

# Processing of propane-butane fraction on zeolite-containing catalysts

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**Abstract.** Processing of propane-butane and propane-propylene fractions in light hydrocarbons on the zeolite catalysts modified by zinc, manganese, cobalt, lanthanum was studied. It was shown that the degree of conversion on the Zn-La-Co-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst increases from 40.2 to 99.0% as the temperature increases from 450 to 600 °C. The maximum yield of aromatic hydrocarbons was 31.4%. As the temperature increases from 450 to 600C, the cracking of hydrocarbons intensifies resulting in the formation of methane and ethane. New generation catalysts based on zeolites have the prospect of being used in technologies for processing various types of hydrocarbon raw materials. The activity of catalysts in the processing of light hydrocarbons depends on the structure and state of the active centers. The physicochemical characteristics of the developed catalysts have been studied. One of the possible ways to control the catalytic properties is to introduce a variable valence catalyst as modifiers into the composition.

## 1 Introduction

Energy resources play an important role in the economy today. The level of the productive forces of a developed country is largely determined by the scale of energy consumption. A testament to the importance of energy resources is the fact that more than 70% of the world's minerals are energy sources.

The main types of known energy resources are coal, oil, natural gas, hydropower and nuclear power. Since oil and its products are the main raw materials for energy production, its global economic and political importance has increased. The presence of oil reserves in the country, the ability to export oil and oil products allows the country to achieve great success in economic and social development. At the same time, fluctuations in world oil prices, along with oil-producing countries, will require significant changes in economic policy and large-scale measures for oil importing countries.

The Republic of Kazakhstan is one of the leading countries in the world in terms of hydrocarbon reserves, and also ranks second among the republics of the Commonwealth of Independent States (CIS) after Russia. Kazakhstan has made great strides in the development of the oil and gas industry, using international experience. However, the economy of Kazakhstan has a unique way of development, so it is necessary to make optimal use of its

advantages and individual methods of civilized and effective management of the oil and gas industry [1-5].

Lower alkanes C<sub>3</sub>–C<sub>4</sub> are the main components of the propane – butane fraction of natural and associated petroleum gases and cheap hydrocarbon feed stock for the production of lower olefins C<sub>2</sub>–C<sub>4</sub> aromatic hydrocarbons and other valuable petrochemical products.

Aromatic hydrocarbons are obtained by treating low molecular weight alkanes in zeolite-containing catalysts. At present, there is a growing interest in zeolites with high silica content, such as pentasil, as a catalyst for the aromatization of low molecular weight hydrocarbons. A promising direction for the use of associated petroleum gas is the development of gas processing facilities at oil production facilities, which make it possible to obtain aromatic hydrocarbons from gas with the participation of catalysts [5-11].

This paper presents the results of studying the process of conversion of propane-butane and propane-propylene fractions into aromatic hydrocarbons on zeolite-containing catalysts modified with zinc, manganese, cobalt, lanthanum, and phosphorus. 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 conversion of hydrocarbons and the composition of the resulting compounds was investigated.

## 2 Experimental part

In this work, we investigated the processing of propane-butane fraction on zeolite- containing catalysts modified with zinc, manganese, cobalt and lanthanum: Al<sub>2</sub>O<sub>3</sub>-ZSM, Zn-La- ZSM-Al<sub>2</sub>O<sub>3</sub>, Zn-La-Mn-ZSM-Al<sub>2</sub>O<sub>3</sub>, Zn-La-Co-ZSM-Al<sub>2</sub>O<sub>3</sub>. The catalysts were prepared by impregnating a mixture of aluminum hydroxide Al(OH)<sub>3</sub> with decationated zeolite HZSM-5 with aqueous solutions of salts of modifying elements: La, Zn, Co. After molding, the catalyst samples were dried, calcined at a temperature of 500°C for 5 hours. The catalysts were prepared by impregnating a mixture of aluminum hydroxide and zeolite ZSM-5 with aqueous solutions of metal salts, followed by drying at 150°C and calcining at 550°C. The synthesized catalysts were tested during processing of the propane-butane fraction in a flow-through quartz reactor with a fixed catalyst bed at atmospheric pressure and varying the reaction temperature from 400 to 600°C. The reaction products were analyzed on “Chromatic-Crystal” and “Agilent” chromatographs.

