CONVERSIONS OF LOWER OLEFINS IN THE PRESENCE OF A SUPERHIGH-SILICA ZEOLITE CATALYST WITH ADDED V_2O_5

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The addition of V_2O_5 is known [1] to increase the selectivity of formation of p-xylene (PX) from 1-octene in the presence of the Na form of superhigh-silica zeolite (SHSZ). The preferential formation of PX from ethylene, propene, and 1-hexene in the presence of SHSZ of the ZSM type with added Sb_2O_3, MgO, and B_2O_3 has been reported in patents [2].

Continuing our study of the catalytic properties of SHSZ, we have examined the effects of adding V_2O_5 on the conversions of C_3–C_4 olefins. For purposes of comparison, experiments using ethylene with the original and modified catalysts were carried out, since the reactions of ethylene over catalysts of this type have been thoroughly studied [3].

EXPERIMENTAL

The experiments were carried out at 320-580°C and a space velocity of the olefin of 500 h^{-1} using previously studied samples [1] of Na-SHSZ (Cat-1) and Na-SHSZ + 5% V_2O_5 (Cat-2). The catalysts (2 ml) were exposed to air (10 liters/h for 3h at 500°C), which was then displaced by helium (1 h at 500°) before the experiments. The experimental method and GLC analyses have been described [4].

The ethylene, propene, and isobutene were ∿99% pure. In the experiments with n-butene, a butane–butene fraction of composition n-butenes 81.6%, n-butane 17.6%, propene 0.3%, $\Sigma C_2 + C_5$ 0.5%. The n-butane did not react to any significant extent under the reaction conditions.

DISCUSSION OF RESULTS

The liquid catalyzates obtained from C_2–C_4 olefins over Cat-1 and Cat-2 were mixtures of aliphatic (C_6–C_8) and aromatic (C_6–C_{10}) hydrocarbons. The gaseous products contained unreacted olefin, other C_2–C_5 alkenes together with the corresponding alkanes, and small amounts of methane (1-3% with Cat-1 and 0.1-0.3% with Cat-2).

TABLE 1. Aromatization of C_2–C_4 Olefins in the Presence of Na-SHSZ (Cat-1) and 5% V_2O_5-SHSZ (Cat-2) at 500°

Catalyst	Olefin	Conversion of olefin, %	Yield of liquid catalyzate, %		Amount of aromatic hydrocarbons in the catalyzate, %	Yield of aromatic hydrocarbons, %	
			on olefin introduced	on olefin reacted		on olefin introduced	on olefin reacted
Cat-1*	$i\text{-}C_4H_8$	97,0	43,8	45,2	71,9	31,5	32,5
Cat-2	$i\text{-}C_4H_8$	78,4	39,9	43,0	71,2	26,8	34,2
Cat-1	$n\text{-}C_4H_8$	89,9	52,5	58,4	87,3	45,9	51,0
Cat-2	$n\text{-}C_4H_8$	73,4	35,9	48,9	75,3	27,7	37,7
Cat-1*	C_3H_6	86,3	40,0	46,3	79,7	31,9	37,0
Cat-2	C_3H_6	68,3	24,8	36,3	60,3	15,2	22,3
Cat-1	C_2H_4	84,0	44,7	53,2	97,3	43,5	51,8
Cat-2	C_2H_4	23,7	7,1	30,0	91,1	6,5	27,3

*From [5].

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TABLE 2. Composition of the Aromatic Hydrocarbons Formed from C_2–C_4 Olefins over Cat-1 and Cat-2 at 500°

Catalyst	Olefin	Composition of aromatic hydrocarbons, %				Composition of C_8 alkylbenzenes, %			
		benzene	alkylbenzenes			p-xylene	m-xylene	o-xylene	ethylbenzene
			C_7	C_8	C_9—C_{10}				
Cat-1	C_2H_4	12,4	57,8	27,8	2,0	12,5	65,2	13,7	8,6
	C_3H_6	7,9	33,5	46,3	12,3	22,0	50,4	19,0	8,6
	n-C_4H_8	8,0	51,6	39,3	1,1	16,3	69,3	9,7	4,7
	i-C_4H_8	8,3	28,5	46,4	16,8	21,6	48,9	18,6	10,9
Cat-2	C_2H_4	5,8	34,5	48,9	10,8	78,7	6,4	0,1	14,8
	C_3H_6	4,2	40,0	37,8	18,0	75,4	9,1	3,3	12,2
	n-C_4H_8	4,0	30,8	54,2	11,0	82,8	10,0	1,1	6,1
	i-C_4H_8	4,4	35,4	50,4	9,8	79,1	8,6	1,1	11,2

