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Conversion of the Components of Natural and Associated Petroleum Gases over Modified Zeolite Catalysts

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Abstract

The laws governing the conversion of components of natural and associated petroleum gases into aromatic hydrocarbons over zeolite catalysts modified with active metal additives are investigated. According to the data obtained, the catalysts under study exhibit high activity in the course of the aromatization of lower C_2-C_4 alkanes. For almost complete conversion of the feedstock, the selectivity towards the formation of aromatic hydrocarbons over Ga-AC and Zn-ZSM-5 samples at 550 °C is 44.6 and 37.8 %, respectively. The highest catalytic activity and selectivity in the conversion of natural gas into aromatic hydrocarbons is exhibited by Zn-containing zeolites. The yield of aromatic hydrocarbons over them reaches 26.7 % at 650 °C. This is higher by 9.0 and 19.0 % than the yield over Ga-containing and unmodified zeolites, respectively. The revealed differences in the behaviour of the catalysts are due to various functional features of their active sites formed when metals are introduced into the zeolite matrix. The yield of aromatic hydrocarbons from the conversion of a mixture of C_2-C_4 alkanes over zeolite-containing catalysts is significantly higher than that in the case of natural gas conversion, which is due to the high thermodynamic stability of its major component – methane. The nature of coke deposits formed on the surface of the catalysts under study during the aromatization of low-molecular C_2-C_4 paraffins was studied by means of differential thermal analysis. The stability of Zn-ZSM-5 in this process was determined to be higher than that of the Ga-containing zeolite.

Keywords: natural gas, associated petroleum gas, propane-butane fraction, aromatic hydrocarbons, zeolite, activity, selectivity, coke

INTRODUCTION

The problem of utilization of associated petroleum gas (APG) is increasing its importance in the modern world. The amount of proved reserves of APG in Russia is 6.5 trillion m³, and our country remains a leader in burning APG since 2009. According to official statistics, 11 % of associated gas, or about 10 milliard m³, was burnt in flares. The combustion of APG leads to the loss of valuable hydrocarbon raw material, which has a negative effect on the financial state and development of companies dealing with oil and petroleum chemistry. In addition, this causes a substantial hazard to the environment: hazardous substances entering the atmosphere during the combustion of APG include carbon oxides, soot, nitrogen oxides, sulphur dioxide, *etc.* Because of this, an increase in the percentage of rationally utilized APG is urgent both for petrochemical companies and for the country's economy in general. Along with APG, natural gas (NG) may become one of the major sources of raw material for the production of organic compounds (NG): the proved resources of NG in the world are estimated as 144 trillion m³, and in Russia – at 47.6 trillion m³. For this reason, the development of chemical processes for NG processing belongs to the priority problems of the fuel-energy complex. Natural gas may serve as a basis for the production of the majority of organic compounds obtained from petroleum processing. However, the direct conversion of NG into higher hydrocarbons is limited by the high stability and low reactivity of the methane fraction. It is impossible to transform it chemically into liquid organic compounds without the use of highly active polyfunctional catalysts. Of special interest is the catalytic synthesis of strongly needed aromatic compounds from lower alkanes C_1-C_5 , which are the components of natural gas and associated petroleum gas, over zeolite-containing catalysts [1–4].

The goal of the present work was to study the regularities of the transformations of natural and associated petroleum gas components into aromatic hydrocarbons over zeolite catalysts modified by active metal additives.

EXPERIMENTAL

The objects of the investigation were: 1) nonmodified high-silica zeolite with the molar ratio $SiO_2/Al_2O_3 = 40$ (H-ZSM-5); 2) ZSM-5 zeolite modified by impregnation with zinc, with the calculated zinc content equal to 3.0 mass % (Zn-ZSM-5); 3) gallium-containing zeolite of ZSM-5 structural type (molar ratio $SiO_2/(Al_2O_3 + Ga_2O_3)$ = 40, Ga_2O_3 content in the reaction mixture 1.85 mass %, Al_2O_3 3.01 mass %), obtained through hydrothermal crystallization of aluminosilicagel in which a part of aluminium was substituted by gallium (Ga-AS).

