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**TRANSFORMATION OF NATURAL GAS TO AROMATIC  
HYDROCARBONS IN THE PRESENCE OF MODIFIED  
PENTACYL-TYPE ZEOLITES**

Speciality: **2307.01** – Physical chemistry

Field of science: Chemistry

Applicant: **Elnura Abulfaz Gambarova**

**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**NAKHCHIVAN – 2022**

The work was performed at "Chemistry" department of Nakhchivan State University.

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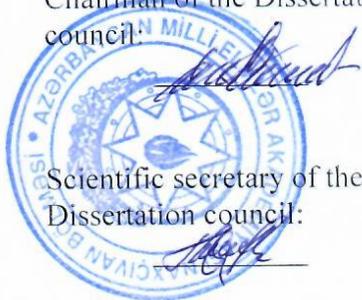
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A handwritten signature in blue ink, which appears to read "Bayram Zulfugar Rzayev", is written over a horizontal line.

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## GENERAL CHARACTERISTICS OF WORK

**The relevance and usage rate of the topic.** Currently, the main source of hydrocarbons is oil. However, due to their limited resources, the development of methods for obtaining hydrocarbons from natural gas, coal, plant biomass is urgent. The most important of these methods is the acquisition of valuable aromatic hydrocarbons from natural gas components. Rational use of natural and associated gases is the first priority issue for the oil and gas complex of the Republic of Azerbaijan. Inefficient use of natural and associated gases causes serious damage to the environment, and the economy suffers huge losses. The conversion of natural and associated gases directly into aromatic hydrocarbons under non-oxidizing conditions in the presence of zeolite catalysts is the most important and promising issue for researchers. The obtained liquid products can be used as a supplement to high-octane gasoline, as a valuable raw material in the petrochemical industry and organic synthesis.

Although there is considerable work on the production and study of the properties of heterogeneous catalysts for the conversion of small molecule C1-C4 alkanes, the effect of the amount and nature of the modifier on the texture and physicochemical properties of catalysts has not been systematically studied, little attention has been paid to the study of the nature and strength of the acid centers of the catalytic properties, the ratio of these centers and the stable service life of the catalyst.

ZSM-5 and their analogues CBM, CBH and ultrasil are medium porous zeolites, the size of the windows is 0.51 x 0.53 nm, and the absence of large gaps prevents the formation of condensed hydrocarbons inside their crystals, which are a source of coke. The catalytic properties of pentacyl zeolites that analogues of ZSM-5 type zeolites from the methods of modification and their combination, the amount and nature of the modifier, the catalytic properties of the synthesized bi and polymetallic catalysts in the process of transformation of texture, physicochemical and natural gas components have not been studied.

Taking these into account, the dissertation is devoted to a

topical issue - the development of bi- and polymetallic catalysts with higher activity and stability using various modification methods based on pentacyl-type zeolites to convert natural gas components directly into aromatic hydrocarbons under non-oxidizing conditions.

**Object and subject of research.** The objects of research are bi- and polymetallic catalysts based on natural gas and its conversion products (benzene, toluene, xylenes, naphthalene), pentacyl (ZSM-5) zeolites modified with Cr, Mo, W, Zr, Zn, Cd and NTE compounds.

**Aims and objectives of the research.** Development of new bi- and polymetallic zeolite catalysts based on pentacyl zeolites with high activity and stability for the process of direct conversion of natural gas components into aromatic hydrocarbons under oxidizing conditions.

The following key issues have been addressed to achieve the purpose:

- Modification of pentacyl zeolites by various methods (absorption, ion exchange, mechanical mixing, solid phase synthesis);
- Study of the effect of texture, acid catalytic and stabilizing properties of monometallic catalysts modified with transition metals;
- Investigation of the effect of the nature and amount of modifiers on their texture, acidity and catalytic properties in bimetallic catalysts modified with rare earth and transition metals;
- Study of the nature and distribution of active centers in modified zeolites by adsorption of molecular probes: acetone, butylamine, ammonia and pyridine;
- Preparation of polymetallic catalysts modified by nano-sized powders, carbonyls and carbonates of transition metals by dry method, their resistance to texture, physicochemical, acid, thermal processing, study of catalytic and stable performance properties.

**Research methods.** The following physicochemical methods were used in the dissertation:

Gas-liquid chromatography, X-ray phase analysis, IR

spectroscopy, thermoprogrammed desorption of  $\text{NH}_3$ , low-temperature adsorption of nitrogen, adsorption of acetone, butylamine and pyridine, and a flow device at atmospheric pressure to determine the activity of the catalyst.

**The main provisions of the defense:**

- Study of the effect of the nature, amount and method of inclusion of modifying additives on the texture, physical and chemical characteristics of the pentacyl-based catalyst and the catalytic properties of natural gas components in the process of aromatization;
- Determination of the interaction of catalytic activities of bi and polymetallic zeolite catalysts with their texture and acid properties;
- Detection of regularities of conversion of natural gas components in the presence of modified catalysts with carbonate of NTE and carbonyls of transition metals;
- Investigation of the effect of thermal processing conditions, catalyst size on the stable service life of polymetallic zeolite catalyst.

**Scientific novelty of the research.** The effect of modifiers on the structure of the catalyst, the active centers in the structure of pentacyl zeolite and its distribution was determined by physicochemical methods.

Based on the systematic study of physicochemical and catalytic properties of high silicon pentacyl zeolites revealed the presence of formation of new active centres that enhance the aromatization reaction on the surface of catalysts and the mechanism of action of modifiers (NTE, transition metals).

For the first time, new Cr-Mo (W), La-Mo (W)-Zn, La-Mo (W)-Cd polymetallic catalysts systems with optimal acid centers, porosity, high activity, selectivity and stability for the process of aromatization of natural gas components have been developed.

By combining methods of heat treatment, ion exchange with transition metals, solid-phase modification of transition metals scientifically substantiated approaches to the development of effective catalysts have been proposed for the process of direct

conversion of natural gas components into aromatic hydrocarbons under non-oxidizing conditions.

**Theoretical and practical significance of the research.** The inclusion of modified NTE and transition metals in pentacyl-type zeolites and the pre-heat treatment of catalysts increases their catalytic activity, selectivity and stable service life in the process of converting natural gas components directly into aromatic hydrocarbons without oxidizing. The obtained results are of great interest to researchers involved in the preparation and study of the properties of zeolite catalysts. Effective polymetallic catalysts have been proposed and shown that their application in the direct aromatization process of natural gas components without oxidizers can increase the production of practical, valuable aromatic hydrocarbons.

