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CATALYTIC TECHNOLOGIES FOR INCREASING QUALITY OF MOTOR FUELS

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The aim of the work was to study the process of hydrodearomatization and alkylation of gasoline fractions under increased hydrogen pressure. It has been used Rh-Pt (9:1)/Al_2O_3 catalyst in the work. It has been studied the hydrogenation of three gasoline fractions of «Atyrau Oil Refinery» LLP and Pavlodar Petrochemical Plant LLP. Technological parameters of the process of hydrodearomatization for the production of environmentally friendly fuels, containing no benzene and low in aromatic hydrocarbons have been worked out (pressure, temperature). Data on group composition of organic substances in gasolines demonstrate that after catalytic hydrogenation benzene in final samples of two fractions is absent. For hydrogenizate, the aromatic content decreased from 11.12 weight % to 2.20 weight %. For stable catalysate, the amount of aromatics decreased from 51.5 weight % to 10.96 weight %. Catalytic systems based on zeolites ZSM5 and Y modified with Mg, La, and Ce were tested during the alkylation of 2 gasoline fractions of Atyrau Oil Refinery LLP. It was established that benzene fractions was removed by 30–37% from gasoline and the content of aromatic hydrocarbons, toluene and cumene decreased by 6–10%.The catalysts were studied by BET, porometry and EM methods, which established a uniform formation of nanoscale particles on the catalyst surface.

KEY WORDS: *catalysts, hydrogenation, hydrodearomatization, alkylation, aromatic hydrocarbons, benzene, gasoline.*

КАТАЛИТИЧЕСКИЕ ТЕХНОЛОГИИ ПОВЫШЕНИЯ КАЧЕСТВА МОТОРНЫХ ТОПЛИВ

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Целью работы являлось изучение процессов гидродеароматизации и алкилирования бензиновых фракций. В работе использовался Rh-Pt(9:1)/Al_2O_3 катализатор. Изучено гидрирование и алкилирование трех бензиновых фракций ТОО «Атырауский нефтеперерабатывающий завод» и ТОО «Павлодарский нефтехимический завод». Отработаны технологические параметры процесса гидродеароматизации и алкилирования для производства экологически чистых топлив, не содержащих бензол и с низким содержанием ароматических углеводородов (давление, температура). Данные по групповому составу органических веществ в бензинах свидетельствуют о том, что после каталитического гидрирования бензол в конечных пробах двух фракций отсутствует. Для гидрогенизата содержание ароматических углеводородов снизилось с 11,12 мас.% до 2,20 мас.%. Для стабильного катализата количество ароматических углеводородов уменьшилось с 51,5 мас.% до 10,96 мас.%. Каталитические системы на основе цеолитов ZSM5 и Y, модифицированных Mg, La и Ce испытаны в процессе алкилирования 2 бензиновых фракций АНПЗ. Установлено, что бензол из бензиновых фракций был удален на 30–37%, а содержание ароматических углеводородов, толуола и кумола снизилось на 6–10%. Катализаторы исследованы методами БЭТ, порометрии и ЭМ, которые установили равномерное образование на поверхности катализаторов наноразмерных частиц.

КЛЮЧЕВЫЕ СЛОВА: *катализаторы, гидрирование, гидродеароматизация, алкилирование, ароматические углеводороды, бензол, бензин.*

