EFFECT OF COMPOSITION AND CALCINATION TEMPERATURE
ON THF CATALYTIC PROPERTIES OF ULTRAHIGH-SILICA
ZEOLITE IN ISOBUTYLENE CONVERSIONS

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We have shown earlier in [1, 2] that domestic ultrahigh-silica zeolites (UHSZ) of the ZSM-11 type display high catalytic activity in reactions of C_3 to C_4 olefins, especially in their aromatization. This paper presents data on a study of the relationship between Na content, calcination temperature (T_c), and the catalytic properties of UHSZ in the conversion of isobutylene (IB) to aromatic and aliphatic hydrocarbons. The results of catalytic tests agree with data on the sorption capacity of zeolites for water obtained by the thermographic method.

EXPERIMENTAL

Five samples of UHSZ were used, differing in Na_2O content* and SiO_2/Al_2O_3 ratio (x). The properties of the catalysts (Ct) are shown in Table 1. Zeolites N-I and N-III were prepared by decationization [2] of samples (I) and (III), respectively.

The tests with IB were performed at 320 and 500°C, enabling us to obtain liquid catalyzates enriched with aliphatic or aromatic hydrocarbons, respectively [2]. These tests lasted 2 h. The procedures for the tests and for reaction product analysis have been described in [3]. All catalyst samples were calcined at 500°C before the test in a current of air (1 h). Catalysts (I) and N-III were also calcined at 700-1000°C in 100-deg steps.

All the UHSZ specimens were examined thermographically by a procedure from [4] on a PRT-1000M instrument in a current of N_2 (3.6 liters/h) at a heating rate of 20 deg/min, using a Ct charge of about 0.30 g. In determining water-sorption capacity, the zeolite samples ($\sim$ 6 mg) were calcined at various temperatures, kept in a hydrostat (p_{H_2O} 17.5 torr) to constant weight ($\sim$ 2 days), and then the weight loss was determined (Δm) on a Perkin-Elmer thermogravimetric apparatus in a current of N_2 (0.6 liter/h).

DISCUSSION OF RESULTS

The results of the tests with IB at 500°C with Ct samples calcined at the same temperature are shown in Table 2; for Ct (I) and (II), which are close in their x values but differ in Na_2O content, the conversions of IB and the liquid catalysate yields are approximately identical. However, in the presence of Ct (I), the liquid catalysate contains > 70% aromatic hydrocarbons (AH), whereas their concentration is $\sim$45% for Ct (II). Catalyst (III) is considerably less active than (I) and (II): IB conversion is 57.6% and the liquid catalysate yield, containing < 5% AH, was about 15%, calculated on the IB passed through. The highest IB conversion ($\sim$ 99%) and the highest catalysate yield ($\sim$ 50%) and AH yield ($\sim$ 50%) were obtained in the presence of Ct N-I and N-III.

These data indicate that the Ct studied can be placed in the following increasing order of IB aromatization: (III) $\ll$ (II) < (I) < N-I < N-III, which corresponds to decreasing Na_2O content in the Ct. Of course, this order reflects the relationship between the Na_2O content of the Ct and its activity only qualitatively. A quantitative expression of this relationship would be much more complicated. In fact, Ct (I) for instance contains at least seven times as much Na_2O as Ct N-I, and (I) is about 1.5 times less active in IB aromatization. The Na_2O content of Ct (II) is about 1.6 times that of Ct (I) (36% relative) and its aromatization activity exceeds the

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* The Na and UHSZ contents were determined by flame photometry in the All-Union Petroleum Processing Scientific-Research Institute.