**Approbation and implementation of research.** The main results of the work were presented at international scientific conferences: VII Всероссийская цеолитная конференция, Тезисы докладов, (Звенигород, 2015 г), Материалы международной заочной научно-практической конференции «Актуальные проблемы естественных наук», Тамбов, 2015; Материалы Международной научно-методической конференции, посвященной 60-летию филиала Уфимского Государственного нефтяного технического университета, г. Салават, 2016; V Российская конференция с международным участием «Актуальные проблемы нефтехимии», посвященная памяти академика В.Н.Ипатьева, г. Звенигород, 2016; Сборник материалов IV Всероссийской студенческой конференции с международным участием, г. Санкт-Петербург, 2017; II Международная конференция «Современные решения научных и производственных задач в химии и нефтехимии» Сборник материалов международной конференции, г. Казань, 2017; Ümummilli Lider Heydər Əliyevin 93, 94, 95, 96, 98 illik yubileyərinə həsr olunmuş respublika elmi konfranslarının materialları, Bakı, 2016, 2017, 2018, 2019, 2021

Catalysts synthesized on the basis of polymetallic ZSM-5 zeolite can be used in the aromatization of small molecule C1-C4 alkanes. The proposed modification methods can also be used in the preparation of effective metaseolite catalysts for various processes.

27 scientific works on the topic of the dissertation were published. 8 of them are articles, 19 reports and conference materials.

Two of the articles were published by a single author, and five were published in periodicals, which are part of the international summary and indexing systems.

**Name of the organization where the dissertation work is carried out.** According to the research work plan the dissertation was carried out at the "Chemistry" department of Nakhchivan State University.

**Personal participation of the author.** The author personally modified zeolite catalysts, prepared them, studied their catalytic, texture, acid, physical and chemical properties and explained the relationship between their catalytic properties. The results of the experiments were analyzed and based on them the author compiled and published articles and theses.

**The volume and structure of the work.** The dissertation consists of an introduction, four chapters, a conclusion and results. The volume of the dissertation consists of 150 pages with computer printing. The dissertation contains 26 figures, 25 tables and a list of 135 references.

## THE MAIN CONTENT OF THE WORK

**The introductory** part reflects the relevance of the research topic, the purpose of the work, the issues to be addressed, scientific innovations, the practical significance of the work, the main provisions of the defense, the summary of individual chapters.

**The first chapter** is devoted to a literature review. In this chapter, the structure of zeolites, their physicochemical and catalytic properties in the conversion of hydrocarbons are given. Transformation of methane and natural gas into aromatic hydrocarbons and kinetic regularities in the presence of zeolites were studied and Based on it, it was concluded that it is possible to regulate the physicochemical and catalytic properties of zeolites by changing the methods of preparation and modification.

**The second chapter** has been described the catalytic device, analysis of reagents and reaction products, methods of preparation of zeolite catalysts, methods of studying their physicochemical and acidic properties, conducting experiments and methods of product analysis.

**The third chapter** has been presented the results of the study of the physicochemical and catalytic properties of modified pentacyls in the transformation of natural gas by the method of impregnation.

**The fourth chapter** has been discussed the results of the physicochemical and catalytic properties of pentacyls modified by nano-sized metal powders and metal nanoparticles in the conversion of natural gas.

**In conclusion**, the results of the research are given.

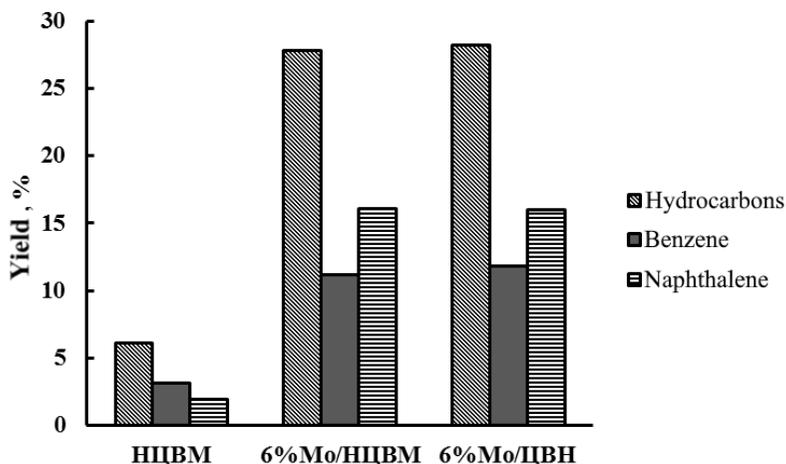
## **PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF PENTACYLS MODIFIED BY IMPREGNATION IN THE TRANSFORMATION OF NATURAL GAS**

**Catalytic properties of H-forms of pentasil-type zeolites in acid and natural gas conversion.** Taking into account the wider application of IJBM, ultrasonic and IJBH zeolites which belong to the ZSM-5 zeolite family and the catalytic properties of their non-modified H-forms have been studied, as catalysts in petrochemical processes. Non-modified forms of zeolites show low catalytic activity in the conversion of natural gas into aromatic hydrocarbons. In their presence, when the volume rate of the raw material is 1000 hrs<sup>-1</sup> and the reaction time is 60 minutes, the rate of conversion of natural gas is 12.8-14.0 wt%, the yield of aromatic hydrocarbons is 5.7-6.2 wt%, selectivity is 46.2-48.3%.

The study of the acidic properties of zeolites showed the presence of two types of active centers on their surface which are weak and strong acid centers. It seems that the strength and concentration of acid centers in these zeolites are different. Unlike H-ultrasyl and CVH zeolites, the concentration of strong acid centres is higher in SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> CVM zeolite with a mole ratio of 33. The concentration of strong acid centers in HIJBM zeolite is 563 μmol/g, which is higher compared to that of H-ultrasyl (542 μmol/g) and IJBH (534 μmol/g).

**Impact of the amount of molybdenum on the physicochemical and catalytic properties of zeolites in the conversion of natural gas.** When 2.0 wt% molybdenum is added to

zeolite ЦВМ, their catalytic activity and selectivity increase significantly. For example, at 750 °C, the yield of aromatic hydrocarbons increases from 6.1% to 15.88%, and the selectivity increases from 46.2% to 72.5%. When the content of molybdenum in zeolites increases to 4.0 wt%, the yield due to aromatic hydrocarbons increases sharply. For instance, at 750 °C it increases to 23.13%, and selectivity increases to 78.2%. When the amount of molybdenum in zeolite is increased to 6.0 wt%, its catalytic activity and selectivity change little. A further increase (8.0 күт.%) in the amount of molybdenum leads to some extent a decrease in its activity and selectivity (the selectivity decreases to 76.2%).



