CATALYTIC AROMATIZATION OF PROPANE-BUTANE FRACTION

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Abstract. In this research work, the propane-butane fractions are aromatized catalytically for the reaction of obtaining aromatic hydrocarbons and liquid fuels.Various types of catalytic catalysts for the productivity of reaction were also studied.

The experiments were carried out in a flow catalytic device in the stationary phase of the catalyst (catalyst volume 6 cm^3), at 450-600ºC, at normal atmospheric pressure (P = 0.1 MPa), under volumetric rate of propane-butane fraction 400-600 h^{-1}.

As the result of the experiment, the best modifying additives were found Zn, Zr,Ga, and Mo. The conversion of propane begins at 450ºC and reaches 100%; where the total conversion of propane reaches 600ºC. Aromatic hydrocarbons are formed in sufficient quantities at 500ºC and a maximum value of 52.5% is reached at 600ºC. The conversion of butane to aromatic hydrocarbons is easier than propane.At 550ºC the yield of aromatic hydrocarbons is 47% while the conversion of butane is 100%. The textural and physicochemical characteristics of the catalysts were also studied in the study.

Introduction

Aromatic hydrocarbons are the primary raw materials in the organic chemical industry, where benzene, toluene and xylenes are widely used.At present, aromatic hydrocarbons are mainly produced methods based on the extraction of crude oil from liquid hydrocarbons in pyrolysis and reforming processes. At the same time the declining supply of crude oil requires to search for alternative sources to replace. These alternative sources could be petroleum gases, natural gas and large fractions of light hydrocarbons [1-2].

High-silicon zeolites are widely used as catalysts in the conversion of low molecular weight hydrocarbons to aromatic hydrocarbons [3-4]. Depending on the reaction conditions, it is possible to synthesize aliphatic C_6-C_{10} hydrocarbons of the gasoline fraction or aromatic hydrocarbons: mainly benzene, toluene, and xylenes (BTX). For this reason, chemical and thermal processing of zeolites used to increase the selectivity of aromatic hydrocarbons production.

In the conversion of low molecular weight hydrocarbons to aromatic hydrocarbons, high silicon zeolites are modified with various metals [5-6].The most active in this reaction are high silicon zeolites containing Zn, Ga, and Pt [6-7]. When aromatizing the propane-butane fraction on high silicon-zeolite promoted with metals, it is not necessary to purify the raw materials from moisture and sulfur-containing compounds, as well as use of circulating hydrogen. The main disadvantages of the catalytic effect of these systems are the formation of significant amounts of methane and high molecular weight arenes (naphthalene and its derivatives). As a result, the stable operation time of the catalyst is reduced [8-9].

The main methods of preparation of modified catalysts are hydrothermal synthesis (absorption) and solid phase synthesis. Metals Zn, Ga, Al, La, Sn, Mo, Co and Zr were used as modifying additives. Experiments have proven that the best modifying additives are Zn, ZrGa, and Mo.

In this research work, the optimal conditions for the aromatization reaction in the presence of a catalytic system containing $(MoO_3)_x \cdot (ZnO)_y \cdot (ZrO_2)_z$ by changing the conditions of the reaction (temperature, contact time, partial pressures of reagents) were studied. We also aim atthe research the real effect of catalyst composition $(MoO_3)_x{\cdot}(ZnO)_y{\cdot}(ZrO_2)_z$ and its activity on the selectivity and yield of liquid hydrocarbons from the propane-butane fraction [10-11].

Experimental

In the study, HSZ s obtained by hydrothermal methods from Navbahor factory bentonite. Synthesis of HSZ consists of the following stages: preparation of aluminum nitrate or sulfate, organic template solutions, the preparation of suspension and aluminosilicate gel; hydrothermal crystallization ofzeolite and its filtration and washing from the primary solution.

The synthesis of zeolites was carried out in containers with a volume of 100 cm^3atthe laboratoryconditions.The mass fraction of sodium oxide in zeolites was detected by flame emission photometry in the PAJ-2 flame photometer.

An important characteristic of zeolites is their statistical capacity, which was determined by the magnitudes of complete saturation of zeolite with water vapor and heptane. Prior toanalysis, the zeolite sample was heated at 500–550ºC for 3 h [19–20].

