordenite (x = 10) with solutions of HCl according to [6], excluding the possibility of destruction of the crystal structure of the zeolite. The concentration of Na_2O in HHSZ and DM did not exceed 0.15 wt.%. For comparison, experiments were also conducted with a structural analog of HHSZ pentasil: silicalite (SL), with x = 600. The values of x will subsequently be indicated in parentheses after the arbitrary symbol for the zeolite.

The experiments with C_3H_6 and i-C_4H_8 of ~99% purity were conducted in a flow-type setup at 270 and 500°C and an olefin feed rate (U) of $1.0 \cdot 10^{-5}$-$5.0 \cdot 10^{-2}$ mole/sec•g. The methods of the experiments and the GLC analysis of the products of the reaction are reported in [8]. The catalytic activity of the zeolites in transformations of olefins was assessed by the initial rates of oligomerization* of the starting olefin (r_{ol}) [2] and with the total yield of C_6-C_{10} aliphatic and aromatic hydrocarbons.

DISCUSSION OF THE RESULTS

On all samples of pentasil and mordenite studied, including the starting HM (10), C_3H_6 and i-C_4H_8 are transformed into gaseous (C_2-C_5 alkanes and alkenes and small amounts of CH_4) and liquid (C_6-C_{10} aliphatic and aromatic hydrocarbons) products (Tables 1 and 2). Zeolite SL (600) is inactive in transformations of C_3-C_4 olefins.

It was shown in [2] on the example of one sample of type HSZ zeolite that a change in the molar feed rate significantly affects the selectivity of transformations of C_3-C_4 olefins. Our experiments showed (Fig. 1a, b) that with low values of the arbitrary contact time (1/U) and low conversions (20-25%), C_6-C_{10} aliphatic hydrocarbons are basically formed on both HHSZ and on DM. With an increase in 1/U, the yield of these products passes through a maximum, while the yield of aromatic hydrocarbons continuously increases, and it is significantly lower on DM zeolite (68) than on HHSZ zeolite (60). The character of these curves is in agreement with the hypothesis in [2] on the sequential transformation of lower olefins on pentasils into aromatic hydrocarbons through the stage of oligomerization [2]. This hypothesis is apparently also valid for zeolites of the mordenite type, although Fig. 1b at first glance significantly differs from Fig. 1a. This difference is due to the low aromatizing activity of DM in this range of values of 1/U. However, as 1/U increases to ~10^5 sec•g/mole, the yield of aromatic hydrocarbons gradually increases to ~13% with a simultaneous decrease in the yield of aliphatic hydrocarbons, as in the case of HHSZ zeolite.

As the data in Table 1, obtained in conditions which favor the formation of aromatic hydrocarbons, indicate, HHSZ pentasils exhibit the highest aromatizing capacity with high conversions of the starting olefin (80-90%). On zeolites DM (32)-DM (240), the yield of aromatic hydrocarbons is ~2.5 times lower than on pentasils. The lowest yields of these products are observed with the starting sample of decationized mordenite HM (10) and on zeolite DM (18), prepared by elimination of ~50% of the Al from the HM (10). The products of the reaction on mordenites contain 30-70% aliphatic hydrocarbons, while this value does not exceed 4 wt.% on pentasils.

The decrease in the concentration of Al in the backbone of pentasils corresponding to a value of x from 37 to 104 virtually does not alter the aromatizing capacity of HHSZ zeolites. The small decrease in the yield of aromatic hydrocarbons takes place only on HHSZ pentasil (280) with a very low concentration of Al. The same also applies to dealuminated mordenites, and a slight tendency toward a decrease in the yield of products of aromatization is observed with an increase in the values of x to 240 and 300.

With the low conversions of alkenes (20-25%) observed at 500°C and high values of U, the products of the reaction on pentasils and mordenites basically contain dimers of the starting olefin (80-90%) and almost no aromatic hydrocarbons. The initial rate of oligomerization of the olefin (r_{ol}) were calculated with the linear segments of the kinetic curves for comparing the activity of zeolites of these two structural types in transformations of C_3H_6 [2]. According to the data obtained (Table 3), the starting sample of HM (10) and zeolite DM (18) exhibit the lowest activity. The activity of the samples of DM prepared with a higher degree of de-

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*Here and below, they are in the form of processes which yield dimers and trimers of the starting olefin.

