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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**BIMETALLIC ZEOLITE CATALYSTS:  
SYNTHESIS, PROPERTIES AND CATALYTIC ACTIVITY IN  
THE CONVERSION OF STRAIGHT-RUN GASOLINE**

Speciality: 2307.01 – Physical Chemistry

Field of science: Chemistry

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**Baku – 2023**

Dissertasiya işi Naxçıvan Dövlət Universitetinin «Kimya» kafedrasında yerinə yetirilmişdir.

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## GENERAL CHARACTERISTICS OF WORK

**Relevance of the topic.** Over recent years, there has been a growing demand for the production of high-octane gasolines with improved environmental properties that meet the Euro-5 standards required for motor fuels. For the transition to the production of this class of gasoline, the share of reforming gasoline has been limited in order to ensure that the amount of aromatic hydrocarbons meets the norm. In "Euro-4" and "Euro-5" class fuels, aromatic hydrocarbons are limited to 35.0 vol.% (benzene 1.0 vol.%), and olefinic hydrocarbons are limited to 14.0 vol. %. To overcome these limitations, the development of isomerization, esterification and alkylation processes and the development of new more effective catalysts are priority directions.

Currently, in our Republic, catalytic cracking, reforming and alkylation processes are applied to produce high-octane components. Motor fuels produced based on these processes do not meet "Euro-4" and "Euro-5" standards in terms of quality. Since the main composition of these fuels consists of reforming gasoline, the amount of aromatic hydrocarbons in its composition is more than 40%, and the amount of benzene is more than 2.0%.

The traditional catalytic reforming process is carried out at a high temperature (500-525°C) in a hydrogen-containing gas environment in the presence of a rhenium-promoted aluminoplatinum catalyst. However, these catalysts have a number of disadvantages: the use of valuable components, low thermal stability, and the need for complex regeneration, high pressure and high-energy consumption. All this necessitates the development of highly efficient catalysts without noble metals in order to carry out the reforming process in fundamentally new conditions without the presence of hydrogen gas. All this necessitates the development of highly efficient catalysts without noble metals in order to carry out the reforming process in fundamentally new conditions without the presence of hydrogen gas. Isomerizates are ideal components of gasolines, and they practically do not contain sulfur, olefins and aromatic hydrocarbons. On the other hand, isomerizates increase the octane number of light gasoline

fractions boiling up to 100°C. The isomerization process is considered a priority direction in solving the problem of improving the quality of modern automobile gasoline.

Although Pt/Al<sub>2</sub>O<sub>3</sub>-Cl type catalysts used in industry have high activity, they do not meet environmental requirements. During their operation, chlorinating agents are constantly required; the equipment corrodes and produces large amounts of acidic waste. These catalysts are very sensitive to nitrogen and sulfur compounds contained in the raw materials, they require purification of the raw materials before the process and they are not regenerated.

Currently, Pt-zeolite catalysts based on chlorinated Pt/Al<sub>2</sub>O<sub>3</sub> and mordenite are used in the isomerization of pentane-hexane fractions in industry.

The activity of Pt-catalysts based on mordenite (Pt-Mor) zeolite is lower than chlorinated Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. However, the advantage of Pt-Mor catalysts compared to Pt/Al<sub>2</sub>O<sub>3</sub>-Cl catalysts is their resistance to additives in raw materials and simple regeneration. Zeolite catalysts are viewed more prospectively due to their high operating qualities.

However, medium-porous mordenite-based catalysts show higher isomerization activity in the isomerization of n-pentane and C<sub>5</sub>-C<sub>6</sub> gasoline fractions with a higher content of n-pentane. When they are used in the isomerization of gasoline fractions rich in n-C<sub>6</sub>-C<sub>8</sub> hydrocarbons, high-octane branched isoparaffins are not obtained, and the hydrocarbons are mainly subjected to hydrocracking.

The analysis of literature data shows that the development of bifunctional catalysts based on high-silica ZSM-5 zeolite in the enrichment of gasoline fractions with straight-run distillation under hydrogen-free conditions, which is an alternative to the reforming process, is a more promising direction.

On the other hand, in order to increase the amount of isostructured C<sub>6</sub>-C<sub>8</sub> hydrocarbons in gasoline, - 70°C and 85°C gasoline requires the development of catalysts based on zeolite with different porous structure (Y, ZSM) for the process of isomerization of fractions.

The above-mentioned advantages are the enrichment of gasoline

fractions by straight distillation at low temperature and atmospheric pressure, the development of catalysts based on Y and ZSM-5 zeolites for the isomerization of narrow gasoline fractions in a hydrogen-free environment, and the improvement of environmental cleanliness and quality of modern automobile gasolines make them a priority in solving the problem and determines the economic efficiency.

**The object and subject of the study.** Research objects are n-hexane, n-heptane, n-octane, light gasoline fractions (b.p. – 70°C, – 85°C), straight-distilled gasoline fractions of gas condensate (b.p. – 70°C), their isomerization and aromatization products and catalysts based on Y and ZSM-5 zeolite modified with compounds of Pt, Ca, La, Gd, Ho, Zn, Ni, Zr, Cu, B, P, Ge, Co.

**The aims and objectives of research.** The main purpose of this work is the development of biseolite based on Y and ZSM-5 zeolites, as well as effective metal zeolite catalysts based on ZSM-5 zeolites for the processes of isomerization of light gasoline fractions, enrichment of gas condensate with straight-run gasoline fractions in a hydrogen-free environment, their catalytic activity with physico-chemical, acid properties, the interaction between selectivity and stability was studied.

In order to achieve the goal, the following main objectives were addressed:

- Preparation of bi- and polymetallic catalysts based on zeolite Y by impregnation and ion exchange methods;
- Investigation of the effect of the nature and amount of transition and rare earth metals on the physicochemical, catalytic properties of Y-based catalysts in the isomerization of acid and n-C<sub>7</sub>-C<sub>8</sub> paraffinic hydrocarbons and light gasoline fractions;
- Preparation of bi- and polymetallic biseolite catalysts based on Y and ZSM-5, study of their physico-chemical properties and isomerization of gasoline fractions of gas condensate (b.p. – 70°C);
- Determination of the dependence between the isomerization selectivity of metal zeolite catalysts, the structural properties of zeolites, the power and concentration of acidic sites, the amount and nature of the modifying metal;

– Preparation of bimetallic catalysts with transition metals and non-metals (B, P) based on ZSM-5 zeolite, study of their physico-chemical and catalytic properties in the process of conversion of gas condensate fraction to high-octane components in a hydrogen-free environment;

– Study of the relationship between the nature and amount of modifying metallic, non-metallic, isoparaffinic and aromatic hydrocarbons (ARCs) in the catalyst;

– Selection of an optimum catalyst with high isomerization selectivity and stability;

**The research methods.** The thesis work has been performed using modern methods of physicochemical analysis (X-ray diffraction, IR, NH<sub>3</sub> TPD, nitrogen adsorption at low temperature, SEM, gas-liquid chromatography).