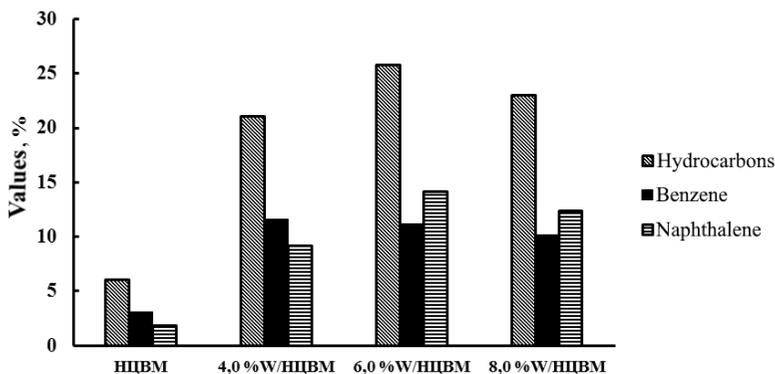
**Figure.1.** Impact of modification and zeolite nature on yield of aromatic hydrocarbons, benzene and naphthalene (T=750 °C, v=1000 hrs<sup>-1</sup>, P=0,1MPa).

1. This regularity is also observed in the presence of molybdenum-modified ЦВН zeolite. Due to their catalytic activity and selectivity, molybdenum-modified ЦВМ and ЦВН zeolites differ slightly from each other. The amount of benzene and naphthalene at 750 °C was 10.5 and 15.3%; 11.1 and 14.6%, respectively, in the presence of 6% Mo/ЦВМ and 6% Mo/ЦВН zeolites, (Fig. 3.1).

Among the catalysts, 4.0% -6% Mo/HЦBM has a higher selectivity due to aromatic hydrocarbons (78,2%) [1,4].

The different catalytic activity and selectivity of zeolites are explained by the redistribution of acid centres according to the strength in zeolite as a result of modification and the formation of new active centers. When the amount of molybdenum in the HЦBM zeolite is increased to 8.0 wt%, the ratio of the amount of weak acid centres ( $C_1$ ) to the amount of strong acid centres ( $C_2$ ) increases from 0.96 to 1.76. However, the samples with acid centres ratio of 1.67-1.69 show higher activity in the transformation of natural gas into aromatic hydrocarbons in the reduction of these samples [11].

**Impact of the amount of tungsten on the physicochemical and catalytic properties of zeolites in the transformation of natural gas.** The inclusion of 2.0 wt.% tungsten into the H-forms of zeolites results in increased efficiency in the transformation of natural gas. As the temperature increases, the conversion rate of natural gas and the yield of aromatic hydrocarbons in the presence of a tungsten-containing catalyst are increasing and at 750 °C, it is 22.3 and 16.6%, respectively, and the selectivity increases from 46.2% to 74.7%.



**Figure. 2.** The effect of modification and the nature of zeolite on the yield of benzene and naphthalene (conditions:  $T=750^{\circ}\text{C}$ ,  $v= 1000\text{hrs}^{-1}$ ,  $P= 0,1 \text{ MPa}$ )

When the amount of tungsten in the zeolite increases to 4.0 wt%, the rate of transformation of natural gas and the yield of aromatic hydrocarbons increases sharply, reaching 26.9% and 21.1%, respectively, at 750 °C, and the selectivity increases to 80.19%. When the amount of tungsten in the zeolite is increased to 6.0 wt%, the activity of the catalyst increases, and the selectivity decreases slightly to 77.5%. When the amount of tungsten is increased to 8.0 wt%, a decrease is observed in the activity and selectivity of the catalyst.

When HIIBM is modified with tungsten, its activity and selectivity for aromatic hydrocarbons increase sharply. Yield of aromatic hydrocarbons increases from 6.1% to 25.18%. 4% - 6% W/HIIBM zeolite shows the highest selectivity [11,12].

**Physicochemical and catalytic properties of bimetallic zeolite catalysts in the transformation of natural gas.** Monometallic catalysts synthesized by the inclusion of Mo and W into the composition of ZSM-5 zeolite by impregnation method using a solution of ammonium paravolframate and paramolybdate salts show significant catalytic activity in the transformation of natural natural gas. To increase their activity and selectivity, monometallic catalysts were modified with NTE and their combined promoter effects were studied.

When the La content of Mo and W-containing catalysts were increased by up to 1.0 wt%, the yield and selectivity of aromatic hydrocarbons significantly increase. At 750 °C and a volume speed of 1000 hrs<sup>-1</sup>, the rate of conversion of natural gas, the yield of aromatic hydrocarbons increases to 30.5-33.2% and 23.8-26.4%, respectively, and the selectivity is 79.7-80.1%. Increasing the amount of lanthanum in zeolite to 1.5 wt% has little effect on the yield and selectivity of aromatic hydrocarbons. When La in the content of zeolite is 2.0 wt%, the rate of transformation of natural gas and the release of aromatic hydrocarbons is significantly reduced. At 750 °C, the natural gas conversion rate is 27.0% and the selectivity is 77.0% (Table 1).

Thus, bimetallic catalysts containing 1.0-1.5% La and 4% -6% Mo (W) have higher activity and selectivity in the transformation of natural gas into aromatic hydrocarbons.

**Table 1.** Acid characteristics of bimetallic zeolite catalysts

Catalyst	T <sub>max.</sub> , form, °C		Concentration of acid centers, μmol/g	
	T <sub>1</sub>	T <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>
HЦБМ	198	418	628	542
4,0% Mo/HЦБМ	190	392	368	213
1.0% La 4,0% Mo/HЦБМ	189	404	358	236
1.5% La 4,0% Mo/HЦБМ	186	408	342	248
2.0% La 4,0% Mo/HЦБМ	173	392	302	201
4,0% W/HЦБМ	189	388	334	204
1,5% La-4,0% W/HЦБМ	185	410	346	240
2,0% La-4,0% W/HЦБМ	170	395	295	198

The study of the effect of the nature of NTE on the activity and selectivity of the catalyst showed that the nature of NTE has little effect on the activity of Mo-containing zeolite at the studied temperatures (700-750°C). All of them (La, Gd and Lu) have a high promoter effect on the activity of the Mo/HЦБМ catalyst. As a result of their impact at 700 °C, the yield of aromatic hydrocarbons increases from 14.7% to 26.5%.

The different activity and selectivity of modified zeolite catalysts can be explained by changes in the acid and texture properties of zeolite as a result of modification. When the amount of lanthanum in bimetallic catalysts is increased to 2.0 wt%, a decrease in the strength of concentration of the weak and strong acid centers of zeolite is observed. The concentration of weak acid centers decreases to 295-302 μmol/g, and the amount of strong acid centers decreases to 198-201 μmol/g.

When HЦБМ zeolite is modified with Mo, W and La redistribution of its acid centers and formation of new active centers

are occur. Changes in the ratio of acid centers in bimetallic catalysts cause changes in their catalytic properties in the conversion of natural gas [6,11,12].

**Physicochemical and catalytic properties of pentacyls modified by nano-sized metal powders and metal nanoparticles in the transformation of natural gas.** More active and stable catalysts are obtained by mechanical mixing of nano-sized powders of metals with carrier powders or by methods of impregnation of carrier multinucleated complexes with solutions of precursors. When the catalyst obtained by these methods is subjected to reduction and oxidation, the probability of the formation of large particles in the active phase is reduced.

