



Catalytic Conversion of Light Hydrocarbons into Aromatic Hydrocarbons over Modified Zeolite Catalysts

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ABSTRACT

The process of conversion of light alkanes into aromatic hydrocarbons on zeolite catalysts, modified with Zn, La, Fe and Zr was investigated in this work. The catalysts were tested in the conversion process of propane-butane and propane-propylene mixtures at atmospheric pressure, variation of temperature and space velocity (SV). It is observed that the maximum amount of aromatic hydrocarbons (34.6%) are formed in the conversion of propane-butane mixture over Zn-La-Fe-ZSM-Al₂O₃ catalyst at 550 °C, selectivity to aromatic hydrocarbons is 39,2%.

Keywords: propane-propylene, propane-butane, zeolite-containing catalyst, aromatic hydrocarbon.

INTRODUCTION

Aromatic hydrocarbon are important starting materials in basic organic synthesis. They are used for manufacturing plastics, synthetic fibers, resins, various-purpose rubbers, dyes, surfactants and pharmaceutical and agricultural products. Rational use of light hydrocarbons that are component of natural, associated and refinery gases, is an actual problem. C₁-C₄ hydrocarbons contained in these gases can be converted into aromatic hydrocarbons over zeolite catalysts. Aromatic hydrocarbons are an important feedstock for many petrochemical processes. However, so

far a significant part of the light hydrocarbon are used as technological and household fuel or flared on torches, causing considerable damage to the environment. Today zeolite-containing catalysts, especially high-silica zeolites such as pentasil are widely used in the petrochemical and refining industries due to unique microporous structure and acid-base properties, capable of converting light hydrocarbons into valuable products of petrochemical synthesis. Researches of catalytic conversions of light hydrocarbon are conducted in many countries of the world. At the same time the direction of recycling process and the yield of products, generally depend on nature, conditions

of preparation of the catalyst and carrying out the process. Catalytic conversions of light hydrocarbon into aromatic hydrocarbons are intensively studied on the modified pentasil-contained catalysts¹⁻¹³.

MATERIALS AND METHODS

Modified zeolite-containing catalysts: Zn-La-Zr-ZSM-Al₂O₃, Zn-La-Co-ZSM-Al₂O₃, Zn-La-Fe-ZSM-Al₂O₃ were prepared by impregnation of mixture of aluminum hydroxide and HZSM-5 zeolite with aqueous solutions of metal salts with subsequent drying at 150 °C and calcinating at 550 °C. The synthesized catalysts were tested in the conversion process of propane-butane and propane-propylene mixture in a flow-type quartz reactor with a fixed-bed catalyst at atmospheric pressure, and variation of the reaction temperature from 450 to 600 °C, SV from 140 to 500 hr⁻¹. The flow -type reactor contained 5 g of the catalyst with particle size of 1-2 mm sandwiched between quartz grit layers. The reaction products were cooled in receiver with a condenser placed in special immersion cooler to collect the liquid fraction.

The reaction products were analyzed by chromatographic (GLC) method on the equipment "Chrom-5" with the column filled with alumina of "Supelco" firm. Liquid organic products were determined by GLS "Agilent 6890" with the capillary column 60m × 0.250mm. Liquid aromatic hydrocarbons and gaseous products are formed during the conversion of propane-butane mixture. Benzene, toluene, ethylbenzene, xylenes and the C₈₊ hydrocarbons were found in the liquid products. C₁-C₄ hydrocarbons are present in the gaseous products of reaction.

Physical and chemical characteristics of the synthesized catalysts were studied. The specific surface area and porosity of the catalysts have

been measured by Brunauer-Emmett - Teller (BET) method on low-temperature adsorption of nitrogen. The acid characteristics of the catalysts were investigated by temperature-programmed desorption of ammonia¹⁴.

RESULTS AND DISCUSSION

The conversion of the propane-butane mixture on a Zn-La-Zr-ZSM-Al₂O₃ catalyst was studied at a space velocity 350 hr⁻¹ (Table 1). With an increase in temperature from 450 to 600 °C the conversion of hydrocarbons (X) rises from 35.1 to 88.3%. The yield of aromatic hydrocarbons (Y) in these conditions increases from 12.3 to 24.2%.

