regeneration of a Type A zeolite immediately after completing the sorption stage.

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INVESTIGATION OF POLYFUNCTIONAL ZEOLITE CATALYSTS. COMMUNICATION 6. INFLUENCE OF PRETREATMENT AND CONDITIONS OF USE ON CATALYTIC PROPERTIES OF NICKEL-ZEOLITE SYSTEMS IN ALKYLATION OF BENZENE WITH ETHYLENE

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Synthetic zeolites of the X and Y types with added nickel in the form of Ni<sup>2+</sup> and NiO are polyfunctional catalytic systems, on which the interaction of benzene with ethylene will go forward to form primarily sec-butylbenzene (SBB), or SBB and ethylbenzene (EB), or SBB and butenes [1-4]. The dependence of the catalyst properties on the catalyst composition and the state of the nickel has been examined in [1, 2, 4-6]. In the work reported here, we studied the influence of pretreatment and the conditions of use of ion-exchanged and impregnated nickel-zeolite catalysts on their activity and selectivity in the alkylation of benzene with ethylene.

#### EXPERIMENTAL

The experiments were performed in a single-pass flow unit, either without any carrier gas or with a stream of N<sub>2</sub> (moisture content 1.5 mg/liter),  $CO_2$  (0.8 mg/liter), or CO (<0.1 mg/liter), with grade ch.d.a. [pure, for analysis] benzene and 98% ethylene (2% ethane by volume). The procedures used in the test runs and in the product analysis have been described in [7]. The zeolites NiNaY, NiCaNaY, and CaNaY were prepared from powdered NaY with a mole ratio  $SiO_2/Al_2O_3 = 4.4$ , by ion exchange [4]. The NiCaNaY specimens were obtained by simultaneous replacement of Na<sup>+</sup> by Ni<sup>2+</sup> and Ca<sup>2+</sup> from solutions of a mixture of their salts. The degree of replacement of Na<sup>+</sup> by  $M^{2+}$  is indicated by the number (fraction replaced) preceding the symbols for the cations in the zeolite designation. Two component catalysts NiO/ CaNaY were synthesized by impregnating dehydrated CaNaY with a solution of Ni acetylacetonate in CHCl3, with subsequent decomposition of the salt in a stream of dry air at 500°C. The IR spectra were taken in a UR-20 spectrophotometer at 20°C [2]. First, the specimens (pellets with a thickness of 9-11 mg/cm<sup>2</sup>) were heated for 4-5 h in a quartz vacuum-flow cuvette in a stream of dry air at the appropriate temperature, and then pumped down while cooling, to an absolute pressure of  $10^{-4}$  torr (30 min). The ethylene and CO<sub>2</sub> were adsorbed at 250°C, PC<sub>2H4</sub> 30 torr, PCO2 25-50 torr, and contact time 30 min; the spectra were recorded before and after pumping off the gas phase (in the case of the  $C_2H_4$ , without a gas phase).

## DISCUSSION OF RESULTS

It can be seen from Fig. 1 that as the treating temperature  $T_o$  is raised from 300° to 600°C, the conversion of  $C_2H_4$  to EB drops off; the conversion to SBB passes through a maximum at 400°C. The greatest overall conversion of ethylene is observed at  $T_o = 400$ °C. Also maximum mal at this  $T_o$  is the selectivity of  $C_2H_4$  conversion to SBB. The manner in which the properties

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Fig. 1. Conversion of  $C_2H_4$  to ethylbenzene (1), sec-butylbenzene (2), alkylbenzenes (3), and total conversion (4) on 0.59NiNaY zeolite, as functions of treating temperature (5 h in dry air). Alkylation process conditions:  $250^{\circ}C$ , v = 1.2 h<sup>-1</sup>,  $C_6H_6:C_2H_4 =$ 3:1 (mole).

of the NiNaY catalyst vary can evidently be explained on the following basis. In the process of heating the zeolite, the aqua complexes Ni(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup>, in the form of which the nickel cations are introduced into the void spaces of the crystals [8], are broken down, and coordinationunsaturated Ni<sup>2+</sup> ions and acidic OH groups appear in the faujasite structure [9], as a result of "hydrolysis" of part of the cations. At 400°C, we apparently find the optimal ratio of these two types of centers that are required for the synthesis of SBB from C<sub>6</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> [5]. Above 400°C, dehydration and dehydroxylation of the zeolite become more pronounced, the protonic acidity of the catalyst decreases, and its alkylating activity drops off.

