

Aromatization of Low-Molecular-Weight Hydrocarbons on Modified Zeolite Catalysts

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Abstract—The processes of converting propane-butane and propane-propylene fractions into aromatic hydrocarbons on zeolite catalysts modified by the introduction of Zn, La, Fe, Co, and phosphorus has been investigated. The behavior of catalysts in the processing of light hydrocarbons depends on the structure and state of active centers. Physicochemical characteristics of the developed catalysts have been investigated. The highest yield of aromatic hydrocarbons has been observed on the Zn-La-Fe-P-ZSM-Al₂O₃ catalyst, where their yield reaches 52.6% in processing the propane-butane fraction at 600°C, while the selectivity for aromatic hydrocarbons is 64.6%. When the propane-propylene fraction is processed in the temperature range of 350–600°C, the yield of aromatic hydrocarbons on the Zn-La-Fe-P-ZSM-Al₂O₃ catalyst is significantly higher than in other investigated catalysts. A comparison of the results of processing propane-butane and propane-propylene fractions has shown that the yield of the aromatic hydrocarbons is higher when using propane-propylene fractions. For example, at a temperature of 550°C on the Zn-La-Fe-P-ZSM-Al₂O₃ catalyst, the liquid phase yield when processing the propane-butane fraction is 43.6% and the propane-propylene fraction is 59.1% at a conversion rate of 70.2 and 88.3, respectively.

Keywords: zeolite, propane-butane fraction, propane-propylene fraction, aromatic hydrocarbons, conversion, selectivity

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INTRODUCTION

The rational use of light alkanes, which are part of natural, associated, and refinery gases, is an urgent task. The C₁–C₄ alkanes contained in these gases can be converted in the presence of zeolite catalysts into aromatic hydrocarbons (AHs), which are important raw materials for many petrochemical processes. However, until now, a significant part of light hydrocarbon gases is used only as technological and household fuel or is burned in flares, causing significant harm to the environment.

Currently, in the petrochemical and oil refining industry, zeolite-containing catalysts based on high-silica zeolites of the pentasil family are widely used, which have a unique microporous structure and acid-base properties capable of converting light alkanes into valuable products of petrochemical synthesis. There is growing interest in high-silica zeolites of the pentasil type as catalysts for the aromatization of low-molecular-weight alkanes [1–8].

Modification of zeolite catalysts by introducing additives of various metals can significantly increase

the yield of aromatic hydrocarbons and increase the stability of the catalyst.

This paper presents the results of studying the process of conversion of C₃–C₄ hydrocarbons into aromatic hydrocarbons on zeolite catalysts modified with variable valence metals (iron and phosphorus), zinc, rare-earth elements (cobalt, lanthanum), and phosphorus to reduce coke formation [9–12]. Most attention was paid to assessing the influence of the nature of the components of the active phase of the catalyst and the conditions of the process on the degree of AH conversion and the composition of the resulting hydrocarbon fractions.

EXPERIMENTAL

The process of aromatization of light AHs was investigated on unmodified and modified ZSM-5 zeolites with a silicate modulus of 35. The catalysts were prepared by impregnating a mixture of aluminum hydroxide and HZSM-5 zeolite with aqueous solutions of zinc, iron(II), cobalt(II), and lanthanum nitrates and phosphoric acid, followed by drying at

Table 1. Temperature-programmed desorption of ammonia

Catalyst	T_{\max} , °C			Amount of desorbed ammonia, 10 ⁻⁴ mol/g of catalyst			Σ NH ₃ , 10 ⁻⁴ mol/g of catalyst
	1	2	3	1	2	3	
ZSM-Al ₂ O ₃	122	170	505	10.85	10.54	6.29	27.68
Zn-Fe-ZSM-Al ₂ O ₃	195	—	510	14.7	—	tr*	14.7
Zn-La-Co-ZSM-Al ₂ O ₃	152	310	480	23.70	8.80	4.00	36.50
Zn-La-Fe-P-ZSM-Al ₂ O ₃	135	450	510	19.0	4.71	6.82	30.53

* tr is trace amount.

150°C and calcining at 550°C. The composition of the catalysts is as follows:

60% ZSM, 40% Al₂O₃;

3% Zn, 1% Fe, 60% ZSM, 36% Al₂O₃;

3% Zn, 1% La, 1% Co, 60% ZSM, 35% Al₂O₃;

3% Zn, 1% La, 1% Fe, 3% P, 60% ZSM, 32% Al₂O₃.