## 3 Results and its discussion

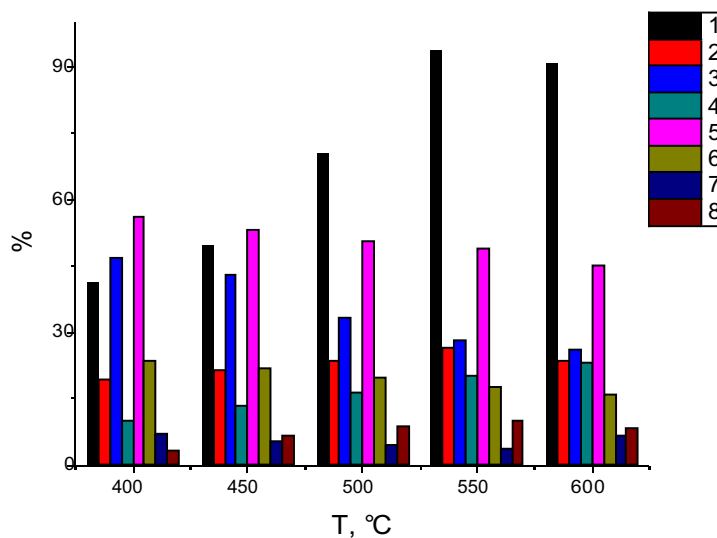
### 3.1 Conversion of propane-butane fraction

When the propane-butane fraction is processed on a zeolite-containing catalyst Al<sub>2</sub>O<sub>3</sub>-ZSM, aromatic hydrocarbons (AH) and gaseous products are formed. Benzene, toluene, ethylbenzene, xylenes, and C<sub>8</sub> + hydrocarbons were found in the liquid phase. The gaseous reaction products contain C<sub>1</sub>-C<sub>4</sub> alkanes (Table 1). With an increase in temperature from 400 to 600°C, the conversion increases from 73.7 to 90.6% and there is an increase in the content of benzene from 10.3 to 30.0%, toluene from 30.9 to 36.5%, and ethylbenzene decreases from 15, 3 to 9.6%. The xylene content ranges from 2.9 to 4.1%. Selectivity for AH - from 9.1 (500°C) to 14.2% (600°C). Under these conditions, cracking intensifies with the formation of C<sub>1</sub>-C<sub>2</sub> hydrocarbons.

**Table 1.** Processing of the propane-butane fraction on the catalyst  $\text{Al}_2\text{O}_3\text{-ZSM}$ ,  $V = 300 \text{ h}^{-1}$ .

$T_{\text{exp}}, ^\circ\text{C}$	400	450	500	550	600
Conversion, %	73.7	82.7	86.3	92.3	90.6
Liquid phase yield,% mas	12.2	10.4	10.4	8.37	12,9
Select. AH%	16.5	12.6	12.0	9.1	14.2
Liquid phase composition, % mas					
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
C5-C6 hydrocarbon	16.6	8.1	2.3	1.7	4.7
C8+	23.1	22.2	29.3	26.7	16.3

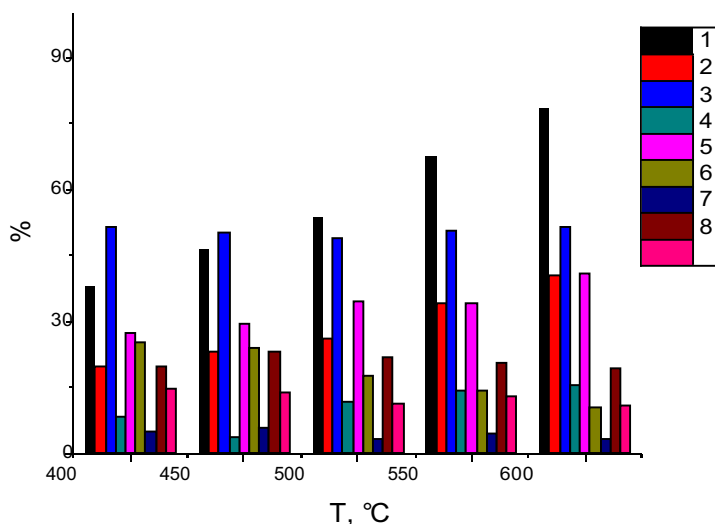
When the propane-butane fraction is converted on the  $\text{Zn-La-ZSM-Al}_2\text{O}_3$  catalyst (Fig. 1), the degree of its conversion increases from 60.2 to 98.4% as the temperature increases from 450 to 600°C. The yield of aromatic hydrocarbons passes through a maximum (31.4%) at 550°C. The selectivity for aromatic hydrocarbons decreases from 37.0 (450°C) to 24.5% (600°C). An increase in the temperature from 450 to 600°C results in an increase in the benzene content in the liquid phase from 16.0 to 49.2%, while the proportion of toluene, ethylbenzene and xylenes decreases from 64.6 to 47.2%, from 13.9 to 2.7% and from 3.8% to 0.9% respectively.