In the process of conversion the propane-butane mixture liquid aromatic hydrocarbons and gaseous products are formed. In the liquid products benzene, toluene, ethylbenzene, xylenes and C₈₊ hydrocarbons were found. In gaseous reaction products, there are C₁-C₄ hydrocarbons.

An increase in temperature of the reaction increases from 400 to 600 °C results in the growth of benzene yield from 18.9 to 38.5% where as the yields of ethylbenzene and xylene are reduced from 17.8 to 7.5% and from 5.8 to 2.4%, respectively. The maximum yield of toluene is 62.1% at 500 °C, with further growth of temperature this value decreases to 50.0% (600 °C).

An increase in temperature leads in increased cracking with formation of C₁-C₂ hydrocarbons. The yield of methane grows from 1.2% to 47.5%, the yield of ethane increases from 1.4% to 52.5% with temperature rise.

Conversion of propane-butane fraction over the Zn-La-Co-ZSM-Al₂O₃ catalyst are shown in Table 2, an increase in temperature from 450 to

Table 1: Conversion of propane-butane mixture over the Zn-La-Zr-Al₂O₃ catalyst

T, °C	X, %	Y, %	Composition of products, %				
			Benzene	Toluene	Ethylbenzene	Xylenes	C ₈₊
450	35.1	12.3	18.9	56.3	17.8	5.8	1.2
500	63.1	21.3	20.9	62.1	10.2	5.3	1.5
550	77.4	25.0	29.5	54.4	9.7	4.6	1.8
600	88.3	24.2	38.5	50.0	7.5	2.4	1.6

600 °C leads to raise of conversion degree from 60.2% to 98.4%. The yield of aromatic hydrocarbons passes through a maximum (31.4%) at 550 °C. The selectivity to aromatic hydrocarbons decreases from 37.0 (450 °C) to 24.5% (600 °C). With increase in temperature from 450 to 600°C the quantity of benzene in a liquid product increases from 16.0 to 49.2%, toluene decreases from 64.6 to 47.2%, ethylbenzene from 13.9 to 2.7% and xylenes from 3.8 to 0.9%. Cracking of hydrocarbons increases with formation of methane and ethane as the temperature grows from 450 to 600°C. The yield of methane and ethane increases from 8.3 to 28.0% and from 2.3 to 42.0%, respectively.

The highest yield of aromatic hydrocarbons (34.6%) during conversion of propane-butane mixture is observed over the zeolite-containing catalyst Zn-La-Fe-ZSM-Al₂O₃ modified with zinc, iron, lanthanum (Table 3). The maximum selectivity to the yield of aromatic hydrocarbons is 39.2% at 550 °C. As the reaction temperature grows in the range of 450-600 °C the degree of conversion increases from 75.4% to 90.2%. There were observed changes in the composition of liquid products. Thus, as process temperature increases the amount of benzene goes up from 12.7 to 44.1%, the yield of toluene and ethylbenzene decreases from 61.6 to 47.7% and from 16.7 to 5.7%, respectively.

Table 2: Conversion of propane-butane mixture over the Zn-La-Co-ZSM-Al₂O₃ catalyst at SV=350 hr⁻¹

T, °C	X, %	Y, %	Composition of products, %				
			Benzene	Toluene	Ethylbenzene	Xylenes	C ₈₊
450	60.2	22.3	16.0	64.6	13.9	3.8	1.7
500	81.3	28.4	35.8	51.7	9.3	2.7	0.5
550	92.6	31.4	41.3	52.0	5.1	1.6	-
600	98.4	24.1	49.2	47.2	2.7	0.9	-

Table 3: Conversion of propane-butane mixture over the Zn-La-Fe-ZSM-Al₂O₃ catalyst at SV=350 hr⁻¹

