TRANSFORMATIONS OF ISOBUTYLENE IN THE PRESENCE OF VARIOUS TYPES OF ZEOLITES

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The Soviet-produced type ZSM-11 zeolite with ultrahigh silica content (UHSZ) in the Na (Na-UHSZ) and decationized (H-UHSZ) forms has much greater ability to aromatize propylene and isobutylene (IB) [1, 2] than all the previously studied nonzeolite catalysts [3-5]. Zeolites of other types (A, X, Y, etc.) have not yet been studied in the aromatization reactions of lower olefins. To find the characteristic features of UHSZ as catalysts in this reaction, we studied the transformations of isobutylene and propylene in the presence of types A, X, and Y zeolites and mordenite (M), as well as catalysts based on them.

EXPERIMENTAL

Zeolites NaA, NaX, NaY, and NaM, HY and HM (degree of decationization $> 90\%$), CaY (produced at the Grozny Scientific-Research Institute), zeolite-containing catalysts CaY + 20% γ-Al_2O_3, NaY + 20% γ-Al_2O_3, and the AShNTs-3 catalyst ($\sim 15\%$ CaY + 85% $Al_2O_3-SiO_2$) from the Salavat Petrochemical Combine and also aluminosilicate (10.4% Al_2O_3 + 87.6% SiO_2) and nonfluorinated γ-Al_2O_3 from the Ryazan' Petrochemical Works were used in the investigation. Several zeolite and zeolite-containing catalysts modified by the addition of Pt and Rh were also used.

Before the experiment, the catalysts were heated for 3 h at 500°C in an air current, and then for 1 h in a He current. The samples containing Pt and Rh were prepared by impregnating the support with aqueous solutions of H_2PtCl_6 and $RhCl_3$, followed by drying at 120°C and calcination at 500°C. Before the experiments, these catalysts were reduced in a H_2 current at 500°C (8 h) and purged with He. The procedure for carrying out the experiments and analysis of the products is described in [3]. The isobutylene (IB) and C_3H_6 used were $> 99\%$ pure.

DISCUSSION OF RESULTS

In experiments with propylene on type A, X, Y, M zeolites and catalysts based on them, the yield of the liquid reaction products, containing only traces of aromatic hydrocarbons (AH), was $< 1\%$. In the case of IB, higher yields of liquid catalysates and AH were obtained on these catalysts.

The data in Table 1 show that the lowest yields of AH are obtained on NaA and NaM zeolites, whose entrance openings have a diameter of ~ 4.0 and ~ 5.0 Å, respectively. A comparison of the size of the openings of the zeolites with minimal kinetic diameter of the IB molecule (~ 5.0 Å) shows that the diffusion of the IB molecules inside the pore structure is impeded. However, at elevated temperatures, the IB molecules can penetrate into the channels and cavities of zeolites and be subjected there to transformations. If molecules are formed whose size exceeds the diameter of the zeolite channels, they cannot be desorbed, and condense with the formation of coke [4].

In the case of the NaX and NaY zeolites with entrance opening diameter of ~ 8 Å, AH are formed in a higher yield (3.3%). The liquid catalysates obtained in the presence of these zeolites in a yield of 4.4% have approximately the same composition: ~ 32% of p-xylene, 18-19% of o- and m-xylene, ~ 1% of benzene, 13-14% of toluene, 6-7% of ethylbenzene and C_9-C_{10} alkylbenzenes, as well as 22-23% of C_6-C_8 aliphatic hydrocarbons.

The decationized HM and HY zeolites give somewhat higher yields of the liquid catalysate than the Na form, and with larger amounts of AH. A certain increase in the yield of the latter is also observed when Na^+ ions are substituted by Ca^{2+} ions in Y-type zeolite. However, the yield of the liquid catalysate scarcely changes as a result.