The transformation of zeolites in the active H-form was performed by means of double decationation with a 25 % aqueous solution of NH_4Cl for 2 h at 90 °C, followed by washing with distilled water and annealing at 550 °C for 6 h.

Zinc was introduced by impregnating the zeolite in H-form with the aqueous solution of zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$.

The acid properties of the obtained catalysts were studied by means of temperature-programmable desorption of ammonia. Ammonia was adsorbed at 100 °C on a sample that was trained preliminarily. Ammonia desorption from the zeolite surface was carried out in the mode of linear heating at a rate of 10 °C/min. The concentration of acid centres in the samples (in μ mol/g of catalyst) was determined from the amount of ammonia desorbed at the moment when desorption peaks appear. Specific surface area $(S_{\rm sp})$ and pore size distribution were measured with the help of ASAP 2020 instrument (Micromeritics, USA). Calculation of $S_{\rm sp}$ for the samples under investigation was carried out using a multipoint BET procedure. Pore volume and size were determined using the Barett-Joyner-Halenda (BJL) model from the data of adsorption and desorption isotherms at the relative pressure of $P/P_0 = 0.99$.

The images taken by means of high-resolution transmission electronic microscopy (HRTEM) were obtained with JEM2010 and JEM-2200FS electron microscopes (JEOL, Japan) with the lattice resolution of 0.14 and 0.1 nm, respectively. The fast Fourier transform (FFT) was used to analyze HRTEM images.

The nature of coke deposits formed on the surface of the catalysts under investigation during the transformation of hydrocarbon gases was studied with the help of a Q-1500 derivatograph of Paulik-Paulik-Erdey system (MOMN, Hungary). Measurement results were processed using the Tanaliz software, which provided control and measurement of temperature (*T*) and rate (*V*) of sample heating, change of sample mass (TG), thermal effects (DTA). Heating rate in the experiments was 10 °C/min, the mass of the sample under investigation was 400 mg, measurements were carried out in the air. Aluminium oxide $(\alpha-Al_{2}O_{2})$ was used as the reference sample.

Propane-butane fraction (PBF) with different compositions (PBF-1 and PBF-2) and NG sampled from the main gas pipeline were used as the initial hydrocarbon material providing approximate simulation of the real APG. The component composition of initial hydrocarbon gases is shown in Table 1.

The regularities of PBF and NG transformations in the presence of the catalysts under study were investigated in a stand set-up of flow type with the steady catalyst bed at atmospheric pressure within temperature range 450-650 °C and the volume flow rate of raw material supply 250 h⁻¹. The duration of an experiment at each temperature point was 60 min; the reactor was blown with nitrogen before and after each experiment. Reaction products were analyzed by means of gas-liquid chromatography using a Khromatek-Kristall 5000.2 chromatograph (GK Novye Teknologii, Russia). The degree of transformation of initial hydrocarbon raw material, the yield of gaseous and liquid products were de-

TABLE 1						
Component	composition	of	initial	hydrocarbon	raw	material

Component	Formula	Conten	t, mass %	
		NG	PBF-1	PBF-2
Methane	CH_4	83.2	0	0
Ethane	C_2H_6	7.9	0	17.5
Propane	$C_{3}H_{8}$	5.0	77.4	49.3
Butanes	$\mathrm{C_4H_{10}}$	3.9	22.6	33.2

termined for each experiment, and the selectivity of product formation was calculated.

