show a low activity in the aromatization reaction of C_3-C_4 olefins at 450-550°C at times of contact of 2-14.4 sec. The zeolites studied become rapidly deactivated as the result of intense coke formation.

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AROMATIZATION OF 1-OCTENE IN THE PRESENCE OF CATALYSIS BASED ON ULTRAHIGH-SILICA ZEOLITE AND ALUMINUM OXIDE

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Ultrahigh-silica zeolite (UHSZ) is known to be highly active in the aromatization of propylene and isobutylene [1, 2], and ethylene as well [3]. The liquid products have been found to contain, besides aromatic hydrocarbons, a considerable amount of C_6-C_8 olefins and paraffins. The only information on the relative activity of UHSZ in the aromatization of aliphatic hydrocarbons C_6 and higher is contained in patent data for zeolites of the ZSM type [4].

In our papers on the aromatization of olefins [1, 2, 5], we studied the catalytic activity of the original form of UHSZ* and of catalysts based on this zeolite containing Pt, Rh, and V_2O_5, in the aromatization of 1-octene. For comparison, we obtained data on the known dehydrocyclization catalysts $Pt-Al_2O_3$, $V_2O_5-Al_2O_3$, and Al_2O_3 as well, which have significant catalytic activity under the adopted conditions.

EXPERIMENTAL

As catalyst (Ct), we used an UHSZ synthesized by a procedure in [6], γ-Al_2O_3 (fluorinated and unfluorinated), and also catalysts prepared by impregnating UHSZ and Al_2O_3 with aqueous solutions of H_2PtCl_6, $RhCl_3$, and $VOSO_4$, with subsequent drying at 120°C and calcination at 500°C. The catalysts containing Pt and Rh were reduced in a current of H_2 at 550°C for 8 h and were purged with He before the test. All the other catalysts were treated before the test successively with air and He at 550°C.

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* The original UHSZ form is a zeolite which has not been decationized.

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TABLE 1. Aromatization of 1-Octene in the Presence of Catalysts Based on UHSZ and Al_2O_3

Catalyst	T., °C	Aromatic hydrocarbon yield, % *	Composition of aromatic products			
			benzene	alkylbenzenes		
				C_7	C_8	C_9—C_{10}
UHSZ	400	8,1	Traces	26,5	44,8	28,7
	500	13,8	10,3	37,5	39,7	12,5
	550	16,0	16,0	45,2	30,6	8,1
5% V_2O_5 – UHSZ	400	14,6	Traces	22,4	57,4	20,2
	500	28,3	8,3	35,8	46,1	9,8
	550	30,4	16,6	34,7	40,6	8,1
0,5% Rh – UHSZ	500	22,9	10,0	42,0	38,1	9,9
0,5% Pt – UHSZ	500	35,3	11,2	39,1	42,6	7,1
Al_2O_3	550	15,6	5,1	31,5	47,5	15,9
5% V_2O_5 – Al_2O_3	550	51,9	8,0	13,3	78,7	Traces
Al_2O_3(F)	500	12,7	1,4	17,4	49,0	32,2
1% Pt – Al_2O_3(F)	500	43,4	19,7	25,5	46,7	8,1

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* Based on the 1-octene passed through.

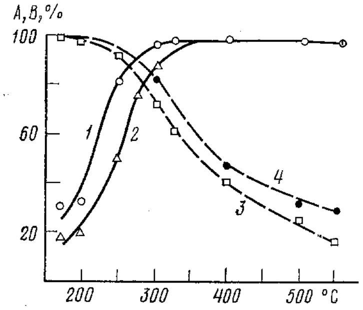


Fig. 1

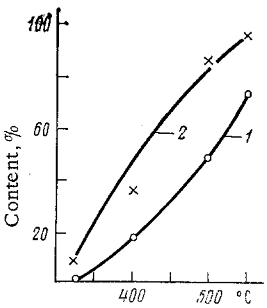


Fig. 2

Fig. 1. Conversion of 1-octene (A, 1, 2) and liquid catalysate yield (B, 3 and 4) vs. temperature. Catalyst: UHSZ (1, 3) and 5% V_2O_5–UHSZ (2, 4).