**Fig. 1.** Influence of temperature on the processing of propane-butane fraction on the catalyst  $\text{Zn-La-ZSM-Al}_2\text{O}_3$ . 1 - conversion; 2 - liquid phase outlet; 3 -selectivity for AH; 4 - benzene; 5 - toluene; 6 - ethylbenzene; 7 - xylenes; 8 - C8+ hydrocarbons.

When processing a propane-butane mixture on the Zn-La-Mn-Al<sub>2</sub>O<sub>3</sub>-ZSM catalyst (Fig. 2) with an increase in temperature from 400 to 600°C, the highest conversion 78.6% occurs at 600°C, while the yield of aromatic hydrocarbons increases to 40.3 %. Selectivity for AH is 51.3%.

It should be noted that in the temperature range 400-600°C, the yields of toluene, ethylbenzene and benzene were 27.2-41.0, 10.3-25.2 and 8.2-15.3% respectively. The xylene content in the catalyst was 3.0-5.9%. The methane yield was low and varied from 0.2 to 6.8%. The ethane yield increased from 2.4% to 20.4% as the temperature increased from 400 to 600°C.



**Fig. 2.** Influence of temperature on processing propane-butane fraction on the catalyst Zn- La -Mn - ZSM - Al<sub>2</sub>O<sub>3</sub>. 1 - conversion; 2 - liquid phase outlet; 3 - selectivity for AH; 4 - benzene; 5 - toluene; 6 - ethylbenzene; 7 - xylene; 8 - C<sub>8</sub>+hydrocarbons.

The stability of the catalyst has been studied. The service life of catalysts depends both on their composition, the nature of modifying additives, and on 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. To restore the activity, the catalysts were regenerated directly in the reactor by oxidative burning of coke [8-11].

The studies were carried out at 550°C and  $V = 300 \text{ h}^{-1}$ . Studies of the stability of the La-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst have shown that with an increase in the duration of operation, its activity decreases, while the yield of the target product after 8 hours of operation significantly decreases from 20.4 to 11.8 wt.%. The study of the stability of the catalysts Zn-La-ZSM-Al<sub>2</sub>O<sub>3</sub> and Zn-La-Mn-Al<sub>2</sub>O<sub>3</sub>-ZSM showed that during seven hours of catalyst operation without regeneration, the conversion changes little: 67.3-61.7%, the yield of aromatic hydrocarbons practically does not change and is 43.2-47.7%. With an increase in the duration of the catalyst, the conversion decreases which is equal to 25.5% after 15 hours.

When the propane-butane fraction is converted on the Zn-La-Co-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst (table 2.) with an increase in temperature from 450 to 600°C, the degree of conversion increases from 40.2 to 99.0%. The yield of aromatic hydrocarbons passes through a maximum (31.4%) at

550°C, the selectivity for aromatic hydrocarbons decreases from 49.0 (450°C) to 24.5 (600°C). An increase in the temperature from 450 to 600°C results in an increase in the benzene content in the liquid phase from 6.0 to 49.2%, while the yield of toluene, ethylbenzene and xylenes decreases from 74.6 to 47.2%, from 13.9 to 2.7% and from 3.8% to 0.9% respectively. As the temperature increases from 450 to 600°C, the cracking of hydrocarbons intensifies and results in 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.

**Table 2.** Processing of LPG on a Zn-La-Co-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst ( $V=370 \text{ h}^{-1}$ )

$T_{\text{exp}}, ^\circ\text{C}$	450	500	550	600
Conversion, %	40.2	81.3	92.6	99.0
Liquid phase yield, % mas	19.3	28.4	31.4	24.1
Selectivity by AH, %	49.0	34.9	33.9	24.5
Liquid phase composition, %				
Benzene	6.0	35.8	41.3	49.2
Toluene	74.6	51.7	52.0	4.2
Ethylbenzene	13.9	9.3	5.1	2.7
Xylenes	3.8	2.7	1.6	0.9
C5-C6 hydrocarbons	1.7	0.5	-	-
C8+ hydrocarbons	6.0	35.8	-	-

During processing of liquefied petroleum gas, liquid aromatic hydrocarbons (AH) and gaseous products are formed. Benzene, toluene, ethylbenzene, xylenes, and C<sub>8+</sub>-hydrocarbons were found in the liquid phase. The gaseous reaction products contain C<sub>1</sub>-C<sub>4</sub> alkanes, C<sub>2</sub>-C<sub>4</sub> olefins and hydrogen.