RESULTS AND DISCUSSION

The data on the effect of temperature on the composition of the products of NG transformation in the presence of the obtained zeolite catalysts are shown in Table 2. One can see that nonmodified zeolite exhibits low activity in the transformation of NG in aromatic hydrocarbons: NG conversion at 650 °C is 18 %, while the yield of aromatic hydrocarbons is 7.7 %. Modification of zeolite with zinc causes changes in its activity in NG transformation. The degree of NG transformation over the Zn-ZSM-5 sample and the yield of aromatic hydrocarbons increase with temperature rise, and at 650 °C these parameters reach 31 and 26.7 %, respectively (Fig. 1). The selectivity of the formation of aromatic hydrocarbons within the range 500–650 °C changes from 69.1 to 85.6 %

(see Table 2). Benzene and naphthalene dominate in the liquid reaction products, and the fraction of these products increases with the rise of the process temperature. The hydrogen concentration in the gaseous reaction products increases with an increase in reaction temperature, while the content of lower alkanes and alkenes decreases.

The Ga-AC sample exhibits lower catalytic activity in NG transformation than Zn-ZSM-5 does, but higher than non-modified zeolite H-ZSM-5. The yield of aromatic hydrocarbons over this catalyst at 650 °C is 17.7 %, which is lower by 9.0 % than the yield over Zn-ZSM-5. This is likely connected with an increase in the rate of hydrogenation of the formed intermediates over active metal-containing centres containing gallium.

The results of the studies into the transformations of PBF of varied composition over Zn-ZSM-5 and Ga-AC catalysts are shown in Table 3. One can see that a noticeable transformation of PBF-1 over the Zn-ZSM-5 sample starts at a reaction temperature equal to 450 °C. With temperature rise, the conversion of the initial raw material increases sharply and reaches 100 % at 600 °C. The formation of aromatic hydrocarbons starts at 450 °C, and their maximal yield is 44.2 % at 600 °C. It should be noted that the composition of the formed aromatic hydrocarbons is essentially affected by process temperature. With its rise, the formation of benzene, methyl- and di-

TABLE 2

Effect of process temperature on the composition of the products of natural gas transformation over non-modified and modified zeolites

T 00	77 07	<u> </u>									<u> </u>
<i>T</i> , °C	X, %	Conten	t, mass %							$Y_{ArHC}, \%$	$S_{\rm ArHC}, \%$
		H_2	Alkanes	Alkenes	C_6H_6	C_7H_8	C_{8-9}	$\mathrm{C_{10}H_8}$	C_{11-12}		
					H-ZSI	M-5 catalys	st				
500	13	1.18	86.83	8.16	2.43	0.99	0.19	0.10	0.12	3.8	29.0
550	16	1.56	84.38	7.96	4.47	0.94	0.11	0.31	0.25	6.1	39.1
600	17	1.72	83.38	7.88	5.20	0.68	0.07	0.70	0.37	7.0	42.2
650	18	1.76	83.15	7.35	5.80	0.72	0.03	0.79	0.40	7.7	43.5
					Zn-ZS	M-5 cataly	st				
500	21	2.71	78.89	3.81	4.53	1.93	0.30	6.44	1.39	14.6	69.1
550	25	3.89	73.70	1.39	5.86	0.73	0.10	10.79	3.54	21.0	83.6
600	28	3.98	72.02	0	7.95	0.27	0.14	13.40	2.24	24.0	84.5
650	31	4.81	68.49	0	8.80	0.28	0.16	15.74	1.72	26.7	85.6
					Ga-A	AC catalyst					
500	19	2.48	80.72	4.90	6.46	1.01	0.09	2.96	1.38	11.9	61.7
550	22	2.82	78.55	4.23	6.65	0.55	0.04	5.76	1.40	14.4	67.0
600	23	3.11	76.95	3.82	7.19	0.27	0.03	7.01	1.62	16.1	70.0
650	25	3.20	75.83	3.23	7.36	0.34	0.01	8.37	1.66	17.7	71.7

Note. T is process temperature; X is gas conversion; Y_{ArHC} is the yield of aromatic hydrocarbons; S_{ArHC} is the selectivity of the formation of aromatic hydrocarbons.