The changes in activity of the contact catalyst in the oligomerization of  $C_2H_4$  are evidently due mainly to changes in the state and location of the nickel in the structure of the crystalline aluminosilicate. Destruction of the hydrate shell of the Ni<sup>2+</sup> cations makes them accessible for interaction with  $C_2H_4$  molecules. At very high treating temperatures, part of the Ni<sup>2+</sup> migrates into the hexagonal prisms [9, 10], and the number of Ni<sup>2+</sup> ions taking part in catalysis drops off quite substantially. The observed dependence of the catalytic properties of the 0.59NiNaY zeolite on T<sub>0</sub> that is shown in Fig. 1 is the resultant of the effects of various processes — dehydration, "hydrolysis," migration of metal cations, and dehydroxylation of crystallites.

This explanation is consistent with the IR spectra of the NiNaY catalyst after heat treatment at various temperatures, these spectra being taken before and after adsorption of ethylene. As can be seen from Fig. 2, in the spectrum of the hydrated zeolite in the region of stretching vibrations of the OH bonds of the water molecules, there are two absorption bands, at 1647 and 1615 cm<sup>-1</sup> (spectrum 1). The first band is due to physically sorbed  $H_2O$ molecules interconnected by a hydrogen bond. The presence of the hydrogen bond is indicated by the broad band in the 3600-3700 cm<sup>-1</sup> region. Along with the physically sorbed H<sub>2</sub>O, the hydrated NiNaY also contains water that is coordination-bonded to Ni<sup>2+</sup> cations, manifested in the form of a band at about 1615 cm<sup>-1</sup>. After heat treatment of the zeolite in a stream of dry air at 100°C, the intensities of the bands decrease, and the low-frequency band is shifted to 1612 cm<sup>-1</sup>, indicating a weakening of the O-H bonds in the H<sub>2</sub>O molecules as a result of stronger interaction of Ni<sup>2+</sup> with the oxygen atoms of water, owing to the decrease in the number of  $H_2O$  molecules in the coordination sphere of the Ni<sup>2+</sup>; in the region of  $O_H$ stretching vibrations, a band appears at 3550 cm<sup>-1</sup> (see Fig. 2, spectrum 2). Evidently, the water molecules that are removed in the initial stage of dehydration include not only those that are physically adsorbed in the void spaces of the faujasite, but also those entering into the composition of Ni(OH2)62+ complexes; simultaneously, part of the H2O dissociates, splitting out H<sup>+</sup> and forming structural OH groups.

With  $T_0 = 200^{\circ}C$ , the maximum in the low-frequency band is located near 1605 cm<sup>-1</sup>, and the intensity of the band of the physically adsorbed water is lower than for the band of Ni(OH<sub>2</sub>)<sub>x</sub><sup>2+</sup> (spectrum 3). In the region of O-H stretching vibrations, bands are present at 3550, 3583, 3640, and 3745 cm<sup>-1</sup>. The band at 3583 cm<sup>-1</sup>, according to [11], can be assigned to Ni(OH)<sup>+</sup> groups.

Further increases in T<sub>0</sub> shift the equilibrium  $Ni(OH_2)_X^{2+} \neq Ni(OH)^+ + H^+ + H_2O + Ni^{2+}$  to the right, and the intensities of the bands for the structural OH groups (at 3550 and 3640 cm<sup>-1</sup>), as well as the intensities of the band for OH groups bound to Ni<sup>2+</sup> cations (3583 cm<sup>-1</sup>), are found to increase (see Fig. 2, spectra 4-7). The contents of acidic hydroxyl groups and



Fig. 2. IR spectra of 0.59 NiNaY zeolite after treatment in a stream of dry air for 5 h at following temperatures, °C: 1) 20; 2) 100; 3) 200; 4) 300; 5) 400; 6) 500; 7) 600.

