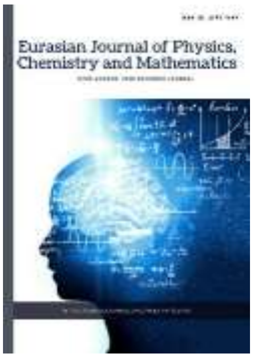

The Possibilities of Use of Catalyst Containing $(MoO_3)_x{\cdot}(ZnO)_y{\cdot}(ZrO_2)_z$/HSZ in Catalytic Aromatization of Propane-Butane Fraction

Sanobar Yunusovna Bobomuratova
PhD, Senior Lecturer, Department of Chemistry, Jizzakh Polytechnic Institute, Jizzakh, Uzbekistan
E-mail: bobomurodovas798@gmail.com

Mukhabbat Botirovna Matchanova
Senior Lecturer, Department of Chemistry, Jizzakh Polytechnic Institute, Jizzakh, Uzbekistan

ABSTRACT

In this work, the application of the catalyst containing $(MoO_3)_x{\cdot}(ZnO)_y{\cdot}(ZrO_2)_z$/HSZ in the catalytic aromatization of the propane-butane fraction was investigated. The experiments were carried out in a flow catalytic device in the stationary phase of the catalyst (catalyst volume 6 cm^3), at 450-600 °C, at normal atmospheric pressure (P = 0.1 MPa), under the volumetric rate of propane-butane fraction 400-600 h^{-1}. As a result of the experiment, the best modifying additives were found Zn, Zr, Ga, and Mo. The conversion of propane begins at 450 °C and reaches 100%; where the total conversion of propane reaches 600 °C. Aromatic hydrocarbons are formed in sufficient quantities at 500 °C and a maximum value of 52.5% is reached at 600 °C. The conversion of butane to aromatic hydrocarbons is easier than propane. At 550 °C the yield of aromatic hydrocarbons is 47% while the conversion of butane is 100%.

Keywords: Aromatic hydrocarbons aromatized catalytically, the productivity of reaction, volumetric rate, propane-butane fraction.

Introduction

Aromatic hydrocarbons are the starting materials in the organic chemical industry, the most commonly used of which are benzene, toluene, and xylenes. At present, aromatic hydrocarbons are obtained in pyrolysis and reforming processes in the processing of liquid hydrocarbons of oil. At the same time, the depletion of oil raw materials requires the search for alternative sources of oil. Alternative sources are petroleum satellite gases, natural gas and broad fractions of light hydrocarbons [1-5].

High-silica zeolites are widely used as catalysts in the processing of low molecular weight hydrocarbons into aromatic hydrocarbons [6-8]. 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 (BTK). Chemical and thermal processing of zeolites used to increase the selectivity of aromatic hydrocarbons is effective. High-silica zeolites are modified with various metals to convert lower molecular weight hydrocarbons into aromatic hydrocarbons [8-14].

Metals Zn, Ga, Al, La, Sn, Mo, Co and Zr were used as modifying additives. As a result of the experiments, it was proved that the best modifying additives are Zn, Zr, Ga, and Mo.

The purpose of this work is to study the effect of $(MoO_3)_x \cdot (ZnO)_y \cdot (ZrO_2)_z$ catalyst composition and activity on the selectivity and yield of liquid hydrocarbons from the propane-butane fraction.

Materials And Methods

In the work, HSZ obtained by hydrothermal method from Navbahor bentonite was used. The synthesis of HSZ consists of the following stages: preparation of aluminium nitrate or sulfate, organic template solutions, suspension, and aluminosilicate gel; hydrothermal crystallization of the zeolite and its filtration and washing from the core solution.

Synthesis of zeolites was carried out in 100 cm^3 vessels in laboratory conditions.

The mass fraction of sodium oxide in zeolites was determined by flame emission photometry on a PAJ-2 flame photometer.

An important characteristic of zeolites is their statistical capacity, which is determined by the values of complete saturation of zeolite with water vapour and heptane. Before analysis, the zeolite sample was heated at 500-550 °C for 3 hours [15-16].

The method of hydrothermal crystallization of alkaline alumino-silica gels is based on the synthesis of high-silica zeolites (HSZ). Hydrothermal crystallization of alumina-silica gels was carried out in the presence of various organic compounds (templates). High silica zeolites in a stainless steel autoclave at 175-200 °C were synthesized according to the following methodology for 6 days.