Fig. 1. Dependence of conversion (1) of natural gas over Zn-ZSM-5 and the yields of alkanes (2), benzene (3), naphthalene (4) and aromatic hydrocarbons C_{6+} (5) on process temperature.

methylnaphthalenes increases, the concentrations of xylenes and $C_{_{8+}}$ alkylbenzenes decrease, while toluene concentration passes through a maximum at a temperature of 550 °C.

The PBF-2 initial raw material with substantial ethane content is prone to transformation to a somewhat lower extent than PBF-1. During PBF-2 conversion, the Zn-ZSM-5 sample is characterized by lower total catalytic activity. For instance, the conversion of PBF-2 at 550 °C is only 82 %, while the conversion of PBF-1 under the same conditions is almost complete; at the optimal process temperature (within the range 550– 600 °C) the yield of aromatic hydrocarbons from PBF-2 transformation insignificantly differs from the yield of aromatic hydrocarbons formed in the transformation of PBF-1.

Similar dependencies of the major parameters characterizing the process on the temperature and composition of initial gaseous raw material are observed for Ga-AC. Over the Ga-AC sample, a noticeable transformation of PBF-1 starts at 450 °C, too, and a rather large amount of aromatic hydrocarbons is formed at this temperature. With an increase in process temperature, the yield of aromatic hydrocarbons increases and reaches 44.1 % at 600 °C. During PBF-2 transformation over Ga-AC, a smaller amount of aromatic hydrocarbons is formed than that formed in the case of PBF-1. This is explained by a decrease in the rate of aromatization of the hydrocarbons with a smaller number of carbon atoms in the molecules of initial gaseous raw material.

The data on the yields and compositions of aromatic hydrocarbons and gaseous products of PBF transformations on modified zeolite catalysts are shown in Table 4. The maximal amount of

TABLE 3

Parameters of the transformation of propane-butane fractions over modified zeolite catalysts

Initial raw material	T, ℃	X, %	$S_{1}^{}, \%$	$S_{2}^{}, \%$	$S_{3}^{}, \%$	$S_4,\%$	$\rm Y_{ArHC},~\%$
		Zn-Z	ZSM-5 ca	talyst			
PBF-1	450	39	5.5	83.9	3.2	7.4	2.9
	500	86	2.5	61.2	1.2	35.1	30.2
	550	99	2.9	58.5	0.8	37.8	37.7
	600	100	3.3	51.3	1.1	44.2	44.2
PBF-2	450	25	7.7	78.6	6.1	7.6	1.8
	500	64	3.1	54.7	2.2	40.0	25.6
	550	82	3.4	52.1	1.1	43.4	35.5
	600	82	4.5	41.2	1.6	52.7	43.5
		Ga	-AC cata	lyst			
PBF-1	450	41	3.8	48.6	4.2	43.4	17.9
	500	74	3.9	47.5	4.1	44.5	32.9
	550	94	3.9	48.1	3.4	44.6	40.9
	600	98	4.1	47.9	3.2	44.8	44.1
PBF-2	450	31	5.8	61.3	4.7	28.2	8.7
	500	64	4.1	48.0	3.4	44.5	28.5
	550	79	4.2	47.7	2.4	45.7	36.2
	600	82	4.5	43.4	2.4	49.7	40.7

Note. S_1 , S_2 , S_3 and S_4 are selectivities of the formation of hydrogen, alkanes, alkanes and aromatic hydrocarbons, respectively.