**The main provisions of the defense:**

– Effect of exchange cation, nature and amount of transition metals in the process of isomerization of n-C<sub>6</sub>-C<sub>8</sub> and gasoline fractions on activity of bi- and polymetallic catalysts based on zeolite Y, as well as isomerization selectivity;

– Study of the correlation between the effect of modification on the physicochemical acidic properties and the isomerisation selectivity of the catalyst;

– Preparation of bimetallic biseolite catalysts based on Y and ZSM-5 zeolites, effect of the nature and amount of zeolite and modifying metals on its catalytic properties in the isomerization of different gasoline fractions;

– Studying the physico-chemical acid and textural properties of catalysts based on modified zeolite and biseolite and determining the interaction with catalytic properties and the principles of developing effective bifunctional biseolite catalysts for the process of isomerization of narrow gasoline fractions;

– Synthesis of bimetallic boron and phosphorus-loaded catalysts on the basis of ZSM-5 zeolite and study of the regularity of the process of enrichment of gas condensate fraction by straight-run distillation in a hydrogen-free environment with their participation, determination of active sites that direct catalysts to isomerizing and aromaticizing

directions, determination of their selectivity and stability researching factors and selecting a highly efficient bifunctional catalyst.

**Scientific innovation of the research.** For the first time in the process of isomerisation of n-paraffin C<sub>5</sub>-C<sub>6</sub> hydrocarbons and light gasoline fractions the regularities of catalytic action of polymetallic biseolite catalysts based on wide-porous Y and medium-porous zeolites ZSM-5 modified with Pt Co, Ni, Ge and NTE metals have been established. It was shown that the isomerisation activity and selectivity of the catalyst can be improved by adjusting the structural type of zeolite made of these metals.

The effect of each component on the catalyst activity and isomerization selectivity was revealed. It has been shown that bi- and polymetallic zeolite (Y) and biseolite (Y-ZSM-5) catalysts modified with two highly charged cations (Ca<sup>2+</sup>-NTE<sup>3+</sup>); transition metals (Pt-Ni, Pt-Co) and germanium are possessing high isomerizing ability. Polymetallic biseolite catalysts provide to obtain high-octane components from the isomerization of light gasoline fractions.

Bimetallic (Zn-Fe, Cu-Zn, Cu-Co, Cu-Zr, Co-Zr) catalytic systems modified with nonmetals (B, P) were obtained for the first time based on zeolite ZSM-5. Moreover, their physicochemical properties and the process of gas condensate processing into high-octane components of straight-run gasoline in a hydrogen-free environment have been studied. It has been shown that in the process of obtaining high-octane components from gasoline fraction by straight-run distillation, the yield of catalyst, amount of isoparaffin, aromatic hydrocarbons, and octane number is regulated by the nature and amount of modifying metal and non-metal in ZSM-5 zeolite. The bimetallic Zr-Cu-B(P)-HZSM and Zr-Co-B(P)-HZSM catalysts show the highest catalytic activity: the gasoline fraction with an octane number of 94.2 (TM) obtained in its presence contains aromatic hydrocarbons (<30.0%), according to the amount of benzene (0.8-1.1%) and olefins (1.2-2.1%), it meets the requirements for "Euro-4" and "Euro-5" car gasoline class.

**Theoretical and practical significance of the research.** The obtained results can be the basis for the development of the method of preparation of active and selective Pt-containing polymetallic biseolite

catalysts for the isomerization of pentane-hexane, hexane-heptane fractions. ZSM-5-based bimetallic catalysts can be an alternative to traditional reforming catalysts for the process of low-temperature enrichment of straight-run distilled gasoline fraction in a hydrogen-free environment.

**Published works and approbation of the work.** The most important achievements of this dissertation have been presented at local and international conferences:

II International scientific conference for students and young scientists (Vinnytsia, 2019); XXI Менделеевский съезд по общей и прикладной химии (Санкт-Петербург, 2019); A collection of abstracts of the VI All-Russian conference (1934-2000) with international participation dedicated to the 85th anniversary of the birth of Y.S. Klyachkina (Perm, 2019); Proceedings of the VIII All-Russian Conference of current issues of chemical technology and environmental protection (Cheboksary, 2020); XIII All-Ukrainian Scientific Conference of Students and Aspirants "Readings of Chemical Karazin" theses collection (Kharkov, 2021); Collection of abstracts of the 9th All-Russian Zeolite Conference on zeolites and mesoporous materials: achievements and prospects (Grozny, 2021); Collection of abstracts of the conference cluster (Ivanovo, Russia, 2021); A collection of abstracts of the XXV All-Russian Conference of Young Chemists with international participation (Nizhny Novgorod, 2022); Materials of scientific conferences of postgraduates, masters and young researchers on "Actual problems of chemistry" dedicated to 96 and 99<sup>th</sup> anniversaries of National Lider Heydar Aliyev, (Baku, 2019, 2022);

There were published nine articles according to the results of the dissertation work (5 of them in periodical scientific journals included in international abstracting and indexing systems) and 20 abstracts of papers.

**Affiliation.** The research was performed at Nakhchivan State University, the department of Chemistry.

**The scope and structure of the work.** The dissertation consists of an introduction (14482 symbols) and four chapters (1st chapter 64401 symbols, 2nd chapter 21588 symbols, 3rd chapter 33450



symbols, and 4th chapter 43454 symbols); main results (4150), 173 cited references, as well as graphs (32), and tables (25) are shown.

**Personal contribution of the author.** The author's personal contribution includes the planning and organisation of the thesis work and the achievement of the main results. The applicant carried out all theoretical and experimental researches, included modification and preparation of zeolite catalysts, as well as the interpretation and synthesis of the results. The analysis and systematisation of the research results were prepared and formalised as scientific reports and articles with the active participation of the applicant.

## CONTENT OF THE WORK

The **introduction** shows the relevance of the dissertation topic, the purpose of the substantiated work, the scientific innovation and practical significance of the results.

**The first chapter** deals with the literature examinations. In this chapter, the structure, physicochemical, and catalytic properties of zeolites in the conversion of hydrocarbons and gasoline fractions are given. The laws of isomerization and aromatization of gasoline fractions of gas condensate with the presence of zeolites were investigated, and it was concluded that it is possible to regulate the physico-chemical and catalytic properties of zeolites by changing the modification methods.