Studies of the conversions of the propane-butane and propane-propylene fractions on the catalyst showed that the degree of conversion of hydrocarbons and the composition of the compounds formed as a result of the processing of the propane-butane fraction on the studied catalysts depend on the temperature of the process and, mainly, on the nature of the components of the catalytic system. The stability of the catalyst also depends on the nature of the components.

### 3.2 Physico-chemical properties of the catalysts for conversion of the propane-butane fraction

The surface of the catalysts under study was determined by the BET method. The activity of catalysts is related to the surface structure, phase composition, and state of modifying additives [15-16]. The surface of the catalysts under study was determined by the BET method. The specific surface area and total pore volume of Al<sub>2</sub>O<sub>3</sub>+ZSMZSM catalyst are equal to 338.0 m<sup>2</sup>/g and 0.40 ml/g, on La-Zn/Al<sub>2</sub>O<sub>3</sub>+ZSM catalyst are equal to 214.9 m<sup>2</sup>/g and 0.43 ml/g, Zn-La-Mn-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst – 255.0 m<sup>2</sup>/g and 0.40 ml/g, Zn-La-Co-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst – 280.0 m<sup>2</sup>/g and 0.40 ml/g, respectively. CoAl<sub>2</sub>O<sub>3</sub>+ZSM catalyst is dominated by the

pores with a size of 1.0-6.0, on La-Zn/Al<sub>2</sub>O<sub>3</sub>+ZSM catalyst – 1.2-3.0 and 6.0 nm, on the catalyst Zn-La-Mn-ZSM-Al<sub>2</sub>O<sub>3</sub> – 2.5-3.0 and 6.0 nm, on the Zn-La-Co-ZSM Al<sub>2</sub>O<sub>3</sub> catalyst – 5.3-3.0 and 6.0 nm.

The acid-base characteristics of catalysts, which are essential for the processing of light hydrocarbons, have been studied by temperature-programmed desorption using ammonia as a probe molecule. Our studies showed that ammonia on the surface of the La-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst is inhomogeneous and adsorbed in three forms, as evidenced by the presence of three maxima on the TPD curve:  $t_{\max} = 155^{\circ}\text{C}$ ,  $t_{\max} = 230^{\circ}\text{C}$ , and the most strongly bound ammonia is desorbed at  $t_{\max} = 460^{\circ}\text{C}$ . Their number is 16.79; 3.79 and  $7.07 \cdot 10^{-4}$  mol/g catalyst. The total content of acid sites is  $27.73 \cdot 10^{-4}$  mol/g of the catalyst.

The introduction of zinc into the La-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst (Zn-La-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst) (Table 3) is accompanied by an insignificant change in the energy characteristics of the acid sites of the system: the desorption maxima of the weakest and most strongly bound forms of adsorbed ammonia are shifted to higher temperatures of 160 and 470°C, respectively. Moreover, the amount of weakly bound ammonia decreases to  $14.43 \cdot 10^{-4}$  mol/g of the catalyst, and the amount of strongly bound ammonia rises to  $7.82 \cdot 10^{-4}$  mol/g of the catalyst. The desorption temperature of the medium-bound forms of NH<sub>3</sub> does not change, but its amount grows almost 1.5 times - up to  $5.39 \cdot 10^{-4}$  mol/g catalyst). The total content of acid sites is  $25.34 \cdot 10^{-4}$  mol/g of the catalyst.