TABLE 4

Composition of the products of the transformation of propane-butane fractions over modified zeolite catalysts (T = 550 °C)

Initial raw	Catalysate	Composition of	Composition of liquid products, mass %			Composition of gaseous products, mass $\%$				
material	yield, mass $\%$	BTX fraction	Alkyl benzenes	Naphthalenes	H_2	CH_4	C_2H_6	Alkenes C_2 - C_4	Alkanes C ₃ –C ₄	
Zn-ZSM-5 catalyst										
PBF-1	37.7	69.5	2.0	28.5	4.6	39.4	54.2	1.3	0.5	
PBF-2	35.5	70.7	3.0	26.3	4.3	31.5	61.6	1.4	1.2	
	Ga-AC catalyst									
PBF-1	40.9	70.1	4.6	25.3	6.5	47.0	30.1	5.7	10.7	
PBF-2	36.2	69.8	4.5	25.7	6.1	36.8	49.1	3.0	5.0	

TABLE 5

Dependence of the catalytic properties of modified zeolite catalysts during the transformation of propane-butane fractions on operation time

Initial raw material	<i>t</i> , h	T, °C	X, %	$Y_{Ar HC}, \%$	$S_{ m Ar~HC},\%$	$S_{ m cr}^{}, \%$	$S_{ m deh}^{},\%$
		Zn	-ZSM-5	catalyst			
PBF-1	1	550	100	33.4	33.4	62.6	0.9
	2	550	100	33.9	33.9	62.1	1.0
	4	550	100	36.3	36.6	59.8	1.0
	8	550	95	33.4	35.3	59.7	2.2
	12	550	75	28.0	37.2	52.7	7.0
	16	550	59	22.9	38.8	43.7	13.9
	17	600	61	24.7	40.5	37.9	20.8
	18	600	57	17.9	31.6	33.4	31.4
	20	600	38	8.5	22.5	24.9	49.7
PBF-2	1	550	82	44.7	54.5	41.5	0.9
	2	550	82	39.5	48.2	47.4	1.0
	4	550	82	35.6	43.6	51.7	1.2
	8	550	81	34.2	42.2	52.9	1.4
	12	550	79	33.4	42.1	52.5	1.8
	16	550	77	30.9	40.4	53.5	2.5
	17	600	82	43.6	53.2	40.7	2.4
	18	600	82	34.3	41.8	51.4	2.9
	20	600	81	25.0	30.9	61.8	3.6
		0	da-AC ca	talyst			
PBF-1	1	550	96	50.2	52.5	41.8	2.3
	2	550	91	41.8	46.1	46.0	4.1
	4	550	85	38.1	44.8	45.3	6.1
	8	550	68	29.3	42.9	42.8	10.7
	12	550	51	17.7	34.8	42.8	18.5
	13	600	55	22.0	40.2	29.7	27.1
	14	600	35	9.0	25.7	29.0	42.5
	16	600	22	3.5	15.6	29.7	52.6
PBF-2	1	550	81	44.6	55.3	38.6	1.8
	2	550	79	36.8	46.8	45.9	2.8
	4	550	76	35.0	46.1	45.3	4.2
	8	550	63	28.9	45.5	41.2	9.0
	12	550	46	20.1	43.7	34.6	17.6
	13	600	46	22.3	48.0	18.6	30.1
	14	600	32	11.5	35.5	17.2	44.3
	16	600	22	4.4	20.1	18.6	58.9

Note. $S_{\rm cr},\,S_{\rm deh}$ is selectivity of cracking and dehydrogenation, respectively.

aromatic hydrocarbons (40.9 %) at 550 °C is formed during PBF-1 transformation over Ga-AC. Catalysates formed over the catalysts under investigation in the transformations of PBF samples of different compositions only insignificantly differ from each other in the quantitative ratios of the groups of hydrocarbons.

With an increase in ethane content in the initial raw material, the fraction of methane in the gaseous products of the transformation decreases, while the fraction of ethane increases. The amount of C_1-C_2 alkanes formed over the Zn-ZSM-5 sample is larger than over the Ga-AC sample.

To reveal the optimal duration of the catalyst reaction cycle after which there would be no difficulties in recovering the catalyst activity through oxidative regeneration, it is important to determine the nature and amount of coke deposits formed on the catalyst surface during the reaction.

