N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.8**
Volume 1, Number 439 (2020), 64 – 71

УДК 541.128.13;665. 644.26; 665.658.62

B.T. Tuktin[1], A.M. Temirova[2], G.T. Saidilda[1], A.A. Omarova[2]

[1] JSC "D. V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry",
050010, Kunaev str. 142, Almaty, Kazakhstan;
[2] al-Farabi Kazakh National University
tuktin_balga@mail.ru

CONVERSION OF PROPANE-PROPYLENE FRACTION INTO AROMATIC HYDROCARBONS ON MODIFIED ZEOLITE CATALYSTS

Abstract. The process of transformation of propane-propylene fraction into aromatic hydrocarbons on zeolite-containing catalysts modified Zn, La, Cr, Zr and P was discovered. The process was carried out in an installation in a flow installation at atmospheric pressure with a temperature variation from 350 to 600°C and a volumetric feed rate of 150-1020 h^{-1}. The catalysts were prepared by impregnation of aluminum hydroxide and zeolite ZSM-5 with aqueous solutions of nitric acid salts of metals and phosphoric acid. The physical and chemical characteristics of the developed catalysts are studied. The BET method established that the surface of the developed catalysts fluctuates within 211.0-274.0 m^2 / g of the catalyst. Catalysts are predominantly mesoporous: pores with d ≈ 2.0-3.0 nm predominate.

It is shown that the developed modified zeolite-containing catalysts have high catalytic activity and selectivity in the process of processing the propane-propylene fraction into aromatic hydrocarbons. The predominant products formed during the processing of C2-C4 alkanes are toluene and benzene. It was found that the highest yield of aromatic hydrocarbons is 52.8% (550°C, 150 h^{-1}) on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3 with a conversion rate of 100.0%, selectivity for aromatic compounds - 52.8%.

Modified zeolite-containing catalysts have multifunctional properties. The composition of liquefied petroleum gas processing products shows that the formation of aromatic hydrocarbons occurs in one stage as a result of cracking, dehydrogenation, oligomerization, dehydrocyclization, alkylation reactions.

Keywords: zeolite-containing catalysts, propane-propylene fraction, aromatic hydrocarbons.

INTRODUCTION

Kazakhstan has large reserves of light hydrocarbon raw materials: gas condensate, natural and petroleum gases, catalytic processing of which is very limited. Efficient processing of light hydrocarbon raw materials to obtain important products of petrochemical synthesis remains one of the important problems in petrochemistry. To date, light hydrocarbons are used as raw materials in only a small number of technological processes.

Catalytic processing of light hydrocarbons into practically important products is one of the ways aimed at their effective use. These products include olefins and aromatic hydrocarbons, important starting products in the basic organic synthesis industry. On their basis, plastics, synthetic fibers, resins, rubbers for various purposes, dyes, surfactants, pharmaceutical and agricultural products are obtained.

Currently, in the petrochemical and oil refining industry, zeolite-containing catalysts based on highly silica zeolites of the pentasil family are widely used, having a unique micro porous structure and acid-base properties, capable of converting light alkanes into valuable products of petrochemical synthesis. Zeolite-containing catalysts can efficiently process low molecular weight alkanes into aromatic hydrocarbons. At present, interest in high silica zeolites of pentasil type as catalysts for aromatization of low molecular weight hydrocarbons has grown [1-21].

Experimental part

In this paper, the process of processing propane-propylene fractions on zeolite-containing catalysts modified with zinc, phosphorus and metals of variable valence: Zn-La-ZSM-Al_2O_3, Zn- La - P-ZSM-Al_2O_3 Zn-La- Zr -ZSM-Al_2O_3, Zn-Zr-ZSM-Al_2O_3, Zn-La-P-Cr-ZSM-AI_2O_3. The catalysts were prepared by impregnation of a mixture of aluminum hydroxide and zeolite HZSM-5 with aqueous solutions of metal salts followed by drying at 150°C and calcination at 550°C. The catalysts were tested in the process of processing propane-propylene fractions in a flowing quartz reactor with a stationary catalyst bed at varying reaction temperature in the range 350-600°C and atmospheric pressure, volume velocity 150-1020 h^{-1}. The reaction products were analyzed on "Crystal-5000M" and "Agilent chromatographs".

Results and discussion

When processing propane-propylene fraction on modified zeolite catalyst Zn- La-ZSM-Al_2O_3 (table 1), aromatic hydrocarbons and gaseous products are formed. Benzene, toluene, ethylbenzene, xylenes and C_{8+} hydrocarbons are found in the liquid phase, and C1-C4 hydrocarbons are found in the gas phase. With an increase in the process temperature from 400 to 650°C, the conversion rate increases from 1.4 to 100.0%. The yield of aromatic hydrocarbons in these conditions increases from 8.9 to 29.2 -28.9%. The maximum selectivity is observed at 600°C and is 29.2%. The quantitative composition of the resulting aromatic hydrocarbons depends significantly on the temperature of the process. Toluene yield in the range of 400 - 650°C varies extremely, reaching a maximum value at 450°C, and is 46.9%. The yield of benzene with increasing temperature increases from 4.1 (400°C) to 39.2% (650°C). The content of xylene in the liquid catalyzate-1,6-7,2%. The yield of ethylbenzene and C5-C6 hydrocarbons decreases with an increase in temperature in the range of 400-650°C from 24.8 to 4.8% and from 21.8 to 4.6 %, respectively. With increasing temperature, cracking increases with the formation of C1-C2 hydrocarbons: the amount of methane increases from 0.1 to 53.1%, ethane-from 1.0 to 44.2%.