Fig. 2. Aromatic hydrocarbon content of aromatization products of 1-octane vs. temperature. Catalyst: UHSZ (1) and 5% V_2O_5–UHSZ (2).

The tests were performed in a continuous reactor. The hydrocarbons were fed in a current of He with the aid of a thermostatted saturator (feed space velocity of 1-octene was 80 h^{-1}). According to gas–liquid chromatography (GLC) data, the impurities in the 1-octene synthesized by a procedure in [7] were not greater than 0.01%. GLC analysis of the liquid reaction products was carried out in a capillary column with squalane.

DISCUSSION OF RESULTS

UHSZ displays high activity at 175 to 250°C in double-bond displacement reactions in 1-octene without significant structural isomerization. The variation of the yield of linear isomerization products to 250°C shown in Fig. 1 corresponds in fact to the 1-octene conversion curve. The liquid catalysate yield is ~100% at 175 to 250°C. Above 250°C, the yield of linear isomers falls to 10%, whereas the conversion of 1-octene continues to increase and approaches 100% at 300°C and the yield of liquid catalyzate drops to 75%; this is related to cracking of both the original olefin and its isomerization products (see Fig. 1, curve 3). At 300°C, the liquid catalyzate contains C_6-C_7 aliphatic hydrocarbons in addition to C_8 olefins.

Results for V_2O_5–UHSZ are shown in Fig. 1 for comparison. The addition of V_2O_5 leads to a decrease in UHSZ activity in the double-bond displacement reaction (the yield of 1-octene linear isomers decreases at 250°C from 85 to 55%) without changing selectivity. Above 275°C, the 1-octene conversion is ~100% and the linear isomer yield drops to 20%. A further increase in temperature is accompanied, as in the case of UHSZ, by structural isomerization and cracking of isomeric octenes, leading to a drop in the liquid catalyzate yield.

In the presence of UHSZ at 400°C, a significant amount of aromatic hydrocarbons is formed from 1-octene (benzene, toluene, C_8-C_{10} alkylbenzenes); the content of these aromatic hydrocarbons in the liquid

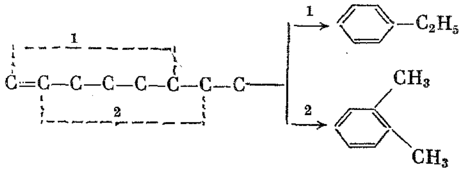
TABLE 2. Composition of the C_8-C_9 Alkylaromatic Hydrocarbons Formed from 1-Octene, %

Catalyst	T, °C	Xylenes			Ethylbenzene	Styrene	p/m ethyltoluene isomer ratio
		p-	*m*-	*o*-			
UHSZ	400	29,5	46,0	10,0	14,5	–	0,71
	500	23,9	45,1	16,9	14,1	–	0,77
	550	21,9	47,0	18,0	13,1	–	0,83
5% V_2O_5 – UHSZ	400	81,7	9,1	1,7	7,5	–	9,10
	500	70,8	13,3	2,4	13,3	0,2	6,70
	550	63,3	13,5	3,6	17,5	2,1	4,80
0,5% Rh – UHSZ	500	22,9	49,1	18,6	9,4	–	0,77
0,5% Pt – UHSZ	500	24,6	49,6	16,9	8,9	–	0,80
Al_2O_3	550	19,2	53,1	19,5	8,2	–	0,56
5% V_2O_5–Al_2O_3	550	6,0	13,1	46,4	28,4	6,1	–
Al_2O_3(F)	500	17,8	60,0	19,0	3,2	–	0,50
1% Pt–Al_2O_3(F)	500	18,6	54,4	23,8	3,2	–	0,43