Results of the investigation into the effect of catalyst operation time on its activity and selectivity in the transformation of PBF of different compositions are presented in Table 5. One can see that PBF-1 and PBF-2 are almost completely transformed over the zeolite catalysts under study at 550 °C, so the duration of the stable operation of catalysts in one reaction cycle was determined at this temperature. For a correct comparison of the results, catalyst tests with the gaseous raw material samples of different composition were carried out for 20 and 16 h of continuous operation with Zn-ZSM-5 and Ga-AC samples, respectively, and the formed reaction products were analyzed after equal time intervals.

It follows from the data shown in Table 5 that the activity of the Zn-ZSM-5 catalyst in the transformation of PBF-1 at a temperature of 550 °C remains almost constant for 8 h, and then a decrease in the conversion of initial raw material and in the yield of aromatic hydrocarbons is observed. At the same time, the selectivity of the formation of lower olefins increases, while the selectivity of the formation of cracking products decreases. With an increase in reaction temperature to 600 °C, after continuous catalyst operation for 16 h, initial activity parameters cannot be achieved. During the operation of the Zn-ZSM-5 catalyst for 20 h, the yield of aromatic hydrocarbons formed over it decreases to 8.5 %, and the degree of initial raw material transformation decreases to 38 %. For PBF-2 transformation over this sample, conversion changes only insignificantly during the entire reaction cycle, while the yield of aromatic hydrocarbons decreases gradually reaching 30.9 % after operation for 16 h at 550 °C. An increase in reaction temperature to 600 °C leads to the recovery of initial activity and selectivity of the catalyst with respect to the formation of aromatic hydrocarbons.

For Ga-AC, an almost linear decrease in PBF-1 conversion and in the yield of aromatic hydrocarbons is observed with an increase in the time of catalyst operation (see Table 5). During 12 h of continuous operation at 550 °C, the degree of transformation and the selectivity of the formation of aromatic hydrocarbons over this catalyst decrease by 45 and 17.7 %, respectively. Similar dependencies of the major process on the time of Ga-AC operation are observed for the transformation of PBF-2.

Results of thermal analysis (DTA and TG) of the catalysts under investigation are shown in Fig. 2 and 3. The thermograms show the changes in sample mass with respect to the mass of the coked catalyst. For a quantitative comparison of the results, it is more convenient to handle the value divided by the mass of the pure catalyst (after coke burning). The values calculated in the proper manner are shown in Table 6.

Endothermic effects in the region of 100-160 °C and the corresponding maxima on DTG curves are due to the removal of adsorbed and weakly bound water. Exothermal effects ob-



Fig. 2. Thermograms of coke deposits on Zn-ZSM-5 catalyst after operation for 20 h in the transofmration of PBF-1 (a) and PBF-2 (b).



Fig. 3. Thermograms of coke deposits on Ga-AC after operation for 16 h in the transformation of PBF-1 (a) and PBF-2 (b).

served above 400 °C and the peaks on DTG curves correspond to coke deposit burning. According to the data of thermal analysis, the largest amount of coke is formed over Ga-AC during the transformation of PBF-2. The total mass of coke deposits for this sample after its operation for 16 h is 12.51 %, the temperature points of the start and maximum of coke burning from this catalyst are within the range of rather high temperatures, which is the evidence of the formation of dense (condensed) deposits (see Table 6). The high-temperature shoulder at 680-710 °C on the DTG curve is close to the temperature of sibunit burning (715 °C) and provides evidence of the formation of coal-like deposits [5]. During PBF-1 transformation over Ga-AC, somewhat less amount of coke is formed than during the transformation of PBF-2, but the maximum of coke burning is shifted to the region of higher temperatures. Coke formations are charac-

TABLE 6

Data of thermal analysis for the catalysts operating in the transformation of propane-butane fractions