The method of hydrothermal crystallization of alkaline silica-aluminagels underlies the synthesis of high-silicon zeolites (HSZ). Hydrothermal crystallization of silica-aluminagels was carried out in the presence of various organic compounds (templates). High-silicon zeolites were synthesized in a stainless steel autoclave at 175-200ºC for 6 days according to the following methodology.

The initial reaction mixture was prepared by rapid mixing of liquid glass (29% SiO_2, 9% Na_2O, 62% H_2O) with the addition of hexamethylenediamine and an alcohol fraction as a template for $Al(NO_3)_3 \cdot 9H_2O$. The pH of the reaction mixture was controlled by adding 0.1 HNO_3 solution to it. Kaolin from Nurabad district was added to the mixture. Upon completion of the crystallization process, the solid phase was separated from the solution using a Büchner funnel and dried at 120ºC for 12 h and burned at 500–550º C for 8 h to remove the template.

To decant the obtained high-silicon zeolite, 100 g of 25% ammonium chloride was added to 10 g of zeolite. The solution was kept in a water bath at 90–100ºC for 2 h then the precipitate (NH_4^+/zeolite) was filtered, washed with distilled water, dried, and calcinedat 550–600ºC for 8 h. The decanted zeolite powder was pressed into tablets and cut into granules.

Modified zeolite catalysts were prepared by absorbing certain salts or acids into the zeolite. X-ray analysis of zeolites was performed on an X-ray diffractometr"DRON-3" (Cu-anode, Ni-filter) Identification and analysis of diffractograms of HSZs, the comparative studies of intensities and interplanar distances were used.

Catalyst preparation:

HSZs obtained from kaolin in Pakhtachi district (Republic of Uzbekistan) were used as porous substrate in the study. The catalyst was prepared as follows: 30% solution of $(NH_4)_2MoO_4$, Zn $(NO_3)_2$, $ZrO(NO_3)_2$ was ingested to 100g of HSZs for 12 hours. Then the obtained catalyst wasseparated from the solution and dried at 350-400ºC in a nitrogen stream for 3 hours and reduced to a granule size of 5-7 mm.

The catalyst sample was placed in a 12 mm diameter tubular reactor made of (V=1.0 cm^3)quartz glass. Before beginning of the reaction, the catalyst was heated to 750ºC in a helium stream then the propane-butane fraction at a volumetric rate of 1000 h^{-1} was sent for 30 minutes.

The experiments were carried out in a flow catalytic device in the stationary phase of the catalyst (catalyst volume 6 cm^3), at 450-600ºC, at normal atmospheric pressure (P = 0.1 MPa), under volumetric rate of propane-butane fraction 400-600 h^{-1}.

Qualitative and quantitative content of propane-butane fraction and reaction products were analyzed on the chromatograph "Chromate-Crystal 5000M" under the following favorable analysis conditions: separation of gaseous products in a column thermal conductivity (DTP) detector with a length of 3 m and a diameter of 3 mm filled with 8% $NaOH/Al_2O_3$ was carried out. Separation of liquid products was carried out in a DV-1 capillary quartz column (30 m × 0.25 mkm), and detection was conducted in a flame ionization detector.

Results and discussion

In the process of catalytic aromatization of propane-butane fraction, high-silicon zeolites have shown high catalytic activity.It was proved thatthe selectivity of catalystconversion of propane-butane fraction and aromatic hydrocarbon increase in the presence of 5.0% Mo/HSZ catalyst.Thepromoter properties of various metals in the molybdenum-based catalyst were also tested. As a result, the highest results were obtained when zirconium was added to the molybdenum-based catalyst.

A bentonite catalyst containing 1.0% Zr and 5.0% Mo has high catalytic activity.When the content of zirconium in the catalyst prepared on the basis of Mo changed in the range of 0.25% to 2%, the best result was obtained when the content of zirconium was 1.0%. Zr and Zn metals were added to the selected catalyst in order to further increase the efficiency of the reaction. With the introduction of zinc and gallium oxides in the catalyst containing Zr-Mo, the catalytic activity of the catalysts increased. As a result of the experiment, an optimal catalyst with the following composition was selected: 5.0% Mo· 1.0% Zr · 1.0% Zn.