TABLE 1. Influence of Reaction Conditions on Intensity and Selectivity of Benzene Alkylation by Ethylene in the Presence of 0.59NiNaY Zeolite [process conditions:  $250^{\circ}$ C, v = 1.2 h<sup>-1</sup>, C<sub>6</sub>H<sub>6</sub>:C<sub>2</sub>H<sub>4</sub>:gas = 3:1:2.4 (mole)]

			C <sub>2</sub> H <sub>4</sub> conv	ersion, %		S <sub>1</sub> (A/B)	S <sub>1</sub> (A/C)
Conditions	Time, h	to EB	to SBB (A)	to alkyl- benzenes (B)	total,* (C)		%
Without carrier gas	2 3 4 5 6 Average †	$0,9 \\ 1,5 \\ 1,4 \\ 1,0 \\ 1,0 \\ 1,3$	$\begin{array}{c} 17,0\\ 15,6\\ 11,5\\ 9,0\\ 7,8\\ 11,9\end{array}$	17,9 17,1 12,9 10,0 8,8 13,2	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	95,0 91,2 89,1 90,0 88,6 90,1	68,5 65,0 63,9 72,0 70,9 69,1
In stream of N <sub>2</sub>	2 3 4 5 6 Average†	1,4 1,8 1,8 1,8 1,8 1,8 1,8	8,2 12,9 13,6 15,7 14,2 11.8	9,6 14,7 15,4 17,5 16,0 13,6	11,3 16,4 17,6 19,2 18,6 15,3	85,4 87,8 88,3 89,7 88,7 86,8	72,5 78,6 77,2 81,7 76,4 77,1
In stream of CO	2 3 4 5 6 Average†	2,9 2,7 2,5 2,5 2,3 2,5	Traces 5,4 6,4 7,1 4,6 4,5	2,9 8,1 9,6 6,9 7,0	3,8 9,3 10,6 11,3 7,8 8,5	66,6 71,9 74,0 66,6 64,2	58,1 60,4 62,8 59,0 52,9
In stream of CO <sub>2</sub>	2 3 4 5 6 Average <b>†</b>	3,0 3,2 3,0 2,6 2,6 2,8	0,7 13,7 14,3 11,8 11,0 9,7	3,7 16,9 17,3 14,4 13,6 12,5	4,5 17,8 19,4 16,1 15,3 14,2	18,9 81,0 82,6 81,9 80,8 77,6	15,5 76,9 73,7 73,3 71,9 68,3

\*Here and subsequently: to ethylbenzene (EB) + sec-butylbenzene (SBB) + butenes. \*Average for 6 h, determined by analysis of mixture of all samples of liquid product.

TABLE 2.	Influence of	f Cc	onditi	ons c	)f Us€ r	uo :	Activi	ity ar	td Se	lectiv	ity 9	of Nic	ckel	Zeolit	te Ca	talys	ts ir	с. С.
(mole)]	י חד מבווצבווב	TM		iytene	id]	Babo	s conc	111101	:S1	<b>່</b> ກຸກຕ	 ‼ ⊳	- - - -	ວັ 1	6 Н <b>6 :</b> С2	2.H4:30	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	с. Т. Т.	7•4