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TABLE 1. Transformations of Isobutylene in the Presence of Types A, X, Y, M, Na-UHSZ, and H-UHSZ Zeolites (550°C, $\tau = 14.4$ sec)

Catalyst	Yield, % based on olefin passed through		Conversion, %	Composition of liquid catalysate, %					
	of liquid catalysate	of aromatic hydrocarbons		benzene	toluene	aromatic hydrocarbons		Σ hydrocarbons	
						C_8	C_9—C_{10}	aromatic	aliphatic
NaA	1,9	Traces	14,0	—	—	—	—	—	100,0
NaM	3,8	0,7	73,9	1,3	8,5	7,2	1,7	18,7	81,3
NaX	4,3	3,3	48,6	1,3	14,0	55,1	6,3	76,7	23,3
NaY	4,3	3,3	47,1	1,0	12,9	57,8	6,2	77,9	22,1
HM	4,8	1,8	46,9	3,0	8,1	14,0	12,5	37,6	62,4
HY	6,6	3,7	70,9	2,1	14,4	22,6	17,6	56,7	43,3
CaY	4,2	4,1	93,2	10,1	54,7	25,9	5,5	97,8	2,2
Na-UHSZ*	34,6	31,7	95,9	13,9	32,8	35,3	8,6	91,6	8,4
H-UHSZ†	48,1	47,9	92,5	18,3	44,1	30,1	7,2	99,7	0,3

* According to data in [1].

† According to data in [2], $\tau = 7.2$ sec.

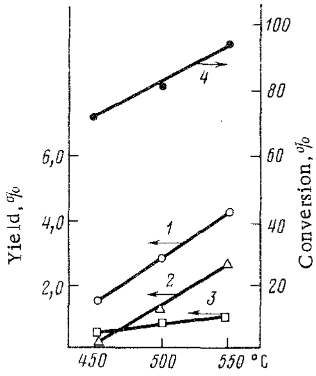

Fig. 1

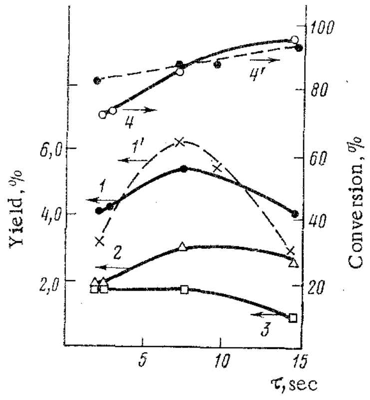

Fig. 2

Fig. 1. Influence of temperature on change in total yield of aromatic hydrocarbons (1), benzene and toluene (2), xylenes (3), and on conversion of initial isobutylene (4) in presence of CaY zeolite ($\tau = 14.4$ sec).

Fig. 2. Influence of time of contact on change in total yield of aromatic hydrocarbons (1), benzene and toluene (2), xylenes (3), and conversion of initial isobutylene (4) in presence of CaY (1-4) and CaY + 20% Al_2O_3 (1', 4') at 550°C.

Decationization and cation exchange lead to a relatively small increase in the yield of the liquid catalysate, but considerably influence the total content of AH. Thus, as a result of the decationization of the NaY zeolite, the total content of these products in the catalysate decreases from 77.9 to 56.7%, and after substitution of Na^+ ions by Ca^{2+}, it increases to 97.8%.

Together with dehydrocyclization, coke formation, cracking, isomerization, and other transformations of the initial olefin take place on the zeolites studied. Because of these reactions, for NaY, the least active zeolite in dehydrocyclization, the conversion of IB is 14% only. In experiments with NaX, NaY, NaM, HY, and HM zeolites, the conversion of IB varies within 47-94%, and in the presence of CaY zeolite, with the highest dehydrocyclization activity, it is 93.2%.

With increase in the reaction temperature from 450 to 550°C at $\tau = 14.4$ sec, the total yield of AH on the CaY zeolite linearly almost doubles, mainly due to an increase in the yield of benzene and toluene (Fig. 1). At the same time, the conversion of the initial olefin increases due to a more intense gas formation, in particular, formation of CH_4, whose content in the gas increases from 2.5% at 450°C to 12% at 550°C. With increase in time of contact from 2 to 14.4 sec at 550°C (Fig. 2), the total yield of AH increases, reaching a maximum at $\tau = 7.2$ sec, and then decreases to almost the initial level (curve 1). On curve 2 of the change in the total yield of benzene and toluene, this maximum is absent, and the total yield of xylenes (curve 3) decreases with increase

TABLE 2. Transformations of Isobutylene in Presence of Type Y Zeolites Modified by Addition of Al_2O_3, $Al_2O_3-SiO_2$, Pt, and Rh (550°C, $\tau = 14.4$ sec)