Table 1 - Processing of propane-propylene fraction on catalyst Zn-La-ZSM-Al_2O_3

T, °C	400	450	500	550	600	650
Conversion, %	1,4	38,6	97,2	99,5	100	100
The yield of liquid phase, %	8,9	12,4	18,4	26,2	29,2	28,9
Select. ArC, C_4%	-	32,1	18,9	26,3	29,2	28,9
Liquid phase,%						
Benzene	4,1	10,1	16,5	20,7	32,2	39,2
Toluene	31,8	46,9	44,5	32,1	37,2	32,6
Ethylbenzene	24,8	22,2	21,0	8,8	6,6	4,8
Xylene	7,2	6,6	6,6	2,8	2,2	1,6
C_{5-6}	21,8	1,5	0,3	27,2	9,1	4,6
C_{8+}	10,3	12,7	11,1	8,4	12,7	17,2

The process of processing propane-propylene fraction on the catalyst Zn-La-P-ZSM-Al_2O_3 was investigated. From the data presented in table 2, it can be seen that with an increase in temperature from 350 to 600°C, the conversion increases from 27.8 to 98.9%. With an increase in temperature from 350 to 550°C, the yield of aromatic hydrocarbons increases from 19.3 to 38.1%, but at a higher temperature (600°C), there is a decrease in the yield of ArC to 27.1%. In the interval 350-600°C toluene yield is 27.4-39.1%, and benzene-0.5-23.0%. The content of xylene in the liquid catalyzate - 1,6-4,3%. The yield of ethylbenzene decreases with temperature increase in the range of 400-600°C from 22.9 to 5.9%. The yield of C_5-C_6 hydrocarbons decreases with increasing temperature in the range 350-550°C from 37.2 to 17.0%, then increases to 32.0 (600°C). The maximum selectivity for ArC is observed at 500°C and is 54.0%. At higher temperatures, the ArC selectivity is slightly lower-38.7-27.4%. With increasing temperature, cracking with the formation of C_1-C_2 hydrocarbons is observed.

In the process of processing the propane-propylene fraction on the catalyst Zn-La- Zr -ZSM-Al_2O_3 with an increase in temperature from 350 to 600°C, the conversion increases from 7.0 to 100.0%. With an increase in temperature from 350 to 550°C, the yield of aromatic hydrocarbons increases from 4.6 to 28.8%, at 600°C there is a decrease in the yield of aromatic hydrocarbons to 23.2%. With increasing temperature, the selectivity of the formation of target products decreases: the maximum selectivity for

ArC is observed at 350°C and is 65.7%. At higher temperatures, ArC selectivity is lower. Toluene and ethylbenzene prevail in the liquid catalysate. Toluene yield grows from 14.4 to 43.9% in the range 350-550°C, at 600°C toluene yield is slightly lower-40.9%. The yield of ethylbenzene monotonically decreases from 24.0 to10, 6%. The amount of benzene in these conditions increases from 1.7 to 27.2%. The content of xylene ranges from 3,1 to 7,9%. With increasing temperature, cracking with the formation of C_1-C_2 hydrocarbons is observed (table 3).

Table 2 - Processing of propane-propylene fraction on catalyst Zn-La- P-ZSM-Al_2O_3

T, °C	350	400	450	500	550	600
Conversion, %	27,8	36,7	58,6	69,5	98,5	98,9
The yield of liquid phase, %	18,7	19,3	30,6	37,5	38,1	27,1
Select. ArC, %	18,8	52,6	52,2	54,0	38,7	27,4
Liquid phase, %						
Benzene	2,6	3,9	9,2	14,7	23,0	19,1
Toluene	27,4	27,9	31,9	39,1	34,3	28,2
Ethylbenzene	22,9	16,2	15,9	17,5	9,4	5,9
Xylene	4,3	3,8	3,9	4,2	2,5	1,6
C_{5-6}	26,8	37,2	30,7	17,0	17,0	32,0
C_{8+}	16,0	11,0	8,4	7,5	13,8	13,2

Table 3 - Effect of temperature on the process of processing propane-propylene fraction Zn-La-Zr-ZSM-Al_2O_3

T,°C	350	400	450	500	550	600
Conversion, %	7,0	52,2	63,8	92,3	100	100
The yield of liquid phase , %	4,6	10,5	23,0	26,9	28,2	23,2
Select. ArC, %	65,7	20,1	24,5	29,1	28,2	23,2
состав жидкой фазы, % мас						
Benzene	1,7	4,7	9,7	13,6	21,9	27,2
Toluene	14,4	35,0	40,3	42,3	43,9	40,9
Ethylbenzene	24,0	27,7	23,1	21,5	15,0	10,6
Xylene	3,9	7,9	6,6	6,3	4,7	3,1
C_{5-6}	15,8	3,1	7,2	3,1	0,2	1,4
C_{8+}	40,2	21,6	13,1	13,2	14,3	16,8