							-			Ö	ndition	S							
			with	out carr.	ler gas				<u>,</u>	stream	of $N_2$				în st	ream c	of CO2		
Catalyst	Time, h	0	2H4 CO	nversior	1, %	<b>'(</b>	<b>"(</b> 2	$C_{2}$	H <sub>4</sub> con	version	. %			$C_{2}H$	t conve	srsion,	70		
		to EB	to SBB (A)	to alkyl- ben-	total (C)	₽/¥) <sup>r</sup> S	0/∀) 2 <sup>5</sup> (∀\0	o EB to	, SBB a	ukyl-t en-	otal	S1. %	S2. %	to EB	b SBB	o alkyl- cen-	total	S1. %	S2, %
				(B)					<u>N</u>	enes						zenes			
0.10 Ni 0.58 CaNaY	থ	1,4	1,1	2,5	4,5	44,0	24,5	0,7		0,7	1,6			9,0	1	9,0	10,7	1	١
$(\sim 1.4\% \text{ Ni}), 275^{\circ}$	ŝ	2,5	13,7	16,2	24,9	84,5	55,0	1,4	0,4	1,8	2,7	22, 2	14,8	10,2	1	10,2	12,2	(	t
	4	2,5	17,6	20,1	31,3	87,6	56,7	1,4	1,4	2,8	4,5	50,0	31,1	11,8	0,1	11,9	14,5	0,8	0.7
	ĸ	2,5	15,6	18,1	27,2	86,1	57,4	1,4	3,2	4,6	7,2	69,69	46,5	12,9	0.7	13,6	16,8	5,2	4.2
	9	2,3	14,1	16,4	25,4	86,0	55,5	1,4	3,6	6,0	7,6	60,0	47,4	11,1	0,2	11,3	13,2	1,8	1,5
	Average	$^{2,1}$	10,8	12,9	17,7	83,8	61,0	1,0	1,5	2,5	4,3	60,0	34, 9	9,5	0,1	9,6	12,0	1,0	0,8
0.24 Ni 0.38 CaNaY	53	3,8	18,5	22,3	33,1	83,0	55,9	3,2	0,7	3,9	5,6	18,0	12, 5	9,4 ]]	Iaces	9,4	11,1	1	I
(3.3% Ni)	<del>ر</del> م	4,2	18,1	22,3	33,6	81,1	53,9	5,2	7,1 ] 1	12,3	14,9	57,7	47,6	10,2	3,2	13,4	15,8	23,9	20,2
	4	3,9	12,4	16,3	22,4	76,1	55,4	5,0	8,6	13,6	17,0	63, 2	50,5	9,4	4,0	13,4	16,8	29,9	23,8
	ഹ	3,8	10,7	14,5	21,0	73,8	51,0	4,5	7,5	12,0	15,4	62,5	48,7	9,0	3,6	12,6	17,3	28,6	20,8
	9	3,2	8,2	11,4	15,7	71,9	52,2	3,8	5,4	9,2	11,8	58,7	45,7	8,1	3,5	11,6	15,0	30,2	23,3
	Average	3,8	15,1	18,9	26,3	79,9	57,4	3,8	5,4	9,2	12,6	58,7	42,9	9,0	2,8	11,8	14,4	23,7	19,5
2.5%NiO	57	8,6	34,2	43,0	46,5	79,5	73,5	9,2 2	3,4	34,0	36,6	68,9	64,0	15,0	20,0	35,8	38,8	55,8	51,5
0.93CaNaY	eo	7,3	42,5	50,2	54,6	84,6	77,8	7,9 3	0,9	39,9	42,9	77,5	72,1	12,0	25,5	38,5	40,9	65,2	62, 4
(~Z%) NI)	4	6, 6	39,7	47,3	51,8	84,0	76,6	6,9 3	32,8 4	i0,2	43,2	81,5	75,9	11,0	27,6	39.5	41,9	69,8	66,0
	ñ	5,4	38,3	45,9	50,0	83,5	76,6	5,9 3	1,9	39,3	42,8	81,1	74,5	9,5	26,3	38,0	38,9	69,1	67,6
	9	4,5	35,6	40,8	46,6	87,2	76,3	4,5 2	9,6	35,8	38,0	82,6	73,0	8,2	25,4	34,3	37,0	74,0	68, 6
	Average	6,1	34,8	41,6	45,1	83,5	77,0	5,9 2	36,0 3	32,6	34,5	79,8	75,4	9,7	22,0	32,5	34,7	67,7	63,5
							•		-	-	-		-	-	•				

 $Ni(OH)^+$  are the greatest in the zeolite that was heated to 400-500°C.