TABLE 3. Changes in the Composition of C_8 Alkylbenzenes with Temperature in the Aromatization of C_3–C_4 Olefins in the Presence of Cat-2

Olefin	T., °C	Conversion, %	Composition of alkylbenzenes, %			
			p-xylene	m-xylene	o-xylene	ethylbenzene
C_3H_6	380	88,5	83,0	4,1	2,8	10,1
	500	68,3	75,4	9,1	3,3	12,2
	550	53,9	70,2	7,1	2,7	20,0
	580	45,4	71,2	8,5	1,8	18,5
n-C_4H_8	380	67,6	88,4	5,1	—	6,5
	500	73,4	82,8	10,0	1,1	6,1
	550	65,2	78,9	6,2	1,5	13,4
	580	60,3	77,4	7,5	2,0	13,1
i-C_4H_8	380	83,8	79,1	8,9	1,5	10,5
	500	78,4	79,1	8,6	1,1	11,2
	550	73,3	76,1	6,9	2,5	14,5
	580	79,0	76,7	7,6	2,5	13,2

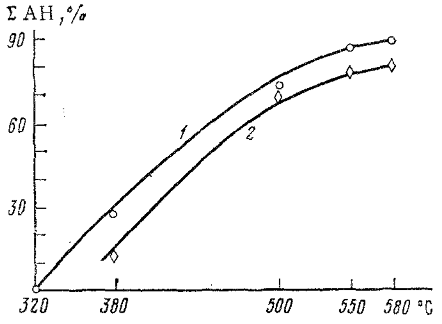

Fig. 1. Effect of temperature and the addition of V_2O_5 on the total amounts of aromatic hydrocarbons in catalyzates obtained from isobutylene in the presence of SHSZ catalysts: 1) SHSZ; 2) 5% V_2O_5–SHSZ.

It will be seen from Table 1 that the addition of V_2O_5 to SHSZ reduces the overall yield of liquid catalyzate and of aromatic hydrocarbons (AH), these effects being greatest in experiments with C_2H_4. As the temperature is increased from 380 to 580°, the amounts of AH in the catalyzates increase, as shown in Fig. 1 for isobutene, the amounts of benzene and toluene increasing (Fig. 2a) and those of C_8–C_{10} alkylbenzenes decreasing (Fig. 2b).

Modification of SHSZ by vanadium pentoxide considerably reduces the selectivity of formation of the p isomers of dialkylbenzenes from C_2–C_4 olefins, as previously found in the case of 1-octene [1]. It follows from the data presented in Table 2 that the PX content

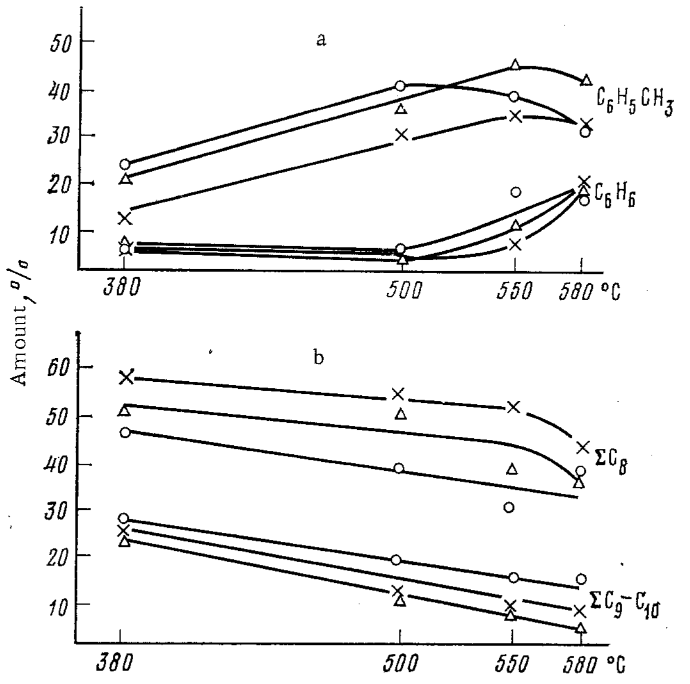

Fig. 2. Effect of temperature on the amounts of benzene and toluene (a) and of C_8 and C_9-C_{10} alkylbenzenes (b) in the aromatic fraction of catalyzates obtained from propylene (○), n-butene (×), and isobutylene (△) in the presence of 5% V_2O_5–SHSZ catalyst.

of the C_8 alkylbenzene fraction of catalyzates obtained using Cat-2 at 500° is 75-83%, whereas at 380° it reaches 80-88% (Table 3). The principal component of the C_9 alkylbenzenes is also p-ethyltoluene, the amounts of which in this fraction of the catalyzates from C_2H_4, n-C_4H_8, i-C_4H_8, and C_3H_6 is 100, 99, 89, and 86%, respectively. In contrast, when Cat-1 is used, the principal component of the C_8 alkylbenzene fraction is m-xylene (MX) (Table 2).