The reaction of the catalytic aromatization of the propane-butane fraction in the presence of a catalyst containing $(MoO_3)_x \cdot (ZnO)_y \cdot (ZrO_2)_z$increases the amount of gas products methane and ethane as soon as temperature increases. On the otherhand the amount of propane and butanedecreases with increasing temperature.

Gaseous aromatization products consist mainly of hydrogen and methane; benzene and toluene predominate in liquid products. In all caseswith an increase in the content of strontium or gallium in Zn-ZSM catalysts with a relatively small decrease in the conversion, the selectivity of the formation of ARs increases (~ 10% rel.). The main effect of the Zn-HSZ modification with zirconium and gallium is a significant decrease in the yield of ARs of the $C_{10} - C_{11}$ + composition. Thus, the introduction of even a very small amount of strontium (Zr / Zn = 0.05) leads to an almost twofold decrease in the concentration of naphthalene and its homologs (see Fig. 1). The greatest effect was obtained on a Ga-containing catalyst. In the presence of these metals, the content of condensed ARs decreased by more than three times, and when the ratio Ga/Zn = 0.1, it decreased by four times (from 20.6% in the initial Zn-HSZ to 5.1% in the Ga-containing catalyst). It should be noted that methane yield on bimetallicpentacil varies little with increasing concentration of Zr and Ga, i.e., the introduction of these metals does not significantly affect the cracking activity of the catalysts.The results obtained are presented in Tables 1-4.

Table -1

Influence of zirconium content on the catalyst $(MoO_3)_x \cdot (ZnO)_y$/HSZ to the main contents during aromatization of compressed hydrocarbon gases at 600°C

Zr/Zn ratio, mol	Zr amount,% mass	Conversion, %	Selectivity, %	Productivity, %		
				ArU	CH_4	C_{10+}
0	0	90.3	57.9	53.8	13.1	9.5
0.05	0.45	83.5	56.7	49.6	15.5	5.9
0.10	0.9	80.5	58.9	49.1	14.3	4.8
0.15	1.35	81.8	55.1	46.6	15.8	4.4
0.25	2.0	53.4	61.2	33.4	14.1	2.4

Table 2

Influence of zirconium content on catalyst $(MoO_3)_x \cdot (ZnO)_y$/HSZto the gas content during aromatization of compressed hydrocarbon gases at 600°C

Zr/Zn ratio, mol	Zramount, %mass	Composition of gas products					
		H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_4
0	0	53.6	23.8	15.6	2.4	5.8	1.4
0.05	0.45	50.3	23.9	16.8	2.6	6.8	2.6
0.10	0.9	49.8	23.9	14.9	3.3	6.8	3.9
0.15	1.35	51.9	20.6	12.2	3.7	9.2	3.3
0.25	2.0	39.5	21.1	12.6	4.2	20.4	3.1

Table 3

Influence of gallium content on catalyst $(MoO_3)_x \cdot (ZnO)_y/HSZ$ to the main parameters of the aromatization process of compressed hydrocarbon gases at 600°C

Ga/Zn ratio, mol	Ga amount, %mass	Conversion%	Selectivity %	Productivity%		
				ArU	CH_4	C_{10+}
0	0	89.8	57.9	52.8	12.9	11.5
0.05	0.8	80.2	57.2	45.5	16.1	7.2
0.10	1.6	79.3	57.4	45.4	12.9	3.4
0.15	2.4	74.6	51.9	38.2	11.7	3.8
0.25	4.0	64.8	62.2	38.9	11.2	3.4

Table 4

Influence of gallium content on catalyst $(MoO_3)_x \cdot (ZnO)_y/HSZ$ to the main parameters of the aromatization process of compressed hydrocarbon gases at 600°C

Ga/Zn ratio, mol	Ga Amount, % mass	Composition of gas hydrocarbon					
		H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_4
0	0	53.4	25.8	16.0	2.4	6.3	2.2
0.05	0.8	49.5	25.0	15.4	2.8	9.1	3.1
0.10	1.6	55.4	21.1	14.2	3.0	9.7	3.9
0.15	2.4	49.9	18.8	13.2	2.7	11.4	8.5
0.25	4.0	50.2	18.9	15.1	2.1	11.0	5.8