Taking these into account, bimetallic catalysts were obtained by mechanical mixing of nano-sized forms of Cr, Mo, Zr, Cu and W metals and forms of pentacyl zeolites, and their physicochemical properties were studied in the direct conversion of natural gas into aromatic hydrocarbons.

Mono- and bimetallic catalysts have two types of acid centers: weak and strong acid centers. The amount of weak and strong acid centers increases when 1.0 wt% Zirconium is added to the 4.0% Mo/H $\beta$ BM catalyst; this is confirmed by the shift of low and high temperature peaks to the higher temperature range of the maximums. The amount of weak acid centers is 377  $\mu\text{mol/g}$  and the amount of strong acid centers is 240  $\mu\text{mol/g}$  for the 1.0% Zr-4.0% Mo/H $\beta$ BM sample and this is 48 and 42  $\mu\text{mol/g}$  higher, respectively, compared to the 4.0% Mo/H $\beta$ BM catalyst. The subsequent increase in the amount of zirconium leads to a decrease in the amount of both acid centers. However, new stronger acid centers are formed as a result of the modification of zirconium. The same regularity is also observed when modified by Cr. (Table. 2).

Thus, the study of the properties of the acid centres of the catalyst shows that redistribution of acid centres occurs due to their strength and concentration as a result of modification of 4.0% Mo/H $\beta$ BM catalyst with zirconium and chromium.

The addition of a second element (Cr, Zr) - a modifier to the Mo-containing catalyst causes a change in its catalytic properties in

the conversion of natural gas. The addition of 1.5 wt% nano-sized Zr (Cr) zirconium powder to a 4%Mo/HI $\beta$ BM catalyst increases the conversion rate of natural gas and the yield of aromatic hydrocarbons. At 750 °C, the conversion rate of natural gas increases to 41.0%, the yield of aromatic hydrocarbons increases to 33.5%, and the selectivity increase from 80.7% to 81.7%. Increasing the amount of Zr (Cr) in the 4% Mo/HI $\beta$ BM catalyst to 2.0 wt% reduces its activity (Table 3).

Thus, nano-sized powders of zirconium and molybdenum have a combined promoter effect on the catalytic properties of HCBM zeolite in the transformation of natural gas. Maximum yield of aromatic hydrocarbons from natural gas (27.3-33.5%) and selectivity (81.7-83.5%) in the temperature range of 700-750 °C is formed in 1.5% Zr - 4% Mo/HI $\beta$ BM bimetallic catalyst. This is due to the redistribution of zeolite acid centers as a result of modification. This pattern is also observed in the presence of pentacyls modified with Cr-W and Zr-W nano-sized powders.

**Table 2.** Acid properties of bimetallic zeolite catalysts

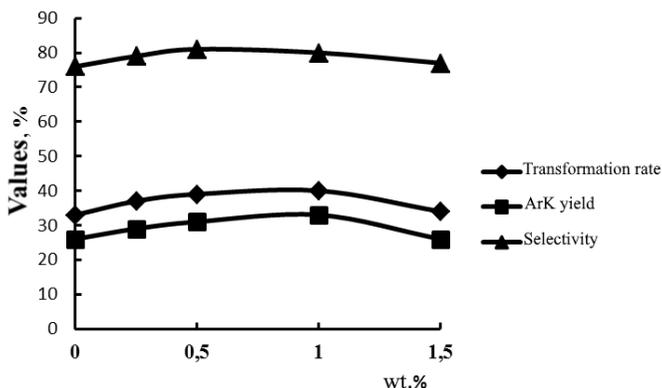
Catalyst	T <sub>max.</sub> , form, °C		Concentration of acid centers, μmol/g	
	T <sub>1</sub>	T <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>
4.0%Mo/HI $\beta$ BM	188	390	330	198
1.0%Zr – 4,0% Mo/HI $\beta$ BM	195	398	377	240
1.5%Zr – 4,0% Mo/HI $\beta$ BM	205	410	355	210
2.0%Zr – 4,0% Mo/HI $\beta$ BM	212	400	300	120
1.0%Cr – 4,0% Mo/HI $\beta$ BM-33	200	403	347	208
1.0%Cr – 4,0% Mo/HYC-103	215	350	148	77

C1 - weak acid centers, C2 - strong acid centers

**Table 3.** The effect of process temperature on the composition of products in the conversion of natural gas in the presence of modified bimetallic zeolite catalysts Cr and Zr

T <sup>o</sup> , C	X, %	Reaction products							yield of ArK, %	S <sub>APY</sub> %
		H <sub>2</sub>	Alkane s C <sub>2</sub> -C <sub>4</sub>	Alkene s C <sub>2</sub> -C <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>10</sub> H <sub>8</sub>	Ar K C <sub>11</sub> - C <sub>12</sub>		
4,0% Mo/HI <sub>2</sub> BM										
65 0	19.6 4	3.1 2	80.36	1.34	4.88	0.05	9.96	0.29	15.1 8	77.3
70 0	25.3 7	3.8 8	74.63	0.98	6.67	0.10	12.74	0.26	19.7 7	77.9
75 0	37.9 1	6.5 8	62.09	0.82	11.2 3	0.12	18.84	0.32	30.5	80.0
1.0% Zr-4,0% Mo/HI <sub>2</sub> BM										
65 0	22.0	3.5 5	78.0	1.23	5.35	0.07	11.42	0.38	17.2 1	78.2
70 0	27.8	4.6 5	72.2	0.95	7.42	0.15	14.25	0.43	22.2 5	80.1
75 0	39.4	6.8 2	60.64	0.78	12.7 4	0.12	18.44	0.54	31.8 4	80.7
1.5% Cr-4,0% Mo/HI <sub>2</sub> BM										
65 0	25.7 8	3.6 5	74.22	0.96	8.86	0.07	11.85	0.39	21.1 7	82.1
70 0	32.7 3	4.6 8	71.61	0.71	12.1 4	0.17	14.62	0.41	27.3 4	83.5
75 0	41.0	6.8 7	59.0	0.62	14.8 7	0.18	17.78	0.68	33.5 1	81.7
2.0% Cr-4,0% Mo/HI <sub>2</sub> BM										
65 0	21.7 5	3.2 3	78.25	1.13	6.86	0.09	10.23	0.21	17.3 9	79.9
70 0	30.2 3	4.5 2	69.77	0.94	11.8 7	0.12	12.46	0.32	24.7	81.9
75 0	38.1 1	6.7 4	61.89	0.78	13.5 2	0.14	16.64	0.28	30.5 8	80.2

When the amount of Cr (Zr) is 0.5-1.0 wt% in the 4%W/HIÇBM catalyst, the rate of transformation of natural gas increases to 39.2-41.4%, and the yield of aromatic hydrocarbons increases to 33.1-34.3%. Selectivity increases from 76.3% to 81.4%. When the amount of modifier is increased to 1.5%, its rate decreases to 31.3-36.5%, the yield of aromatic hydrocarbons reduces to 28.1%, and selectivity diminishes to 78% (Fig. 3) [5,7,10,13,16,17].