Changes in the quantity of Ni<sup>2+</sup> ions capable of interacting with ethylene to form butenes was judged from the IR spectra of 0.59 NiNaY that had been heat-treated at various temperatures, after the adsorption of  $C_2H_4$ . These studies showed that the integral intensity of the group of bands in the 2800-3000 cm<sup>-1</sup> region (characterizing C-H deformation vibrations of CH<sub>2</sub> and CH<sub>3</sub> groups in hydrocarbons), which is directly proportional to the number of Ni<sup>2+</sup> cations located in the large void spaces of the faujasite [7], passes through a maximum at 400-500°C. Thus, the quantity of nickel ions accessible for C<sub>2</sub>H<sub>4</sub> molecules is the greatest in the 0.59-NiNaY zeolite that had been heated to 400°C, this zeolite manifesting the highest catalytic activity in the reaction of C<sub>6</sub>H<sub>6</sub> with C<sub>2</sub>H<sub>4</sub> (see Fig. 1). Let us note that the heat of adsorption of C0 on the faujasite 0.77NiNaY (x = 5.0) was also found to increase up to 400°C, then remaining unchanged as the temperature was further increased [12].

The catalytic properties of NiNaY zeolite are also highly dependent on the conditions of use of the material (Table 1). In experiments without any carrier gas, the main product from the interaction of  $C_6H_6$  with  $C_2H_4$  is SBB, accounting for 88-95% of the alkylbenzenes. In a stream of N<sub>2</sub>, the ratio of rates of  $C_2H_4$  dimerization and  $C_6H_6$  alkylation by olefins is different, owing to dilution of the reaction mixture and a shorter contact time with the catalyst; because of these factors, the maximum conversion of  $C_2H_4$  to SBB and the total conversion decrease slightly, and the conversion to EB increases. This shows up in the tabulated values as a significant increase in S<sub>2</sub>, with little change in S<sub>1</sub>. In a CO atmosphere, we find the lowest yields of products from the alkylation of  $C_6H_6$  with ethylene. A poisoning effect of CO on NiNaY as a catalyst for  $C_2H_4$  dimerization has been reported previously [13]; the obvious reason for this behavior is that CO as a ligand can compete with  $C_2H_4$  molecules for interaction with Ni<sup>2+</sup> cations and thereby retard the reaction of the olefin (at high temperatures, it is also possible that part of the Ni<sup>2+</sup> may be reduced to Ni<sup>+</sup> and Ni<sup>o</sup>, with a decrease in concentration of the active centers for  $C_2H_4$  dimerization).

The activity of X and Y zeolites with bivalent metal cations  $M^{2+}$  in carbonium-ion reactions is much greater when CO<sub>2</sub> is present [14]. We should expect a substantial effect of CO<sub>2</sub> on the alkylating and dimerizing functions of the NiNaY and hence on the selectivity of the reaction of C<sub>6</sub>H<sub>6</sub> with C<sub>2</sub>H<sub>4</sub>. It can be seen from Table 1 that, even though the conversion of C<sub>2</sub>H<sub>4</sub> to EB in a stream of CO<sub>2</sub> is 1.5-2 times greater than in N<sub>2</sub>, the basic process indices in these two carrier gasses differ but little; i.e., there is only a weak effect of CO<sub>2</sub> on the NiNaY in the alkylation of C<sub>6</sub>H<sub>6</sub> with ethylene.