The possible explanation of there sultsisdueto change catalytic properties of strong electron-withdrawing Zn-containing active centers in their interaction with Zr and Ga. It cannot be ruled out thatin this case, we are dealing with the manifestation of cluster and ligand effects. Without giving preference to one of them, we assume thatthe cluster effect is more probable, i.e., a change in the size and shape of Zn-containing active centers and their partial blocking of Zr or Ga. As for the ligand effect, the basis of which is the formation of alloys and a change in the electronic state of zinc, such processes seem unlikely, although their occurrence based on only catalytic data cannot be ruled out.

Modified zeolites exhibit low catalytic activity in the conversion of propane to aromatic hydrocarbons. The conversion of propane to aromatic hydrocarbons produces large amounts of methane and low molecular weight alkenes.

An important issue in the conversion of propane and butane to aromatic hydrocarbons is to increase the yield of aromatic hydrocarbons and reduce the formation of methane and ethane.

In the $(MoO_3)_x\cdot(ZnO)_y\cdot(ZrO_2)_z$catalyst, the conversion of propane begins at 450ºC and the conversion of propane increases with increasing temperature and reaches 100% when it reaches 600ºC. Aromatic hydrocarbons are formed in sufficient quantities at 500ºC and demonstrate their maximum value of 52.5% when the temperature is reached 600ºC. The conversion of butane to aromatic hydrocarbons is easier than propane’s conversion, and at 550ºC the yield of aromatic hydrocarbons is 47% while the conversion of butane is 100%. The results obtained are presented in Table 5.

Table 5

The main indicators of the aromatization process of propane and butane in zeolite catalysts

Product	T, ºC	X, %	S_1, %	S_2,%	S_3, %	S_4, %	S_5, %	A, %
Zn-HSZcatalyst								
Propane	400	8	0.6	24,9	65.6	6.2	2.7	0.2
	450	20	1.2	43,5	40.9	9.5	4.9	0.9
	500	40	2.3	65,1	12.3	12.9	7.4	3.0
	550	78	2.5	50,0	1.0	9.6	36.9	28.6
	600	94	3.2	51,5	0.1	8.7	36.5	34.4

Butane	400	76	0.1	4,5	91.6	2.4	1.4	1.0
	450	91	0.4	12,4	63.6	3.6	20.0	18.3
	500	96	1.2	26,9	39.6	6.5	25.8	24.8
	550	99	2.0	38,9	15.5	8.4	35.2	34.9
Zn-Zr-Mo- HSZcatalyst								
Propane	400	11	4.8	27.9	47.0	5.8	14.5	1.6
	450	26	7.8	51.9	16.1	7.7	16.5	4.3
	500	68	4.6	34.6	1.9	4.6	54.3	36.6
	550	92	4.4	34.7	0.3	4.0	56.6	51.8
	600	100	4.4	37.6	0.1	5.4	52.5	52.5
Butane	400	75	0.9	6.3	77.1	2.0	13.7	10.3
	450	92	1.8	13.8	50.6	3.0	30.8	27.5
	500	98	2.9	24.1	28.7	4.4	39.9	39.1
	550	100	3.4	31.2	12.8	5.6	47.0	47.0

Note: X-conversion, selectivity of formation of S_1-hydrogen, S_2-methane and ethane, S_3-S_3-S_5-alkanes; S_4-S_2-S_4-alkenes and S_5-aromatic hydrocarbons; A- productivity of aromatic hydrocarbons

Table 6 shows the composition of the gaseous products of the aromatization reaction of propane and butane in zeolite catalysts.

Table 6

The content of gas products after aromatic reaction of of propane and butane on the high silicon zeolitecatalysts (T=550ºC)

Catalyst					
	H_2	CH_4	C_2H_6	Alkene C_2-C_4	Alkane C_3-C_5
Propane					
Zn-HSZ	2.7	36.2	18.0	10.4	32.7
Zn-Zr-HSZ	8.1	45.3	20.9	7.6	18.1
Butane					
Zn-HSZ	3.1	30.8	28.5	12.8	24.8
Zn-Zr-HSZ	6.3	32.2	26.2	10.5	24.8

As can be seen from Figure 1 and Table 6, the main products in the catalytic conversion of propane and butane are C_1-C_5 gaseous alkanes, C_2-C_4 alkenes, and liquid aromatic hydrocarbons, mixture of aromatic hydrocarbons (benzene, toluene and xylenes-BTX-fraction) and small amounts of alkylbenzenes, naphthalene and alkylnaphthalene.