**The second chapter** outlines methods for the synthesis of zeolite catalysts, describes the experimental catalytic unit, the methodology of the experiments, the analysis of reaction products and methods of physico-chemical investigation of the catalysts.

The thesis concludes with conclusions, a list of references and a list of abbreviations.

### Summary of chapter 3

#### **Catalytic properties of mono- and bimetallic catalysts based on zeolite Y in n-Hexane isomerization reaction.**

Catalysts were systematically prepared based on Y and ZSM-5 zeolites modified with Y zeolite Ca-, cation and bication forms of REE metals, transition metals (Ni, Co), Sn and Ge metals and their physicochemical properties and catalytic activity were systematically

studied in the isomerization reaction of n-hexane, n-octane, industrial n-pentane, C<sub>5</sub>-C<sub>6</sub> gasoline fractions (b.p. – 70<sup>0</sup>C and b.p. – 85<sup>0</sup>C) and n-C<sub>7</sub>-C<sub>8</sub> paraffin hydrocarbons mixture.

Monometallic Pt/CaY zeolite has low activity and selectivity in n-hexane isomerization reaction. The maximum yield of isohexanes (58.5 wt.%) is achieved at 350<sup>0</sup>C, the inclusion of 0.3-0.8 wt.% of holmium in the composition of the Pt/CaY catalyst has a promoting effect on its activity and selectivity. When the catalyst is modified with holmium, the isomerisation reaction temperature decreases by 10-40<sup>0</sup>C depending on the amount of holmium. When increasing the amount of modifier to 0.5 wt.%, this time the optimal temperature drops to 320<sup>0</sup>C and yield of isohexanes increases to 71.1% and isomerization selectivity increases to 94.8% at this temperature. When the amount of holmium in bimetallic catalyst is increased to 0.8 wt.%, its isomerization activity and selectivity decrease slightly. At the optimum temperature (320<sup>0</sup>C), the yield of isohexanes is 69.2%, and the selectivity is 92.8%. Thus, holmium metal has a promoting effect on the activity and selectivity of the Pt/CaY catalyst. The optimum amount of holmium in the bimetallic Pt Ho/CaY catalyst is 0.5 wt.%.

When adding nickel to the 0.5% Pt 0.5% Ho/CaY catalyst, its amount, activity and selectivity change significantly. The addition of 0.2 wt.% nickel to its composition increases the activity and isomerizing selectivity of the catalyst. At the optimal temperature (320<sup>0</sup>C), the yield of isohexanes increases to 73.5 wt.% and the selectivity of isomerization to 96.2 wt.%. When increasing the amount of nickel in the catalyst to 0.3 wt.%, its isomerization decreases activity and selectivity.

**Catalytic properties of bi- and polymetallic catalysts based on zeolite Y in the process of isomerization of C<sub>5</sub>-C<sub>6</sub> gasoline fraction (b.p. – 70<sup>0</sup>C).** It can be seen from Table 1 that bimetallic BMSKT (0.5% Pt 0.5% Ho/CaY) shows enough isomerization activity. In its presence, the amount of isopentane to 18.8 wt.%, the amount of iso-C<sub>5</sub>-C<sub>6</sub> hydrocarbons increases to 50.6 wt.% and for this reason, the octane number of the obtained gasoline fraction rises to 77.2.

When the bimetallic BMSKT catalyst was modified with 0,2 wt.%

Ni (PMSKT-1; 0,5% Pt 0,5% Ho 0,2% Ni/CaY) və 0,2 wt.% Ge (PMSKT-2; 0,5% Pt 0,5% Ho 0,2% Ge/CaY), its isomerization activity and selectivity become higher.

In the presence of polymetalzeolite catalysts, the amount of isopentane in the gasoline fraction to 20.1-21.5 wt.%, the amount of iso-C<sub>5</sub>-C<sub>6</sub> hydrocarbons increases to 53.0-54.7 wt.%, also the octane number rises to 80.3-81.0. Benzene, containing 0.9 wt.% of the raw material, undergoes complete conversion.

**Table 1.** Parameters of the process of isomerization of gas condensate gasoline fraction (b.p.-70°C) in the presence of bi- and polymetallic Y zeolite catalysts; *Condition:* T=320°C, V=1.0 h<sup>-1</sup>, H<sub>2</sub>/raw material=3:1(mol)

Parameters	Raw material, wt.%	Catalyst		
		BMSKT	PMSKT-1	PMSKT-2
ethane+ propane	0,1	6,3	5,3	5,0
isobutane	0,6	2,1	2,9	3,0
n- butane	3,5	2,0	2,1	1,9
isopentane	14,2	18,8	20,4	21,5
n- pentane	28,9	22,1	21,5	20,7
cyclopentane	5,7	5,9	5,2	4,8
2,2- dimethylbutane	0,2	5,3	5,9	6,1
2,3- dimethylbutane + 2 methylpentane	15,6	16,1	16,4	16,6
3- methylpentane	10,8	10,4	10,5	10,7
n- hexane	15,8	7,2	7,5	8,1
methylcyclohexane	3,6	2,4	2,1	1,6
cyclohexane	0,1	0,3	0,1	-
benzene	0,9	0,2	-	-
iso-C <sub>5</sub> -C <sub>6</sub> amount	40,8	50,6	53,0	54,7
Octane number	69	77,2	80,3	81,0

The isomerizing activity of polymetallic zeolite catalysts was studied in the conversion of the gasoline fraction of gas-condensate (b.p. – 70°C) in the temperature range of 320-350°C and it has been

shown that process temperature has a significant effect on hydrocarbon conversion. When the reaction temperature is increased from 320°C to 350°C, the decomposition of hydrocarbons included in the C<sub>5</sub>-C<sub>6</sub> fraction and the amount of gas products increases from 8.7 wt.% to 14.6-15.6 wt.%. At 320°C, the amount of isopentane in the C<sub>5</sub>-C<sub>6</sub> fraction from 16.4 wt.% to 26.3-27.2 wt.%, the amount of isohexanes increases from 25.2 wt.% to 28.6-29.1 wt.% and the octane number increases from 69.4 to 79.2-80.2. When the process temperature is raised to 330°C, the amount of iso-C<sub>5</sub>-C<sub>6</sub> hydrocarbons in the fraction increases from 54.9-56.0 wt.% to 57.3-59.0 wt.% and as a result, its octane number increases to 82.1-82.6. When the temperature is increased to 350°C, the decomposition reaction accelerates and decreases the amount of isoparaffins. The obtained results show that 0.5% Pt 0.5%Ho 0.2% Ge/CaY polymetallic catalyst shows higher activity. A comparison of the composition of the C<sub>5</sub>-C<sub>6</sub> fraction shows that it is possible to obtain a gasoline fraction with a higher octane number as a result of the isomerization of the fraction containing more n-pentane and n-hexane hydrocarbons.