**Table 3.** Temperature-programmed ammonia desorption

Catalyst	Tmax, °C			Ammonia adsorbed, 10 <sup>-4</sup> mol/g catalyst			ΣNH <sub>3</sub> , 10 <sup>-4</sup> mol/g of catalyst
	1	2	3	1	2	3	
Al <sub>2</sub> O <sub>3</sub> -ZSM	122	170	505	10.85	10.54	6.2	27.68
Zn- La-ZSM- Al <sub>2</sub> O <sub>3</sub>	160	230	470	14.73	5.39	6.92	25.34
Zn-La-Mn-ZSM-Al <sub>2</sub> O <sub>3</sub>	188	-	500	2.,2	-	7.6	34.8
Zn-La-Co-ZSM-Al <sub>2</sub> O <sub>3</sub>	152	310	480	23.70	8.80	4.00	33.50

The study of the acidic characteristics of Zn-La-Co-ZSM-Al<sub>2</sub>O<sub>3</sub> showed that ammonia is desorbed in three regions at T = 152, 310 and 480°C; their amounts are 23.70, 8.80 and  $4.00 \cdot 10^{-4}$  mol/g catalyst, respectively. The total number of the acid sites is  $36.50 \cdot 10^{-4}$  mol/g of the catalyst. The introduction of manganese into the composition of Zn-La-ZSM-Al<sub>2</sub>O<sub>3</sub> leads to the significant changes in the energy characteristics of the acid sites. Thus, the desorption maxima of the most weakly and strongly bound forms of the adsorbed ammonia are shifted to higher temperatures of 188 and 500°C, respectively; their amounts are  $27.20 \cdot 10^{-4}$  and  $7.60 \cdot 10^{-4}$  mol/g catalyst. No moderately bound forms of adsorbed ammonia were found. The total number of the acid sites on the Zn-La-Mn-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst is significantly higher than that of the other catalysts which is equal to  $34.80 \cdot 10^{-4}$  mol/g of the catalyst.

The analysis of the obtained results shows that under the same conditions (550°C), the maximum AH yield is characteristic for the Zn-La-Mn-Al<sub>2</sub>O<sub>3</sub>-ZSM catalyst was 34.2%. Toluene and benzene are the predominant products formed during the processing of a propane-butane mixture on catalysts: their yield ranges were 34.0-48.9% and 14.3-27.8%, respectively.

In the IR spectrum of ammonia adsorbed on the surface of the Al<sub>2</sub>O<sub>3</sub>+ZSM catalyst at

room temperature, the following absorption bands were found: 3500, 3450, 3320, and 3200  $\text{cm}^{-1}$ , as well as 1700, 1660, 1600, 1550, and 1450  $\text{cm}^{-1}$ . Absorption bands 3500, 3450  $\text{cm}^{-1}$  refer to stretching vibrations of the OH-group. According to [15, 17], Bronsted acid centers (BACs) are characterized by the appearance of absorption bands in the IR spectra of chemisorbed ammonia. 1450 and 1700  $\text{cm}^{-1}$ , and Lewis acid centers (LAC) – a.b. 3320, 3200, 1660, 1600  $\text{cm}^{-1}$ . The doublet of absorption bands at 1550 and 1450  $\text{cm}^{-1}$  indicates the presence of an amide group, which appears in the case of strong adsorption of ammonia on oxygen-containing sites of the catalyst. Intensity a.b. corresponding to the Lewis (1600, 3320  $\text{cm}^{-1}$ )  $\text{NH}_3$  adsorption centers on the  $\text{Al}_2\text{O}_3 + \text{ZSM}$  surface are higher than a.b. typical for Bronsted centers. After evacuation, a.b. remain in the IR spectrum: 3550, 3400, 1600 and 1400  $\text{cm}^{-1}$ . With an increase in the adsorption temperature of  $\text{NH}_3$  to 200°C, the position of the absorption bands in the IR spectrum changes - broad absorption bands with maxima at 3450, 3320, and 3200  $\text{cm}^{-1}$ , as well as pp. 1700, 1650, 1600, 1500 and 1300  $\text{cm}^{-1}$ . It should be noted that at 200°C, the adsorption capacity of the  $\text{Al}_2\text{O}_3 + \text{ZSM}$  catalyst with respect to ammonia increases, and the intensity of all absorption bands increases. In the IR spectra of  $\text{NH}_3$  adsorbed at 200°C is higher than at 30°C. After evacuation, the absorption bands remain in the IR spectra – 1600 and 1400  $\text{cm}^{-1}$ .