The addition of V_2O_5 reduces the stability of SHSZ. In experiments with C_3-C_4 olefins at 320-380°, Cat-2 was deactivated to the extent of the total cessation of the formation of liquid products, although at >380° its activity was constant over a period of 6 h. In experiments with ethylene, however, Cat-2 lost some of its activity even at 500°. It is noteworthy that the original activity of deactivated samples of Cat-2 was fully regained on treatment with an oxygen-free inert gas (helium, 8 h, 500°).

Consider the effects of adding V_2O_5 on the properties of SHSZ with respect to possible pathways for the conversion of lower olefins into AH. According to [6], catalysts for the aromatization of olefins must possess oligomerizing and dehydrogenating properties such as those exhibited by SHSZ [1, 5]. In the first stage of the reaction, the lower olefins must be converted into di- or oligomers, which then undergo isomerization and dehydrocyclization. Consequently, the structures of the AH formed, and their proportions, must be determined by the structures of the oligomers and their isomerization products.

In the case of the original SHSZ, the yields and proportions of the AH formed (Tables 1 and 2) enable the olefins investigated to be provisionally divided into two groups: ethylene and n-butene (44-46% AH containing 8-12% of benzene, 52-58% of toluene, ∿29-39% of C_8 alkylbenzenes, and 1-2% of C_9-C_{10} alkylbenzenes), and propene and isobutene (31-32% AH containing ∿8% of benzene, 28-33% of toluene, ∿46% of C_8 alkylbenzenes, and 12-17% of C_9-C_{10} alkylbenzenes). It is suggested that the first stages in the conversion of ethylene and n-butene involve the formation of oligomers which on dehydrocyclization afford toluene and MX [7, 8]. In the case of propene and isobutene these isomers are apparently formed to a lesser extent, larger amounts of oligomers being formed which are the precursors of the C_9-C_{10} alkylbenzenes.

The addition of V_2O_5 to SHSZ substantially reduces the differences in the proportions of the AH in the C_2-C_4 olefin catalyzates and considerably increases the amounts of PX. As in the case of 1-octene, the selective formation of PX is apparently explained by the partial blockage of the pores of the SHSZ by vanadium pentoxide, resulting in a decrease in the rate of diffusion of MX and o-xylene molecules into the gas phase. Thus, the conversion of C_2-C_4 olefins over Cat-2, as in the case of 1-octene, occurs in the internal diffusion region, the rate of the process being limited by the diffusion of the molecules of product into the channels of the zeolite.

These concepts also provide an explanation for the deactivation of Cat-2 in experiments with olefins at temperatures below 380°. The possibility of regenerating deactivated catalyst samples without the use of oxygen shows that the drop in activity is not caused by carbonization, but by the formation in the channels of the zeolite of branched macromolecular oligomers whose desorption is hindered. Under regeneration conditions, these oligomers decompose, and their fragmentation products are removed from the catalyst pores by a stream of inert gas. Confirmation of these views is provided by the composition of the hydrocarbon gases evolved during the regeneration of Cat-2 deactivated in an experiment with propene at 320°. These gases contained $\sim$40% of C_5 alkanes and alkenes, 50% of butanes and butenes, and a total of $\sim$10% of C_1-C_3 hydrocarbons. The possible formation of such macromolecular compounds in the channels of SHSZ (type ZSM-5) has been shown in the case of ethylene [9].

The addition of V_2O_5 to SHSZ may, in addition to the creation of diffusion barriers, result in the partial blockage of the active sites of the zeolite and to the observed reduction in the conversion of the olefin and the yields of liquid reaction products.

CONCLUSIONS

1. Modification of the Na form of superhigh-silica zeolite by the addition of 5% V_2O_5 considerably increases the selectivity of this catalyst with respect to the formation of p-xylene from C_2-C_4 olefins, but reduces the overall yields of aromatic hydrocarbons.

2. The addition of V_2O_5 apparently changes the pore structure of the zeolite, hindering the desorption in the gas phase of some of the conversion products of the olefins, in particular m- and o-xylenes, resulting in an increase in the yields of p-xylene.

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