TABLE 1. Composition and Yield of C_6–C_{10} Hydrocarbons from i-C_4H_8 on Zeolites of type HSZ and Mordenite of Varying Composition (500°C, u = $1.0 \cdot 10^{-5}$ mole/sec•g)

Zeolite	Composition of C_6-C_{10} hydrocarbons, wt. %					Yield of hydrocarbons, wt. %	
	aromatic				aliphatic	aromatic	aliphatic
	C_6	C_7	C_8	C_9—C_{10}			
HM(10)	1.9	8,9	12.0	11.1	66.1	7.1	13,7
DM (18)	1.8	7.9	12.6	6.9	70.8	6.5	15.6
DM (32)	7.0	22.9	26.1	12.7	31.3	18.9	8.6
DM (68)	5.1	26.4	27.6	11.6	29.2	19.8	8.1
DM (240)	4.8	18.3	20.6	10.2	46.1	15.8	13.6
DM (300)	3.2	23.5	16.5	10.4	46.7	13.7	12,0
HHSZ (37)	15.0	49.2	30.0	3.8	2.0	48.0	1.0
HHSZ (60)	14.7	43.3	32.4	8.1	1.5	48.6	0,8
HHSZ (104)	15.4	45.8	30.2	7.0	1.6	48.7	0,8
HHSZ (280)	9.7	41.4	40.2	4.8	3.9	43.8	1.4

TABLE 2. Composition of Gaseous Products Formed from C_3H_6 at 500°C on DM (32) and HHSZ (37)

Zeolite	Conversion, %	Composition of gases, wt. %						
		CH_4	C_2	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	C_5
DM (32)	20	–	0.2	1.5	91.9	–	3.9	2,4
HHSZ (37)	20	–	0.6	2.2	89.2	–	4.9	3.0
DM (32)	80	0.7	5.0	11.2	30.0	15.2	28.6	8.7
HHSZ (37)	80	3.0	13.2	34.3	15.0	17.6	11.3	5.6

TABLE 3. Values of r_{ol} in Transformations of C_3H_6 above Pentasils and Mordenites of Varying Composition (500°C)

Zeolite	$\frac{Al}{Al+Si}$	$r_{ol} \cdot 10^4$, mole/sec·g)	Zeolite	$\frac{Al}{Al+Si}$	$r_{ol} \cdot 10^4$, mole/sec·g)
HM (10)	0.165	0.2	HHSZ (37)	0.054	13.4
DM (18)	0.100	0.1	HHSZ (60)	0.032	11.9
DM (32)	0.059	1.3	HHSZ (104)	0.019	13.6
DM (68)	0.030	1.2	HHSZ (280)	0.007	5.5
DM (240)	0.008	1.3	SL (600)	0.003	–
DM (300)	0.007	1.3			

alumination is ~7 times higher than the activity of the starting HM (10). All samples of DM are ~10 times less active in oligomerization of C_3H_6 than pentasils HHSZ (37)-HHSZ (104).

This relationship between the activity of pentasils and mordenites in the oligomerization of the olefins studied is also preserved at lower temperatures, i.e., in conditions favoring dimerization of the olefins. According to the data from the experiments with i-C_4H_8 at 270°C and conversion of the starting olefin of <20%, where the products of the reaction basically contain isomeric octenes (93-98%), the initial rate of oligomerization on pentasils is not a function of the concentration of Al in the zeolite and is $2.7 \cdot 10^{-4}$ mole/sec•g for all samples of HHSZ (Fig. 2a). For mordenites HM (10) and DM (32)-DM (240), r_{ol} is also not a function of the composition of the zeolite and is equal to $3.3 \cdot 10^{-5}$ mole/sec•g (Fig. 2b), i.e., ~10 times lower than for pentasils of similar composition.

Gaseous C_2-C_5 hydrocarbons are formed on pentasils and mordenites due to cracking and disproportionation reactions in the entire range of values of U studied, and the reactions take place on HHSZ to a much greater degree than on DM. The data in Table 2 indicate that with ~20% conversion of C_3H_6, these products have approximately the same composition and are characterized by a similar ratio of the concentrations of C_3-C_4 alkanes and olefins. With elevated conversion of the olefin (80%), the gaseous products formed on HHSZ and DM differ significantly in composition, and the products of the reaction on pentasil are characterized by a higher concentration of C_3-C_4 alkanes. The reactions of redistribution of hydrogen ap-