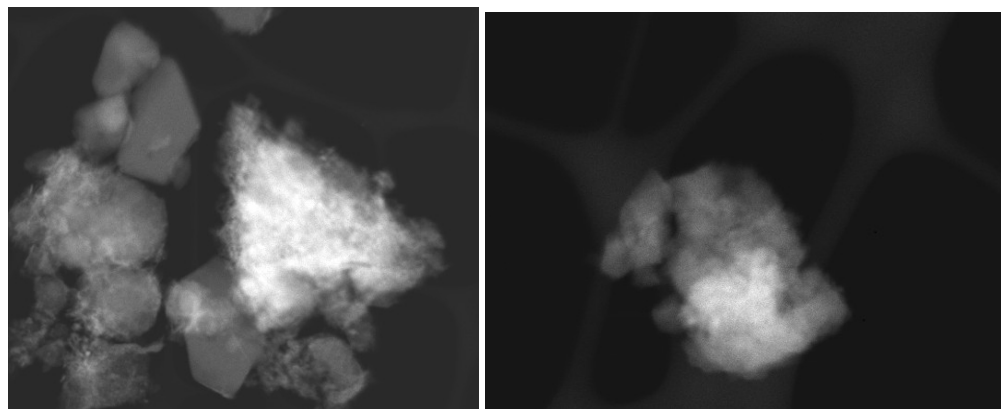
The structure and state of the acid sites La- $\text{Al}_2\text{O}_3$ +ZSM and La-Zn- $\text{Al}_2\text{O}_3$ +ZSM of the catalysts were studied using the method of IR-spectroscopy by adsorption of a molecule - an ammonia probe. On the La- $\text{Al}_2\text{O}_3$ +ZSM catalyst, absorption bands were found. In the range 3600-3000  $\text{cm}^{-1}$ , as well as a.b. 3400-3320  $\text{cm}^{-1}$ . In addition, there are pp 1700, 1600, 1560 and 1450  $\text{cm}^{-1}$ , which correspond to the adsorption of ammonia at the Bronsted and Lewis centers.

In addition to ammonia, carbon monoxide was used as a spectral probe, which, on the one hand, is a generally recognized IR spectroscopic test for Lewis acid sites, and on the other hand, using COads, one can assess the state of the metal that is part of the catalyst. In the IR spectra of carbon monoxide chemisorbed on the La- $\text{Al}_2\text{O}_3$ +ZSM catalyst, absorption bands 3700-2700, 2140, 2085, 1600, 1420  $\text{cm}^{-1}$  are present, weak a.b. 1980, 1850  $\text{cm}^{-1}$ . Wide a.b. 3700-2700  $\text{cm}^{-1}$  indicates the presence of OH-groups with different binding energies with the catalyst centers, a.b. 2140  $\text{cm}^{-1}$  corresponds to linear adsorption of CO on Lewis centers, which include oxidized forms of  $\text{M}^{n+}$  (in this case,  $\text{La}^{n+}$ ), weak absorption bands. 2085, 1980 and 1850  $\text{cm}^{-1}$  are formed due to CO adsorbed on  $\text{M}^0$ -centers, respectively, in linear and bridged forms. The presence in the IR spectrum of CO ads a.b. in the region 1600-1400  $\text{cm}^{-1}$  can be associated with the formation of format structures.

When zinc is introduced into the La- $\text{Al}_2\text{O}_3$ +ZSM catalyst, the state of the acid sites on the catalyst surface changes. In the IR spectra of CO on the La-Zn/ $\text{Al}_2\text{O}_3$ +ZS catalyst, a shift of the absorption bands was found: 1700 is shifted to 1720  $\text{cm}^{-1}$ , 1600 to 1630  $\text{cm}^{-1}$ , 1450 to 1550  $\text{cm}^{-1}$ . The maxima in the region of 3600-3000  $\text{cm}^{-1}$  shift to 3500 and 3380  $\text{cm}^{-1}$ . These changes indicate an increase in the acidic properties of active sites upon the addition of zinc to the composition of the La/ $\text{Al}_2\text{O}_3$ +ZSM catalyst, which leads to a change in the activity of the catalyst upon the conversion of n-hexane. IR spectroscopic studies have shown that the concentration of proton-donor groups in zeolites, the ratio and concentration of Bronsted and Lewis acid sites change with increasing temperature. Metal-containing structures can be anchored inside zeolite cavities or on the outside of zeolite crystals. As the temperature rises, the particles of the metal phase tend to grow larger, and the nature of the electronic interaction between the metal and the matrix changes [8-12].