In contrast, on the NiCaNaY (Table 2) in a stream of  $CO_2$ , the EB yields are much greater than in N<sub>2</sub>, and the differences are greater for greater degrees of replacement of Na<sup>+</sup> by Ca<sup>2+</sup>. Thus, in a CO<sub>2</sub> atmosphere, the alkylating activity of the catalyst 0.1NiO.58CaNaY is much greater. This leads to a change in the process selectivity. In the case of the 0.24NiO.38-CaNaY, which contains more Ni<sup>2+</sup> and less Ca<sup>2+</sup>, the total yields of alkylbenzenes and the total conversions of C<sub>2</sub>H<sub>4</sub> are very similar for the runs in N<sub>2</sub> and CO<sub>2</sub>, but the ratios of EB and SBB in the products are very much different (see Table 2).

In the case of the catalyst that is the more efficient in the synthesis of SBB from  $C_6H_6$ and  $C_2H_4$ , the two-component catalyst NiO/CaNaY, the relative quantities of EB and SBB that are formed also depend on the reaction conditions (Table 2). In a stream of  $CO_2$ , the EB yield is higher and the SBB yield is lower. The total conversion of  $C_2H_4$  to alkylbenzenes is the same as in the experiments with N<sub>2</sub>.

The IR spectroscopic studies showed that when the  $CO_2$  used as the carrier gas (0.8 mg/ liter H<sub>2</sub>O) is adsorbed on NiCaY zeolites in the system NiO/CaNaY, their H<sup>+</sup> acidity increases (as a result of interaction of  $Ca^{2+}$  with  $CO_2$  and H<sub>2</sub>O). These effects of the  $CO_2$  can be explained by the change brought about by the  $CO_2$  in the ratio of the rates of  $C_2H_4$  dimerization and subsequent alkylation of the C<sub>6</sub>H<sub>6</sub> by the butenes that are formed, on the one hand, and the rate of alkylation of C<sub>6</sub>H<sub>6</sub> by ethylene, on the other hand. On catalysts of the NiO/CaNaY type, the formation of carbonate-like compounds with the Ni component is also possible, with the result that their dimerizing function is weaker and the selectivity shows a further change. The character of interaction of the contact catalysts with  $CO_2$  depends on the temperature, the  $CO_2$  partial pressure, and the moisture content.

When pyridine is added, the concentration of acidic centers of the catalyst is reduced, and the Py interacts with the  $Ni^{2+}$  cations, so that contact is hindered between the  $C_2H_4$ 

TABLE 3.	Effect of I	Pyridine (1	y) on Catal?	ytic Properti	es of
0.59NiNaY	Zeolite in	Alkylation	1 of Benzene	by Ethylene	[process
conditions	s;225°C v =	$= 1.2 h^{-1};$	$C_6H_6:C_2H_4 =$	3:1 (mole)]	

		$C_2H_4cc$	mversion, %		
Reactants	to C <sub>4</sub> H <sub>8</sub>	to EB	to SBB (A)	total (B)	S (A/B), %
C <sub>6</sub> H <sub>6</sub> (C <sub>•</sub> P <sub>•</sub> ) +C <sub>2</sub> H <sub>4</sub> C <sub>6</sub> H <sub>6</sub> +0,5 % Py+C <sub>2</sub> H <sub>4</sub>	3,4 0,9	0,7 0,2	12,1 7,5	$\begin{array}{c} 17,2\\ 8,6 \end{array}$	70,4 87,1

molecules and the dimerization centers; this lowers both the alkylating and the oligomerizing activities of the NiNaY zeolite (Table 3). Here, the timewise changes in  $C_2H_4$  conversion in the experiments with pure  $C_6H_6$  and with  $C_6H_6$  containing 0.5% Py were found to be symbatic, and the selectivity of olefin conversion to SBB was found to be higher in the case of  $C_6H_6$  + Py.

The results obtained in the present work support the concepts of the nature of bifunctionality and the mechanism of action of nickel-zeolite alkylation catalysts that were developed in [15]; these results can be used for purposeful regulation of the properties of various systems in reactions of aromatic compounds with ethylene.

## CONCLUSIONS

1. The ratio between the acid (alkylating) function and oligomerizing function, as well as the activity and selectivity of the bifunctional catalysts NiNaY, NiCaNaY, and NiO/CaNaY, depend to a great degree on the catalyst pretreatment and on the conditions of catalyst use in the reaction of benzene with ethylene.