Gaseous products consist mainly of methane and ethane, as well as small amounts of hydrogen, C_3-C_5 alkanes and C_2-C_4 alkenes. It can be seen that the BTX fraction is formed more as a result of the catalytic conversion of propane than butane.

Electron-microscopic study shows that when the surface of dispersed MoO_3 particles is coated with ZrO_2 shells, the particle size suddenly increases. The latter can occur not only due to the presence of a shell with ZrO_2 but also due to the aggregation of hybrid particles, as evidenced by the large difference in the shape of the “core-shell” type particles and the original molybdenum oxide nuclei.

X-ray phase study has shown that the main phase of a hybrid oxide is hexagonal MoO_3, which in small amounts contains a mixture of its monoclinic dihydrate $MoO_3 2H_2O$, as well as ZrO_2.

The presence of bound water in the samples is apparently the result of hydrated oxide encapsulation in the inner layers of the heterophase particles.

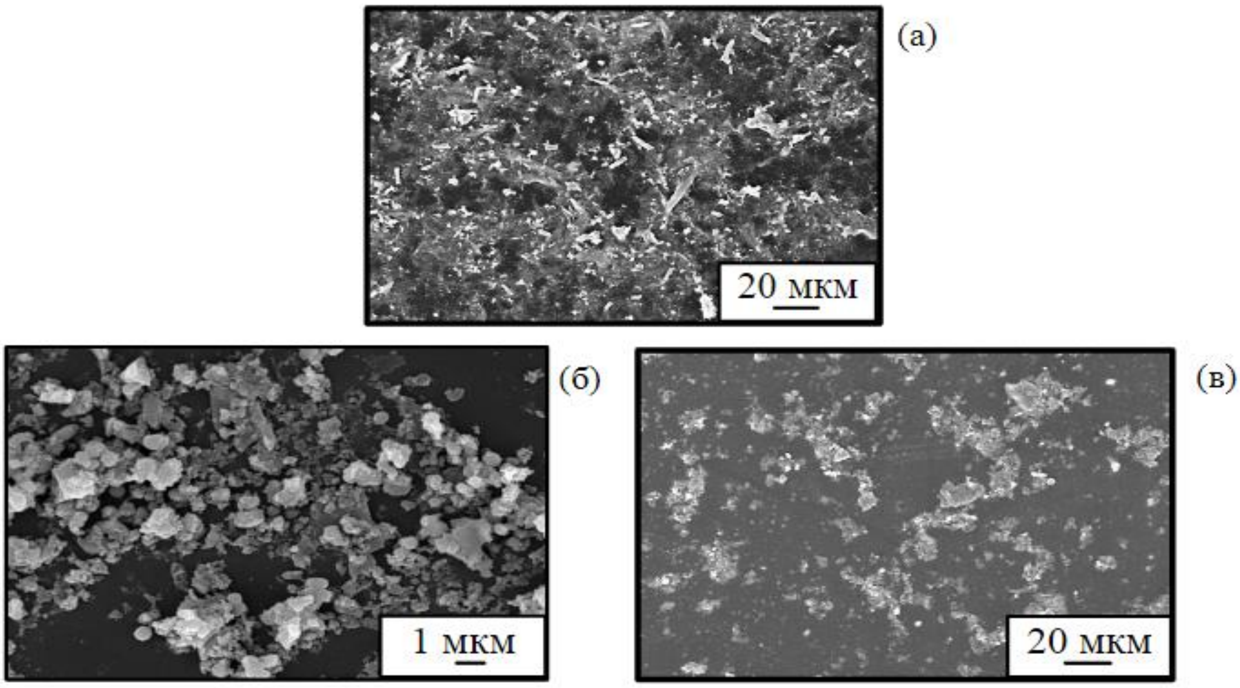
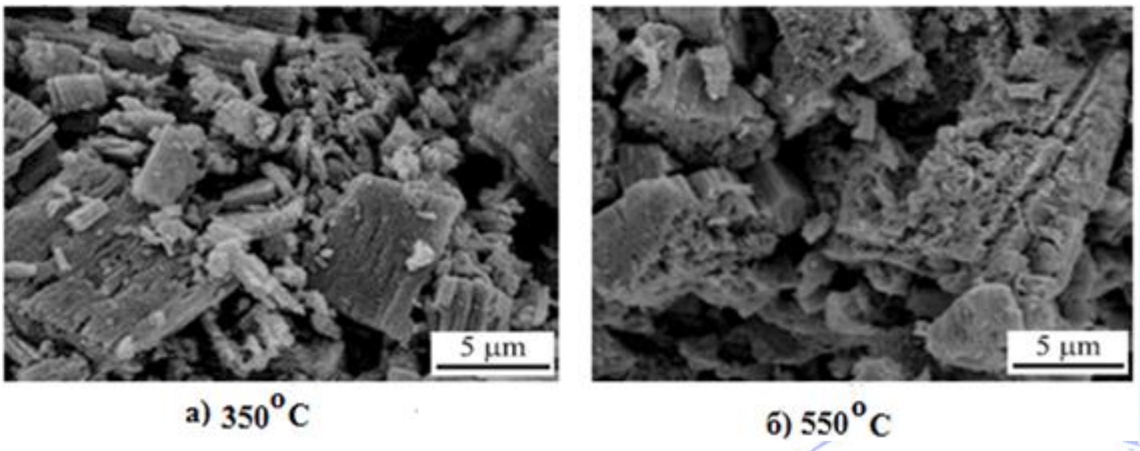