The physicochemical characteristics of the synthesized catalysts were investigated by BET methods on an AccuSorb setup (Micromeritics, United States). The dispersity, structure, and state of the active centers of the catalysts were investigated using electron microscopy [13] on an EM-125K transmission electron microscope with the use of electron microdiffraction. Decoding of microdiffraction images was carried out using standard ASTM tables [14, 15].

To determine the number of acid sites and their distribution by strength, the method of temperature-programmed desorption of ammonia was used [16].

The synthesized catalysts were tested during the processing of propane-butane and propane-propylene fractions in a flow-through quartz reactor with a stationary catalyst layer at atmospheric pressure and reaction temperature varying from 400 to 600°C. The composition of the propane-butane fraction, %, was 0.1 methane; 0.4 ethane; 0.1 ethylene; 25.2 propane; 69.9 isobutane, 2.9 *n*-butane; and 1.4 C₅-C₆-AH. The composition of the propane-propylene fraction, %, as ethane 3.1, propane 36.2, propylene 27.8, isobutylene 0.4, butylene 2.9, cis-2-butene 2.0, and trans-2-butene 2.8.

The reaction products were analyzed on Khromatek-Kristall and Agilent chromatographs.

RESULTS AND DISCUSSION

The behavior of catalysts in the processing of light hydrocarbons mainly depends on the structure and state of active centers. In the course of this work, the physicochemical characteristics of the developed catalysts, namely, specific surface area and porosity, were obtained. For all catalysts, the specific surface area is

in the range of 283.0–307.2 m²/g, pores with $d = 1.5$ –3.0 nm prevailing.

The acid-base characteristics of catalysts are essential for the processing of light hydrocarbons. The acid-base properties of the catalysts were investigated by the temperature-programmed desorption of ammonia. Studies have shown (Table 1) that ammonia chemisorbed on the surface of the Al₂O₃-ZSM catalyst is inhomogeneous and present in three forms with desorption maxima temperatures equal to $t_{\max} = 122^\circ\text{C}$, $t_{\text{des}} = 170^\circ\text{C}$, and $t_{\max} = 505^\circ\text{C}$. Their total amount is equal to 10.85×10^{-4} , 10.54×10^{-4} , and 6.29×10^{-4} mol/g of catalyst. The total content of desorbed ammonia, which corresponds to the number of acid sites, is 27.68×10^{-4} mol/g of catalyst.

The introduction of zinc and iron into the composition of the Al₂O₃-ZSM catalyst changes its acidic characteristics. The desorption maxima of adsorbed forms of ammonia shift to higher temperatures, the temperature of the most strongly bound ammonia shifts from 122 to 195°C, and its amount is 14.70×10^{-4} mol/g of catalyst. In this case, ammonia, which is chemisorbed in the region of medium and high temperatures, practically disappears.

The study of the acidic characteristics of the Zn-La-Co-ZSM-Al₂O₃ showed that ammonia is desorbed in three regions with $T_{\text{des}} = 152$, 310, and 480°C; their amount is 23.70×10^{-4} , 8.80×10^{-4} , and 4.00×10^{-4} mol/g of the catalyst, respectively. The total number of acid sites is 36.50×10^{-4} mol/g of catalyst.

The most weakly bound ammonia from the Zn-La-Fe-P-ZSM-Al₂O₃ surface is desorbed with a maximum at 135°C, and the temperature of the more

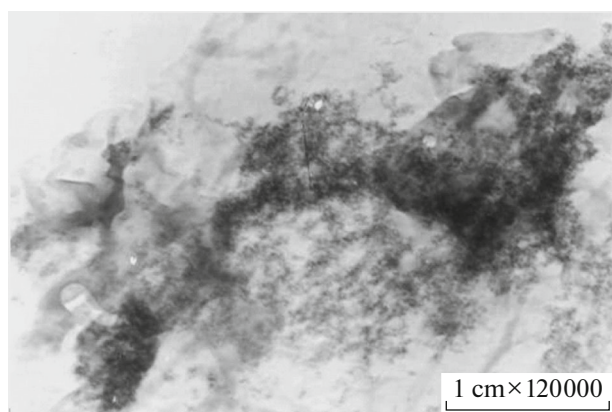


Fig. 1. Scanning electron images of Zn-Fe-ZSM- Al_2O_3 catalyst.