T, °C	X, %	Y, %	Composition of products, %				
			Benzene	Toluene	Ethylbenzene	Xylenes	C ₈₊
450	75.4	28.4	12.7	61.6	16.7	6.9	2.1
500	83.5	31.4	30.7	45.9	14.9	5.6	2.9
550	88.3	34.6	40.7	47.0	8.4	3.3	0.6
600	90.2	28.1	44.1	47.7	5.7	2.5	-

Table 4: Stability testing of the modified zeolite-containing Zn-La-Fe-ZSM-Al₂O₃ catalyst in conversion of propane-butane mixture at 550 °C, SV = 370 hr⁻¹

Catalyst running time, hr.	X, %	Y, %	Composition of products, %			
			Benzene	Toluene	Ethylbenzene	Xylenes
1	81.1	30.9	36.6	43.8	15.5	4.1
2	78.9	32.5	33.0	45.5	14.2	7.3
3	79.0	31.5	31.6	45.9	14.5	8.0
5	80.2	30.0	32.7	47.0	12.5	7.8
7	81.2	32.0	32.2	46.0	13.8	8.0

The influence of the SV (140, 350, 450, 500 hr⁻¹) on the degree of conversion and the yield of products over the catalyst Zn-La-Fe-ZSM-Al₂O₃ at 550 °C has been studied. With the increase SV of propane-butane mixture from 140 to 500 hr⁻¹, a decrease occurs in the yield of aromatic hydrocarbons from 49.1 to 20.7% and the degree of conversion from 88.7 to 75.8%, which connected with the reduction of time of contact of active centers of the catalyst with a feed.

With increase of feed rate from 140 to 500 hr⁻¹ the yields of benzene and xylenes are reduced from 31.7 to 19.3% and from 8.8 to 2.3%, respectively the yield of toluene increases from 38.7 to 70.8% and ethylbenzene passes through a maximum at 350 hr⁻¹. Cracking is limited as the SV grows, the yields of methane and ethane are

decreased from 21.1 to 4.2% and from 29.2 to 16.6%, respectively.

Stability of the Zn-La-Fe-ZSM-Al₂O₃ catalyst was studied at conversion of propane-butane mixture (Table 4). It was observed that continuous work of the catalyst from 1 to 7 h the yield of aromatic hydrocarbons (30.0-32.5%) and the degree of conversion (81.0-78.9%) change slightly. The selectivity to the yield of aromatic hydrocarbons fluctuates within 37.4-41.2%. The qualitative composition of the liquid products remains practically unchanged. Toluene (47.0%) and benzene (36.6%) are formed in the prevailing quantity.

It should be noted that the cracking of hydrocarbons proceeds less intensively over the catalyst Zn-La-Fe-ZSM-Al₂O₃ than over the catalysts

Table 5: Conversion of propane-propylene mixture over the Zn-La-Fe-ZSM-Al₂O₃ catalyst at SV = 350 hr⁻¹

T, °C	X, %	Y, %	Composition of products, %			
			Benzene	Toluene	Ethylbenzene	Xylenes
450	61.8	35.2	24.8	53.7	16.3	5.2
500	72.9	35.8	39.1	46.9	10.9	3.1
550	88.4	38.4	40.4	49.1	8.1	6.0
600	100.0	33.9	55.1	37.8	6.0	1.1

Table 6: Specific surface area and porosity of the catalysts

Catalyst	Specific surface area, m ² /g	Pore volume, ml / g	Pore size, nm
Zn-La-Fe-ZSM-Al ₂ O ₃	283.0	0.25	1.5
Zn-La-Co-ZSM-Al ₂ O ₃	289.7	0.24	1.5; 3.0
Zn-La-Zr- ZSM-Al ₂ O ₃	310.7	0.24	2.0

Table 7: Temperature-programmed desorption of ammonia

Catalysts	T _{max} , °C			The quantity of desorbed ammonia, 10 ⁻⁴ mol / g of catalyst			ΣNH ₃ , 10 ⁻⁴ mol/g of cat.
	1	2	3	1	2	3	
Zn-La-Fe-ZSM-Al ₂ O ₃	115	320	470	22.60	7.80	4.80	35.20
Zn-La-Co-ZSM-Al ₂ O ₃	152	310	480	23.70	8.80	4.0	36.50
Zn-La-Zr- ZSM-Al ₂ O ₃	175	-	490	24.0	-	9.4	33.4