catalysate increases sharply as the temperature rises (Fig. 2, curve 1). Modification of the UHSZ by the addition of V_2O_5 brings about a significant increase in the content of the aromatic products (curve 2). The data in Table 1 indicate that in the presence of UHSZ a temperature rise from 400 to 550°C increases the benzene and toluene concentration in the 1-octene aromatization products but decreases the C_8-C_{10} alkylbenzene concentration. At the same time, the o-xylene (OX) content of the C_8 aromatic fraction increases and the p-xylene (PX) content decreases, but the m-xylene (MX) and ethylbenzene (EB) contents hardly change. The same tendencies are also found for V_2O_5–UHSZ (Table 2).

Adding Pt, Rh, and V_2O_5, which have dehydrogenation properties, to either UHSZ or Al_2O_3 brings about an increase in the aromatic hydrocarbon yields. Moreover, the distribution of C_8 alkylbenzenes (see Table 2) depends strongly on the catalyst used. Although the aromatic C_8 fraction contained 60-80% PX in the presence of V_2O_5–UHSZ and the basic products of 1-octene in the presence of V_2O_5–AL_2O_3 were OX, EB, and styrene, the major fraction of the C_8 alkylbenzenes (45-60%) was MX in all the other Ct studied. The formation of the p-isomer predominantly on V_2O_5–UHSZ was also observed for C_9 alkylbenzenes (the p- and m-ethyltoluene concentration ratio increased as a result of an approximately 6- to 10-fold modification).

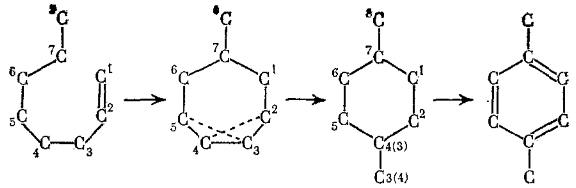
Let us consider possible reasons for the predominant formation of one or another isomeric xylene on a Ct studied. According to the mechanism of direct C_6-cyclization of 1-octene [8], the major aromatization products should be OX and EB:



Scheme 1

Apparently, the reaction proceeds according to this scheme in the presence of V_2O_5–Al_2O_3. This is confirmed by the composition of the C_8 alkylbenzene fraction, > 80% of which is accounted for by OX, EB, and styrene, respectively 46, 28, and 6%. However, Scheme 1 is not helpful in explaining the predominant formation of MX on most of the Ct studied, since the latter cannot be obtained by direct C_6-cyclization of 1-octene. The increased MX content may be related either to structural isomerization of the original olefin before cyclization or to isomerization of OX, the primary product of 1-octene aromatization. Note that for all Ct that do not contain V_2O_5, the C_8 alkylbenzene composition is close to the equilibrium composition [9].

It is harder to explain the predominant formation of PX in the presence of V_2O_5–UHSZ. It might be assumed that the aromatization reaction proceeds on a Ct atom by some mechanism, for instance by the scheme proposed in [10, 11]. This mechanism calls for intermediate formation of a methylcycloheptane ring (I) and subsequent narrowing of the ring:



Scheme 2

However, all the other C_8 alkylbenzenes can be formed by this mechanism along with PX. Actually, PX should be obtained only when a seven-membered ring narrows by rupture of bonds 2–3 or 4–5, as shown in Scheme 2. If the ring constriction proceeds by some other way, the reaction products can be both OX and MX or EB. In turn, these alkylbenzenes can undergo mutual transformation by isomerization. Inasmuch as selective splitting of compound (I) exclusively at the 2–3 (or 4–5) bond is of low probability, the mechanism considered cannot serve as a convincing explanation of the predominant formation of PX from 1-octene in the presence of V_2O_5–UHSZ. It can be assumed that in this case selective formation of PX is caused by a reaction that occurs in the internal diffusion region, where the reaction rate is limited by diffusion of product or reagent molecules within the zeolite Ct pores. Since the size of the entrance apertures of UHSZ is commensurable with the size of the reacting molecules, it is extremely probable that the reaction may take place by an internal diffusion mode. Examples of diffusional retardation of reactions on a zeolite Ct are given in [12, 13].