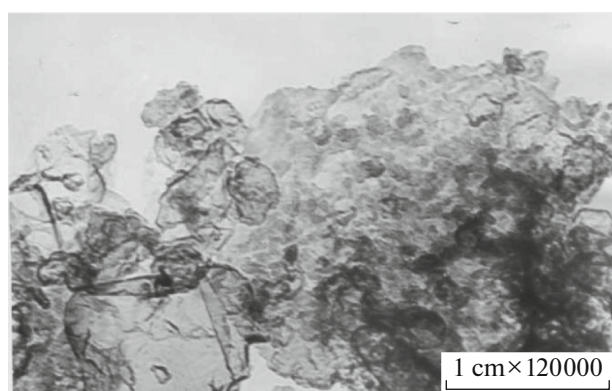


Fig. 2. Scanning electron images of La-Zn-Co-ZSM- Al_2O_3 catalyst.

strongly bound forms shifts higher up to 450 and 510°C when compared to other studied catalysts. On the surface of the Zn-La-Fe-P-ZSM- Al_2O_3 catalyst, weakly bound forms of ammonia predominate. Their amount reaches 19.4×10^{-4} mol/g of catalyst; the content of more strongly bound forms is much less and is equal to 4.71×10^{-4} (450°C) and 6.82×10^{-4} mol/g of catalyst (510°C). The total acidity of the catalyst is 30.50×10^{-4} mol/g of catalyst.

Using electron microscopy and microdiffraction analysis, it was established that the structure of the catalysts is rather complex. The particle size, structure, and phase composition of the active centers of the surface depend on the nature and ratio of the metals of the active phase.

According to electron microscopy data, highly dispersed structures with $d \approx 2.0$ – 4.0 nm prevail on the surface of the unmodified ZSM- Al_2O_3 catalyst. On the surface of the modified Zn-Fe-ZSM- Al_2O_3 catalyst, large semitransparent structures with a hexagonal facet prevail, identified by the electron diffraction as FeFe_2O_3 . Their size ranges from 50 to 100 nm. The

combination of electron microscopy with electron diffraction, which makes it possible to determine the composition of the formations, shows that on the catalyst surface there are also accumulations of particles identified as Fe_3Al , FeOOH , Fe_2SiO_4 , Fe_4O_5 , Fe_2O_3 , FeAl_2O_4 , ZnFe_2O_4 with $d \approx 1.0$ – 2.0 nm.

The electron microscopy image of the Zn-Fe-ZSM- Al_2O_3 catalyst is shown in Fig. 1.

It was found that, on the surface of the Zn-La-Co-ZSM- Al_2O_3 catalyst, formations with $d \approx 3.0$ – 5.0 nm, consisting of La_2O_3 and La_2CoO_4 , prevail. There are also structures with a size ranging from 5.0 to 7.0 nm, formed by La_2O_3 , ZnO , and $\text{Zn}(\text{OH})_2$. The introduction of zinc and lanthanum atoms into the structure of zeolite and Al_2O_3 with the formation of $\text{La}_4\text{Zn}_2\text{Si}_3\text{O}_{10}$ and LaAlO_3 was observed. The electron microscopic image of the Zn-La-Co-ZSM- Al_2O_3 catalyst is shown in Fig. 2.

On the surface of the Zn-La-Fe-P-ZSM- Al_2O_3 catalyst, there are evenly spaced vast accumulations of La_2O_3 , ϵ - Fe_2O_3 , and FeAl_2 particles with $d \approx 3.0$ – 5.0 nm. There are clusters of aggregates of rounded particles with $d = 10.0$ – 30.0 nm consisting of smaller particles with $d = 0.2$ – 0.3 nm, identified as a mixture of α - FeO , Fe_2O_3 , ZnFe_2O_4 , FeO , ZnAl_2O_4 , LaO , and $\text{LaAl}_{11}\text{O}_{18}$. On the catalyst surface, there are structures formed by AlPO_4 , SiP_2O_7 , and ZnO with $d = 0.3$ – 0.5 nm. It should be noted that the compounds ZnAl_2O_4 , ZnFe_2O_4 , $\text{LaAl}_{11}\text{O}_{18}$, FeAl_2 , AlP , AlPO_4 , and SiP_2O_7 , which indicate the direct interaction of matrix atoms with modifying additives, were also found in the composition of catalysts by electron microscopy and electron diffraction. These structures, according to [17], can work as Lewis acid centers, which can provide a high activity of this catalyst in the aromatization process of light hydrocarbons. The electron microscopy image of the La-Zn-Fe-P-ZSM- Al_2O_3 catalyst is shown in Fig. 3.