Figure 2. Electron microscopic images of the MoO_3 - ZrO_2 disperse phase obtained by coating the shells with ZrO_2 on MoO_3 particles of different morphologies: (a) – needle-shaped, (b) – ultra microprisms and (c) microprisms. (mkm)

Zn $(NO_3)_2$, distilled water and ammonia were used for ZnO synthesis. Zinc nitrate was diluted in distilled water and mixed. Then ammonia was added to the resulting solution for precipitation, after that filtration was carried out and the resulting bound disperse mass was placed in a muffle furnace. The solution was heated to the given temperature by subsequent holding in the oven. Then cooling and grinding of the obtained nanostructured ZnO powder was carried out.



a) 350°C

б) 550°C

Figure 3. Electron photograph of nanostructured zinc oxide burned at different temperatures

Figure 3 shows a typical morphological structure of ZnOheated at 350ºC and 550ºC. Surface images of the samples were taken using a JEOL JSM 55-10 (Japan) scanning electron microscope. As can be seen, the synthesized powder was formed from nanocrystalline agglomerates. Their average size increases with increasing firing temperature. Analysis of the described electron microphotographs shows that during the heating process, the specific surface area of the nanostructured ZnO, the concentration of defects, and as a result, the width of the band gap of the material changed.

X-ray structural analysis was carried out to determine the amount oftetragonal and monoclinic forms of zirconia(IV). Modification of alkali zirconium ions $\mathrm{MoO_4^{2-}}$ allows metastable tetragonal form of ZrO_2. Monoclinic form of zirconium(IV) oxidecatalytic inactive in the whole reactions, its permeability in the catalytic system leads to a decrease in the effectiveness of $\mathrm{MoO_4^{2-}}$/ ZrO_2.

Conclusion

Catalytic aromatization of propane-butane fractions, the catalytic activity of various catalysts on the reaction yield in the reaction of aromatic hydrocarbons and liquid fuels was studied. Experiments have shown that the best modifying additives are Zn, ZrGa, and Mo. The conversion of propane starts at 450ºC and reaches 100% when it reaches 600ºC.

Aromatic hydrocarbons are formed in sufficient quantities at 500ºC and a maximum value of 52.5% is reached at 600ºC. Based on the results obtained, it was proved that the conversion of butane to aromatic hydrocarbons is easier than that of propane, and at 550ºC the productivity of aromatic hydrocarbons is 47%, while the conversion of butane is 100%.

The textural and physicochemical characteristics of the catalysts were also studied in this research work.

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