The influence of the bulk feed rate on the activity and selectivity of the catalyst Zn-La-Zr-ZSM-Al_2O_3 in the processing of propane-propylene fraction was studied (table 4). At 550°C and volume feed rate of 150 h^{-1} conversion is 100%, yield of aromatic hydrocarbons-37,9%. With an increase in the volume feed rate of raw materials up to 825 h^{-1} conversion does not change and is equal to 100%, but the output of the liquid phase is reduced to 10.8%. The qualitative and quantitative composition of the liquid catalyzate does not change much when the volumetric feed rate of the raw material changes. The yield of benzene is in the range of 21.9 to 25.1%, of toluene, from 42.8 to 46.4%. The yield of ethylbenzene is in the range of 13,2 - 15,0%. The maximum selectivity of aromatic hydrocarbons formation reaches 37.9% at V=150 h^{-1}.

Table 4 - Effect of volumetric feed rate on the process
of processing propane-propylene fraction on the catalyst Zn-La-Zr-ZSM-Al_2O_3

V, h^{-1}	150	300	470	675	825
Conversion, %	100	100	97,9	100	100
The yield of liquid phase, %	37,9	28,2	19,4	11,3	10,8
Select. ArC, %	37,9	28,2	19,8	11,3	10,8
Liquid phase, %					
Benzene	23,4	21,9	25,1	23,7	24,9
Toluene	43,2	43,9	42,8	44,9	46,4
Ethylbenzene	13,3	15,0	13,6	14,9	15,0
Xylene	4,0	4,7	4,2	4,7	4,6
C_{5-6}	2,4	0,2	1,3	0,9	0,2
C_{8+}	13,7	14,3	13,0	10,9	8,9

The stability of the modified zeolite-containing catalyst Zn-La-Zr-ZSM-Al_2O_3 in the process of processing gaseous hydrocarbons formed during catalytic cracking was studied. Studies were carried out at 550°C and V=300h^{-1} (table 5). From the data presented in table 5, it can be seen that during 11 hours of operation of the catalyst, the conversion does not change and is 100%. The yield of the liquid phase in the first 5 hours of operation changes little-20.6-17.9%, then after 11 hours of operation, it decreases to 10,8%.

Under these conditions, the yield of benzene varies in the redistribution of 25.0 to 28.9%. The yield of toluene is higher than benzene – 40.9 - of 44.4%. The yield of ethylbenzene-10.9-13.0%, xylene-3.4-6.0%. C_1-C_4 hydrocarbons were found in the gas phase.

Table 5 - Stability of the modified zeolite-containing catalyst Zn-La-Zr-ZSM-Al_2O_3 in the process of processing propane-propylene fraction

Time, h	1	2	3	4	5	6	7	8	9	10	11
Conversion,%	100	100	100	100	100	100	100	100	100	100	100
The yield of liquid phase, %	20,6	20,4	19,0	18,0	17,9	15,7	12,5	12,7	12,3	11,1	10,8
Select. ArC, C_3%	64,2	55,0	44,1	35,4	88,6	-	-	35,8	26,2	64,5	54,8
Select. ArC, C_4%	20,6	20,4	90,0	18,0	17,9	15,7	12,5	12,7	12,3	11,1	10,8
	Liquid phase, %										
Benzene	26,3	27,7	28,7	28,9	26,7	25,9	26,9	24,0	25,0	25,9	26,4
Toluene	42,7	40,9	42,2	41,3	42,9	42,0	43,3	43,2	40,4	44,4	44,2
Ethylbenzene	12,8	11,8	10,9	11,3	12,4	12,1	12,3	13,0	11,6	11,1	12,3
Xylene	4,1	3,7	3,4	3,6	3,9	4,7	3,9	6,0	3,6	4,3	3,9
C_{5-6}	1,4	0,6	1,7	0,8	0,9	2,4	2,0	3,0	8,0	1,0	1,8
C_{8+}	12,7	15,3	13,1	14,1	13,2	12,9	11,6	10,8	11,4	12,3	11,4

When processing the propane-propylene fraction on the catalyst Zn-Zr-ZSM-Al_2O_3, the conversion rate increases from 6.3 to 100% with an increase in temperature from 400 to 600°C. From the data of table 6 it can be seen that the products of processing of propane-propylene fraction contain aromatic hydrocarbons, mainly benzene, toluene, ethylbenzene and xylenes. The total yield of aromatic hydrocarbons (ArC) increases from 8.8 (350°C) to 21.3% (600°C). Maximum ArC selectivity is 29.2% at 450^{0}C. With an increase in temperature from 400 to 600°C, there is an increase in the content of benzene from 1.0 to 33.3%. Toluene yield varies, increasing from 30.2% (350°C) to 44.3% (500°C) and decreasing to 37.6% (600°C). The content of xylene is small-2,3-5,2%. Ethylbenzene yields vary from 30.3 (400°C) to 7.6% (600°C). Product composition the temperature in the gas phase indicates that as the temperature increases, the cracking direction increases with the formation of methane and ethane.