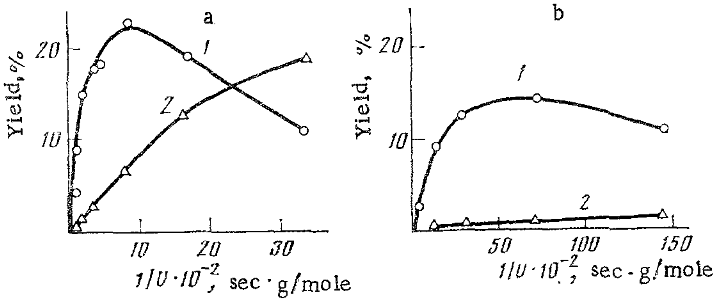

Fig. 1. Change in the yield of aliphatic (1) and aromatic (2) C_6-C_{10} hydrocarbons as a function of 1/U in transformations of C_3H_6 on zeolites HHSZ (37) (a) and DM (32) (b) at 500°C.

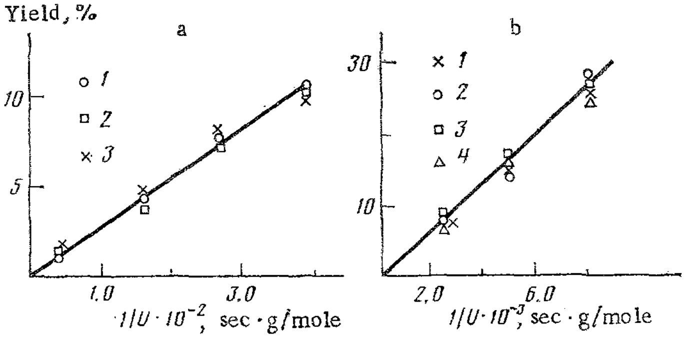

Fig. 2. Change in the yield of oligomers of i-C_4H_8 as a function of 1/U in transformations of this olefin on pentasils: a) HHSZ (37) (1), HHSZ (60) (2), HHSZ (104); b) HM (10) (1), DM (32) (2), DM (68) (3), DM (240) (4) at 270°C.

parently also take place less intensely on DM, which exhibits lower activity in the aromatization of olefins than pentasils.

Let us examine the possible causes of the differences in the catalytic properties of zeolites of the pentasil and mordenite type. The catalytic activity of zeolites is usually related to the presence of acid sites of different strength on their surface, and the number of these sites is determined by the concentration of Al in the backbone of the zeolite. For this reason, it could be hypothesized that differences in the acid properties of the surface of these zeolites could be one of the causes. However, based on the data from the calorimetric study of the acidity of HS zeolites by determining the heats of adsorption of ammonia, these differences are not very large and decrease as the concentration of Al in the backbone of the pentasils and mordenites decreases [9, 10]. The data obtained in the present study (see Table 3) show that zeolites HM (10) and DM (18), characterized by a high concentration of strong acid sites [1, 7, 9, 10], exhibit low activity in the oligomerization reaction. This is apparently related to the fast deactivation of these zeolites during operation. A significant decrease in the concentration of Al (i.e., a decrease in the concentration of acid sites) in the backbone of pentasils and mordenites has almost no effect on their activity in the formation of C_6-C_{10} aliphatic hydrocarbons. Such pentasils and mordenites as HHSZ (104), HHSZ (280), DM (240), and DM (300), which have a very low concentration of Al, even exhibit high activity in this reaction. Nevertheless, the sample of silicalite SL (600) containing only traces of Al did not exhibit marked activity in transformations of C_3-C_4 olefins in a wide range of temperatures and molar feed rates. This suggests that a small number of weak acid sites in the zeolites is sufficient for oligomerization of lower olefins. The reaction of aromatization of such olefins, for which stronger acid sites are required [11], is slightly more sensitive to a change in the SiO_2/Al_2O_3 ratio in the backbone of the zeolites. A certain tendency toward a decrease in the yield of aromatic hydrocarbons is actually observed with a very low concentration of Al as in zeolites HHSZ (280) and DM (300), for example (see Table 1).