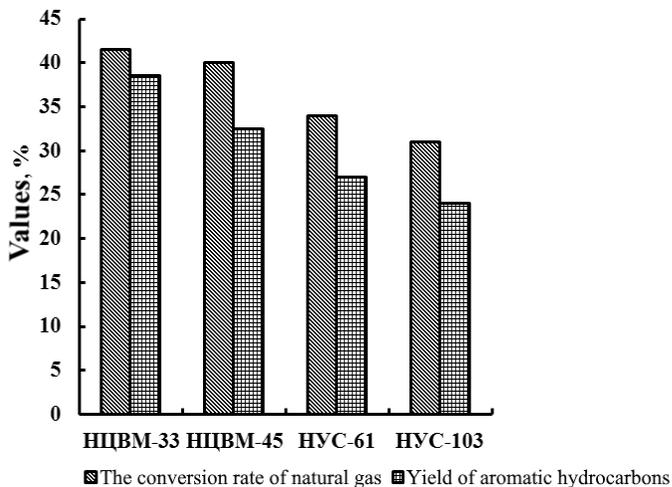


**Figure 3.** The effect of the amount of zirconium on natural gas transformation rate, aromatic hydrocarbon yield and selectivity in Cr-4% W/HIÇBM catalyst (conditions:  $T=750^{\circ}\text{C}$ ,  $v=1000 \text{ hrs}^{-1}$ )

**The effect of the value of zeolite silicate module on the properties of modified catalysts.** due to determine the effect of the price of zeolite silicate module on the properties of modified catalysts in the process of natural gas conversion, pentacyl zeolites with modulus values of 33, 45, 61, and 103 were taken and modified with 4.0 wt% Mo and 1.0 wt% Cr nano-sized powders, respectively, and their catalytic properties were investigated.

Silikat modulun qiyməti əmələgələn məhsulların keyfiyyət tərkibinə mühüm dərəcədə təsir etmir, lakin katalizatorun ümumi və aromatikləşdirici aktivliyini təyin edir (şək. 4). Silikat modulu 33 və 45 seolitlər daha yüksək aktivlik göstərir. Bu seolitlər əsasında

katalizatorların iştirakında 750°C-də təbii qazın aromatik karbohidrogenlərə çevrilmə dərəcəsi 39.8-41.4%, seçicilik isə 80.2-80.7 % təşkil edir. Silikat modulu 103-ə qədər artırdıqda, yeni seolitın karkasında alüminiumun azalması təbii qazın çevrilmə dərəcəsinə və aromatik karbohidrogenlərin çıxımını aşağı salır [8,12]

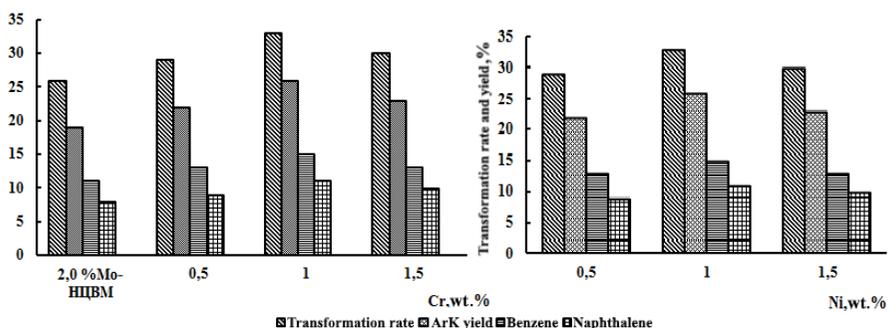


**Figure. 4.** The effect of the silicate module on the rate of transformation of natural gas and the release of aromatic hydrocarbons in the bimetallic 1.0% Cr - 4% Mo/H -pentacycl catalyst.

**Catalytic properties of bimetallic catalysts modified with chromium, copper, nickel, molybdenum and tungsten carbonyls in gas transformation.** As a result of research, it was determined that bimetallic catalysts modified with nano-sized metal powders have higher catalytic activity and selectivity than bimetallic catalysts prepared by the impregnation method in the conversion of natural gas. The stable operating time of these catalysts is 10 hours. Carbonyls of metals were used to increase the lifetime of bimetallic catalysts in their preparation. It was found that when Mo and W are 2.0 wt% blunt in the HİBM the higher the transformation rate of natural gas and the yield of aromatic hydrocarbons is observed. At 700 °C, the conversion rate of

natural gas is 26.3-27.5%, and the yield of aromatic hydrocarbons is 19.4-20.6%. When H<sub>2</sub>QBM zeolites containing 2.0 wt% Mo are modified with chromium and nickel carbonyls, their catalytic properties change significantly.

The addition of small amounts (0.5 wt%) of chromium to the content of Mo/H<sub>2</sub>QBM increases the rate of transformation of natural gas and the yield of aromatic hydrocarbons. The transformation rate of natural gas increases from 26.3% to 33.2%, and the yield of aromatic hydrocarbons increases from 19.4% to 26.3%. Under the same conditions, the amount of benzene increases from 11.2% to 15.4%. When the amount of chromium in the composition of catalyst is increased to 1.5 wt%, natural gas conversion rate and reduction of aromatic hydrocarbon yields are observed. The conversion rate of natural gas is reduced to 30.4%, and the yield of aromatic hydrocarbons is reduced to 23.3%. (Fig. 5).



**Figure 5.** The relationship between the amount of chromium and nickel in the composition of Mo/H<sub>2</sub>QBM between the transformation of natural gas and the reaction products.

Unlike chromium, the promoter effect of nickel on the activity of Mo/H<sub>2</sub>QBM the catalyst is somewhat weak. When Mo/H<sub>2</sub>QBM is added to the catalyst in the amount of 1.0-1.5 kg.%, the conversion rate of natural gas increases to 29.4-30.1%, and the yield of aromatic hydrocarbons increases to 22.3-23.1%. In this case, the amount of benzene in the composition of reaction products varies little, and the amount of naphthalene increases from 8.2 to 12.1%. The same pattern

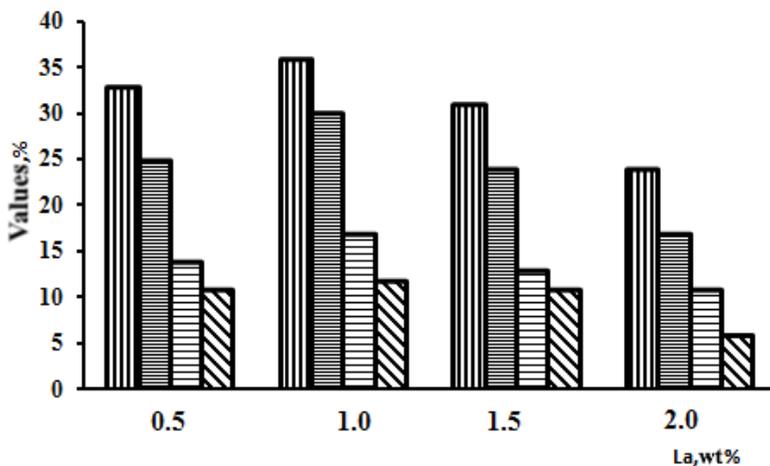
is observed in the presence of a catalyst containing Mo and W, modified with Cr and Cu carbonyls. Unlike chromium, the inclusion of copper in 2.0% W/HI $\alpha$ BM zeolite does not significantly affect its activity. When 0.5-0.75 wt% copper is added to the composition of 2.0% W/HI $\alpha$ BM catalyst, the rate of conversion of natural gas and the yield of aromatic hydrocarbons increases by only 1.5-2.0%. When the amount of copper in the catalyst is increased to 1.0 wt%, The rate of conversion of natural gas and the yield of aromatic hydrocarbons decreases.