TABLE 1. Characteristics of Zeolites Employed

Zeolite	Conditional designation	SiO_2/Al_2O_3 (x)	Na_2O content, %
Na — UHSZ	(I)	70,5	0,7
Na — UHSZ	(II)	73,2	1,1
Na — UHSZ	(III)	60,3	1,3 *
N — UHSZ	N-I	70,5	0,1
N — UHSZ	N-III	60,3	—

* In addition to Na_2O, zeolite (III) also contained 0.25% Fe_2O_3. This impurity was absent in the other zeolites.
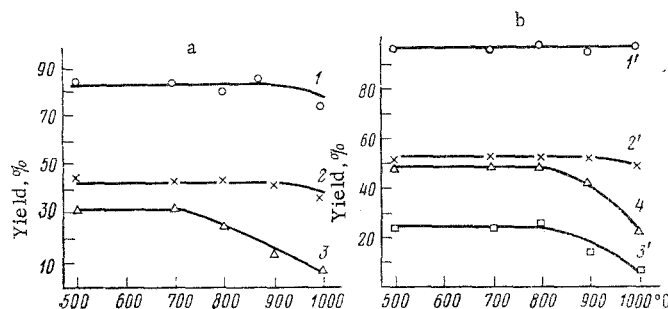

Fig. 1. Effect of T_C of UHSZ on liquid catalysate yield (1, 2, 1', 2') and aromatic hydrocarbon yield (3, 3', 4) in tests with isobutylene at 320°C (1, 1', 3') and 500°C (2, 3, 2', 4) on catalysts (I) (a) and N-III (b).

activity of Ct (I) by a factor of at least 1.7. The IB aromatization activity of Ct (III) is lower than that of Ct (II) by a factor of about 26, although these samples differ in Na_2O content by only ~ 17 relative % (1.2 times). Obviously, the very low activity of Ct (III) is caused not only by its higher Na_2O content, but also by additional poisoning due to the Fe_2O_3 impurity. Note that decationization of Ct (III) brought about complete removal of these oxides and resulted in the most active Ct N-III.

Lowering the Na_2O concentration in the UHSZ affects the AH yield much more than it does the yield of liquid catalyzate, whose aliphatic reaction product level decreases at the same time. Apparently, Na^+ ions essentially occupy those portions of the active UHSZ surface that are responsible for AH formation.

Figure 1 shows the data obtained in studying the effect of T_C on the catalytic activity of Ct (I) (a) and Ct N-III (b) at 320 and 550°C and indicates that on Ct (I) the liquid catalysate yield is practically independent of T_C at both temperatures and decreases only slightly after the sample has been calcined at 1000°C. The yield of AH formed on Ct (I) only at 500°C, decreases from 31.5 to 25% after calcination of the zeolite at 800°C, but after calcination at 1000°C it falls to 5 to 6%. Catalyst N-III is less subject to the influence of T_C. Calcination of N-III even at 1000°C does not affect the liquid catalysate yield at 320°C and decreases it only from 51 to 47% at 500°C. At the same time, the AH yield at 320 and 500°C drops only after calcination of the Ct at 900 and 1000°C. Moreover, the aromatization activity of the Ct is not reduced during the test at 500°C with IB saturated with water vapor (at 20°C).

Along with the decrease in total AH yield, calcination of Ct (I) and N-III at 1000°C leads to an almost twofold increase in the p-xylene content of the liquid catalysate and accordingly to a decrease in the concentration of m- and o-xylene (Table 3). We observed the same change in the ratio of xylene isomer concentrations in the catalysate in tests with n-butene over Ct N-III calcined at 1000°C.

We have also established that as T_C increases, the content of gaseous IB conversion products decreases considerably. Thus, for Ct N-III, as T_C increases from 700 to 1000°C, the content of saturated hydrocarbons in the gas decreases and the olefin content increases (Fig. 2a, b). Similar observations were made with Ct (I). Evidently, as T_C increases, leading to a decrease in the dehydrocyclization activity of the UHSZ, its activity in hydrogen redistribution reactions also decreases.