Thus, polymetallic catalysts based on Y zeolite exhibit high activity in the isomerization of the medium-temperature light fraction C<sub>5</sub>-C<sub>6</sub> (b.p.-70°C) and gasoline fraction C<sub>6</sub>-C<sub>7</sub> (b.p-85°C) and increase its octane number to 12,0-13.2 “in one pass”, provides obtaining of the high-octane non-aromatic isomerates C<sub>5</sub>-C<sub>6</sub> and C<sub>6</sub>-C<sub>7</sub>.

**Isomerization of a mixture of n-octane and n-C<sub>7</sub>-C<sub>8</sub> paraffin hydrocarbons in the presence of polymetallic catalysts based on zeolite Y.** The broad gasoline fraction (b.p – 125°C) is shown with C<sub>5</sub>-C<sub>8</sub> alkanes along with naphthenes and aromatic hydrocarbons. Since the diameters of molecules of n- and isoalkanes vary in the range of 0.55-0.8 nm, it is more available to use catalysts prepared on the basis of Y zeolite with pore sizes of ~0.9 nm for their isomerization. For this reason, new polymetallic catalysts were synthesized based on Y zeolite and their catalytic properties were studied in the isomerization reaction of a mixture of n-heptane and n-octane as a model raw material (table 2).

**Table 2.** Isomerization of a mixture of n-C<sub>7</sub>-C<sub>8</sub> paraffinic hydrocarbons based on zeolite Y in the presence of polymetallic catalysts. *Condition:* T=280°C, P=1atm, V=1.0 h<sup>-1</sup>, H<sub>2</sub>/raw material=3:1. The composition of mixture: n-C<sub>7</sub>H<sub>16</sub>: n-C<sub>8</sub>H<sub>18</sub> (1:1 wt.%)

Catalyst	Yield of products, %			Σi-C <sub>7</sub> -C <sub>8</sub>	S <sub>iso</sub> %
	C <sub>2</sub> -C <sub>6</sub>	Σi-C <sub>7</sub> H <sub>16</sub>	Σi-C <sub>8</sub> H <sub>18</sub>		
PMSKT-2	4,2	33,9	27,7	61,6	93,6
PMSKT-3	4,5	32,7	26,8	59,5	92,9
PMSKT-4	4,0	34,3	28,4	62,7	94,0

PMSKT-2 (0,5%Pt 0,2%GeHoCaY<sup>xx</sup>); PMSKT-3 (0,5%Pt 0,2%GeLaCaY<sup>x</sup>); PMSKT-4 (0,5%Pt 0,2%GeLaCaY<sup>xx</sup>); Isomerization selectivity – S<sub>iso</sub> %; The amount of Ho and La is 0.8wt.% and the exchange rates with <sup>x</sup>Ca<sup>2+</sup> and <sup>xx</sup>Ca<sup>2+</sup> are 86 and 91%, respectively.

It can be seen that polymetalzeolite catalysts show high catalytic activity in the isomerization reaction of a mixture of n-C<sub>7</sub>-C<sub>8</sub> paraffin hydrocarbons.

Polymetallic catalysts modified with Ho or La (0.8 wt. %) with an exchange rate of 91% with Ca<sup>2+</sup> cations show higher activity and selectivity. The catalytic properties of these catalysts are very close to each other. In their presence, the total yield of i-C<sub>7</sub>-C<sub>8</sub> hydrocarbons at 280°C is 61.6-62.7wt.% and the selectivity is 93.6-94.0.

The change in the catalytic properties of the Pt-zeolite catalyst after REE modification can be explained by the formation of additional Brønsted (B) and Lewis (L) acid sites as a result of the modification. La<sup>3+</sup>, La<sub>2</sub>(OH)<sub>2</sub><sup>+</sup> La(OH)<sub>2</sub><sup>2+</sup> cations are an additional source of L-acid. The NTE form of zeolite always contains OH groups of the Brønsted type. Around the La cation, the L-acid site can hold two OH-groups (La(OH)<sup>+</sup>). This cation localizes near the central group of atoms by forming two B-acid sites and compensates its charge. Therefore, the formation of B-acidic sites in REE-CaY zeolites is due to the presence of water molecules surrounding REE cations with L-sites. The promoting effect of lanthanum on the catalytic properties of Pt/0.86 CaY and Pt/0.91 CaY catalysts in the isomerization of n-octane is determined by the change in the ratio of B- and L-acid sites. Ca-

forms of Y zeolite have weak ( $E < 95$  kC/mol) and medium ( $95 < E < 130$  kC/mol) acid sites. However, the amount of weak and medium acid sites is 33.7-38.5  $\mu\text{mol/g}$  and 80.3-88.5  $\mu\text{mol/g}$ , respectively. The platinum-zeolite catalyst does not exhibit high activity due to the small number of medium-strong sites (table 3). When adding 0.5-0.8 wt.% La to CaY zeolite, the amount of medium-strong acid sites increases sharply (178.7-186.5  $\mu\text{mol/g}$ ). As a result of modification with germanium, the ratio of medium-strong acid sites to strong acid sites increases (6.5-6.9), the density of strong B-sites decreases, and new L-sites are formed.

Thus, both sites are involved in the isomerization reaction. However, the main role is played by medium-strong B-acid sites. Isomerization selectivity is regulated by the ratio of medium and strong B-acid sites and the amount of new formed L-acid sites.

**Table 3.** Distribution of the amount of La and Ge in the Pt-zeolite catalyst according to the activation energy of the number of acid sites.

Sample №	The amount of modifier, wt. %		E < 95 kJ/mol	95 < E < 130 kJ/mol	E > 130 kJ/mol
	La	Ge			
0,86 CaY	-	-	38,5	80,3	-
0,91 CaY	-	-	33,7	88,5	-
0,86 CaY	0,5	-	27,2	132,2	25,4
0,86 CaY	0,8	-	20,6	178,7	31,2
0,86 CaY	1,0	-	14,7	184,5	42,1
0,91 CaY	0,8	-	18,8	186,5	33,7
0,86 CaY	0,8	0,1	30,1	190,3	29,1
0,86 CaY	0,8	0,2	32,4	192,5	27,7

**Investigation of catalytic properties of bimetallic Pt-Me/HZSM-5 catalysts in isomerization of n-pentane and industrial n-pentane fraction.** High-silica ZSM-5 zeolites with medium porosity and three-dimensional structure belong to the class of effective catalysts in the conversion of n-paraffins.