МОТОР ОТЫНДАРЫНЫҢ САПАСЫН АРТТЫРУҒА АРНАЛҒАН КАТАЛИТИКАЛЫҚ ТЕХНОЛОГИЯЛАР

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Жұмыстың мақсаты – бензин фракцияларын сутектендіру және алкилдеу процесінде сутегінің жоғары қысымында зерттеу. Жұмыс барысында Rh-Pt(9:1)/Al_2O_3 катализаторы қолданылды. ЖШС «Атырау мұнай өңдеу зауытының» және «Павлодар мұнайхимия зауытының» ЖШС бензин фракцияларын сутектендіру процесі зерттелінді. Құрамында бензол жоқ және төмен мөлшердегі хош иісті көмірсутектері бар экологиялық таза жанармайлар өндіру үшін гидродеароматизация процесінің технологиялық параметрлері жасалынды (қысым, температура). Жанармайдағы органикалық қосылыстардың топтық құрамының көрсеткіштері бойынша каталитикалық сутектендіру процесінен соң бензол компоненті екі бензин фракцияларының құрамынан толығымен жойылды. Гидрогенизат фракциясы бойынша хош иісті көмірсутектер мөлшері 11,12 мас.%-дан 2,20 мас.%-ға дейін төмендеді. Тұрақты катализат фракциясы бойынша хош иісті көмірсутектер мөлшері 51,5 мас. %-дан 10,96 мас. %-ға дейін төмендеді. Mg, La және Ce-мен модификацияланған ZSM5 және Y цеолиттеріне негізделген каталитикалық жүйелер ЖШС «Атырау мұнай өңдеу зауытының» 2 бензин фракциясын алкилдеу кезінде сыналды. Бензин фракцияларынан бензол 30–37% -ға дейін төмендеді, ал хош иісті көмірсутектер, толуол және кумол 6–10%-ға дейін төмендегені анықталды. Катализаторлар БЭТ әдісі, порометрия және электрондық микроскопта зерттелінді.

НЕГІЗГІ СӨЗДЕР*: катализаторлар, сутектендіру, гидродеароматизация, алкилдеу, хош иісті көмірсутектер, бензол, бензин.*

Technical progress in various fields of engineering, operating machinery and the laws on the protection of the biosphere are tightening requirements for the quality of fuels and oils. Continuously deteriorating environmental conditions in the world dictate the need of exploitation of environmentally friendly and high-quality fuel [1]. The quality of fuels largely depends on the hydrocarbon composition. Aromatic hydrocarbons in fuels are represented by monoaromatic compounds: benzene, toluene, xylene isomers and polyaromatic ones – naphthalene, tetraline and other condensed aromatic compounds.

The sources of benzene in automotive gasoline at the modern refinery are the following components: catalytic reforming gasoline – 78.2%; catalytic cracking gasoline residue – 10.2%; light hydrocracking gasoline – 10.9%; coking gasoline – 0.7%. At reforming plants 58% aromatics are formed and the benzene content can exceed 3%.

However, these compounds are the most toxic of all hydrocarbon groups; they form toxic substances at combustion. Particularly dangerous is benzene, which forms benzopyrene during combustion, which, according to its degree of toxicity, belongs to the first hazard class with a maximum permissible concentration of 0.000001 mg/m^3 and it is a strong carcinogen. When 1 liter of gasoline is burned, benzpyrene is formed up to 81 μg in the exhaust gases, and up to 170 μg in case of liter of diesel fuel. According to gasoline standards EURO-6 the content of benzene must be less than 0.1%, and aromatic hydrocarbons is 11%.

Benzene reduction in reforming products is possible by the following methods [2–4]:

– hydrogenation of benzene with the formation of cyclohexane, leading to some decrease in the octane number of the component;

– extraction of pure benzene, cost-effective only with its further effective use;

– alkylation with low molecular weight olefins, which allows not only to solve the problem of benzene removal, but also to increase the yield of the target high-octane component;

– hydroisomerization of benzene to cyclohexane followed by isomerization to methylcyclopentane with a slight increase in the octane number and yield of the target component;

– transalkylation of benzene and aromatic hydrocarbons C9 +, leading to a decrease in the yield of the target product;

– fractionation of the reformate to obtain a set of fractions, then mixed in various proportions to achieve the desired result,

– reforming + hydroisomerization of benzene – hydrogenation of benzene to cyclohexane followed by isomerization to methylcyclopentane (RIGIZ).

The authors of RIGIZ [1] explain the benefits of hydroisomerization of cyclohexane to methylcyclopentane with a higher octane number of the latter 92, while cyclohexane has 88 units.

The most effective methods for improving the operational properties of fuels, in our opinion, are their hydrodearomatization and alkylation in the presence of effective catalysts. Catalytic hydrogenation and alkylation of aromatic hydrocarbons allows to change the chemical structure of hydrocarbons in the right direction and to improve the operational characteristics of motor fuels [5–9].

In industry, for the hydrogenation processes, both catalysts based on metals of group VIII and sulfide are used, but in the latter, the hydrogenation of benzene and aromatic hydrocarbons is carried out under more severe conditions. For industrial alkylation processes, catalysts based on different zeolites are used.

The aim of this work is to study the catalytic hydrodearomatization and alkylation of three gasoline fractions of Atyrau Oil Refinery LLP and Pavlodar Petrochemical Plant LLP in order to reduce the content of benzene and aromatic hydrocarbons on supported catalysts based on group VIII metals and alkylation on zeolite-containing catalysts.