2. When the NiCaNaY and NiO/CaNaY are used in a stream of  $CO_2$ , the  $C_2H_4$  conversion to ethylbenzene is considerably higher, and the conversion to sec-butylbenzene is considerably lower, than in experiments without carrier gas or with N<sub>2</sub> or CO.

3. The IR spectra of the catalysts and  $C_2H_4$  and  $CO_2$  adsorbed on these catalysts have been investigated in order to clarify the reasons for the phenomena that have been observed.

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CATALYTIC PROPERTIES OF SUPERHIGH-SILICA ZEOLITES IN

# CONVERSIONS OF CERTAIN HYDROCARBONS

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One of the basic trends in the synthesis of zeolites is the development of crystalline aluminosilicates with higher and higher silica contents [1].

Superhigh-silica zeolites of the ZSM type that have been developed in other countries, as well as the TsVK and Ul'trasil that are manufactured in the USSR, are classed as narrow-pore zeolites with  $SiO_2/Al_2O_3$  ratios up to 200 or even higher; these materials, despite the small amounts of aluminum and the consequent small amounts of protons and cations, are high in acidity and hydrophobicity (they interact weakly with polar molecules) and are highly resistant to acid media [2]. Even with such obvious advantages, the catalytic properties of these zeolites have been investigated very little.

Here we are reporting on a study of the catalytic activity of type TsVK zeolites with various  $SiO_2/Al_2O_3$  ratios in reactions of isomerization of  $C_4$ - $C_6$  n-paraffins, hydrogenation and hydroisomerization of benzene, and the side reactions of hydrocracking and disproportion-ation. The studies reported previously in [3] were confined to isomerization and hydrocracking of n-decane on Pt/ZSM catalyst at atmospheric pressure.

# EXPERIMENTAL

The catalysts were prepared from these different zeolites: TsVK-1 with  $SiO_2/Al_2O_3 = 83$ , synthesized with the participation of an organic cation; TsVK-2 with  $SiO_2/Al_2O_3 = 33.3$ ; and TsVK-3 with  $SiO_2/Al_2O_3 = 47$ ; the last two of these catalysts were synthesized without an organic cation. The hydrogen forms of the zeolites were obtained by ion exchange with an NH<sub>4</sub>Cl solution with subsequent calcination at 600°C. Pd-containing catalysts were prepared from HTsVK\* by impregnation with an H<sub>2</sub>PdCl<sub>4</sub> solution and by ion exchange with a Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> solution. The hydrocarbons used in this reaction were n-butane, n-pentane, n-hexane, and benzene, grade "ch." [pure].

The experiments were performed in a single-pass flow reactor with a catalyst charge of 7.5 g. Before use in the experiments, the catalysts were pretreated as follows: The H forms of the zeolite were calcined at 520°C in a stream of air; the Pd-containing catalysts were calcined at 380°C and then reduced by  $H_2$  at this same temperature. The catalytic properties of the zeolites were investigated over a temperature range of 250-380°C at 30 atm and a hydro-carbon feedstock space velocity of 1 h<sup>-1</sup>.

The products from these runs were analyzed in an LKhM-8M chromatograph with a column containing Celite 545 with 18% triethylene glycol dibutyrate.

## DISCUSSION OF RESULTS

In order to determine the acid function of the catalysts, i.e., the ratio between their isomerizing and hydrocracking (or cracking) activities, the HTsVK and Pd/HTsVK catalysts were investigated in the reaction of n-pentane isomerization (Table 1). It will be noted that the H forms of the zeolite give high levels of n-pentane conversion, for example, 55% on the HTsVK-2 at 300°C. A common feature of the HTsVK catalysts is their high hydrocracking activity and low isomerizing activity; another feature is the occurrence of disproportionation to

\*HTsVK is the hydrogen form of the high-silica zeolite.

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