Zn-La-Zr-Al₂O₃ and Zn-La-Co-ZSM-Al₂O₃. During conversion propane-butane mixture over the Zn-La-Fe-ZSM-Al₂O₃ catalyst as the temperature increases from 400 to 600 °C, the yield of methane grows from 9.0% to 19.1% and the yield of ethane increases from 17.7% to 25.8%.

The Zn-La-Fe-ZSM-Al₂O₃ catalyst was tested at conversion of propane-propylene mixture. Aromatic hydrocarbons, C₁-C₄ hydrocarbons were found in the reaction products during conversion propane-propylene mixture over this catalyst (Table 5). A significant increase in the yield of aromatic hydrocarbons is observed at conversion of propane-propylene mixture, particularly at low temperatures (450-550 °C) in comparison when using a propane-butane mixture under similar conditions. Thus, when processing propane-butane mixture on the Zn-La-Fe-ZSM-Al₂O₃ at 450 °C the yield of aromatic hydrocarbons was 28.4%, while the processing under the same conditions a propane-propylene mixture the yield of aromatic hydrocarbons increased to 35.2%. With increase of reaction temperature in the range of 450-500 °C the yield of aromatic hydrocarbons increases from 35.2% (450 °C) to 38.4% (550 °C), but with the further growth of temperature their amount decreases to 33.9% (600 °C). The degree of conversion is 61.8% at 450 °C and it reaches 100% with temperature growth to 600 °C.

Comparison of the results obtained during processing of propane-butane and propane-propylene mixtures over the Zn-La-Fe-ZSM-Al₂O₃ catalyst shows that the composition of the feedstock practically does not affect the conversion. The amount of aromatic hydrocarbons formed is higher when using a propane-propylene mixture. At a temperature of 550 °C, the yield of the liquid products during processing of the propane-propylene mixture is 38.4% and the propane-butane yield is 34.6% (Table 3 and 5).

Physical and chemical characteristics of the synthesized catalysts were studied. The specific surface area and porosity of the catalysts have been measured by BET method on low-temperature adsorption of nitrogen. The specific surface of catalysts ranges within 283.5 – 310.7 m²/g and pores dominate with $d = 1.5-3.0$ nm (Table 6).

The acid-base characteristics of the catalysts are also essential for the conversion process of light hydrocarbons. The acidic characteristics of catalysts were studied by temperature-programmed desorption of ammonia. From the data provided in Table 7 it is seen that ammonia on the surface of the catalyst Zn-La-Fe-ZSM-Al₂O₃ is non-uniform and adsorbed in three forms. The weakly bound ammonia is desorbed from $t_{\text{max}} = 115$ °C, tightly bound from $t_{\text{des}} = 320$ °C and more tightly bound ammonia is desorbed at $t_{\text{max}} = 470$ °C. Their quantity is equal to 22.60; 7.80 and 4.80×10^{-4} mole/g of catalyst. The total content of acidic sites is equal to 35.20×10^{-4} mole/g of catalyst.

Introduction of cobalt into the composition of the catalyst changes its acidic properties. The maximum desorption of weakly bound and strongly bound forms of ammonia in the Zn-La-Co-ZSM-Al₂O₃ shifted to the area of higher temperatures from 115 to 152 °C and from 470 to 480 °C, where as the maximum desorption of ammonia with an average binding energy is shifted to the area of lower temperatures till 310 °C. However, their content changes slightly - 23.70, 8.80 and 4.00×10^{-4} mol/g of catalyst, respectively. The total amount of acidic sites is equal to 36.50×10^{-4} mole/g of catalyst.