The tests of the catalysts in the process of hydrodearomatization and alkylation were carried out on an autoclave of Amar Equipment Ltd and Finetech 4000, intended for hydrogenation processes with heating and under hydrogen pressure above atmospheric. Analysis of the reaction products was carried out on a Crystallux-4000M chromatograph: Zebron ZB-1 column filled with dimethylsiloxane, column length 30 mm, column diameter

0.53 mm. The hydrodearomatization products of gasoline fractions were also studied by IR spectroscopy.

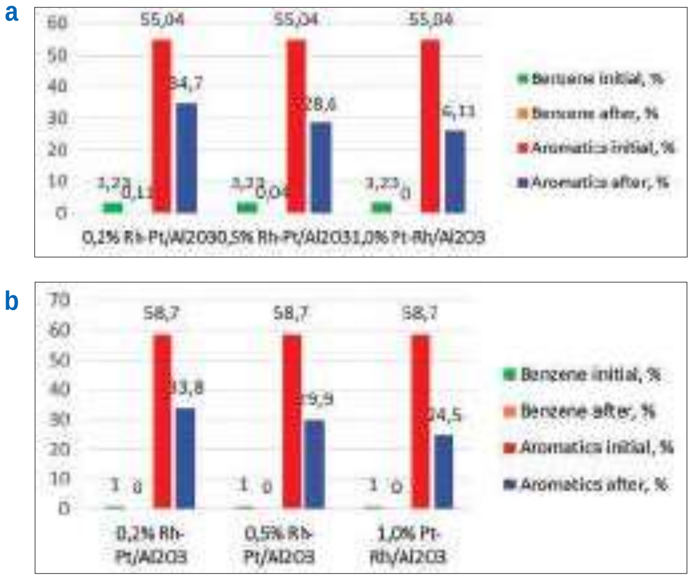
The process of hydrodearomatization of two gasoline fractions was studied: Stable catalysate AOR (Atyrau Oil Refinery LLP)and Stable catalysate PPP (Pavlodar Petrochemical Plant LLP) on the prepared Rh-Pt/Al_2O_3 catalysts. The content of benzene and aromatic hydrocarbons in different gasoline fractions is given in *table 1*. The aromatics content is high, because these fractions after reforming.

Table 1 – **Content of benzene and aromatic hydrocarbons in the gasoline fractions of AR LLP and POCR LLP**

Name of fraction	Content of benzene, mass%	Content of aromatics, mass%
Stable catalysate AOR	3.23	55.04
Stable catalysate PPP	1.0	58.68

The catalyst used was Rh-Pt(9:1)/Al_2O_3, which was most effective in the hydrogenation of individual benzene and toluene [10]. The effect of temperature and pressure of hydrogen on the process of hydrogenation of benzene and aromatic hydrocarbons for two gasoline fractions was studied.

The effect of the content of the active catalytic phase on the composition of the components of 2 gasoline fractions was studied during hydrodearomatization on 0.2% Rh-Pt/Al_2O_3, 0.5% Rh-Pt/Al_2O_3 and 1.0% Pt-Rh/Al_2O_3 catalysts at 50°C and 0.4 MPa *(Fig. 1)*. With an increase in the content of the active phase, the conversion of aromatic hydrocarbons increases, their content decreases from 55.04 to 34.7% for the catalyst 0.2% Rh-Pt/Al_2O_3, up to 28.60% for the catalyst 0.5% Rh-Pt/Al_2O_3 and up to 26.11% for the



a – Stable catalysate of AOR, b – Stable catalysate of PPP

Figure 1 – **Hydrogenation of gasoline fractions on catalysts 0.2%, 0.5% and 1.0% Rh/Al_2O_3 at 50°C and 0.4 MPa**

catalyst 1.0% Pt-Rh/Al_2O_3. On all three catalysts, benzene is completely removed from the two fractions.