Catalyst (raw material,	Mass changes, %					
operation time)	Water	Coke				
Zn-ZSM-5 (PBF-1, 20 h)	-1.97 (133 °C)	-11.77 (636, shoulder 700 °C)				
Zn-ZSM-5 (PBF-2, 20 h)	-3.47 (107 °C)	−11.08 (608, shoulder 665 °C)				
Ga-AC (PBF-1, 16 h)	-2.04 (112 °C)	-12.24 (658, shoulder 740 °C)				
Ga-AC (PBF-2, 16 h)	-1.33 (110 °C)	−12.51 (650, shoulder 706 °C)				

Note. Mass changes are presented with respect to the mass of pure catalysts (after coke burning out up to 900 °C). The corresponding temperature points for the maxima of peaks on DTG curves are given in parentheses.

terized by lower homogeneity, which is confirmed by the presence of a shoulder on DTA curve in the high-temperature region after the temperature maximum at 658 °C.

Less coke is formed over Zn-ZSM-5 samples after the treatment of PBF for 20 h, and the formed products are not so dense, which is confirmed by the lower temperature of the termination of coke burning (see Table 6). The smallest amount of coke deposits is formed over the Zn-ZSM-5 catalyst during PBF-2 transformation: 11.08 %. For this sample, more narrow peaks on DTG and DTA curves with the exo effect at 608 °C are observed (see Fig. 2, *b*), which is the evidence of the homogeneity of the carbon deposits present in the samples.

So, the studies showed that the composition of initial raw material has a substantial effect on the yield of aromatic hydrocarbons. It is much higher in the case when PBF is used than in the case of NG. This is explained by an increase in the rate of aromatization with an increase in the content of hydrocarbons with a larger number of carbon atoms in the molecule. With an increase in the temperature of PBF and NG transformation, an increase in the yield of the target product over the catalysts under study is observed. The discovered differences in catalyst behaviour may be connected with different functional features of the active centres formed in these catalysts as a result of the introduction of metals in the zeolite matrix.

The Zn-ZSM-5 catalyst is characterized by the developed specific surface area with an average pore diameter of 2.6 nm (Table 7). The Ga-AC sample possesses a lower specific surface area but it is characterized by a larger average pore diameter, which is equal to 5 nm. According to the data of ammonia thermodesorption, the cata-

Characteristics	s of the catalys	sts under investigat	tion				
Catalyst	$S_{\rm sp},{\rm m^2/g}$	Average pore	$T_{\rm max}$, c	°C	Conce	ntration, µ	umol/g
		diameter, nm	T_{I}	$T_{\rm II}$		$C_{\rm II}$	C_{Σ}
Zn-ZSM-5	393	2.6	165	420	447	128	575
Ga-AC	344	5.0	200	425	531	330	861

TABLE 7

Note. $T_{\rm II}$, $T_{\rm II}$ are temperature points of the maxima of low- and high-temperature peaks on thermodesorption curves, respectively; $C_{\rm p}$, $C_{\rm m}$ and $C_{\rm s}$ are the concentrations of weak and strong acid centres and their sum, respectively.

lysts under investigation possess two types of acid centres, which is evidenced by the presence of two maxima on thermodesorption curves. The high-temperature peak is usually assigned to acid OH groups bound with Al atoms of the zeolite framework. They provide Bronsted acidity of zeolite and are responsible for its activity in the transformations of hydrocarbons. One can see in the data presented in Table 7 that the catalysts are characterized by the presence of strong acid centres that are close to each other in the strength, but the amount of these centres is substantially larger for Ga-AC. In addition, the Zn-ZSM-5 sample contains a smaller amount of weak acidic centres characterized by substantially lower force in comparison with the force of centres in Ga-AC.