An analysis of the electron microscopy results and thermal desorption of ammonia showed that acid sites coexist with metal ones on the surface of the developed catalysts. Depending on the nature of the modifier, their size ranges from 0.2 to 10.0–20.0 nm. All catalysts are characterized by the introduction of modifier metals into the structure of the matrix. Metals are in various oxidation states and can be fixed both inside zeolite cavities and outside. These structures can function as Lewis acid sites. The functioning of various types of centers in catalytic processes is often described as independent, without considering the possibility of their joint action on the reactant molecule. However, it can be assumed that their simultaneous presence ensures the polyfunctionality of the catalytic system [15, 16].

It has been shown that the degree of conversion of C_2 – C_4 alkanes into aromatic hydrocarbons and the composition of compounds formed during their pro-

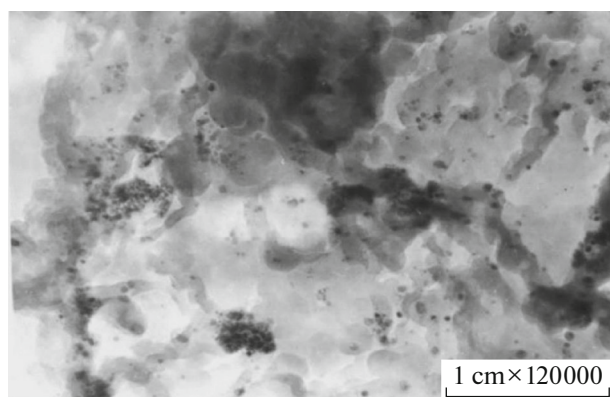


Fig. 3. Scanning electron images of La-Zn-Fe-P-ZSM- Al_2O_3 catalyst.

cessing on zeolite-containing catalysts depend on the composition of the mixture, the temperature of the process, and the nature of the components of the catalytic system. Therefore, when processing a propane-butane fraction on the unmodified ZSM- Al_2O_3 catalyst, aromatic hydrocarbons and gaseous products are formed. The liquid phase contains benzene, toluene, ethylbenzene, xylenes, and C^{8+} hydrocarbons (Table 2).

When the propane-butane fraction is converted on the Zn-La-Co-ZSM- Al_2O_3 catalyst (Table 3), the degree of conversion increases from 40.2 to 98.4% with an increase in temperature from 450 to 600°C. The yield of aromatic hydrocarbons passes through a maximum (31.4%) at 550°C; selectivity for these hydrocarbons decreases from 48.0 (450°C) to 24.5 (600°C). With an increase in temperature from 450 to 600°C, the content of benzene in the liquid phase increases from 6.0 to 49.2%, the yield of toluene decreases from 74.6 to 47.2%, that for ethylbenzene decreases from 13.9 to 2.7%, and for xylenes from 3.8 to 0.9%. With an increase in temperature from 450 to 600°C, hydrocarbon cracking increases with the formation of methane and ethane. The yield of methane

and ethane increases from 8.3 to 28.0% and from 2.3 to 42.0%, respectively.

When the propane-butane fraction is processed on the Zn-La-Fe-P-ZSM- Al_2O_3 catalyst, the conversion at 400°C is 16.8% and, with an increase in temperature to 600°C, it increases to 81.4% (Table 4). At 400°C, the total yield of aromatic hydrocarbons was 13.3%. With an increase in the reaction temperature to 600°C, the yield of aromatic hydrocarbons increases to 52.6%. Under conditions of maximum conversion, the catalyst contains 17.6% benzene, 41.7% toluene, 17.7% ethylbenzene, and 5.7% xylenes. The gas phase contains C_1 – C_4 -AH and hydrogen. The maximum selectivity for aromatic hydrocarbons is 80.3% at 450°C. Its value decreases to 64.6% (600°C) with an increase in temperature.

Thus, the composition of the products of processing the propane-butane mixture shows that the formation of aromatic hydrocarbons occurs as a result of simultaneously and parallel occurring reactions of cracking, dehydration, oligomerization, and dehydrocyclization.