It has been studied the influence of technological parameters of the process of hydrodearomatization of gasoline fractions (pressure 1–5 MPa, temperature 50–200°C) on the content of benzene and aromatic hydrocarbons. At temperatures of 50–200°C and hydrogen pressures of 2–5 MPa, benzene is completely removed from 3 fractions, and the amount of aromatic hydrocarbons is reduced to 1.5–2 times *(table 2)*. During gasoline hydrogenation of Stable catalysate AOR, the content of aromatic hydrocarbons at 50–200°C decreased from 55.04% to 20.21%, and with increasing pressure from 1.0 to 5.0 MPa it decreased from 55.04 to 22.91%. At gasoline hydrogenation of Stable catalysate PPP in the temperature range of 25–200°C the aromatics content reduced from 58.68% to 24.89%, and when the pressure changed from 1.0 to 5.0 MPa, it decreased from 58.68% to 26.55%.

Table 2 – **Hydrodearomatization of fractions of Stable catalysate AOR and Stable catalysate PPP on 0.5% Pt-Rh/γ-Al_2O_3**

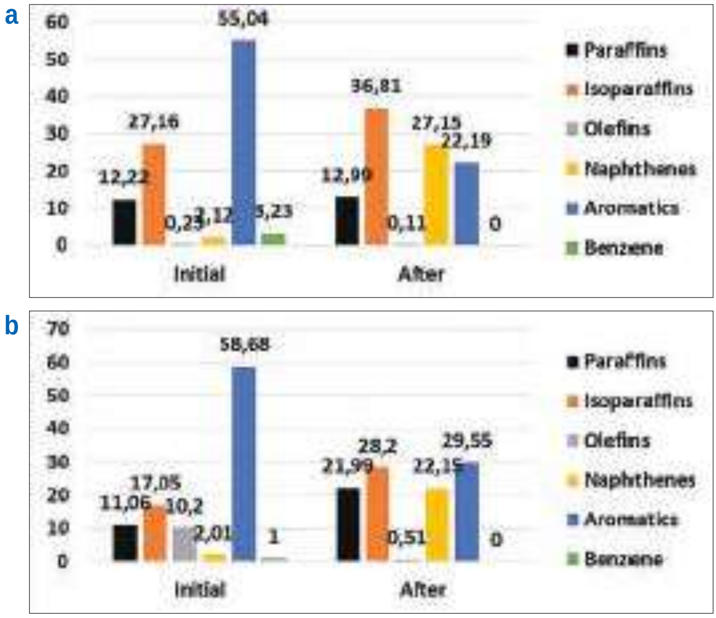
Conditions		Benzene, % mas.		Aromatics, % mas.	
		Initial, %	After experiment, %	Initial, %	After experiment, %
Stable catalysate AOR					
P, MPa at 50°C	1,0	3,23	0,11	55,04	41,11
	2,0		0,04		37,62
	3,0		0,01		34,55
	4,0		-		28,56
	5,0		-		22,91
T, °C at 4 MPa	25	3,23	-	55,04	35,69
	50		-		28,56
	100		-		25,87
	150		-		23,54
	200		-		20,21
Stable catalysate PPP					
P, MPa at 50°C	1,0	1,0	0,62	58,68	50,77
	2,0		0,05		47,21
	3,0		0,01		32,95
	4,0		-		29,98
	5,0		-		26,55
T, °C at 4 MPa	25	1,0	-	58,68	35,83
	50		-		29,98
	100		-		28,34
	150		-		25,98
	200		-		24,89

In addition to chromatographic analysis, we analyzed the change in the composition of the catalysate before and after hydrodearomatization by IR spectroscopy. *Table 3* shows the absorption bands in the IR spectrum of two gasoline fractions. Absorption bands related to the C = C bonds of the benzene ring (3014–3017 cm^{-1} and 1378, 1342 cm^{-1}) are absent after the reaction, which once again proves the complete removal of benzene and a significant reduction in aromatics.

Table 3 – **IR spectra of gasoline fractions PPP and AOR (cm^{-1})**

Gasoline PPP		Gasoline AOR		Attributions
initial	**after experiment**	**initial**	**after experiment**	
			3088	Valent fluctuations CH at double bond of benzene ring =CH–
	3020		3030	
3017		3014		
0,5	0,5	0,2		
1609	1613	1606	1606	Valent fluctuations of bond –C=C– benzene ring.
0,15	0,3	0,3	0,1	
1506	1505 1455	1516 1497	1506 1458	
1455	1378 1304	1465	1378 1345	
1378 1342	-	1378 1342	-	