In the dehydrogenation cyclization of 1-octene on V_2O_5–UHSZ, it is more probable that the reaction rate is limited by diffusion of aromatic product molecules from the zeolite pores, since C_8-C_{10} alkylbenzenes show a larger kinetic diameter than the original olefin. Moreover, the steric configuration of the molecules of the original substance and the reaction products may also play some role. The measurements we made of PX, OX, and MX sorption on UHSZ and V_2O_5–UHSZ showed that adding V_2O_5 reduces the sorption capacity of zeolite and the initial adsorption rate of xylenes. Furthermore, the values of the sorption properties measured for both Ct decrease in the order PX > MX > OX. These results agree with data from [14], according to which the sorption capacity of type ZSM-5 zeolites and the sorption rate are greater for PX than for OX.

The collection of catalytic and adsorption data enables us to suggest relatively fundamental reasons for the anomalous distribution of C_8-C_9 alkylbenzenes on aromatization of 1-octene in the presence of UHSZ modified by V_2O_5. Adding the latter oxide apparently causes blockage of a portion of the zeolite pores. The change in the pore structure of the UHSZ can in turn retard the reaction or its individual stages as a result of diffusion of product molecules from the Ct pores. The internal diffusion mode comes into being because of the presence of a product concentration gradient inside and outside the Ct pores [15]. According to the adsorption data we obtained, PX has the highest sorption rate. Therefore, diffusion difficulties should arise first in MX and OX desorption. The diffusion difficulties are probably also related to the preponderant formation of p-ethyltoluene.

Thus, limitation of the aromatization rate by product diffusion leads to a change in reaction selectivity in favor of the preponderant formation of the p-isomers of the dialkylbenzenes. Similar conclusions were reached in [16] on the basis of data on the preponderant formation of PX in the alkylation of toluene by methanol and the disproportionation of toluene in the presence of zeolite ZSM-5 treated with H_3PO_4 and $Mg(CH_3COO)_2$. Indirect confirmation of this hypothesis of a diffusional basis for the selectivity change is given by data that we obtained in tests on the isomerization of OX in the presence of UHSZ and V_2O_5–UHSZ. Addition of V_2O_5 to UHSZ sharply decreases the isomerization activity of this zeolite. For example, a notable transformation of OX is observed on UHSZ by 400°C, and at 500°C and higher a mixture of all the isomeric xylenes is formed in a proportion practically corresponding to the equilibrium proportion. At the same time, the catalyst containing V_2O_5 showed low activity in the isomerization of OX even at 550°C (OX conversion 8.9%), which may also be related to a change in the zeolite's pore structure which makes it hard for the OX molecules to enter the Ct cavities.

We should note in conclusion that selective formation of PX from olefins (ethylene, propylene, 1-hexene) was observed earlier in [17] in the presence of ZSM zeolites to which Sb_2O_3, B_2O_3, and MgO were added. Apparently, the effect of selective formation of PX is basically caused by a change in the Ct pore structure during the modification, whereas the nature of the modifying additive plays a secondary role. Further study of the phenomenon that has been observed may be promising in selecting selective Ct based on UHSZ.

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CONCLUSIONS

1. The original form of ultrahigh-silica zeolite shows activity in the aromatization of 1-octene at 400-500°C and atmospheric pressure. Modification of the zeolite by adding Pt, Rh, and V_2O_5 increases the aromatic hydrocarbon yield.

2. In the presence of V_2O_5-modified ultrahigh-silica zeolite, 1-octene is predominantly converted to p-xylene. The p-xylene content in the catalysate increases with decreasing temperature.

3. The hypothesis is proposed that selective formation of p-xylene is caused by blockage of the zeolite channels by the V_2O_5 additive, leading to difficulty in the desorption of the meta and ortho isomers of the dialkylbenzenes.

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