Catalyst	Yield, % based on olefin passed through		Conversion, %	Composition of liquid catalysate, %					
	of liquid catalysate	of aromatic hydrocarbons		benzene	toluene	aromatic hydrocarbons		Σ hydrocarbons	
						C_8	C_9—C_{10}	aromatic	aliphatic
NaY+20% Al_2O_3	7,3	6,2	71,7	3,3	21,7	44,3	13,4	84,8	15,2
CaY+20% Al_2O_3 *	6,4	6,2	85,6	4,4	25,6	41,3	24,2	95,5	4,5
AShNTs-3	10,4	8,2	76,1	3,9	18,2	36,2	20,8	79,1	20,9
NaY+0,5% Pt	2,9	2,8	61,4	3,8	16,9	65,0	11,8	98,1	1,9
HY+0,5% Pt	7,1	5,9	51,2	2,3	11,0	36,0	34,2	83,5	16,5
NaY+0,5% Rh	1,9	1,8	63,5	19,5	28,3	36,0	12,9	96,7	3,3
NaY+20% Al_2O_3+ +0,5% Pt	3,9	3,9	54,4	40,3	28,2	22,6	8,9	100,0	–
NaY+20% Al_2O_3+ +0,5% Rh	2,6	2,5	54,6	5,0	22,0	62,6	4,9	94,5	5,5
Al_2O_3 †	13,8	13,2	73,8	6,2	26,3	47,8	11,5	94,3	5,7
$Al_2O_3-SiO_2$ †	11,8	9,2	57,2	0,8	8,3	34,9	34,2	78,2	21,8

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* At $\tau = 7.2$ sec.

† According to data of [3].

in the time of contact. Increase in the time of contact is also accompanied by increase in conversion of IB, due to intensification of gas and coke formation.

In Table 2 data are listed which were obtained by introducing additives with aromatizing activity to Y-type zeolites. It follows from these data that addition of 20% γ-Al_2O_3 to NaY and CaY zeolites increases the yield of the liquid catalysate and the content of AH in it. The catalysate formed has almost the same composition as that obtained when Al_2O_3 is used as the catalyst. The influence of this additive is also apparent in the change in the shape of the curve for the dependence of the yield of AH on time of contact for CaY zeolite (see Fig. 2, curves 1 and 1'). The introduction of 0.5% Pt or Rh into NaY and HY zeolites, and also into NaY + 20% Al_2O_3 catalyst, leads to a considerable increase in the AH content in the liquid catalysates. However, the yield of the latter decreases as the result of cracking and coke formation. Among the modified zeolite catalysts studied, the highest yield of AH is observed on AShNTs-3 catalyst. However, under conditions of IB transformation (see Table 2), this catalyst differs little in its properties from pure aluminosilicate, and hence in this case the role of the zeolite is very small.

Type A, X, Y, and M zeolites studied in the present work have thus a low activity in the aromatization reaction of C_3-C_4 olefins. Modification of these zeolites by decationization, cation exchange, or introduction of additives, or a change in the reaction conditions, does not make it possible to obtain AH in yields approaching those observed in the case of UHSZ (see Table 1). The zeolites studied and the catalysts based on them become completely deactivated in the course of 1-1.5 h of operation, as the result of deposition of coke on them in amounts reaching 10-20%, calculated for the olefin passed through. In contrast, the UHSZ, together with high aromatization ability, show high stability under similar conditions [1, 2].

High stability and inappreciable coke formation are characteristic of UHSZ also under conditions of other reactions, for example, oligomerization and isomerization of olefins at 100-350°C [1, 2], in which zeolites of other types lose their activity as the result of intense clogging by coke [5-7]. Similar data were obtained during comparative investigation of cracking n-hexane in the presence of a type H-ZSM-5 UHSZ and type Y and M zeolites [8].

It is assumed [8, 9] that the less intense clogging by coke in the case of UHSZ and their higher stability under transformation conditions of hydrocarbons are due to weak electrostatic interactions characteristic of them. As a result of these, products preceding the formation of coke are readily removed from the zeolite channels. In contrast to mordenite, because of the limited free volume of the channels, large cations of the diphenyl, naphthalene, and anthracene type are not formed in the H-ZSM-5 zeolite [9]. Therefore, we can assume that in UHSZ, molecules of condensed AH are not formed, which could diffuse from the pore structure, condense, and convert into coke.

CONCLUSIONS

In contrast to zeolites with ultrahigh silica content, type A, X, Y, and M zeolites in the Na form and also those modified by decationization, cation exchange, and addition of γ-Al_2O_3, $Al_2O_3-SiO_2$, Pt, and Rh 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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