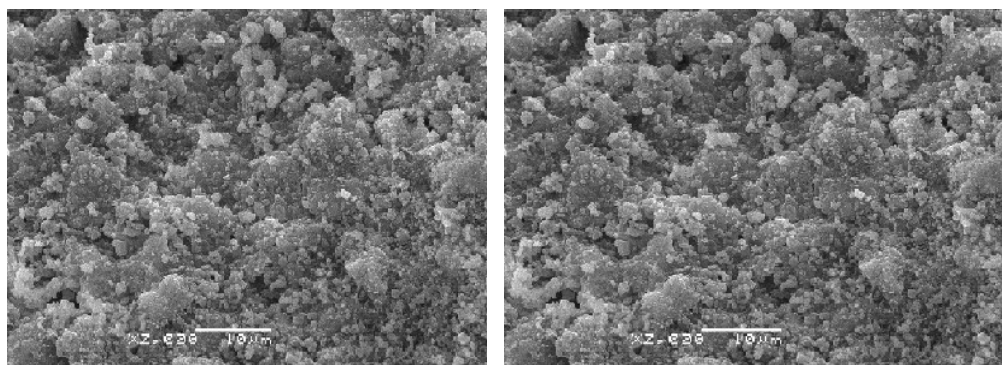
]Using the methods of electron microscopy and electron diffraction, the structure and state of the active centers of the catalysts were investigated. According to the electron microscopy data, the surface of the La-ZSM- $\text{Al}_2\text{O}_3$  catalyst is rather uniform: highly dispersed structures with  $d \approx 2.0$ -4.0 nm, formed by the oxide states of the rare-earth elements  $\text{La}_2\text{O}_3$  and  $\text{La}_2\text{O}_{11}$ , prevail. There are also the formations with  $d \approx 100.0$  nm, identified as  $\text{AlSi}_2\text{O}_6$  and

$\text{Al}_4\text{Si}_4\text{O}_{17}$  (Fig. 3).



**Fig. 3.** Electron microscopic images of the La-ZSM- $\text{Al}_2\text{O}_3$  catalyst. Increase 100 000.

On the surface of Zn- La-ZSM- $\text{Al}_2\text{O}_3$ , particles with  $d \approx 5.0\text{-}7.0$  nm were found. Zinc and a rare earth element are in an oxidized state, mainly in the form of  $\text{La}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{Zn}(\text{OH})_2$ . There is an introduction of zinc and lanthanum atoms into the structure of zeolite and  $\text{Al}_2\text{O}_3$  with the formation of  $\text{Zn}_2\text{Si}_3\text{O}_{10}$  and  $\text{LaAlO}_3$  (Fig. 4).



**Fig. 4.** Electron microscopic images of the Zn-La-ZSM- $\text{Al}_2\text{O}_3$  catalyst. Increase 100 000.

The dispersion of the particles of the active phase of the catalyst Zn-La-Mn-ZSM- $\text{Al}_2\text{O}_3$  is higher than that of Zn-La-ZSM- $\text{Al}_2\text{O}_3$ . The structures with  $d \approx 2.0\text{-}3.0$  nm are mainly present, consisting of a mixture of more highly dispersed particles  $\text{MnO}_2$ ,  $\text{Mn}(\text{OOH})_2$ ,  $\text{ZnMnO}_3$ ,  $\text{MnSiO}_3$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{Zn}(\text{OH})_2$  and  $\text{ZnAl}_2\text{O}_4$ ,  $\text{Zn}_{0.75}\text{Al}_{1.5}\text{Si}_{1.5}\text{O}_6$ . In addition, on the catalyst surface there are large accumulations of small  $\text{La}_2\text{O}_3$  and  $\text{MnO}_2$  particles with  $d \approx 3.0\text{-}5.0$  nm and small aggregates of highly dispersed particles with  $d \approx 3.0\text{-}5.0$  nm, formed by  $\text{Mn}_3\text{O}_4$  and  $\text{Zn}_7\text{SiO}_4$ ,  $\beta\text{-Zn}_2\text{SiO}_4$ ,  $\text{Mn}(\text{OOH})_2$ ,  $\text{LaMnO}_3$  and  $\text{ZnMnO}_4$ .