Table 6 - Processing of propane-propylene fraction on catalyst Zn -Zr -ZSM-Al_2O_3

T, °C	350	400	450	500	550	600
Conversion, %	-	6,3	68,8	95,5	100	100
The yield of liquid phase, %	8,8	10,8	20,1	21,8	20,6	21,3
Select. ArC, %	-	-	29,2	22,8	20,6	21,3
Liquid phase, %						
Benzene	1,0	4,0	9,8	14,6	25,1	33,3
Toluene	36,2	31,2	41,7	44,3	43,4	37,6
Ethylbenzene	30,0	28,0	22,6	19,9	12,3	7,6
Xylene	2,8	5,2	3,6	2,3	3,8	2,5
C_{5-6}	8,0	9,6	3,6	3,5	1,4	0,6
C_{8+}	22,0	22,0	18,7	15,4	14,0	18,4

Table 7 presents the results obtained during the processing of propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3 (KTK -15).

When processing propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3 at a volumetric rate of 350 h^{-1} with a temperature increase from 400 to 600°C, an increase in the conversion rate from 85.2 % (450°C) to 100% at 600°C is observed (table 7). Under these conditions, the highest yield of aromatic

hydrocarbons is 34.5% at 550°C. the Selectivity for aromatic hydrocarbons for C3 is maximum at 400°C and is 64.3%, and for C_4 is maximum at 450°C-38.6%.

With increasing temperature, there is an increase in the yield of benzene and toluene from 4.3% (400°C) to 24.1% (550°C) and from 41.5% (400°C) to 44.1% (550°C), with a further increase in temperature to 600°C, the yield of these products decreases to 12.3 and 18.2%, respectively.

As with most of the catalysts studied (tables 1-6), on Zn-La-P-Cr-ZSM-Al_2O_3 in the range 400 - 600°C toluene yield is higher than benzene.

Yields of ethylbenzene and xylenes with increasing temperature decrease from 29.5 and 4.5% (400°C) to 4.1 and 1.0% (600°C), respectively. During processing of propane-propylene fraction on Zn-La-P-Cr-ZSM-AI_2O_3 cracking of alkanes with formation of methane and ethane is observed.

Table 7 - effect of temperature on the process of processing propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-AI_2O_3

T, °C	400	450	500	550	600
Conversion, %		85,2	100	100	100
The yield of liquid phase, %	25,0	32,9	32,1	34,5	27,0
Select. ArC, %		38,6	32,1	34,5	27,0
Liquid phase, %					
Benzene	4,3	9,4	19,8	24,1	12,3
Toluene	41,5	35,1	40,3	44,1	18,2
Ethylbenzene	29,5	16,9	13,3	12,3	4,1
Xylene	4,5	3,1	2,8	3,0	1,0
C_{5-6}	5,0	25,0	16,3	5,7	47,0
C_{8+}	15,2	10,5	7,5		17,4

At a temperature of 550°C, the effect of the volumetric feed rate on the processing of propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3 was studied (table 8). At 550°C and a volume feed rate of 150h-1, the conversion of software is 100.0%, the output of ArC is 52.8% with selectivity-52.8%. With an increase in the volumetric feed rate to 1020 h^{-1} conversion is reduced to 52.4%, the yield of aromatic hydrocarbons is reduced to 17.2%. Under these conditions, the yield of benzene varies from 30, 8 to 17.9%, toluene – from 40.5 to 47.4%, ethylbenzene - from 7.0 to 20.2%. The yield of xylene is in the range of 1.8 to 3.0%.

Table 8 - effect of volumetric feed rate on the process of processing propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-AI_2O_3

T, °C	150	300	470	675	825	1020
Conversion, %	100	100	100	65,7	90,4	52,4
The yield of liquid phase, %	52,8	34,5	20,4	21,2	20,5	17,2
Select. ArC, %	52,8	34,5	20,4	32,3	22,6	32,8
Liquid phase, %						
Benzene	30,8	24,1	20,0	24,4	21,4	17,9
Toluene	40,5	44,1	46,0	42,5	43,4	47,4
Ethylbenzene	7,0	12,3	15,1	12,1	16,5	20,2
Xylene	1,9	3,0	2,4	1,8	1,8	2,2
C_{5-6}	3,9	5,7	8,8	12,4	5,5	6,0
C_{8+}	15,9		7,7	6,8	11,4	

The developed modified zeolite-containing catalysts have high catalytic activity and selectivity in the process of processing the propane-propylene fraction into aromatic hydrocarbons. It was found that the highest yield of aromatic hydrocarbons is 52.8% (550°C, 150 h^{-1}) on the catalyst Zn-La-P-Cr-ZSM-AI_2O_3 with a conversion rate of 100.0%, selectivity for aromatic compounds-52.8%.