The initial reaction mixture was prepared by adding hexamethylenediamine and alcohol fraction to liquid glass (29% SiO_2, 9%Na_2O, 62%H_2O) as $Al(NO_3)_3 \cdot 9H_2O$ template and stirring rapidly. The pH value of the reaction mixture was controlled by adding 0,1 N HNO_3 solution to it. Kaolin brought from the Nurabad district was added to the resulting mixture. After the crystallization process was completed, the solid phase was separated from the solution using a Buchner funnel and dried at 120 °C for 12 hours and calcined at 500-550 °C for 8 hours to remove the template.

For decationization of the obtained high-silica zeolite, 10 g of zeolite was treated with 100 g of 25% ammonium chloride. The solution was kept in a water bath at 90-100 °C for 2 hours with constant stirring. Then the precipitate (NH_4^+/zeolite) was filtered. Washed with distilled water, dried and calcined at 550-600 °C for 8 hours. Then, the decationized zeolite powder was pressed into tablets and cut into granules. Modified zeolite catalysts were prepared by absorbing certain salts or acids into zeolite [17-20]

Results And Discussion

In the process of catalytic aromatization of the propane-butane fraction, high-silicon zeolites have high catalytic activity, and in the presence of a 5.0% Mo/HSZ catalyst, it was found that the conversion of the propane-butane fraction and the yield of aromatic hydrocarbons increased. After that, the promoting properties of various metals on the molybdenum-based catalyst were investigated. As a result, the highest results were obtained when zirconium was added to the molybdenum-based catalyst.

Bentonite catalyst containing 1.0% Zr and 5.0% Mo has high catalytic activity. Then, when we tried changing the amount of zirconium in the Mo-based catalyst from 0.25% to 2%, the best result was obtained when the amount of zirconium was 1.0%. To further increase the yield of the reaction, Zr and Zn metals were added to the selected catalyst. Adding zinc and gallium oxides to the Zr–Mo catalyst increased the catalytic activity of the catalysts. As a result of the research, an optimal catalyst with the following composition was selected: 5.0% Mo*1.0% Zr*1.0% Zn.

Catalytic aromatization of the propane-butane fraction in the presence of a $(MoO_3)_x \cdot (ZnO)_y \cdot (ZrO_2)_z$ catalyst increases the amount of methane and ethane in the gas products with increasing temperature. The amount of propane and butane, on the contrary, decreases with increasing temperature[16-25].

The obtained results are presented in tables 1-4.

Table 1. The influence of the amount of zirconium in the $(MoO_3)x\cdot(ZnO)y$/HSZ catalyst on the main parameters of the aromatization process of compressed hydrocarbon gases at 600 ?

Zr/Zn ratio, mol	Amount of Zr, % mass	Conversion, %	Selectivity, %	Yield, %		
				ArU	CH4	C10+
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. The influence of the amount of zirconium in the $(MoO_3)_x\cdot(ZnO)_y$/HSZ catalyst on the gas composition during the aromatization of compressed hydrocarbon gases at 600 ?

Zr/Zn ratio, mol	Amount of Zr, % 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. The influence of gallium content in the $(MoO_3)_x\cdot(ZnO)_y$/HSZ catalyst on the main parameters of the aromatization process of compressed hydrocarbon gases at 600 ?

Ga/Zn ratio, mol	Amount of Ga, % mass	Conversion, %	Selectivity, %	Yield, %		
				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. The influence of gallium content in the $(MoO_3)_x\cdot(ZnO)_y$/HSZ catalyst on the main parameters of the aromatization process of compressed hydrocarbon gases at 600 ?

Ga/Zn ratio, mol	Amount of Ga, % mass	Composition of gas hydrocarbons					
		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

Modified zeolites show low catalytic activity in the conversion of propane to aromatic hydrocarbons. A large amount of methane and lower molecular alkenes are formed during the conversion of propane to aromatic hydrocarbons.

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 starts at 450 °C, and the conversion of propane increases as the temperature rises and reaches 100% when it reaches 600 °C. Aromatic hydrocarbons are formed in sufficient quantity at 500 °C and reach a maximum value of 52.5% at 600 °C. The conversion of butane to aromatic hydrocarbons is easier than that of propane, and the yield of aromatic hydrocarbons is 47% while the conversion of butane is 100% at 550 °C. The obtained results are presented in Table 5.