Thus, 2.0% Mo/HI $\alpha$ BM and 2.0% W/HI $\alpha$ BM which are modified with chromium carbonyl has a higher promoter effect among the bimetallic catalysts studied. The optimal amount of chromium in this catalyst is 1.0 wt% [22,23,26].

#### **Catalytic properties of Mo (W) carbonyls and pentacyls modified with La carbonate in the transformation of natural gas.**

As a result of research, it was determined that NTE-Mo/H-pentacyl and NTE-W/H-pentacyl obtained by impregnation show high catalytic activity at 750 °C in the conversion of natural gas. Taking this into consideration, this type of catalytic system was obtained on the basis of molybdenum, tungsten carbonyls and lanthanum carbonates, and their catalytic properties were studied in the conversion of natural gas (Fig. 6). La has a promoter effect on the activity of catalysts and its optimal amount is 1.0 wt%. It has been shown that the yield of aromatic hydrocarbons increases with increasing temperature in the presence of 1%La2.0%Mo/HI $\alpha$ BM catalyst. However, the yield of benzene exceeds the maximum. Its maximum yield which is 17.2% observed at 700 °C. When the reaction temperature is raised to 750 °C, the yield of benzene decreases and the yield of naphthalene increases sharply. At 750 °C, the amount of naphthalene increases to 19.3%.

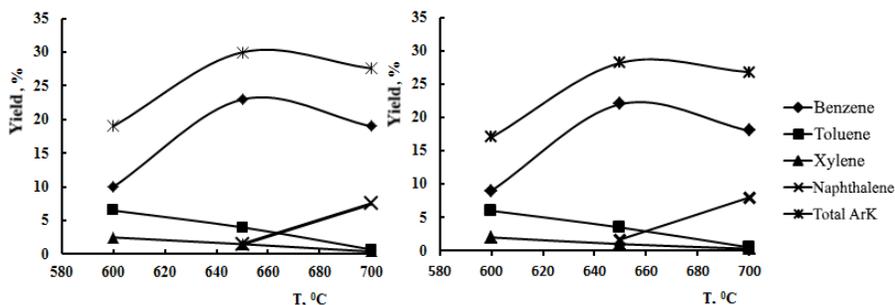
The optimum temperature for the 1% La 2.0% Mo/HI $\alpha$ BM catalyst can be selected at 700 °C depending on the yield of benzene. The bimetallic catalyst prepared by this method has a high activity compared to bimetallic catalysts obtained by other methods in the transformation of natural gas. The yield of benzene is 5.0-6.0% higher at temperatures below 50 °C, namely at 700 °C [19,20,22,26].



**Figure 6.** The dependence between the amount of lanthanum, the rate of natural gas conversion in the composition of 2.0% Mo / HCVM catalyst and the yield of aromatic hydrocarbons, benzene and naphthalene in the conversion of natural gas ( $T=700^{\circ}\text{C}$ ,  $v=1000\text{saat}$ )

**Catalytic properties of polymetallic zeolite catalysts in the transformation of natural gas.** Catalysts synthesized on the basis of Mo, W carbonyls and La carbonates show high activity in the conversion of natural gas at  $700^{\circ}\text{C}$ . In their presence, the yield of aromatic hydrocarbons is 30-32%. Aromatic hydrocarbons consist mainly of benzene and naphthalene. The catalyst maintains high activity for 10 hours. When the transformation of natural gas is carried out at high temperatures a significant portion of aromatic hydrocarbons converted to naphthalene series hydrocarbons by condensation and as a result, the amount of more valuable benzene is reduced and the stable lifetime of the catalyst is reduced. It is necessary to increase its dehydrogenation capacity and minimize the strength of the bransted acid centers to maintain a high level of catalyst activity at relatively low temperatures. Taking these into account, the bimetallic La-Mo-H-pentacyl and La-W/H-pentacyl catalysts were modified with Zn and Cd, which have high dehydrogenation properties. Zn and Cd were incorporated into pentacyls by ion exchange method to reduce the strength of the

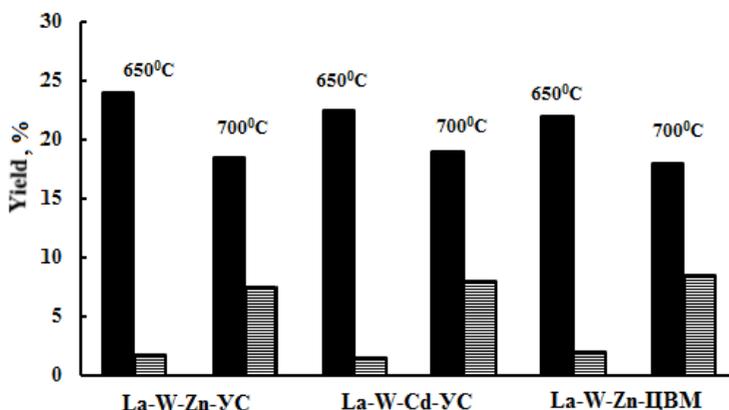
branded acid centers. Their ion exchange rate was 71-73% eq. After exchange, 0.73 Zn-pentacyl and Cd-pentacyl are modified with the metal carbonyls mentioned above. La-Mo-Zn-pentacyl, La-Mo-Cd-pentacyl, La-W-Zn-pentacyl and La-W-Cd-pentacyl polymetallic catalysts were synthesized and their catalytic properties were studied in natural gas conversion. Şək. 7-də 1% La-2%Mo-Zn-İİBM və 1% La-2%Mo-Cd-İİBM katalizatorun iştirakında təbii qazın çevrilməsinin temperaturdan asılılığı verilmişdir. The temperature dependence of the conversion of natural gas in the presence of 1% La-2% Mo-Zn-İİBM and 1% La-2% Mo-Cd-İİBM catalyst are given in the figure 7.



**Figure 7.** Temperature dependence of the yield of aromatic hydrocarbons obtained from the transformation of natural gas in the presence of 1% La-2% Mo-Zn-İİBM and 1% La-2% Mo-Cd-İİBM catalysts.