Unlike the catalyst Zn-La-Co-ZSM-Al₂O₃ and Zn-La-Fe-ZSM-Al₂O₃ for the Zn-La-Zr-ZSM-Al₂O₃ is characteristic presence of more strong acid centers. At a temperature of desorption of 490 °C, the amount of stripped ammonia makes $9.4 \cdot 10^{-4}$ mol/g of the catalyst (Table 7).

CONCLUSION

The results shows that the catalyst Zn-La-Zr-ZSM-Al₂O₃ has low catalytic activity during the processing of the propane-butane fraction compared to Zn-La-Co-ZSM-Al₂O₃ and Zn-La-Fe-ZSM-Al₂O₃. The replacement of the modifying iron additive with cobalt results in an increase in the activity of the catalyst. The maximum activity is exhibited by the catalyst Zn-La-Co-ZSM-Al₂O₃, the conversion is 92.6% (500 °C). Under equal conditions, the highest yield of aromatic compounds and selectivity are observed on catalyst Zn-La-Fe-ZSM-Al₂O₃: respectively 34.6% and 39.2%.

The structure and composition of the products formed during the processing of propane-butane propane-propylene mixtures indicate that modified zeolite-containing catalysts have polyfunctional properties. Several zeolite-containing Zn-La-Zr-ZSM-Al₂O₃, Zn-La-Co-ZSM-Al₂O₃ and Zn-La-Fe-ZSM-Al₂O₃ catalysts simultaneously and in parallel proceed with cracking, dehydrogenation, oligomerization, dehydrocyclization, alkylation. Cracking and dehydrogenation of the starting hydrocarbons occur with the formation of intermediate activated complexes with a reduced content of carbon atoms and adsorbed olefinic structures. In the future, depending on the nature of the active center of the

catalyst, various transformation directions develop with the participation of intermediate activated

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REFERENCES

- LIU Ru-ling, ZHU Hua-ging, WU Zhi-wei, QIN Zhang-feng., *J. of Fuel Chem. and Techn.*, **2015**, *43*, 961-969.
- Shets V.F., Sapunov V.N., Kozlovskii R.A., Staroverov D.V., Gartman T.N., *Petroleum Chemistry*, **2015**, *55* (8), 632-639.
- Shiryazdanov R.R., Rakhimov M.N., Mansurov I.S., *Petroleum Chemistry*, **2010**, *1* 32-42.
- Choudhary T.V., Kinage A., Banerjee S., Choudhary V.R., *J. of Mol. Catal. A: Chemical*, **2006**, *246*, 79-84.
- Solymosi F., Zzechenyi A., *Applied Catalysis A: General*, **2004**, *278*, 111-121.
- Dergachev A.A., Lapidus A.L., *Russian Chemical Journal*, **2008**, *12*, 15-22 (in Russ.).
- Lubango M., Scurrill M.S., *Applied Catalysis A: General*, **2002**, *235*, 265-272.
- Tuktin B.T., Zakumbayeva G.D., Smagulov R., Toktabayeva N.F., *J. of refining and petrochem.*, **2008**, *6*, 35-43 (in Russ.).
- Bulkatov A.N., *J. oil processing and petrochem.*, **2008**, *10*, 30-38 (in Russ.).
- Akhmetov A.F., Karatun O.N., *J. of Chem. and Techn. of Fuels and Oils.*, **2001**, *5*, 35-41 (in Russ.).
- Dedov A.G., Moiseyev I.I., Loktev A.S., Kuznetsov N.T., Ketsko V.A., Parkhomenko K.V., *J. Chem. and Techn. of Fuels and Oils*, **2007**, *2*, 35-42 (in Russ.).
- Rasulov S.R., Mustafayeva G.R., Makhmudova L.A., *J. of refining and petrochem.* **2012**, *2*, 36-43 (in Russ.).
- Mustafayeva G.R., Salimova N.A., Rasulov S.R., *J. of refining and petrochem.*, **2012**, *5*, 36-42 (in Russ.).
- Yushchenko V.V., Zakharov A.N., Romanovsky B.V., *Kinetics and catalysis*, **1986**, *27* (2), 474-478.