For this reason, the development of new, more selective catalyst

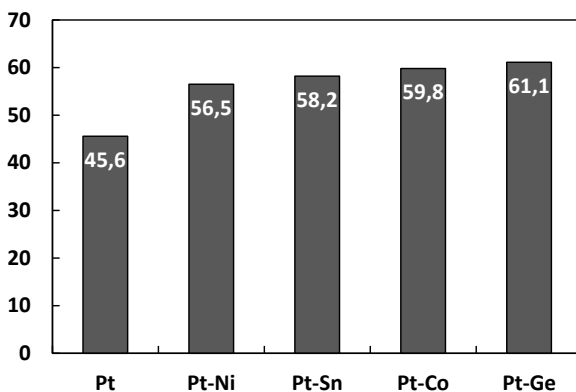
based on ZSM-5 zeolite for the process of isomerization of n-paraffin hydrocarbons and light gasoline fractions has become one of the important issues of the work.

Considering these, the effect of modification with cobalt, nickel and other metals (Sn, Ge) on the activity and selectivity of the catalyst based on Pt-containing ZSM-5 in the isomerization reaction of n-pentane and industrial n-pentane fraction was studied. It was shown that the monometallic Pt/HZSM-5 catalyst exhibits high activity in the isomerization of n-pentane and the yield of isopentane at 300°C is 57.4wt. %. However, its selectivity is low (91.2%).

When adding 0.15 wt.% cobalt to the Pt/HZSM-5 catalyst, the yield of isopentane and the isomerizing selectivity of the catalyst increase in the temperature range of 280-320°C. At the optimal temperature (300°C), the yield of isopentane to 58.6-60.8 wt.% and the isomerizing selectivity increases to 93.7-95.6%.

0.5% Pt 0.15% Co/HZSM-5 bimetallic catalyst tested in industrial n-pentane fraction isomerization reaction and it was determined that increasing the reaction temperature from 280°C to 320°C increases its isomerizing activity. Higher isomerization activity is observed at 300°C. The amount of isopentane in the catalyst increases to 53.9wt.%, the amount of isopentane in the C<sub>5</sub> fraction increases to 59.8%. During the process, the sulfur and nitrogen compounds in the raw materials are completely removed and cyclopentane is partially decomposed. The presence of these compounds in the raw material does not affect the activity and selectivity of the bimetallic catalyst.

The effect of other metals (Sn, Ge, Ni) in a small amount (0.15wt.%) on the activity of 0.5% Pt/ HZSM-5 catalyst was studied in the isomerization of industrial isopentane fraction at 300°C and the obtained results are given in figure 1. The adding Ni, Sn, Co, Ge in the amount of 0.15 wt.% to the Pt/HZSM-5 catalyst has a promoting effect on its isomerizing activity.



**Fig. 1.** The effect on the amount of isopentane of the nature of the second metal in the isomerization of the pentane fraction of the 0.5% Pt/HZSM-5 catalyst ( $T=300^{\circ}\text{C}$ ,  $v=1,0\text{ h}^{-1}$ ,  $\text{H}_2/\text{raw material}=3:1$ )

At  $300^{\circ}\text{C}$ , the amount of isopentane in the  $\text{C}_5$  fraction increases from 45.6 wt.% to 61.1 wt.%. Higher isomerizing activity is shown by bimetallic Pt-Co and Pt-Ge catalysts.

**Medium-temperature isomerization of light gasoline fraction of gas condensate in the presence of bimetallic bisolite catalysts.** In the process of isomerization of the light  $\text{C}_5\text{-C}_7$  gasoline fraction of gas condensate, it is very important and relevant to study the catalytic properties of Pt-containing bisolite catalysts prepared by combining wide-pore (Y) and medium-pore (ZSM-5) zeolites and the effect of the modifier on its isomerization activity and selectivity.

It can be seen that hydrocracking of paraffin, naphthenic hydrocarbons and isomerization of n-pentane takes place in the presence of a Pt-containing catalyst on the basis of medium-porous ZSM-5 zeolite. At  $280^{\circ}\text{C}$ , the yield of  $\text{C}_2\text{-C}_4$  gaseous hydrocarbons is high and is 13.3wt.%. There is no increase in the yield of isohexanes in the products. The kinetic diameters of 2,2-dimethylbutane and 2,3-dimethylbutane ( $\sim 0.62\text{ nm}$ ) are larger than the channel cross section of ZSM-5 zeolite and it creates steric difficulties for its formation. In the presence of the Pt/HZSM-5 catalyst, only n-pentane isomerization proceeds selectively (table 4).



**Table 4.** Parameters of isomerization of gasoline fraction of gas condensate (at-70°C) in the presence of Pt-containing mono- and biseolite catalysts. *Condition:* 280°C (KT-1, KT-2); 300°C (KT-3, KT-4)  $V=2h^{-1}$ ,  $H_2/\text{raw material}=3:1(\text{mol})$

Parameters	The composition of raw material, wt. %	The yield of products, wt. %			
		KT-1	KT-2	KT-3	KT-4
Ethane + propane	0,1	8,2	0,9	2,9	2,5
Isobutane	0,6	2,3	0,8	1,4	0,9
n-butane	3,5	2,8	2,1	2,4	1,9
isopentane	14,2	22,6	17,6	23,1	26,7
n-pentane	28,9	21,6	26,1	19,8	16,6
Cyclopentane	5,7	6,3	6,0	5,3	5,1
2,2-dimethyl butane	0,2	0,3	5,2	6,5	7,1
2,3-dimethyl butane+2-methyl pentane	15,6	15,0	16,6	16,6	17,0
3-methyl pentane	10,8	10,4	11,0	11,4	11,2
n-hexane	15,8	7,5	10,5	8,2	8,6
Methyl cyclohexane	3,6	2,2	2,3	1,8	1,8
Cyclohexane	0,1	0,7	0,8	0,6	0,6
Benzene	0,9	0,1	0,1	-	-
Amount of C <sub>5</sub> -C <sub>6</sub> isomers in the fraction	40,8	48,3	50,4	57,6	62,0
Octane number	69	78,4	77,2	81,8	86,0

*Note.* KT-1 (0,5% Pt-HZSM-5); KT-2 (0,5% Pt-Gd Ca Y); KT-3 (0,5% Pt-Gd Ca Y+20 %HZSM-5); KT-4 (KT-3+0,15% Ge)

Isomerisation of n-pentane and n-hexane into branched isomers proceeds selectively in the presence of Pt-containing expanded Y-zeolite (channel cross-section 0.7-0.8 nm), in contrast to the ZSM-5-based catalyst. In the presence of this catalyst (KT-2), the amount of more valuable 2,2-dimethylbutane increases to 5.2 wt.%. Hydrocracking of hydrocarbons takes place partially in the presence

of that catalyst. Thus, the Pt-containing catalyst based on ZSM-5 zeolite has high hydrocracking and n-pentane isomerizing activity. The Pt-containing catalyst based on zeolite Y is characterized by low hydrogenation property and high isomerization activity against n-hexane.