The influence of the composition of the processed raw materials on the aromatization process was studied on the example of comparison with the processing of the propane-propylene fraction on the most active Zn-La-Fe-P-ZSM- Al_2O_3 catalyst (Table 5). It is shown that in this case the degree of conversion of the mixture with an increase in temperature from 350 to 600°C increases from 6.4 to 91.0%. Under these conditions, the total yield of aromatic hydrocarbons increases from 45.8 to 63.9%. The maximum selectivity for aromatic hydrocarbons is 70.2% at 600°C. The benzene yield increases from 1.2 to 23.7%; the toluene, and ethylbenzene yields change extremely. Thus, the toluene yield increases from 9.6 to 45.6% in the range 350–450°C, then drops to 37.5% at 600°C. The maximum xylene yield is 16.4% and is observed at 350°C.

Table 2. Processing propane-butane fraction on ZSM- Al_2O_3 catalyst, gas velocity $V = 300 \text{ h}^{-1}$

$T_{\text{exp}}, ^\circ\text{C}$	400	450	500	550	600
Conversion, %	73.7	82.7	86.3	92.3	90.6
Liquid phase yield, wt %	8.2	10.4	10.9	12.9	8.4
Selectivity for aromatic hydrocarbons, %	11.1	12.6	12.6	13.9	9.3
Liquid phase composition, wt %					
Benzene	10.3	15.6	19.5	22.3	30.0
Toluene	30.9	35.6	36.0	32.9	36.5
Ethylbenzene	15.3	14.5	12.9	12.3	9.6
Xylenes	3.8	4.0	4.1	4.1	2.9
C_5 – C_6 hydrocarbons	16.6	8.1	2.3	1.7	4.7
C^{8+} hydrocarbons	231	22.2	29.3	26.7	16.3

Table 3. Processing propane-butane fraction on Zn-La-Co-ZSM-Al₂O₃ catalyst, gas velocity $V = 300 \text{ h}^{-1}$

$T_{\text{exp}}, ^\circ\text{C}$	450	500	550	600
Conversion, %	40.2	81.3	92.6	98.4
Liquid phase yield, %	19.3	28.4	31.4	24.1
Selectivity for aromatic hydrocarbons, %	48.0	34.9	33.9	24.5
Liquid phase composition, wt %				
Benzene	6.0	35.8	41.3	49.2
Toluene	74.6	51.7	52.0	47.2
Ethylbenzene	13.9	9.3	5.1	2.7
Xylenes	3.8	2.7	1.6	0.9
C ⁸⁺ hydrocarbons	1.7	0.5	—	—

Table 4. Processing propane-butane fraction on Zn-La-Fe-P-ZSM-Al₂O₃ catalyst, gas velocity $V = 380 \text{ h}^{-1}$

$T_{\text{exp}}, ^\circ\text{C}$	400	450	500	550	600
Conversion of C ₄ , %	16.8	23.6	32.2	70.2	81.4
Liquid phase yield, wt %	13.3	20.5	26.2	43.6	52.6
Selectivity for aromatic hydrocarbons, C ₄ %	79.2	80.3	81.4	62.1	64.6
Liquid phase composition, wt %					
Benzene	1.1	6.2	14.5	20.4	17.6
Toluene	30.0	40.1	47.4	36.8	41.7
Ethylbenzene	41.6	23.9	20.6	11.4	17.7
Xylenes	9.3	6.0	5.4	3.2	5.7
C ₅ –C ₆ hydrocarbons	11.9	—	22.0	—	10.0
C ⁸⁺ hydrocarbons	15.0	11.9	6.7	6.2	17.3

An analysis of the results of studying the process of processing light hydrocarbons on the prepared catalysts showed that the highest yield of aromatic hydrocarbons was achieved for the Zn-La-Fe-P-ZSM-Al₂O₃ catalyst. The maximum quantity of aromatic hydrocarbons (52.6%) during the processing of the propane-butane fraction is formed on the Zn-La-Fe-

P-ZSM-Al₂O₃ catalyst at 600°C, while the selectivity for aromatic hydrocarbons is 64.6%. When the propane-propylene fraction is processed in the temperature range of 350–600°C, the yield of aromatic hydrocarbons on the Zn-La-Fe-P-ZSM-Al₂O₃ catalyst is more than two times higher than in other investigated catalysts (see Table 4).