It seems that in the presence of a polymetallic zeolite catalyst, at 600 °C the amount of benzene reaching the maximum is 22.3-23.4%. Under the same conditions, the amount of benzene in the presence of a bimetallic catalyst is 17.4-18.5%. High catalytic activity is shown in 1% La-2,0% W-Zn-ultrasil, 1% La-2,0% W-Cd-ultrasil and 1% La-2,0% W-Zn-İİBM polymetallic catalysts (fig. 8).

Thus, in contrast to bimetallic catalysts, polymetallic catalysts have a higher catalytic activity in the transformation of natural gas into aromatic hydrocarbons (şək. 8). In the presence of polymetallic catalysts, the conversion of natural gas occurs at relatively lower temperatures, and therefore the yield of benzene is higher.



**Figure 8.** Yield of benzene and naphthalene in the presence of polymetallic catalysts.

The results show that the aromatization capacity of the catalyst depends significantly on the nature of the modifier and its compounds and the method of their inclusion into the zeolite [23,25,26].

**Texture characteristics and physicochemical properties of modified catalysts.** X-ray structure studies confirm the phase stability of zeolite modified with La and Mo. The inclusion of modifiers does not cause structural and phase changes in pentasil, and thus the change in catalyst activity cannot be related to the modifier's replacement of Al atoms in the zeolite structure. La, Zn, Cd are located as compensating cations of  $\text{AlO}_4^-$  tetrahedron in the lattice, while molybdenum and tungsten are located as oxides on the surface and channels of the zeolite. Modifiers penetrating the zeolite in the form of cations can change the acid centres of zeolite, and modifiers that are penetrating in the form of oxides can change its texture properties.

It seems that when Zn is added into the HIIIBM zeolite by ion exchange method, its surface area and pore volume does not change practically. When 1.0 wt% of lanthanum and 2 wt% of molybdenum are added to zeolite by the impregnating method, its surface area and

pore volume are significantly reduced. The surface area decreases from 266.3 m<sup>2</sup>/g to 242.4 m<sup>2</sup>/g, and the pore volume decreases from 0.246 cm<sup>3</sup>/g to 0.208 cm<sup>3</sup>/g. When 1.0 wt% of lanthanum, 2.0 wt% of molybdenum and 0.68 wt% of zinc were added to the composition of zeolite, these values decrease to 238.2 m<sup>2</sup>/g and 0.189 cm<sup>3</sup>/g, respectively. The change in the volume of the pores of zeolite as a result of modification undoubtedly affects also its sorption capacity variations. It has been determined that when Zn<sup>+2</sup> ions are introduced into the zeolite by the ion exchange method, its sorption capacity has changed less compared to benzene and n-heptane. As the amount of modifier in zeolite increases, its sorption capacity compared to benzene and n-heptane decreases. When three modifiers were added to the composition of zeolite, its sorption capacity varies significantly compared to benzene and n-heptane. The sorption capacity of La-Mo/ZnIIBM and La-W/ZnIIBM catalysts according to benzene and n-heptane decreases from 0.142 cm<sup>3</sup>/g and 0.168 cm<sup>3</sup>/g to 0.065-0.069 cm<sup>3</sup>/g and 0.079-0.084 cm<sup>3</sup>/g, respectively, compared to the initial IIBM zeolite.

The obtained results show the chemical interaction of the modification in zeolite. Therefore, the sorption capacity of zeolite varies in accordance with benzene, n-heptane and methane, which manifests itself in the molecular grid properties of zeolite. (Table. 5) Having narrower pores of polymetallic zeolite catalysts makes impossible the formation of naphthalene in their channels. Naphthalene can only form on its surface at high temperatures.

**Table 5.** The adsorption capacity of modified catalysts in accordance with methane (cm<sup>3</sup>/g)

IIIB M	IIIBM+ Mo	IIIBM+Mo ,La	IIIBM+W, Cr	ZnIIBM+W ,La	ZnIIBM+W ,Cr
0.047	0.054	0.069	0.071	0.082	0.080

Thus, the amount of methane sorbed increases as a result of the modification of the catalyst, which directly affects the rate of transformation and the yield of aromatic hydrocarbons.

According to M.M. Dubini's opinions, molecules of paraffin

C1-C5 are not able to form sufficiently long, densely packed chains in the zeolite channels and the increase in the amount of adsorbate in the channels and pores of zeolite greatly simplifies the process of aromatization of methane and its homologues due to the regular convergence of molecules.

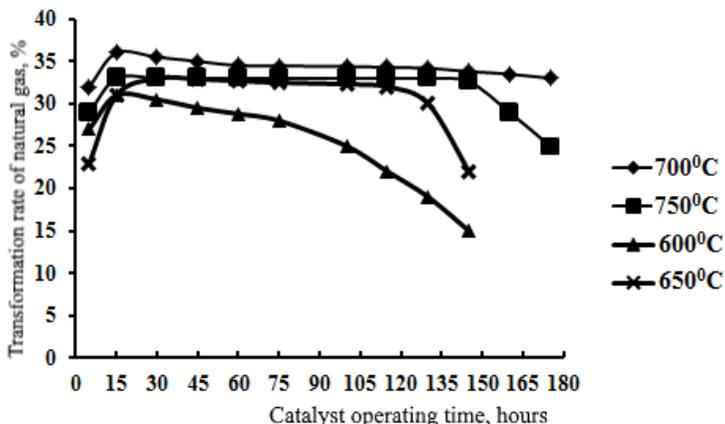
It is also one of the reasons for the change in the activity of zeolites in the conversion of hydrocarbons may be a variation in the strength and concentration of acid centres in the zeolite. Considering that the decomposition of paraffin hydrocarbons occurs in the Brensted and Lewis acid centres of zeolite, a change in their ratio may lead to a change in the activity of the catalyst.

The acidic properties of the catalysts were studied by the TPD method of ammonia to confirm the nature of the catalytic activity of modified zeolites. It was found that the amount of strong and weak acid centres decreases when metal adds into the composition of HIQBM zeolite. When the amount of metal in the content of zeolite is increased the number of strong acid centres with the activation energy of  $E > 130$  (kJ/mol) decreases. However, when Mo and La are added to the content of zeolite, the value of the activation energy of ammonia desorption increases in these samples. The increase in activation energy confirms the formation of strong aprotic acid centers of zeolite as a result of modification. Stronger aprotic centers are formed on the 1%La 2% Zn-2%Mo/HIQBM catalyst. It is clear from the results obtained that the catalytic activity of zeolite depends not only on the proton and aprotic centres of both acid centres, but also on their proportion. Both centers are involved in the catalytic process.

Thus, changes in the texture characteristics of zeolite, redistribution of acid centres and the formation of new stronger aprotic acid centres, C-H bonds in the molecules of methane and its homologues are able to polarize as a result of the modification [16,18,22,23,24].