In *figure 2* there are shown data on the group composition of organic substances in two gasolines of the initial fractions and after hydrogenation on Rh-Pt (90:10)/Al_2O_3 at 3 MPa and 50°C. For the Stable catalysate AOR, the benzene content in the initial state was 3.23 wt.%, after the reaction, benzene is absent, i.e. 100% benzene conversion. The amount of aromatics decreased from 55.04 wt.% to 22.19 wt.%. It should be noted that the number of olefins decreased almost 2 times from 0.23% to 0.11 wt.%, which is very favorable for gasolines, since the presence of olefins leads to instability (in the chemical expression, the oligomerization and polymerization reaction proceeds). The amount of paraffins slightly increased from 12.22 wt.% to 12.99 wt.%. And the content of isoparaffins increased from 27.16 wt.% to 36.81 wt.%. Apparently, the isomerization of paraffins to isoparaffins occurred. The content of naphthenes increased sharply from 2.12 wt.% to



a – Stable catalysate of AOR, b – Stable catalysate of PPP

Figure 2 – **Group composition of gasoline fractions on Pt-Rh/Al_2O_3**

27.15 wt.%. The picture is similar for the Stable catalysate PPP: benzene is absent, aromatics decreased from 58.68 to 29.55%, olefins from 10.2 to 0.51%, isoparaffins increased from 17.05 to 28.2%. It should be noted that an increase in the content of paraffins of the isostructure indicates not only the hydrogenation reaction, but also hydroisomerization.

Data on the octane number and the density of the initial gasoline fractions before and after the catalytic treatment are given in table 4 (LLP "Independent Center for the Examination of Petroleum Products ORGANIC"). According to the research method, the octane number after treatment of the Stable catalysate AOR has not changed and is equal to 94 units.And the octane number according to the motor method increased from 82.6 to 82.7, i.e. in this case also, the octane number has not changed. For Stable catalysate of PPP, the octane number decreased from 90 to 89.9. This indicates that the processing of gasolines practically does not affect the octane number. The density slightly increased after treatment, which is understandable from the point of view of changing the hydrocarbon composition to a heavier region – naphthenes have a higher density compared to aromatic hydrocarbons.

Table 4 – **Characteristics of gasoline fractions of Stable catalysate of AOR and Stable catalysate of PPP before and after catalytic treatment**

Gasoline	Octane number RM	Octane number MM	Density, g/cm3
Stable catalysate AOR			
Initial	94,0	82,6	0,771
After experiment	94,0	82,7	0,780
Stable catalysate PPP			
Initial	90,0	Not measured	0,793
After experiment	89,9	Not measured	0,798

In transmission electron microscopy image *(Fig. 3)*, the Rh-Pt(9:1)/Al_2O_3catalyst is represented by fine particles with a size of 2–2.5nm and a small number of denser and larger particles of 5 nm, the microdiffraction patterns of which are represented by diffuse rings corresponding to metals. Metal particles are distributed on the surface of alumina and are mixed bimetallic agglomerates Rh-Pt together with Rh particles. The high activity of the catalyst is possibly due to the formation of alloys of these metals.

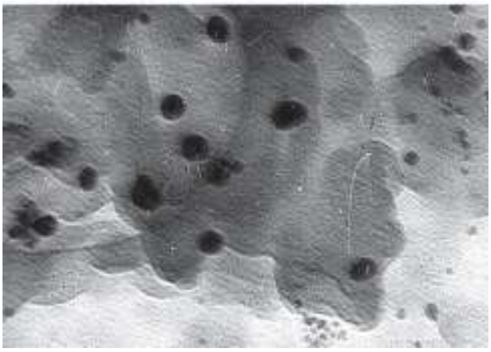


Figure 3 – **EM image of 2% Rh-Pt (9: 1) / Al2O3 (magnification 160,000)**

Alkylation is one of the most important petrochemical processes of hydrocarbon processing, allowing to produce high-octane components of gasoline, intermediate products for synthesis of many important chemical products, in particular monomers for production of polymers and plastics. In Western countries, the specific weight of the alkylation process in the entire oil refining industry is 16–20%, in Russia – 0.1%, in Kazakhstan there is no such process at all, even scientific research in this area has not been carried out.It has been selected the catalytic systems based on zeolites ZSM5 and Y modified with Mg, La, and Ce for alkylation of benzene [11]. The catalysts were tested in the alkylation process of 2 gas oline fractions of refinery. It was found that benzene from gasoline fractions was removed to 30–37%, and the content of aromatic, toluene and cumene decreased to 6–10%.