Physical and chemical characteristics of the developed catalysts were studied using various methods (EM, BET, TPD of ammonia). By the BET method it was established that the surface of the developed catalysts fluctuates within 211,0-274,0 m^2/g of cat. Catalysts are predominantly mesoporous: pores with d

≈ 2.0-3.0 nm predominate. The total pore volume of catalysts depends little on their composition and does not exceed 0.13-0.21 ml/g of catalyst. According to electron microscopy data, there are active centers on the surface of catalysts, which include metals - components of the active phase and Lewis and Bronsted acid centers, the presence of which is mainly due to the presence of zeolite ZSM in the catalysts. The active phase particles on the surface of the developed catalysts are highly dispersed. Metals of the active phase are predominantly in the oxidized state, forming clusters on the surface-associates, dispersion, structure and condition of which is determined by the nature of the catalyst components.

The composition of the products formed during the processing of propane-propylene fraction on the developed modified zeolite-containing catalysts indicates that the synthesized catalysts have multifunctional properties. On the developed modified zeolite-containing catalysts, several reactions occur simultaneously and in parallel: cracking, dehydrogenation, isomerization, dehydrocyclization, alkylation.

Б.Т. Туктин[1], А.М. Темирова[2], Ғ.Т. Сайділдә[1], А. А. Омарова[2]

[1] Д.В. Сокольскийатындағыжанармай, катализ және электрохимия институты,
050010, Алматы, Қазақстан, Қонаевк-сі 142;
[2] Әль-Фарабиатындағы Қазақ ұлттық университеті

ПРОПАН-ПРОПИЛЕН ФРАКЦИЯСЫНАН МОДИФИЦИРЛЕНГЕН ЦЕОЛИТТІ КАТАЛИЗАТОРЛАРДА АРОМАТТЫ КӨМІРСУТЕКТЕР АЛУ

Аннотация. Zn, La, Cr Zr, және P модифицирленген цеолиті бар катализаторларда пропан-пропилен фракциясын өңдеп ароматты көмірсутектер алу процесі зерттелді. Процесс ағынды қондырғыда атмосфералық қысымда 350 – 600°С температурада және шикізатты берудің көлемдік жылдамдығы 150-1020 сағ$^{-1}$-де жүргізілді. Катализаторлар алюминий гидроксидін және ZSM-5 цеолитін металдардың азот қышқылды тұздарының және фосфор қышқылының судағы ерітінділерін сіңіру әдісімен дайындалды. Катализаторлардың физика-химиялық сипаттамалары зерттелді.БЭТ әдісімен катализаторлардың беті 211,0-274,0 м^2/г мөлшерінде болатындығы анықталды. Катализаторлар негізінен мезокеуекті:басым кеуектер d ≈ 2,0-3,0 нм.

Дайындалған модифицирленген құрамында цеолиті бар катализаторлардың ароматты көмірсутектерге пропан-пропилен фракциясын өңдеу процесінде жоғары каталитикалық белсенділікке және селективтілікке ие екендігі көрсетілді. C_2-C_4 алкандарды өңдеу кезінде пайда болатын басым өнімдер толуол және бензол болып табылады. Модифицирленген цеолитті катализаторда Zn-La-ZSM-Al_2O_3пропан-пропилен фракциясын өңдеу кезінде ароматты көмірсутектер (АрК)және газ тәрізді өнімдер пайда болды.

Процесс температурасының 400-ден 650°С-қа дейінөскенде конверсия дәрежесі 1,4-тен 100,0%-ға дейін көтерілді. Бұл жағдайда ароматты көмірсутектердің шығымы 8,9-дан 29,2-28,9%-ға дейін өседі. АрК бойынша ең жоғары селективтілік 600°С-та байқалады және 29,2% құрайды. Түзілгенароматты көмірсутектердің сандық құрамы процестің температурасына байланысты. 400-650°С аралығында толуолдың шығымы экстремальды түрде өзгереді, 450°С-та ең жоғарғы мәнге жетеді және 46,9% құрайды. Температураның өсуімен бензолдың шығымы 4,1 (400°С) бастап 39,2% (650°С)дейін артады. Сұйық катализаттағы ксилолдың мөлшері - 1,6-7,2%. Этилбензол мен C_5-C_6көмірсутегінің шығымы температура 400-650°С аралығында өскенде тиісінше 24,8-ден 4,8%-ға дейін және 21,8-ден 4,6%-ға дейін төмендейді. Zn-La-P-ZSM-Al_2O_3 катализаторында пропан-пропилен фракциясын өңдеу процесі зерттелді. 2-кестеде ұсынылған деректерден температура 350-ден 600°С-қа дейін өсуімен конверсия 27,8-ден 98,9%-ға дейін артқанын көруге болады. Температураның 350-ден 550°С-қа дейін артуы кезінде ароматты көмірсутектердің шығымы 19,3-тен 38,1%-ға дейін өседі, бірақ жоғары температурада (600°С) АрК шығымының 27,1%-ға дейін төмендеуі байқалады. 350-600°С аралығында толуолдың шығымы 27,4-39,1%, ал бензолдың шығымы 0,5 - 23,0% құрайды. Сұйық катализаттағы ксилолдың мөлшері–1,6-4,3%-ке тең. Этилбензолдың шығымы температураның 400 - 600°С аралығында артқанда 22,9-ден 5,9%-ға дейін төмендейді. C_5-C_6 көмірсутектерінің шығымы 37,2-ден 17,0%-ға дейін 350- 550°С аралығында температураның өскенде төмендейді де, содан кейін 32,0% (600°С) дейін артады. АрК бойынша ең жоғары селективтілік 500°С кезінде байқалады және 54,0% құрайды. Жоғары температураларда АрК бойынша селективтілік біршама төмен–38,7-27,4%.Zn-La-Zr-ZSM-Al_2O_3 катализаторында пропан-пропилен фракциясын өңдеу процесінде температураның 350-ден 600°С-қадейінөсуімен конверсия 7,0-ден 100,0%-ға дейін көтеріледі. Температураның 350-ден 550°С-қа дейін артуы кезінде ароматты көмірсутектердің шығымы 4,6-дан 28,2%-ға дейін өседі, 600°С кезінде ароматты көмірсутектердің шығымының 23,2% - ға дейін төмендеуі байқалады. Температура жоғарылағанда мақсатты өнімдердің түзілу селективтілігі төмендейді: АрК бойынша ең жоғары селективтілік 350°С кезінде байқалады және 65,7%-ды құрайды.Жоғары температураларда АрК