Table 5. The main parameters of the aromatization process of propane and butane on zeolite *catalysts*

X-conversion, selectivities of formation of S_1-hydrogen, S_2-methane and ethane, S_3-C_3-C_5-alkanes, S_4-C_2-C_4-alkenes and S_5-aromatic hydrocarbons; A product of aromatic hydrocarbons

Product	T, °C	X, %	S_1, %	S_2,%	S_3, %	S_4, %	S_5, %	A, %
Catalyst Zn-HSZ								
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
Bhutan	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
Catalyst Zn-Zr-Mo-HSZ								
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
Bhutan	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

Table 6 shows the composition of the gas products of the aromatization reaction of propane and butane on zeolite catalysts.

Table 6. The composition of gas products of the aromatization reaction of propane and butane on high-silica zeolite catalysts (T = 550 ?)

Catalyst	H_2	CH_4	C_2H_6	Alkenes are C_2-C_4	Alkanes C3-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
Bhutan					
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

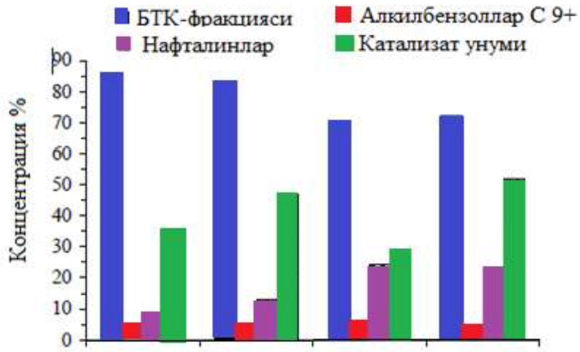

Figure 1. Composition and catalyst yield of liquid products of the aromatization reaction of propane and butane on zeolite catalysts (T=550 ⍰)

The composition of the liquid products of the aromatization reaction of propane and butanes on zeolite catalysts and the catalyst yield (T = 550 °C) are presented in Fig. 1.
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. The composition of the catalyst is a mixture of aromatic hydrocarbons (benzene, toluene and xylenes-BTK-fraction) and a small amount of alkylbenzenes, naphthalene and alkylnaphthalenes [16-22].
The 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. As can be seen from the above, the BTK fraction is more formed as a result of the catalytic conversion of propane than butane.

Conclusion

Thus, the catalytic activity of various catalysts was studied for the reaction yield in the catalytic aromatization reaction of propane-butane fractions. As a result of the experiments, it was proved that the best modifying additives are Zn, Zr, Ga, and Mo. Propane conversion starts at 450°C and reaches 100% when it reaches 600 °C. Aromatic hydrocarbons are formed in sufficient quantity at 500 °C and reach a maximum value of 52.5% at 600 °C. Based on the obtained results, it was proved that the conversion of butane to aromatic hydrocarbons is easier than propane, and the yield of aromatic hydrocarbons is 47% with the conversion of butane at 100% at 550 °C.

References

1. Dudley, B. (2018). BP statistical review of world energy. *BP Statistical Review, London, UK, accessed Aug*, *6*(2018), 00116.
2. Миначев, Х. М., & Дергачев, А. А. (1990). Итоги науки и техники. Сер. *Кинетика и катализ*, *23*, 3.
3. Восмерикова, Л. Н., Литвак, Е. И., Восмериков, А. В., & Ушева, Н. В. (2010). Превращения природного газа на la mo-содержащих высококремнеземных цеолитах. *Нефтехимия*, *50*(3), 212-216.
4. Ахметов А.Ф., Белоусова О.Ю., Курмаев С.А. (2007). Нефтепереработка и нефтехимия. 11. С. 30-31.
5. Белоусова О.Ю., Кутепов Б.И. (2000). Ароматизация углеводородов на пентасил-содержащих катализаторах. *М.: Химия*, 94 с.
6. Казанский, В. Б. (1988). Современные представления о механизмах гомогенного и гетерогенного кислотного катализа: сходства и различия. *Успехи химии*, *57*(12), 1937-1962.
7. Ахметов А.Ф., Белоусова О.Ю., Курмаев С.А. (2007). Влияние содержания промо-тора на кислотные свойства пентасилсодержащих катализаторов в превраще-нии углеводородов C_3-C_4. *Башкирский химический журнал*. Т. 14(5). С. 101.