Compared to monozeolite catalysts, Pt-containing biseolite catalyst (KT-3) has a higher isomerizing ability towards n-pentane and n-hexane. When it is increased to 300<sup>0</sup>C in its presence, the amount of isoparaffins is up to 57.6 wt.% and the octane number of gasoline is up to 81.8 (table 4). The inclusion of 0.15 wt.% Ge (KT-4) in the composition of the biseolite catalyst leads to a significant increase in its isomerizing activity. In the presence of KT-4 catalyst at a temperature of 300C, the amount of isoparaffins to 62.0 wt.% and the octane number increases to 86. The octane number of gasoline increases by 17. When increasing the temperature to 320C, its isomerizing activity decreases slightly. Increasing the amount of Ge in the biseolite catalyst to 0.3 wt.% (KT-5) does not increase its isomerizing activity, on the contrary, it reduces the amount of C5-C6 isoparaffins to 60.3%.

Thus, the isomerizing activity of the catalyst depends on the nature of the zeolite and amount of the modifier. The amount of isoparaffinic hydrocarbons and the octane number of gasoline are regulated by the compatibility of wide-porous and medium-porous (Y, ZSM-5) zeolites and the amount of modifying additive (Ge) in the Pt-containing bimetallic catalyst.

#### **Summary of chapter 4**

**Acidic and catalytic properties of mono- and bimetallic Fe- and Me (Cu, Zn, Ni)-Fe-P catalysts based on ZSM-5 zeolite in the enrichment of straight-run distillation gasoline fraction.** As it is carried out in catalytic hydrogen environment and at high temperature (490-530<sup>0</sup>C), the octane number of the obtained gasoline fraction is provided mainly at the expense of ArHC.

For this reason, the synthesis of new bimetallic catalysts with higher isomerizing ability and the study of their properties were conducted on the basis of ZSM-5 zeolite for the conversion process of straight-run distillation gasoline fractions without using them at low

temperatures, relatively.

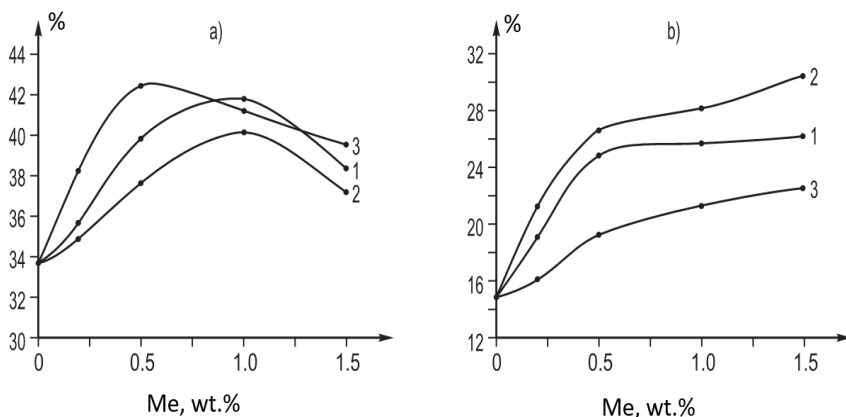
Straight-run distillation fraction with the following hydrocarbon composition was used as raw material (wt.%): Paraffins – 28,3; isoparaffins – 29,5; naphthenes – 33,4; ArHCs– 8,8; octane number (MM) – 58.

In the presence of HZSM-5 zeolite, the straight-run distillation gasoline fraction is mainly cracked, and therefore, when the reaction temperature is increased from 350°C to 430°C, the yield of liquid products decreases from 71.8% to 64.2%. When the temperature increases, this time the amount of ArHC increases in liquid products. The octane number increases from 58 to 74 due to aromatic hydrocarbons. Adding 1.0-3.0% of Fe to the composition of HZSM-5 zeolite increases the amount of isoparaffins to 34.2-36.2% and the amount of ArHC to 22.8-26.8% at the optimal temperature (380°C). The yield of liquid products varies a little. When the 3% Fe HZSM-5 catalyst is modified with 1.0-2.0 wt.% phosphorus, the yield of liquid products increases significantly (74.1-77.4%), the amount of isoparaffins and ArHC changes a little. When the 3% Fe 2% P-HZSM-5 catalyst is modified with 0.5-1.5% Cu, Zn and Ni, the yield of liquid products increases, the amount of isoparaffins and ArHC changes in the catalyst. In addition, as a result of modification, the amount of coke is reduced significantly.

It can be seen from Figure 2 that the isomerizing and aromaticizing ability of the catalyst depends to a great extent on the nature and amount of the metal. A bimetallic catalyst modified with Ni metal shows a higher isomerizing ability. Increasing the amount of metal above 1.0 wt.% increases the aromaticity of the catalyst. A higher aromatization selectivity is shown by the catalyst modified with Zn.

According to the isomerization selectivity, bimetallic zeolite catalysts are arranged in the following order:

Ni – Fe – P/HZSM-5 > Cu-Fe-P/HZSM-5 > Zn-Fe-P/HZSM-5.



**Fig. 2.** Dependence between the concentration of the modifying metal and the amount of isoparaffins (a) and ArHC (b) in the catalyst in 3.0%FeMe2.0%P/HZSM-5 catalysts.

According to the aromatization selectivity, bimetallic catalysts are arranged in the following order:



In order to explain the effect of modification on the catalytic properties of HZSM-5 zeolite, the acidic properties of catalysts were studied by TPD method of ammonia.