бойынша селективтілік төмен. Сұйық катализатта толуол мен этилбензол басым. Толуолдың шығымы 14,4 - тен 43,9% - ға дейін 350- 550°С аралығындаөседі, 600°С-татолуолдың шығымы біршаматөмен - 40,9%. Этилбензолдың мөлшері монотонды түрде 24,0-ден 10,6% - ға дейін төмендейді. Бұл жағдайда бензолдың шығымы 1,7-ден 27,2% - ға дейін өседі.Ксилол мөлшері – 3,1-7,9% аралығында ауытқиды.

Ароматты көмірсутектердің ең жоғары шығымы Zn-La-P-Cr-ZSM-AI_2O_3катализаторында байқалып 52,8%-ға (550°С, 150 $сағ^{-1}$) тең болып конверсия дәрежесі 100%-ға жетеді. Модифицирленген цеолиті бар катализаторлар көп функционалды қасиеттергеие. Пропан пропилен фракциясын өңдеу өнімдерінің құрамы ароматты көмірсутектердің түзілуі крекинг, дегидрлеу, олигомеризациялау, дегидроциклдеу, алкилдеу реакцияларының жүруі нәтижесінде бір сатыда жүретінін көрсетеді.

Түйін сөздер: катализатор, цеолит, пропан-пропилен фракциясы, ароматты көмірсутектер

Б.Т. Туктин[1], А.М. Темирова[2], Г.Т. Сайдилда[2], А. А. Омарова[2]

[1]Институт топлива, катализа и электрохимии им. Д.В. Сокольского, 050010,
Алматы, Казахстан, ул. Кунаева 142;
[2]Казахский национальный университет им.аль-Фараби

ПРЕВРАЩЕНИЕ ПРОПАН - ПРОПИЛЕНОВОЙ ФРАКЦИИ В В АРОМАТИЧЕСКИЕ УГЛЕВОДОРОДЫ НА МОДИФИЦИРОВАННЫХ ЦЕОЛИТНЫХ КАТАЛИЗАТОРАХ

Аннотация. Исследован процесс превращения пропан-пропиленовой фракции в ароматические углеводороды на цеолитсодержащих катализаторах модифицированных Zn, La, Cr Zr, и P. Процесс проводили в установке в проточной установке при атмосферном давлении при варьировании температуры от 350 до 600^{0}С и объемной скорости подачи сырья 150-1020 $ч^{-1}$. Катализаторы готовили методом пропитки гидроксида алюминия и цеолита ZSM-5 водными растворами азотнокислых солей металлов и фосфорной кислоты. Изучены физико-химические характеристики разработанных катализаторов. Методом БЭТ установлено, что поверхность разработанных катализаторов колеблется в пределах 211,0-274,0 $м^2$/г к-ра. Катализаторы преимущественно мезопористые: преобладают поры с d ≈ 2,0-3,0нм.

Показано, что разработанные модифицированные цеолитсодержащие катализаторы обладают высокой каталитической активностью и селективностью в процессе переработки пропан-пропиленовой фракции в ароматические углеводороды. Преобладающими продуктами, образующимся при переработке C_2-C_4 алканов, являются толуол и бензол.

