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**ABSTRACT**

of the dissertation for the degree of Doctor of Science

**NOVEL POLYFUNCTIONAL POLYMETALZEOLITE  
CATALYSTS: SYNTHESIS, PROPERTIES IN C<sub>7</sub>-C<sub>8</sub>  
AROMATIC HYDROCARBONS CONVERSIONS AND  
C-C BOND PROCESSING REACTIONS**

Speciality: 2307.01 – Physical Chemistry

Field of science: Chemistry

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**BAKU – 2024**

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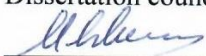


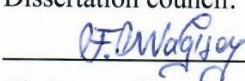
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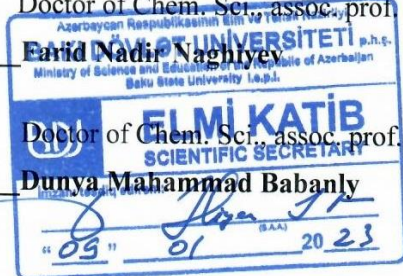
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## INTRODUCTION

**The actuality of the theme and degree of elaboration.** The optimization of the selectivity of catalytic systems is one of the most crucial challenges in catalysis.

The development of scientific fundamentals for the preparation of paraselective catalysts for isomerization, disproportionation, trans-alkylation of alkylaromatic hydrocarbons and conversion of methanol and bioethanol into hydrocarbons, which are an alternative to petroleum feedstock, is one of the most important directions.

The para-isomers of alkylaromatic hydrocarbons are very valuable products and are widely used in organic and petrochemical synthesis. Among these hydrocarbons, p-xylene and p-diethylbenzene occupy a special place. P-Xylene is used as a raw material in the production of terephthalic acid, polyethylene terephthalate, fibers, and plasticizers. In recent years, the processes of toluene disproportionation and C<sub>8</sub>-aromatic fraction isomerization in the presence of mor-denite-type zeolite catalysts have been used to increase the production of p-xylene. However, since the amount of p-xylene in the xylene fraction in these processes is 22-24%, it is difficult to separate it from m-xylene<sup>1</sup>.

p-Diethylbenzene, another isomer of alkylaromatic hydrocarbons, is used as a valuable raw material mainly in the production of ion exchange resins and p-divinylbenzene, and as a desorbent in the process of separating p-xylene from the C<sub>8</sub>-aromatic fraction by the adsorption method<sup>2</sup>.

In industry, p-diethylbenzene is produced both by the adsorption method from a mixture of economically unfavorable alkylaromatic hydrocarbons, and by the process of disproportionation of ethylbenzene in the presence of aggressive Friedel-Crafts catalysts, which do not meet environmental requirements.

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<sup>1</sup> Albahar, M. The effect of ZSM-5 zeolite crystal size on p-xylene selectivity in toluene disproportionation / M.Albahar, L.Chaozhou, V.L.Zholobenko [et al] // Microporous and Mesoporous Materials, – 2020. vol.302, – p.110221-110225.

<sup>2</sup> Glotov, A. Bizeolite Pt/ZSM-5:ZSM-12/Al<sub>2</sub>O<sub>3</sub> catalyst for hydroisomerization of C-8 fraction with various ethylbenzene content / A.Glotov, N.Demikhova, M.Rubtsova [et al.] // Catalysis Today, – 2021. vol.378, – p.83-95.

The application of zeolites in the development of the production of mono- and dialkylbenzenes in the presence of a heterogeneous catalyst is a more promising direction because it prevents the formation of toxic volatile organic compounds, which is characteristic to Friedel-Crafts catalysts. Since zeolite-based catalysts are characterized by very low tar formation and waste generation, they are highly active, selective and regenerative.

The study of literature sources shows that catalysts based on mordenite (channel size 6.5×7.0Å; 2.6×5.7Å) and Y (channel size 7.4×7.4Å) zeolites with a 2D channel system quickly lose their sufficient activity in the conversion of alkylaromatic hydrocarbons and alcohols, heavy aromatic hydrocarbons prevail in the composition of the obtained products. Higher activity and stability are shown by medium-porous ZSM-5, ZSM-11 and BEA (beta) zeolites with a system of medium 3D channels. Zeolites with a pore diameter of 5.1-6.0Å belong to the medium-pored zeolites, and catalysts based on this group of zeolites show selectivity for molecules of reagents and products.

ZSM-5 zeolite with straight and sinusoidal channels (dimensions 5.1×5.3Å) intersected between high-silica zeolites allows the synthesis of small-sized aromatic hydrocarbon molecules, prevents the accumulation of polycondensed aromatic hydrocarbons in the pores, and therefore provides conditions for the stable operation of the catalyst<sup>3</sup>.

Although there are a large number of works on the conversion of methanol and ethanol to aromatic hydrocarbons in the presence of zeolite catalysts, studies focusing on their conversion towards p-xylene are quite limited<sup>4</sup>.

Not enough attention has been paid to the study of the depend-

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<sup>3</sup> Farshadi, M., Falamaki C. Ethylbenzene disproportionation and p-xylene selectivity enhancement in xylene isomerization using high crystalline desilicated HZSM-5 // Chinese Journal of Chemical Engineering, – 2018. vol.26, –p.116-126.

<sup>4</sup> Bai, Y. Conversion of Methanol to Para-Xylene over ZSM-5 Zeolites Modified by Zinc and Phosphorus / Y.Bai, X.Niu, Y.-E.Du [et al.] // Molecules, – 2023. vol.28, – p.4890-4906.

ence of the paraselectivity of ZSM-5 zeolites on the method of introduction of promoters, their nature and density, the strength and distribution of acid sites of the catalyst, ratios of Lewis and Brønsted acid sites, pores and textural properties of the zeolite.