DTA curves of all the UHSZ were obtained in a thermographic study. The DTA curves of previously uncalcinated Ct samples contained two endothermic peaks with maxima at 180 and 450°C. The former peak

TABLE 2. Conversion of Isobutylene in the Presence of UHSZ Calcined at 500°C (500°C, $v = 500 \ h^{-1}$)

Catalyst	Liquid catalysate yield, % based on the olefin		Aromatic hydrocarbon yield, % based on the olefin		Con-version, %	Liquid catalysate composition, %							
								xylenes			ethyl-benzene	C_9-C_{10} alkyl-benzenes	aliphatic hydro-carbons
	passed through	reacted	passed through	reacted		benzene	toluene	p-	m-	o-			
I	43,8	50,8	34,5	35,3	89,2	6,0	20,5	7,2	16,3	6,2	3,6	12,1	28,1
II	40,1	45,4	18,1	20,5	88,3	1,8	11,9	5,0	10,8	3,4	3,2	9,0	54,9
III	15,0	26,1	0,7	1,2	57,6	0,2	1,6	0,4	1,2	0,5	0,4	0,5	95,5
N-I	49,4	50,1	48,6	49,4	98,6	14,7	43,2	7,3	16,1	6,6	2,4	8,1	1,6
N-III	40,2	50,8	49,8	50,4	98,8	19,2	41,2	7,1	16,1	6,5	2,3	6,9	0,7

TABLE 3. Conversion of Isobutylene on UHSZ Calcined at 500–1000°C (500°C, $v = 500 \ h^{-1}$)

Catalyst	Tc, °C	Aromatic hydrocarbon yield % based on olefin	Aromatic hydrocarbon distribution, %							
			benzene	toluene	xylenes			ethyl-benzene	C_9-C_{10} aromatics	
					p-	m-	o-			
I	500	34,5	8,3	28,5	10,0	22,7	8,6	5,0	16,8	
	800	25,0	7,0	31,0	9,5	20,1	5,6	6,0	20,8	
	900	13,6	5,7	34,0	12,2	21,2	6,2	6,0	17,9	
	1000	9,4	7,7	29,1	23,8	11,5	3,1	6,1	16,5	
N-III	500	49,8	19,3	41,5	7,2	16,2	6,5	2,3	6,9	
	800	50,4	11,7	42,2	9,3	18,3	7,6	3,3	7,7	
	1000	24,6	4,7	42,2	18,9	19,1	4,2	5,8	5,1	

TABLE 4. Sorption Capacity of UHSZ vs. Calcination Temperature

T_c, °C	Water sorption capacity, % of zeolite sample weight				
	(I)	(II)	(III)	N-I	N-III
Before calcination	9,8	10,2	12,5	—	—
500	—	—	—	5,4	4,8
700	3,2	4,5	2,7	2,4	3,0
800	2,1	3,4	1,4	0,9	1,3
1000	0,8	0,9	0,5	0,7	0,8
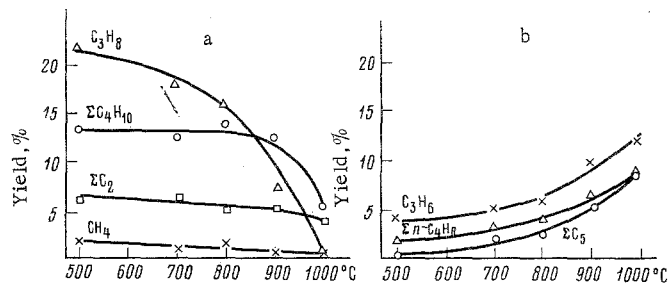
Fig. 2. Effect of T_C of zeolite N-III on the change in content of saturated (a) and unsaturated (b) hydrocarbons in the gaseous conversion products of isobutylene at 500°C.

represents the dehydration of the zeolite and the latter desorption of the products of an alkylammonium base captured by the zeolite during the synthesis. The thermograms of samples first calcined at 500-900°C, as well as Ct N-I and N-III, which had been calcined at 500°C while they were being prepared by decationization of Ct (I) and (III), showed only one peak, the dehydration peak. The thermogravimetric analysis results (Fig. 3 and Table 4) show that the highest value of Δm is obtained for the previously uncalcined Ct (I)-(III) samples, since not only water is desorbed from them but organic substances as well. As T_C increases, Δm for each sample gradually decreases, which is evidence of a decrease in the sorption capacity of the zeolite for water or an increase in their hydrophobicity.