При переработке пропан-пропиленовой фракции на модифицированном цеолитном катализаторе Zn- La-ZSM-Al_2O_3 образуются ароматические углеводороды (АрУ) и газообразные продукты. В жидкой фазе обнаружены бензол, толуол, этилбензол, ксилолы и C_{8+}-углеводороды, а в газовой фазе содержатся C_1-C_4 углеводороды. С увеличением температуры процесса от 400 до 650°С степень конверсии повышается от 1,4 до 100,0%. Выход ароматических углеводородов в этих условиях растет от 8,9 до 29,2 -28,9%. Максимальная селективность по АрУ наблюдается при 600°С и составляет 29,2%. Количественный состав образующихся ароматических углеводородов существенно зависит от температуры процесса. Выход толуола в интервале 400- 650°С меняется экстремально, достигая максимального значения при 450°С, и составляет 46,9%. Выход бензола с ростом температуры возрастает от 4,1 (400°С) до 39,2% (650 °С). Содержание ксилола в жидком катализате - 1,6-7,2%. Выход этилбензола и C_5-C_6 углеводородов снижается с ростом температуры в интервале 400- 650°С от 24,8 до 4,8% и от 21,8 до 4,6 % соответственно

Исследован процесс переработки пропан-пропиленовой фракции на катализаторе Zn-La-P-ZSM-Al_2O_3 С ростом температуры от 350 до 600°С конверсия повышается с 27,8 до 98,9%. При увеличении температуры от 350 до 550 °С выход ароматических углеводородов растет от 19,3 до 38,1%, но при более высокой температуре (600 °С) наблюдается снижение выхода АрУ до 27,1%. В интервале 350 - 600^{0}С выход толуола составляет 27,4-39,1%, а бензола - 0,5 - 23,0%. Содержание ксилола в жидком катализате - 1,6-4,3%. Выход этилбензола снижается с ростом температуры в интервале 400- 600°С от 22,9 до 5,9%. Выход C_5-C_6 углеводородов снижается с ростом температуры в интервале 350- 550°С от 37,2 до 17,0%, затем увеличивается до 32,0 (600 °С). Максимальная селективность по АрУ наблюдается при 500°С и составляет 54,0%. При более высоких температурах селективность по АрУ несколько ниже – 38,7-27,4%.

В процессе переработки пропан-пропиленовой фракции на катализаторе Zn-La- Zr -ZSM-Al_2O_3 с увеличением температуры от 350 до 600°С конверсия повышается с 7,0 до 100,0%. При повышении температуры от 350 до 550°С выход ароматических углеводородов растет от 4,6 до 28,8%, при 600°С наблюдается снижение выхода ароматических углеводородов до 23, 2%. Установлено, что наибольший выход ароматических углеводородов составляет 52,8% (550°С, 150 $ч^{-1}$) на катализаторе Zn-La-P-Cr-ZSM-AI_2O_3 при степени конверсии 100,0%. Модифицированные цеолитсодержащие катализаторы обладают

полифункциональными свойствами. Состав продуктов переработки пропан-пропиленовой фракции показывает, что образование ароматических углеводородов происходит в одну стадию в результате протекания реакций крекинга, дегидрирования, олигомеризации, дегидроциклизации, алкилирования

Ключевые слова: цеолитсодержащие катализаторы пропан-пропиленовая фракция ароматические углеводороды.

Information about the authors:

Tuktin Balga Tuktiyevich – Head of the sector of motor fuels, Doctor of Chemical Sciences, JSC "D.V.Sokolskiy Institute of Fuel, Catalysis and Electrochemistry", e-mail: tuktin_balga@mail.ru, w.tel. 8-727-2916826, tel. 8(702)641-35-97, https://orcid.org/0000-0003-3670-4010;

Temirova Aiman Maksatovna - PhD of petrochemistry, "al-Farabi Kazakh National University", e-mail: aika179@mail.ru, tel. 8-701-392-9090, https://orcid.org/0000-0002-7357-8204;

Omarova Aizhan Auelkhanovna - Senior lecturer, PhD (chemistry) al-Fababi Kazakh National University, e-mail: aika_03_79@mail.ru, tel: 87762387210, https://orcid.org/0000-0001-7167-3526;

Saidilda Galymzhan Talgatuly - Lead Engineer of the Motor Fuel Sector, JSC "D.V.Sokolskiy Institute of Fuel, Catalysis and Electrochemistry", e-mail: galym711@mail.ru, w.tel. 8-727-2916826, tel. 8(775)126-42-14, https://orcid.org/0000-0001-7468-7421.

REFERENCES

[1] Dergachev A.A., Lapidus A.L. Kataliticheskaya aromatizatsiya nizshikh alkanov [Zhurnal Ross. khim. obshchestva im.D.I.Mendeleyeva] 2005. LII 4:15-21. (In Russian).

[2] Akhmetov A.F., Karatun O.N. Modifitsirovannyye pentasilsoderzhashchiye katalizatory dlya aromatizatsii uglevodorodnykh gazov [Khimiya i tekhnologiya topliv i masel] 2001, 5:33-36. (In Russian)

[3] Lapidus A.L., Kozlov A.M., Khudyakov D.S., Dergachev A.A. Aromatizatsiya propan-butanovoy fraktsii na modifitsirovannom pentasile [Gazokhimiya] 2010, 6: 16-18. (In Russian).

[4] Lapidus A.L., Dergachev A.A., Kostina V.A., Silakova A.A. Aromatizatsiya etana na galliyplatinovykh tseolitakh semeystva pentasila [Neftekhimiya] 2008, 48: 2:83-86. (In Russian).