According to the data of electron microscopic investigation, the particles of Zn-containing zeolite have a shape characteristic of high-silica zeolites: polycrystalline spheroids composed of single crystals grown together, with a size of several micrometres (Fig. 4, a, b). The bands of the lattice correspond in their orientation and periodicity to the internal channel structure of zeolite; no separate zinc particles were detected (see Fig. 4, c).

According to the results of EDX analysis, the nonuniform distribution of zinc over zeolite crystals was established. Results of the elemental analysis show that zinc content in different zeolite crystals varies within the range 0-5 at. % (Fig. 5). As a rule, zinc concentration is substantially higher in defectbearing zeolite crystals.

According to electron microscopic data, Ga-AC particles possess the morphology of block crystals with the stepped surface, $\sim 1 \mu m$ in size (Fig. 6, *a*). An HRTEM image shows a lattice region transparent for electrons, with the parameter $d_{200} \approx 1.0$ nm, which is characteristic of zeolite with ZSM-5 structure (see Fig. 6, b). These results suggest that the internal structure of the zeolite is uniform, and foreign particles are completely absent from the surface of its crystals, which cor-



Fig. 4. Microscopic images of the Zn-ZSM-5 sample: a, b particle morphology; c - HRTEM image of zeolite lattice.

Fig. 5. EDX spectrum of the Zn-ZSM-5 sample: a – complete absence of zinc in one crystal; b – presence of zinc, with the atomic ratio Zn/Si = 5 : 95 in another zeolite crystal.

Fig. 6. Microscopic images of the Ga-AC sample: a – particle morphology; b – HRTEM image of zeolite lattice.

responds to the idea of a cation-dispersed state of gallium in the Ga-AC sample.

According to [6, 7], there are principal differences in the mechanisms of aromatization of lowmolecular paraffins over H-ZSM-5 zeolites and over the zeolites modified with Zn and Ga. The aromatization activity of H-ZSM-5 not modified with metals is determined by the presence of strong Bronsted acid centres over which the cracking of saturated molecules occurs, followed by the transformations of the formed olefins: oligomerization, hydrogen redistribution, oligomer cracking.

Zeolites containing zinc and gallium possess clearly pronounced dehydrating capacity of aprotonic acid centres formed during modification. Lewis acid centres exhibit electron-accepting properties and are able to detach hydride ions from saturated molecules, These centres accelerate the dehydration of lower paraffins, olefins, naphthenes and exhibit low activity in the oligomerization of unsaturated molecules, for which proton acid centres are responsible [7, 8]. So, over pentasil-type zeolites containing strong Lewis acid centres, the formation of aromatic hydrocarbons from saturated molecules with less than six carbon atoms proceeds through the stage of dehydrogenation of initial paraffins, olefin oligomerization, the formation of alkyl cations, cyclization-aromatization of oligomers; these processes are accompanied by cracking, isomerization and hydrogen redistribution.

CONCLUSION

The analysis of the obtained data allows us to conclude that both catalysts under study exhibit

high activity in the aromatization of lower $C_2^{-}C_4^{-}$ alkanes. The selectivity of the formation of aromatic hydrocarbons at 550 °C over Ga-AC and Zn-ZSM-5 samples is 44.6 and 37.8 %, respectively, with an almost complete transformation of initial raw material. The benzene-toluene-xylene fraction dominates in the liquid reaction products: its content is more than 70 %, while the

not exceed 30 %. The studies showed that the yield of aromatic hydrocarbons from the transformation of a mixture of lower C_2-C_4 alkanes over zeolite-containing catalysts is substantially higher than in the case if natural gas is used, which is connected with the high thermodynamic stability of methane, its major component.

concentration of naphthalene hydrocarbons does

To achieve the high efficiency of the transformation of lower alkanes, the catalysts should possess not only increased dehydrogenating and aromatizing activity but also a low disposition to coking. In comparison with Ga-containing zeolite, Zn-ZSM-5 is characterized by the higher performance stability in the aromatization of low-molecular $C_2^{-}C_4$ paraffins.

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