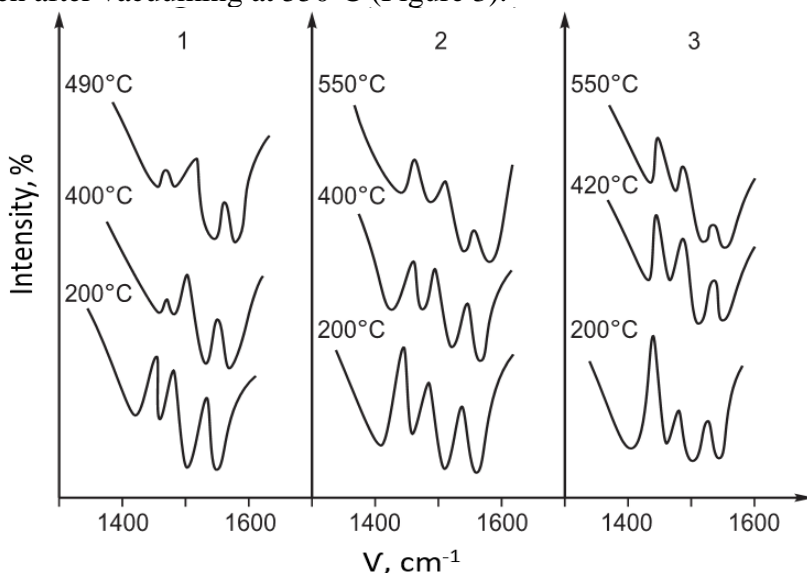
HZSM-5 zeolite has strong B-acid sites (538  $\mu\text{mol/g}$ ) and weak L-acid sites. When adding 3.0%Fe to its composition, the concentration of strong Brønsted acid sites drops to 312  $\mu\text{mol/g}$ , but at this time, new strong Lewis acid sites are formed (55  $\mu\text{mol/g}$ ). When the catalyst is additionally modified with phosphorus (2.0 wt.%P), the concentration of strong B-sites decreases to 126  $\mu\text{mol/g}$ . When the 3.0%Fe/HZSM-5 catalyst is individually modified with Zn, Ni, Cu, metals and P, there is a sharp reduction of strong B-sites and the formation of new strong L-sites.

The change of acid properties as a result of modification of zeolite catalysts can be explained as followings.

In the process of modification and thermal processing of zeolite, metal ions in contact with its acidic hydroxyl groups replace part of the proton with metal ions, and as a result, the density of strong B-acidic sites decreases and new stronger ( $\text{Me}^{\delta+}\text{O}^{\delta-}$ ) L-acid sites are formed. In addition, the metal and part of its various oxidized

structures are located in the micropores of zeolite and on its surface in the form of nanoparticles, forming additional L-acidic sites with the coordination-unsaturated ions of aluminum in the crystal lattice.

As a result of modification with transition metals, the IR spectra of pyridine from Fe and Cu modified catalyst confirm the formation of new and stronger L-sites in contrast to the L-acid sites of the original zeolite (H-ultrasil). Desorption of adsorbed pyridine from aprotic sites of modified samples is not completely desorbed from the surface even after vacuuming at 550°C (Figure 3).



**Fig. 3.** IR-spectra of pyridine adsorbed on modified H-ultrasils: 1 – H-ultrasil; 2 – Fe-ultrasil; 3 – Cu-ultrasil.

Thus, when HZSM-5 zeolite is modified with transition metals, redistribution of acid sites occurs: the density of strong B-acid sites decreases and new stronger L-acid sites are formed.

The main role in the catalytic activity of modified catalysts in the dehydrogenation of n-paraffins and naphthenes is played by L-acid sites of the type  $Me^{\delta+} O^{\delta-}$  formed as a result of modification with transition metals. These sites have strong polarizability against n-paraffin, naphthene and hydrogen molecules and are responsible for the dehydrogenation activity of the catalyst in the transformation of

these hydrocarbons. The main role of B-sites is the formation of carbocation. However, a small number of zeolite "bridging" OH-groups are required to obtain the carbocation.

**Obtaining high-octane gasoline from the straight-run distillation gasoline fraction of gas condensate in the presence of mono- and bimetallic catalysts based on ZSM-5 zeolite modified with Zr, Cu and B.** In order to study the influence of the nature and amount of modifiers on the acidic and catalytic properties of HZSM-5 zeolite, bimetallic Zr-Cu and Zr-Cu-B-HZSM-5 catalysts were prepared on its basis and their catalytic properties were studied.

When the monometallic 2% Cu/HZSM-5 catalyst is modified with orthoboric acid, the yield of liquid products increases up to 73.7%, but the amount of isoparaffins practically does not change, while the amount of ARK decreases significantly (22.8% ). 2%Cu1% B/HZSM-5 monometallic catalyst was modified with 0.5-1.0 wt.% Zr to increase the amount of high-octane isoparaffins in liquid products.

When the amount of Zr in the catalyst content is increased to 1.0 wt.%, the amount of isoparaffins in the liquid products increases significantly and makes up 43.5 wt.%, the amount of ArHC increases by only 2.5%. Compared to the original gas condensate, the octane number increases by 34.5. When the amount of Zr in the bimetallic catalyst increases to 1.5 wt.%, the amount of isoparaffins does not increase, but the amount of ArHCs increases slightly (28.3%).

Thus, 1.0% Zr 2% Cu 1% B/HZSM-5 bimetallic catalyst has optimal isomerizing and dehydrogenating functions, the yield of catalyst at 380<sup>0</sup>C is 78.2%, the octane number is 94.2 and it allows you to buy gasoline with a high content of isoparaffin hydrocarbons.

**Influence of the working time without regeneration of bimetallic catalysts on the indicators of the enrichment process of the straight-run distillation gasoline fraction.** The most important of the operational properties of the catalyst is its stable operating time without regeneration. For this reason, the influence of the operating time of bimetallic zeolite catalysts was studied on process parameters (table 5).

**Table 5.** The influence of the operating time of bimetallic zeolite catalysts without regeneration on the parameters of the process of enrichment of the straight-run distillation gasoline fraction.

Parameters	Operating time, hour				
	10	50	100	150	200
<b>1,0% Zr 2% Cu /HZSM-5 (cat. 1)</b>					
Reactor temperature, °C	380	400	420	440	460
Catalyst yield, wt.%	74,2	76,8	78,8	80,2	82,1
<b>Hydrocarbon composition of the catalyst, wt.%</b>					
n-paraffin+naphten	28,0	31,4	37,2	39,2	43,5
Isoparaffin	41,4	39,8	35,1	33,2	30,8
Olefin	0,9	1,6	3,6	5,2	6,0
Aromatics	29,7	27,2	24,1	22,4	19,7
Benzene	1,2	1,3	1,7	1,9	2,3
Octane number	91,6	88,1	84,3	80,2	76,8
<b>1,0% Zr 2,0% Cu 1,0% B/HZSM-5 (cat 2)</b>					
Reactor temperature, °C	380	400	420	440	460
Catalyst yield, wt.%	78,2	79,3	82,1	84,5	85,6
<b>Hydrocarbon composition of the catalyst, wt.%</b>					
n-paraffin+naphten	28,7	29,2	31,4	32,7	35,5
Isoparaffin	43,5	42,8	41,9	40,8	40,1
Olefin	0,7	1,2	1,6	2,1	2,7
Aromatics	27,1	26,8	25,1	24,4	21,7
Benzene	0,8	1,1	1,4	1,9	2,3
Octane number	94,2	93,5	91,2	88,4	85,1

To maintain high catalyst yield, the reaction temperature was gradually increased from 380°C to 460°C during the experiments. In the presence of bimetallic 1.5% Zr 2% Cu//HZSM-5 (cat. 1), the catalyst yield is 74.2-82.1 wt.% in the temperature range 380-460°C. When the operating time of this catalyst exceeds 50 hours, the amount of isoparaffin and ArHC decreases significantly in the catalyst. During 200 hours of operation, the amount of isoparaffins in the catalyst decreases from 41.4 wt.% to 30.8 wt.% and the amount of ArHC decreases from 29.7 wt.% to 19.7 wt.%. For this reason, the octane number of the catalyst drops from 91.6 to 76.8 points.