Since the acid properties of HS pentasils and dealuminated mordenites are approximately the same, the differences in the catalytic properties of these zeolites can be due to the

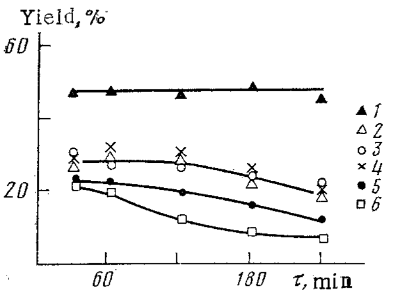

Fig. 3

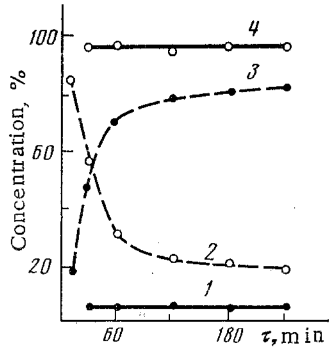

Fig. 4

Fig. 3. Change in the total yield of C_6-C_{10} hydrocarbons in time in transformations of i-C_4H_8 on type HHSZ (1) and mordenite zeolites: DM (32) (2), DM (68) (3), DM (240) (4), DM (18) (5), HM (6) at 500°C.

Fig. 4. Change in the concentration of aliphatic (1, 3) and aromatic (2, 4) C_6-C_{10} hydrocarbons in time in the products of transformation of i-C_4H_8 on zeolites HHSZ (37) (1, 4) and DM (32) (2, 3) at 500°C and $U = 1.0 \cdot 10^{-5}$ mole/sec•g.

features of their structure. In particular, it is known [12, 13] that zeolites of different structural types exhibit different stability of operation in the conditions of a catalytic reaction. The data in Fig. 3 show that the total yield of C_6-C_{10} hydrocarbons on pentasils HHSZ (37)-HHSZ (240) remains at a high level (~50%) during the entire experiment. On dealuminated mordenites in analogous conditions, the yield of liquid hydrocarbons decreases by ~1.5 times after 4 h. The starting zeolite HM (10) is characterized by the lowest stability. Elimination of Al from the backbone of mordenites slightly increases their stability and activity. However, beginning with the sample of DM (32), an increase in the degree of dealumination does not result in a change in either the activity or the stability of the mordenites, and zeolites DM (18)-DM (240) are significantly inferior to pentasils in this respect.

As a consequence, dealumination, which permits obtaining HS mordenites of the same chemical composition as pentasils, only results in a change in the acid properties of the zeolites but has almost no effect on their structure. As shown by EPR, the structure of the zeolites determines the nature and localization of the coke formed during the catalytic reaction [13-15]. In the case of pentasils, the coke is localized on the external surface of the crystallites. The active sites located inside the pores of pentasils remain accessible to the reacting molecules, and zeolites of this type are not deactivated during operation. In contrast to pentasils, strongly chemisorbed molecules of aromatic compounds of the type of diphenylalkanes and condensed polynuclear structures accumulate in the pores of mordenites and block the active sites of the zeolite. It was shown on the example of transformations of i-C_4H_8 on zeolite DM (32) (Fig. 4) that during the deactivation of this catalyst, the ratio of C_6-C_{10} aliphatic and aromatic hydrocarbons changes significantly in the products of the reaction. Primarily aromatic hydrocarbons are formed in the first 15-30 min of the experiment, and their distribution virtually does not differ from the distribution observed in transformations of i-C_4H_8 on HHSZ pentasils. However, the concentration of aliphatic hydrocarbons increases by ~3 times 60 min after the experiment begins, and the concentration of products of aromatization correspondingly decreases. These results indicate that in the deactivation of mordenite due to the formation of coke, the stronger acid sites where the aromatization reaction takes place are blocked first.

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CONCLUSIONS

1. The properties of high-silicon pentasils and mordenites of varying composition were compared in transformations of propylene and isobutylene and it was shown that mordenites are ~10 times less active in the oligomerization reaction; they are also less active in the reactions of aromatization and redistribution of hydrogen and are deactivated during operation. Dealumination slightly increases the activity and stability of mordenites.

2. The activity of pentasils and mordenites in oligomerization of olefins virtually does not change with an increase in the SiO_2/Al_2O_3 ratio from ~30 to 280-300, while the aromatization reaction is more sensitive to a change in the concentration of Al in the backbone of the zeolites with $SiO_2/Al_2O_3 \simeq 300$, the yield of aromatic hydrocarbons decreases.

3. The differences in the catalytic properties of high-silicon pentasils and mordenites in transformations of lower olefins are primarily due to the features of the structure of these zeolites, which determine their different stability in the conditions of a catalytic reaction.

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