**The impact of thermal process and particle size on catalytic activity and stability of the polymetallic catalyst.** 1%La-2%Zn/2%Mo/HIQBM catalyst was processed at 600 °C, 700 °C and 750 °C for 4 hours and its catalytic activity and stability were studied

in the natural gas transformation to study the impact of the thermal process. It appears that unlike polymetallic catalysts thermally processed at 400 °C, 650 °C and 750 °C for 4 hours, polymetallic catalysts thermally processed at 700 °C have a more stable performance. In the presence of this catalyst, the natural gas conversion rate increases to 35.7% and the catalyst activity change slightly during 180 hours of operation (Fig. 9).



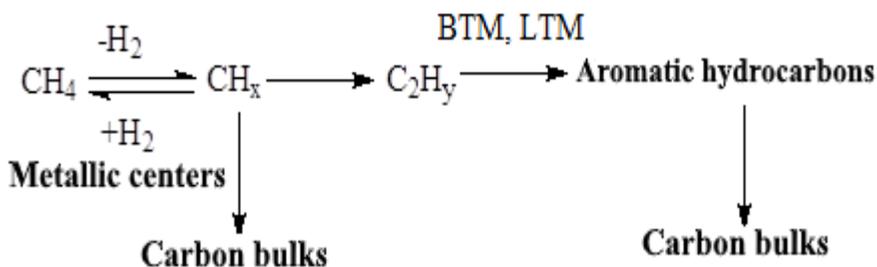
**Figure. 9.** Dependence of the rate of conversion of natural gas in the presence of thermally processed polymetallic zeolite catalyst on its operating time (the particle size of catalyst - 3 mm).

The dependence between the rate of transformation of natural gas in the presence of polymetallic catalysts of various sizes and its operating time was studied and it was determined that the size of the catalyst particles significantly affects its catalytic activity. The catalyst shows higher activity when the particle size is 2.5mm. When the catalyst is thermally processed at 700 °C and the particle size is 2.5 nm, its operating time increases to 180 hours.

The aromatization function of modified pentacyls is more sensitive to the transformation of active centres, and its change can occur considerably under the impact of various factors (temperature, environment, reagents).

The stable operation time of the catalyst is reduced due to H-

pentacyls modified with La, Cr, Ni, Mo and other metals are unable to maintain the required acidity to carry out the aromatization reaction during the reaction. After the thermal process of pentacyl zeolites, when ion exchange with Zn or Cd salts and then modifying them with Mo or W carbonyls and La carbonate the required L/B ratio for the aromatization of methane to intermediate products from the non-oxidative conversion is formed. Stable operation of the catalyst is ensured when this ratio is 1.1-1.2. Thus, along with the Brensted acid centres of zeolite, Lewis acid centres also play an important role in the aromatization process of natural gas components [18,19,23,24]. Taking this into account, the non-oxidative conversion of the methane molecule, the major component of natural gas, can be described as follows:



BTM-Brensted acid centers, LTM-Lewis acid centers

## KEY FINDINGS

1. For the first time, the effect of systematic preparation methods and modification conditions on the physicochemical and catalytic properties of pentacyl-type high-silicon zeolites modified with rare earth and d-elements (Mo, W, Zr, Cr, Ni, Zn, Cd) in the process of conversion of natural gas into aromatic hydrocarbons was studied [1,4,7,8,9,10,13].
2. The combined promoter effect of the metals NTE, Cr, Zr, Fe with Mo and W on the catalytic properties of pentacyl was found. The combined promoter effect of the metals NTE, Cr, Zr, Fe, Mo and

W on the catalytic properties of pentacil was found. It has been shown that the addition of NTE and d-elements to the zeolite containing Mo and W increases the activity and selectivity of the catalyst in the acquisition of aromatic hydrocarbons from natural gas components [11,12,15,16,17].

3. It has been determined that the concentration of the metal and the method of its application to the surface of the catalyst considerably affect the physicochemical and catalytic properties of pentacillin. Bimetallic catalysts obtained by mechanical mixing of metal nanopowders with pentacil and adsorption of metal precursors with pentacyl show the highest activity and selectivity in the acquisition of aromatic hydrocarbons [14,19,20,21,26].
4. Based on the results obtained by the derivatography, X-ray, ammonia TPD, IR spectroscopy and BET methods, it has been reported that the modifier chemically interacts with the crystal lattice of zeolite in the process of modification and it leads to redistribution of acid centres and changes in the porous structure and activity of the catalyst [2,7,11,13].
5. It is reported that modification of H-pentacillin with metals leads to a decrease in the total amount of acid centres and the destruction of strong Brensted acid centres due to blockade of "bridge" hydroxyl groups with metal cations, molybdate and tungstate groups, as well as an increase in medium-strength acid centres and the formation of new, stronger aproton centres on the surface of the zeolite that these aproton centres also combine with proton centres to selectively obtain aromatic hydrocarbons and form complex active centres. Lewis acid centres also play an important role in the conversion of natural gas into aromatic hydrocarbons along with Brensted acid centres. Polymetallic zeolite ensures stable operation of the catalyst when the L/B ratio is 1.1-1.2 [19,22,23].
6. For the first time, new Cr-Mo (W), La-Mo(W)-Zn, La-Mo(W)-Cd polymetallic catalytic systems have been developed for the conversion of natural gas into aromatic hydrocarbons, which provide high yield (32-35%), selectivity (82-85%) and capable of stable operation time (200 hours) of aromatic hydrocarbons at

relatively low temperatures (600-650 °C) [18,23,24,25].

**The main results of the dissertation study are published in the following scientific works**

1. Ганбарова Е.А., Алиев Т.А., Мамедов С.Э. Превращение природного газа на модифицированных пентасилах / *Ümummilli lider Heydər Əliyevin anadan olmasının 91-ci ildönümünə həsr olunmuş VIII Respublika Elmi Konfransı, Bakı:- 2014,- s.109-110.*
2. Ганбарова Е.А., Масмалиева Т.А., Мамедов С.Э., Алиев Т.А. Превращение природного газа и метанола на цеолитах типа пентасила, модифицированных нанопорошками хрома и молибдена // *Актуальные проблемы естественных наук, Россия, Тамбов:- 2015,- с.108-114.*
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The defense will be held on 30 June 2022 at 11:00 at the meeting of the Dissertation council FD.010252 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Nakhchivan Branch of the National Academy of Sciences of Azerbaijan.

Address: Az 7000, Nakhchivan city, Haydar Aliyev avenue 76.

Dissertation is accessible at library of the Nakhchivan Branch of the National Academy of Sciences of Azerbaijan.

Electronic versions of dissertation and its abstract are available on the official website of the <http://www.e-kitab.ameanb.nmr.az>

Abstract was sent to the required addresses on 11 february 2022.

Signed for print: 07.02.2022

Paper format: 60×90<sup>1/16</sup>

Volume: 45.079

Number of hard copies: 30