[5] Khasanova E.I., Nazmiyeva I.F., Ziyatdinov A.SH., Salakhov I.I., Kopylov A.YU. Izucheniye protsessa aromatizatsii propana na tseolitsoderzhashchem katalizatore s razlichnym otnosheniyem Si/Al7 [Neftekhimiya] 2012, 2:97-103. (In Russian).

[6] Rasulov S.R., Mustafayeva G.R., Makhmudova L.A. Perspektivnyye katalizatory aromatizatsii propana [Neftekhimiya] 2012, 1:36-41. (In Russian).

[7] Dedov A.G., Moiseyev I.I., Loktev A.S., Kuznetsov N.T., Ketsko V.A., Parkhomenko K.V., Kartashev I.YU. Kataliticheskiy sintez bazovykh neftekhimicheskikh produktov na osnove alkanov S1-S4 [Khimiya i tekhnologiya topliv i masel] 2005, 2:35-40. (In Russian).

[8] Shiryazdanov R.R., Rakhimov M.N., Mansurov I.S. Osnovnyye problemy, osobennosti i perspektivy pererabotki neftezavodskikh gazov [Neftekhimiya] 2010, 1: 32-35. (In Russian).

[9] Mustafayeva G.R., Salimova N.A., Rasulov S.R. Tekhnologiya pererabotki gazov kataliticheskogo krekinga [Neftepererabotka i neftekhimiya] 2012, 5: 36-38. (In Russian).

[10] Fal'kevich G.S., Rostanin N.N, Vilenskiy L.M., Inyayeva G.V., Nemira K.B., Nefedov B.K. Novyye tekhnologii «SAPRneftekhim» pererabotki uglevodorodnogo syr'ya s ispol'zovaniyem tseolitsoderzhashchikh katalizatorov. Soobshcheniye 1. Pererabotka poputnykh neftyanykh gazov, shirokikh fraktsiy legkikh uglevodorodov i otkhodyashchikh neftezavodskikh parafinsoderzhashchikh gazov v aromaticheskiye uglevodorody [Kataliz v promyshlennosti] 2002, 2:44-50. (In Russian).

[11] Lu H., You H. Aromatization reaction of liquefied petroleum gas [Petrol. Sci. and Technol] 2010, 28, 8: 816-825. (In Eng).

[12] Meged' A.A., Adzhiyev A.YU., Korsakov S.N., Sevost'yanova S.F. Aromatizatsiya nizshikh parafinov v protsesse arkon [Neft', gaz i biznes] 2003, 3:55-57. (In Russian).

[13] Yechevskiy G. Polucheniye aromaticheskikh uglevodorodov iz PNG i drugikh legkikh fraktsiy. [Neftegaz. tekhnol] 2012, 4: 92-96. (In Russian).

[14] Minachov KH.M., Dergachev A.A. Mekhanizm aromatizatsii nizshikh parafinov na pentasilakh [Uspekhi khimii]. 1990, 9:1522-1549. (In Russian).

[15] Terent'yev A.I., Yurkin N.A., Khlytin A.L. Katalizatory na osnove elementoalyumosilikatov tseolitnoy struktury dlya neftepererabatyvayushchey promyshlennosti [Khim. tekhn]. 2012, 1: 34-37. (In Russian).

[16] Viswandham N., Saxena S.k., Kumar M. The transformation of light paraffins to LPG and aromatics over a Ni/ZSM-5 catalyst [Petrol. Sci. and Technol]. 2011, 29, 4: 393-400. (In Eng).

[17] Tuktin B., Zakumbayeva G.D., Smagulov R., Toktabayeva N.F. Kataliticheskoye prevrashcheniye szhizhennogo neftyanogo gaza v aromaticheskiye uglevodorody [Neftepererabotka i neftekhimiya]. 2008, 6:35-37(In Russian).

[18] Ctepanov V.G.,Litvinenko N.G.,Ione K.G. Prevrashcheniye alkanov S2-S4 na modifitsirovannom tsinkom tseolitakh tipa pentasila [Neftekhimiya]. 1992, 10:14-22. (In Russian).

[19] Akhmetov A.F., Belousova O.YU., Kurmayev S.A. Vliyaniye soderzhaniya promotora na kislotnyye svoystva pentasilsoderzhashchikh katalizatorov v prevrashchenii uglevodorodov S3-S4 [Bashkirskiy khimicheskiy zhurnal]. 2007, 14, 5: 101. (In Russian).

[20] Akhmetov A.F., Karatun O.N., Stabil'nost' pentasilsoderzhashchikh katalizatorov pri aromatizatsii butanovoy fraktsii [Khimiya i tekhnologiya topliv i masel]. 2002, 2:32-33. (In Russian).

[21] Vosmerikov A.V. Yermakov A.Ye., Vosmerikova L.N., Fedushchak T.A., Ivanov G.V. Prevrashcheniye nizshikh alkanov v prisutstvii nanochastits metallov, nanesennykh na tseolitnuyu matritsu [Kinetika i kataliz]. 2004, 45, 2: 232-236 (In Russian).