These studies have shown that particles on the surface of La-ZSM- $\text{Al}_2\text{O}_3$ , Zn-La-ZSM- $\text{Al}_2\text{O}_3$  and Zn-La-Mn-ZSM- $\text{Al}_2\text{O}_3$  catalysts are highly dispersed. Metals-components of the active phase are predominantly in an oxidized state, forming clusters-associates on the surface, the dispersion, structure and state of which are determined by the nature of the catalyst components. These catalysts are characterized by the introduction of modifier metals into the structure of the zeolite and  $\text{Al}_2\text{O}_3$  with the formation of  $\text{MnSiO}_3$ ,  $\text{ZnAl}_2\text{O}_4$ ,  $\text{Zn}_{0.75}\text{Al}_{1.5}\text{Si}_{1.5}\text{O}_6$ ,  $\text{Zn}_7\text{SiO}_4$ ,  $\beta\text{-Zn}_2\text{SiO}_4$ ,  $\text{Zn}_{0.75}\text{Al}_{1.5}\text{Si}_{1.5}\text{O}_6$ ,  $\text{AlPSiP}_2\text{O}_7$ . These structures can function as Lewis acid sites [14]. Thus, on the surface of catalysts, acid sites coexist with



metal sites: the presence of acid (Bronsted and Lewes),  $M^{n+}$  - metal and mixed sites is characteristic. The acid sites can include metals in different oxidation states, fixed both inside the zeolite cavities and on their outer side, which is consistent with [12-14] and is confirmed by the data of electron microscopy.

The composition of the products formed during the processing of propane-butane and propane-propylene fractions on the developed modified zeolite-containing catalysts shows that the synthesized catalysts have polyfunctional properties. The structure and composition of the products formed during the processing of light hydrocarbons indicates the simultaneous and parallel course of several reactions on the developed modified zeolite-containing catalysts: cracking, dehydrogenation, isomerization, dehydrocyclization, and alkylation. Cracking and dehydrogenation of the starting alkanes occur with the formation of intermediate activated complexes with a reduced content of carbon atoms and adsorbed olefin structures.

Subsequently, depending on the nature of the activesite of the catalyst, various directions of transformation develop with the participation of intermediate activated complexes [13-16].

## 4 Conclusions

In this review, the process of the conversion of the propane-propylene fraction into aromatic hydrocarbons on zeolite-containing catalysts modified with Zn, La, Mn, Co, P has been studied. The process was carried out in a unit in a flow-through unit at atmospheric pressure with a temperature variation from 350 to 600°C and a volumetric feed rate of 150-1020 h<sup>-1</sup>. The catalysts were prepared by impregnating aluminum hydroxide and zeolite ZSM-5 with aqueous solutions of metal nitrate salts and phosphoric acid. It was found by the BET method that the surface of the developed catalysts varies within the range of 214.9-338.0 m<sup>2</sup>/g. The catalysts are predominantly mesoporous and the pores with  $d \approx 1.2-6.0$  nm prevail.

It was shown that the developed modified zeolite-containing catalysts have high catalytic activity and selectivity in the process of processing the propane-butane fraction into aromatic hydrocarbons. The predominant products formed during the processing of C<sub>2</sub>-C<sub>4</sub> alkanes are toluene and benzene.

On the most active catalyst Zn-La-Co-ZSM-Al<sub>2</sub>O<sub>3</sub>, with an increase in temperature from 450 to 600°C, the degree of conversion increases from 40.2 to 99.0%. The yield of the aromatic hydrocarbons passes through a maximum (31.4%) at 550°C, the selectivity for aromatic hydrocarbons decreases from 49.0 (450°C) to 24.5 (600°C). With an increase in temperature from 450 to 600°C, the benzene content in the liquid phase increases from 6.0 to 49.2%, the yield of toluene decreases from 74.6 to 47.2%, ethylbenzene from 13.9 to 2.7%, and xylenes from 3.8% to 0.9%. As the temperature rises from 450 to 600°C, the cracking of hydrocarbons intensifies 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.

Modified zeolite-containing catalysts have polyfunctional properties. Nanosized catalysts based on high-silica zeolites are used in many oil refining and petrochemical processes, their relevance is mainly determined by the unique acid-base properties. On the surface of the catalyst, the C-C bond breaks, resulting in the formation of light C<sub>1</sub>-C<sub>2</sub> hydrocarbons. At the same time, carbonium ions are formed as highly active catalytic centers. The composition of the products of processing of the propane-butane fraction shows that the formation of aromatic hydrocarbons occurs in one stage as a result of cracking, dehydrogenation, oligomerization, dehydrocyclization, and alkylation reactions. Depending on the nature of the active site of the catalyst, different directions of transformation develop with the participation of intermediate activated complexes.

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