On the most active catalysts modified with magnesium and lanthanum, alkylation of two gasoline fractions of Atyrau Oil Refinery LLP was carried out – Hydrogenated gasoline and Stable catalysate. The data on the content of benzene, toluene, and cumene in the gasolines of the initial fractions and after alkylation with 5% Mg-HY (80) are shown in the *table 5*.

Table 5 – **Composition of the gasoline fraction of the initial and after treatment with 5% Mg-HY (80) catalyst at 200°C**

Name of sample	Content of defined indicator, mass.%			
	Aromatics	Benzene	Toluene	Cumene
Hydrogenated gasoline (initial)	13,70	2,22	5,66	3,44
After treatment	12,26	1,41	0,12	0,2
Stable catalysate (initial)	51,50	4,53	9,89	5,67
After treatment	48,96	3,15	0,78	0,48

In the initial hydrogenated gasoline there was 2.22% benzene, after catalytic treatment 1.41% benzene was found in the catalyzate – i.e. its conversion was 37.5%.The aromatic content of the initial gasoline was 13.70% and then became 12.26%.The amount of aromatics decreased to 10.6%. In the stable catalysate there was 4.53% benzene, and it became 3.15%, the conversion of benzene was 30.5%. The amount of aromatics was 51.5%, and after processing 48.59% – it decreased to 5.6%.

Thus, studies have been carried out on the alkylation of benzene as a model compound and contained in the gasoline fractions of Atyrau Oil Refinery LLP on zeolites HZSM-5, HY and β modified with magnesium and lanthanum. It is shown that as a result of the reaction, benzene was removed from gasolines to 30–37%, and the content of aromatics, toluene and cumene decreased to 6–10%.

Comparing two methods of reducing the content of aromatic hydrocarbons in fuels, we can conclude that hydrogenation is much more efficient:

– removes benzene up to 100%, while during alkylation, the benzene content decreases only to 30–37%;

– reduces the aromatic content to 41–48%, and alkylation reduces only up to 6–10%;

– conducts the process at low temperatures, i.e. this technology is energy saving.

The advantage of this work is the fact that, in addition to the hydrogenation of benzene and olefins, the process of hydroisomerization of normal alkanes and isostructural alkanes with increased octane numbers proceeds on the catalyst. Catalysts have a dual function: redox catalysis (hydrogenation) and acid-base catalysis (isomerization), which proceeds on a part of the surface represented by a zeolite with pronounced acid centers and alumina.

CONCLUSIONS

1. On highly effective catalysts Pt-Rh/γ-Al_2O_3 for the hydrogenation of gasolines, allowing to remove completely benzene and as well as reduce the content of aromatic compounds till 2–4 times. The catalyst was tested in the hydrogenation of 2 gasoline fractions – Stable catalysate Atyrau Oil Refinery LLP and Stable catalysate Pavlodar Petrochemical Plant LLP. By the method of studying the influence of temperature and pressure of hydrogen for two gasoline fractions, optimal parameters (temperature 50°C and pressure 3 MPa) were selected for the production of environmentally friendly fuels that do not contain benzene and with a low content of aromatic hydrocarbons.

2. During the hydrodearomatization of gasoline fractions, the Stable catalysate of Atyrau Oil Refinery LLP and the Stable Catalysis of Pavlodar Petrochemical Plant LLP, it is found that bimetallic Pt-Rh catalysts on γ-Al_2O_3 showed the best activity. The conversion of benzene is 100%, i.e. benzene is completely removed from gasoline fractions.

3. The group composition after catalytic treatment showed that the content of aromatic hydrocarbons is reduced almost 2 times. In addition, the content of paraffins decreases, and iso-paraffins increases, which indicates that the synthesized catalysts, in addition to hydrogenation, carry out the process of hydroisomerization of normal paraffins into branched iso-paraffins. The octane number of gasoline fractions has not changed significantly.

4. On zeolite catalysts modified with magnesium and lanthanum, alkylation of two gasoline fractions of Atyrau Oil Refinery LLP – hydrogenated gasoline and Stable catalysate were carried out. It is shown that as a result of the reaction, benzene was removed from gasolines to 30–37%, and the content of aromatics, toluene and cumene decreased to 6–10%.

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