Table 5. Processing propane-propylene fraction on Zn-La-Fe-P-ZSM-Al₂O₃ catalyst

$T_{\text{exp}}, ^\circ\text{C}$	350	400	450	500	550	600
Conversion of C ₃ , %	6.4	26.6	17.2	58.2	88.3	91.0
Liquid phase yield, wt %	45.8	52.5	55.8	56.3	59.1	63.9
Selectivity for aromatic hydrocarbons, C ₄ , %	—	—	—	96.7	66.9	70.2
Liquid phase composition, wt %						
Benzene	1.2	3.4	9.7	15.3	21.2	23.7
Toluene	9.6	34.8	45.6	40.7	40.2	37.5
Ethylbenzene	2.6	33.9	27.4	18.5	14.4	10.7
Xylenes	16.4	7.7	7.0	5.2	4.1	3.2
C ⁸⁺ hydrocarbons	37.2	13.6	8.8	9.6	9.2	13.2
C ₅ –C ₆ hydrocarbons	33.0	6.6	1.5	10.7	10.9	11.7

Table 6. Effect of the properties of zeolite-containing catalysts on the overall yield of aromatic hydrocarbons

Catalyst	ΣNH_3 , 10^{-4} mol/g (catalyst)	Dominant phases	Size of particles on the surface, nm	Overall yield of aromatic hydrocarbons at $T = 550^\circ\text{C}$, %
ZSM- Al_2O_3	27.68	ZSM- Al_2O_3	2.0–4.0	12.9
Zn-Fe-ZSM- Al_2O_3 ,	14.7	FeFe_2O_3	50–100	20.6
Zn-La-Co-ZSM- Al_2O_3 ,	36.5	La_2O_3 ; La_2CoO_4	3.0–5.0	31.4
Zn-La-Fe-P-ZSM- Al_2O_3	30.53	La_2O_3 , e- Fe_2O_3 , FeAl_2	3.0–5.0	43.6

The results of the study of the process of aromatization of the propane-butane and the propane-propylene mixtures on the developed multicomponent catalysts showed that the introduction (except for zinc) of additives of lanthanum, iron, cobalt, and phosphorus allows increasing the yield of aromatic hydrocarbons to 52.6–59.1% when compared with catalysts containing only zinc (40.9–42.3%) [18–22] (Table 6).

The service life of catalysts depends both on their composition, the nature of modifying additives, and the quality of the processed raw materials. The main reason for the gradual decrease in the activity of catalysts in the process of obtaining aromatic compounds from light hydrocarbons is the accumulation of coke on their surface. The activity of the unmodified ZSM- Al_2O_3 catalyst with an increase in the duration of its operation decreases, while the yield of the target product after 7 h of operation is significantly reduced from 12.9 to 5.8 wt %. Modification has a positive effect on the stability of the catalyst. The study of the stability of the most active catalyst, Zn-La-Fe-P-ZSM- Al_2O_3 , showed that, during 7 h of operation of the catalyst without regeneration, the conversion changes little (from 67.3 to 66.7%); the yield of AHs practically does not change and is 46.2–47.7%. With a further increase in the duration of the catalyst operation, the conversion decreases and after 15 h is equal to 25.5%. The yield of the liquid phase and the selectivity for aromatic hydrocarbons are 19.4 and 66.7%, respectively. To restore the activity, the catalysts are regenerated after 1 h of operation directly in the reactors by the oxidative burning of coke at 550°C (2 h in a stream of air).

CONCLUSIONS

These studies showed that the Zn-Fe-ZSM- Al_2O_3 , Zn-La-Co-ZSM- Al_2O_3 , and Zn-La-Fe-P-ZSM- Al_2O_3 modified zeolite-containing catalysts have polyfunctional properties and high catalytic activity and selectivity in the process of processing liquefied petroleum gas into aromatic hydrocarbons. The composition of the products of the processing of a propane-butane mixture shows that the formation of aromatic hydrocarbons occurs because of the simultaneously occurring parallel reactions of cracking, dehydrogenation,

oligomerization, and dehydrocyclization. A comparison of the results obtained in the processing of the propane-butane and the propane-propylene fractions shows that the yield of the aromatic hydrocarbons is higher for propane-propylene fractions. For example, at a temperature of 550°C on the Zn-La-Fe-P-ZSM- Al_2O_3 catalyst, the yield of the liquid phase when processing the propane-butane fraction and the propane-propylene fraction is 43.6 and 59.1%, respectively, at conversion rates of 70.2 and 88.3, respectively. Since the propane-propylene fraction is an industrially important raw material and is more accessible for experiments, in further studies the most effective modified catalyst will make it possible to obtain a sufficiently high yield of aromatic hydrocarbons and can be recommended for pilot tests at refineries where these gases are used primarily as process fuels.

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