Thus, the catalytic properties of UHSZ depend on both the sodium content and T_C; as the Na_2O content of the zeolite is decreased, its catalytic activity increases, especially the activity in the dehydrocyclization reaction, and the effect of T_C on the catalytic properties decreases; when the UHSZ is calcined, it becomes dehydrated and as T_C increases its hydrophobicity rises; the effect of T_C on the zeolite's catalytic properties begins to be seen only after calcination at 800°C and above; as T_C increases, the aromatization activity of the UHSZ and its activity in the hydrogen redistribution reaction decrease; reactions leading to formation of a mixture of C_6-C_8 aliphatic hydrocarbons (oligomerization of IB, isomerization of the oligomers) are practically independent of T_C; after zeolite calcination at 1000°C, their selectivity for the formation of p-xylene rises. Consequently, the change in the catalytic properties of UHSZ caused by Na_2O and T_C consists essentially of a change in selectivity for AH formation.

According to current hypotheses on the nature of catalytic UHSZ activity, the role of the active centers therein can be fulfilled by the OH groups bound to the Si atoms and by the aluminum ions present in the zeolite's crystal lattice [5-8]. Our data on the effect of T_C on IB conversion in the presence of UHSZ lead us to conclude that there is a link between the catalytic activity of such a zeolite and the degree of dehydroxylation of its surface. However, the change in catalytic properties (drop in selectivity for aromatization with retention of total activity) is observed only in Ct calcined at 800-1000°C containing a total of 20-30% water based on the amount present in the zeolite after calcining at 500°C (Fig. 4, curve 1). Consequently, the total activity of these Ct is apparently due to a small number of OH groups, whose removal is accomplished only by calcination at high temperatures. It is possible that these OH groups themselves constitute that part of the zeolite's surface hydroxyl shell which plays the role of active acid centers.

The results we have obtained agree well with IR-spectroscopy data from a study of zeolite H-ZSM-5 dehydroxylation [5], which showed that as T_C increases from ~ 470 to 800°C, the intensities of the OH-group absorption bands at 3605 and 3720 cm^{-1} decrease (see Fig. 4, curves 2 and 3). Moreover, the OH groups
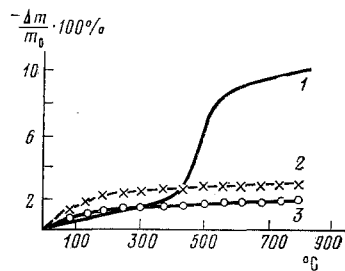
Fig. 3   Fig. 4

Fig. 3. TGA curves of Ct (I) (charge 6.5 mg, heating rate 20°C/min in a current of 0.6 liter/h N_2); 1) uncalcined sample; 2) calcined at 700°C; 3) calcined at 800°C.
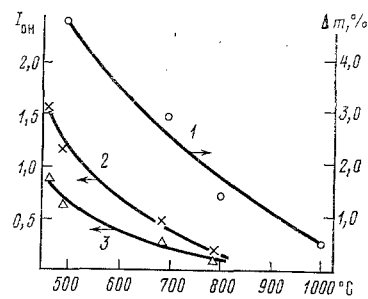
Fig. 4. Change in the amount of water sorbed by zeolite N-III after calcination at 500-1000°C (1) and change in intensity of the absorption bands of the two types of OH groups (I_{OH}) in the IR spectrum of zeolite H-ZSM-5 calcined at 470-800°C (2 and 3, plotted from data in [5]).

corresponding to the Bronsted acid centers (λ_{max} 3605 cm^{-1}), whose number is small even in uncalcined zeolite [7] ($\sim 3 \cdot 10^{19}$ groups/g), are removed irreversibly on calcination.

It is suggested in [7, 8] that the Bronsted acid centers of UHSZ participate in the olefin oligomerization reaction. However, according to our results, this reaction is apparently independent of the concentration of such centers. Consequently, it can be assumed that the oligomerization and dehydrocyclization reactions proceed at different active centers and OH groups probably also enter into the composition of the active dehydrocyclization center. The calcination of zeolite above 800°C can cause destruction of the active centers due to the irreversible removal of OH groups. At the same time, the dehydrocyclization activity of UHSZ may be related to the presence of Al ions which serve as electron-acceptor centers and, as shown by the x-ray photoelectron spectroscopy (XPES) method [5], are partially removed from the zeolite lattice on calcination.