In the presence of the bimetallic 1.5%Zr2%Cu1% B/HZSM-5 (Cat. 2) catalyst, the yield of the catalyst under those conditions is higher and is 78.2-85.6 wt.%. Cat. 1 compared to Cat. 2 works more stable. During 20 hours of operation, the amount of isoparaffins in the catalyst is at a high level and it is 40.1wt.%.

The high stability of the KT-2 bimetallic catalyst means that the catalyst can operate using fixed bed technology without the presence of hydrogen gas. After 200 hours of operation without regeneration, since coke gradually accumulates on the surface of the catalyst, its deactivation is reversible: After oxidative regeneration at 500°C for 2 hours, the catalyst fully recovers its original activity.

## CONCLUSIONS

1. 1. The regularities of catalytic action of polymetallic biseolite catalytic systems based on large-porous zeolite Y and medium-porous ZSM-5 have been studied for the first time in the process of isomerisation of light gasoline fractions. And, it was shown that the way to reconcile the structural type of zeolite with rare earth and transition metals, It is possible to increase the isomerization activity and selectivity of the catalyst.

2. It was determined that bi- and polymetallic zeolite and biseolite catalysts modified with two multi-charged cations ( $\text{Ca}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Ho}^{3+}$ ) and transition metals (Pt, Ni, Ge, Co) are effective in the conversion of n-C<sub>5</sub>-C<sub>8</sub> paraffinic hydrocarbons and they show high isomerizing activity in the isomerization process of light gasoline fraction. The active centers of isomerization are considered medium-strength acid centers (95<E<135 kJ/mol) with a concentration of 178.7-186 mkmol/g.

3. In the process of obtaining high-octane components of motor fuels by isomerization of light gasoline fractions, the regularities of the catalytic effect of bi- and polymetallic catalysts based on their compatibility with Y and ZSM-5 zeolites were studied. It has been shown that the isomerization selectivity of metal zeolite catalysts is determined by the structural characteristics of zeolites, the strength and concentration of acidic centers, the nature and quantity of the modifying metal, and the structure of the intermediate formed in the pores of zeolite. Modification of bimetallic biseolite catalyst (0.5 Pt 0.8 NTE-CaY-HZSM-5) with germanium in the amount of 0.1-0.15 wt.% in the optimal ratio of Y and



ZSM-5 zeolites (4:1) at 300°C It allows to increase the amount of isoparaffins in C up to 62%, and the octane number of the gasoline fraction of the gas condensate up to 86.

4. It was determined that Pt-containing polymetallic catalysts based on medium porosity show high isomerizing activity only in the isomerization of n-pentane. Polymetallic catalysts based on wide-pore Y zeolite have high activity in isomerization of C<sub>6</sub>-C<sub>7</sub> n-paraffin and light gasoline fractions.

5. For the first time, bi-metallic catalysts were prepared on the basis of ZSM-5 zeolite modified with transition metals (Cu, Zn, Fe, Co, Ni, Zr) and non-metals (B, P), and their physico-chemical properties and gas condensate in hydrogen-free environment was studied in the enrichment of straight-run gasolines. It has been shown that in the process of obtaining high-octane components from straight-run gasoline fraction, the yield of catalyst, the amount of isoparaffin, aromatic hydrocarbons and the octane number are regulated by the nature and amount of modifying metal and non-metal in ZSM-5 zeolite. The bimetallic Zr-Cu-B(P)-HZSM and Zr-Co-B(P)-HZSM catalysts show the highest catalytic activity: gasoline fraction with 94.2 (TM) octane number obtained in its presence according to the amount of aromatic hydrocarbons (<30.0%), benzene (0.8-1.1%) and olefins (1.2-2.1%) “euro-4” and “euro-5” meets the requirements for the automobile gasoline class.

6. For the first time, bimetallic catalysts were prepared on the basis of ZSM-5 zeolite modified with transition metals (Cu, Zn, Ni, Co, Fe, Zr) and non-metals (B, P) and it was determined that the addition of these additives in the amount of 0.5-2.0 wt.% leads to the weakening of the strong Brønsted acid sites of zeolite and the formation of new stronger Lewis acid sites and the increase of the amount of isoparaffinic hydrocarbons in the enriched gasoline fraction.

7. It was determined that the change in catalytic properties as a result of modification is related to the redistribution of acid sites and the creation of new active sites: Reduction of density and strength of Brønsted acid sites, creation of newly isolated Me<sup>n+</sup>, Me-O type Lewis acid sites and metallic sites and formation of metallic sites and participation of these sites in isomerization of n-paraffin hydrocarbons and dehydrogenation of naphthenic hydrocarbons included in the

gasoline fraction.

8. It was shown for the first time that HZSM-5 zeolite 1.5% Co; Promotion with 1.0% Zr and 1.0% B in the temperature range of 350-380<sup>0</sup>C enables the increase of the liquid product yield, the increase of the amount of isoparaffins in the catalyst, and the stable operation of the catalyst for 200 hours in the enrichment of straight-run distillation gasoline fraction of gas condensate. 94.2 (TM) octane gasoline fraction obtained by the content of isoparaffins (40.1-43.5%), aromatic hydrocarbons (24.4-27.1%), benzene (0.8-1.1%) and olefins (1.2-2.1%) "Euro-4" and "Euro-5" automobiles fully meet the requirements of gasoline class.

**The main content of the dissertation and obtained results are published in the following works.**

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The defense will be held on **24 November 2023 at 12<sup>00</sup>** at the meeting of the Dissertation council ED 2.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Baku State University.

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Abstract was sent to the required addresses on **23 October 2023**

Signed for print: 13.10.2023  
Paper format: A5  
Volume: 38715 characters  
Number of hard copies: 20 ekz.