8. Курмаев, С. А., Ахметов, А. Ф., & Белоусова, О. Ю. (2008). Влияние содержания промотора на каталитические свойства пентасилсодержащих катализаторов в превращении углеводородов С3-С4. *Башкирский химический журнал*, *15*(1), 40-41.
9. Расулов, С. Р., Мустафаева, Г. Р., & Махмудова, Л. А. (2012). перспективные катализатор ы Ароматизаци И ПРОПана. *Нефтепереработка и нефтехимия. Научно-технические достижения и передовой опыт*, (1), 36-41.
10. Восмерикова, Л. Н., Барбашин, Я. Е., & Восмериков, А. В. (2014). Каталитическая ароматизация этана на цеолитах различного структурного типа, модифицированных цинком. *Нефтехимия*, *54*(6), 430-435.
11. Frey, K., Lubango, L. M., Scurrell, M. S., & Guczi, L. (2011). Light alkane aromatization over modified Zn-ZSM-5 catalysts: characterization of the catalysts by hydrogen/deuterium isotope exchange. *Reaction Kinetics, Mechanisms and Catalysis*, *104*(2), 303-309.
12. Gabrienko, A. A., Arzumanov, S. S., Freude, D., & Stepanov, A. G. (2010). Propane aromatization on Zn-modified zeolite BEA studied by solid-state NMR in situ. *The Journal of Physical Chemistry C*, *114*(29), 12681-12688.
13. Baerlocher, C., McCusker, L. B., & Olson, D. H. (2007). *Atlas of zeolite framework types*. Elsevier. 398 p.
14. Дедов, А. Г., Локтев, А. С., Кунашев, Л. Х., Карташева, М. Н., Богатырев, В. С., & Моисеев, И. И. (2002). Аддитивное влияние оксидов хрома и цинка на активность цеолита марки НЦВМ в ароматизации пропан-бутановой фракции. *Химическая технология*, *3*(8), 15-19.
15. Ibodullayevich, F. N., Yunusovna, B. S., & Anvarovna, X. D. (2020). Physico-chemical and texture characteristics of Zn-Zr/VKTS catalyst. *Journal of Critical Reviews*, *7*(7), 917-920.
16. Fayzullaev, N. I., Bobomurodova, S. Y., Avalboev, G. A., Matchanova, M. B., & Norqulova, Z. T. (2020). Catalytic change of C 1-C 4-alkanes. *International Journal of Control and Automation*, *13*(2), 827-835.
17. Bobomurodova, S. Y., Usmanova, K. A., & Fayzullaev, N. I. (2020). Catalytic aromatization of oil satellite gases. *International Journal of Advanced Science and Technology*, *29*(5), 3031-3039.
18. Бобомуродова, С. Ю. (2020). Каталитические изменения нефтяных попутных газов и текстурные характеристики катализаторов. *Universum: химия и биология*, (9 (75)), 70-75.
19. Fayzullaev, N. I., Akmalaev, K. A., Karjavov, A., Akbarov, H. I., & Qobilov, E. (2020). Catalytic Synthesis Of Acetone And Acetaldehyde From Acetylene In Fluoride-Based Catalysts. *The American Journal of Interdisciplinary Innovations and Research*, *2*(09), 89-100.
20. Бобомуродова, С. Ю., Матчанова, М. Б., & Холмуминова, Д. А. (2020). Разработка цинк, цирконий промотированного цеолитового катализатора конверсии пропан-бутановой фракции. *Universum: химия и биология*, (9 (75)), 65-69.
21. Fayzullaev, N. I., Bobomurodova, S. Y., Karimova, F. S., & Buronov, A. Y. (2020). Catalytic Aromatization of Propane-Butane Fraction. *International Journal of Advanced Science and Technology*, *29*(05), 6532-6540.
22. Fayzullaev, N. I., Bobomurodova, S. Y., Kurbanova, L. M., & Buronov, A. Y. (2020). The Physicochemical and Textural Characteristics of Catalysts in the Catalytic Aromatization Reaction of Propane-Butane Fractions. *International Journal of Control and Automation*, *13*(4), 888-896.

23. Fayzullaev, N. I., Akmalaev, K. A., Karjavov, A., Akbarov, H. I., & Qobilov, E. (2020). Vapor phase catalytic hydratation of acetylene. *ACADEMICIA: An International Multidisciplinary Research Journal*, *10*(7), 88-98.
24. Fayzullaev, N. I., & Bobomurodova, S. Y. (2020). Laws of Catalytic Aromatization Reaction of C1-C4-Carbohydrates and Texture Characteristics of Catalysts. *International Journal of Psychosocial Rehabilitation*, *24*(04), 1475.
25. Matchanova, M., Bobomuratova, S., & Kholmominova, D. (2022). Radiation Polymerization Of Vinyl Fluoride In The Presence Of Freon-113 (F-113). *Journal of Pharmaceutical Negative Results*, 4828-4839.