The increase which we noted above in selectivity of zeolite Ct for formation of p-xylene after calcination at 900-1000°C can be explained by changes in the zeolite pore structure which are not observed in x-ray diffraction analysis [6] but lead to some decrease in the diameter of the zeolite channels and produce diffusion difficulties for m- and o-xylenes.

The hypotheses discussed above do not contradict current information on UHSZ structure and the nature of their catalytic activity. However, they require further experimental verification.

CONCLUSIONS

1. As the Na_2O content of ultrahigh-silica zeolites increases, the yield of liquid catalysate and aromatic hydrocarbons from isobutylene at 500°C decreases.

2. As the temperature of preliminary calcination increases from 500 to 1000°C, the water-sorption capacity of ultrahigh-silica zeolites gradually decreases. Calcination at 800-1000°C hardly affects the total zeolite activity but decreases its activity in the dehydrocyclization and hydrogen redistribution reactions. After zeolite calcination at 1000°C, an increase in selectivity for p-xylene formation is observed.

3. The change in the catalytic properties of ultrahigh-silica zeolites after calcination at 800-1000°C is related to the removal of a small number of OH groups which enter into the composition of the active centers. The selectivity increase for p-xylene formation can be attributed to some changes in the pore structure at high temperature which make the diffusion of m- and o-xylene difficult.

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REGIOSELECTIVE REACTION OF ALKYL DIAZOACETATES
WITH TRIMETHYLSILYLISOPROPENYLACETYLENE AND
CHEMICAL CONVERSIONS OF THE RESULTING ESTERS OF
# TRIMETHYLSILYLETHYNYLMETHYLCYCLOPROPANE-
CARBOXYLIC ACID

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The reaction of alkyl diazoacetates (ADA) with conjugated enynes with an internal triple bond proceeds regioselectively both with respect to the triple and the double bond [1]. The reaction of ADA with enynes with a terminal triple bond such as isopropenylacetylene (I) affords only pyrazoles, the products of 1,3-dipolar addition to the $C \equiv C$ bond [2]. It was therefore of obvious interest to develop a method of synthesis from terminal enynes of ethynylcyclopropanecarboxylate esters, which could be of value as insecticides and drugs [3].

Since the introduction of the trialkylsilyl substituent substantially reduces the reactivity of the triple bond in reactions with ADA [4], it would be expected that similar deactivation of the triple bond in conjugated enynes would direct the attack of ADA on the double bond to form the cyclopropane adduct, from which the Me_3Si group could be removed by alkaline hydrolysis of the Si—C bond [5].

It has been found that reaction of ADA in the presence of $CuSO_4$ at 100-110°C with an excess of trimethyl-silylisopropenylacetylene (II), obtained in 68% yield by the silylation of (I), affords the alkyl esters of the isomeric 2-methyl-2-trimethylsilylethynylcyclopropanecarboxylic acid (III) in yields up to 80%. Products of the addition of alkoxycarbonylcarbenes to the triple bond, or diadducts of the carbenes to the double and triple bonds, were not found, enabling a threefold excess of the enyne (II) to be employed.

R = Me(a), Et(b).
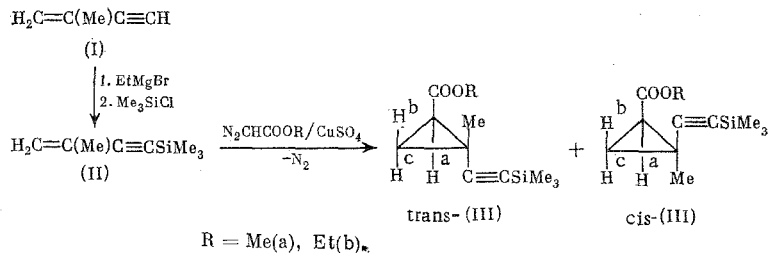
Thus, the introduction of the Me_3Si group reduces the reactivity of the triple bond in the enyne to such an extent as to enable the ADA to react selectively under the usual conditions with enynes exclusively at the double bond.