That is why, the study of ZSM-5 zeolite modified with various transitions, rare earth metals, non-metals and nanopowders of spinel-structured compounds, the development of the scientific basis of the synthesis of paraselective catalytic compositions, the determination of the laws of interaction between their physico-chemical and catalytic properties, the systematization of the obtained results and the selection of a paraselective catalyst for the studied reactions are important scientific issues and of fundamental and applied importance.

**The object and subject of the research.** The objects of research are toluene, m-xylene, ethylbenzene, methanol, bioethanol and their conversion products, as well as catalysts based on ZSM-5 zeolite modified with transition metals, lanthanoid metals and spinel structured  $\text{NTE}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$  nanopowders doped with lanthanides. The subject is the study of the effect of the obtained catalytic systems on the acid properties, strength, distribution, proportion and textural characteristics of Brønsted and Lewis acid sites using modern physico-chemical methods.

**The purpose of the work** is scientific justification of the selection of catalytic systems for disproportionation, isomerization of  $\text{C}_7$ - $\text{C}_8$  aromatic hydrocarbons, and conversion of methanol and ethanol into hydrocarbons, synthesis of catalysts based on ZSM-5 zeolite modified with transition metals, lanthanoid metals and spinel structured  $\text{NTE}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$  nanopowders doped with lanthanides, to determine the interaction between their physico-chemical, acid, textural properties, catalytic activity and paraselectivity, as well as to develop paraselective catalysts with polyfunctional properties for those processes.

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

- Development of new catalytic composition systems with polyfunctional properties and high paraselectivity based on HZSM-5 zeolite modified with transition metals, lanthanoid metals and spinel structured  $\text{NTE}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$  nanopowders doped with lanthanides for

the processes of disproportionation and isomerization of C<sub>7</sub>-C<sub>8</sub> aromatic hydrocarbons, conversion of methanol and ethanol into hydrocarbons, study of their physico-chemical, acid and catalytic properties;

- Study the effect of the modification on the acid properties of the catalytic system, the strength, distribution, ratio and textural characteristics of Brønsted and Lewis acid sites;
- Examination of the dependence of the paraselectivity of the catalytic systems on the nature of the modifier, its amount, the ratio of acid sites and the volume of pores;
- Studying the regularities of reactions of disproportionation, isomerization of C<sub>7</sub>-C<sub>8</sub> aromatic hydrocarbons, and conversion of methanol and ethanol into hydrocarbons with the participation of catalytic composition systems;
- Selection of optimal catalytic systems with high paraselectivity for the studied processes.

**The research methods.** Modern physico-chemical methods of analysis were used in the delivery of the work for a comprehensive approach to the desired objectives. Physico-chemical analysis methods including low-temperature nitrogen adsorption methods (BET and BJH), ammonia chemisorption, IR spectroscopy, X-ray phase analysis, scanning electron microscope, AAC research methods were widely used for catalyst characterization. The determination of the composition of hydrocarbon products was carried out by the Agilent 7890A gas-liquid chromatography method according to GOST R 52714-2007. Testing of catalysts in the process of conversion of aromatic hydrocarbons, methanol and ethanol was carried out in a continuous tubular reactor, which allows the process to be carried out under different conditions.

**The main provisions of the defense.**

- The influence of the nature and quantity of modifiers in the disproportionation, isomerization of C<sub>7</sub>-C<sub>8</sub> aromatic hydrocarbons, the conversion of methanol and bioethanol into hydrocarbons, and the methods of loading them into zeolite on the activity of bi- and polymetallic catalysts based on ZSM-5 zeolite, as well as on the selectivity of disproportionation, isomerization and aromatization;
- Dependence between the nature and quantity of the modifier

of acid and textural properties of zeolite;

- The effect of the modifier on the density, strength, and nature of the acid centers of zeolite;

- Dependence of the paraselectivity of the catalyst on the amount of the modifier, the ratio of acid centers and the volume of the pores;

- Regularities of conversion of toluene, ethylbenzene, C<sub>8</sub> aromatic fraction, methanol and ethanol in the presence of ZSM-5 zeolite-based catalysts modified with transition lanthanoid metals and spinel nanopowders;

- Basic principles of development of paraselective catalysts based on ZSM-5 zeolite;

- The perspective of using the main results of the dissertation.

**Scientific novelty of the work.** Scientific bases of synthesis of highly paraselective catalytic compositions modified with ZSM-5 zeolite for disproportionation and isomerization of C<sub>7</sub>-C<sub>8</sub> aromatic hydrocarbons, conversion of methanol and ethanol into hydrocarbons by various methods, compounds of lanthanoid metals, phosphorus and spinel structure NTE<sub>x</sub>Mg<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> doped with NTE developed.

- New results were obtained on the effect of the nature, amount and modification methods of modifiers on the properties of multi-functional catalytic systems based on ZSM-5 zeolite, on the selectivity of formation of para-substituted aromatic, isoparaffin and C<sub>2</sub>-C<sub>4</sub> olefinic hydrocarbons.

- The effect of the modification on the textural properties of ZSM-5 zeolite, the nature, strength, density, distribution of acid sites and the paraselectivity of the catalytic system was studied. It was determined that the ratio of B/L sites due to the reduction of the density of Brønsted acid sites and the formation of new stronger Lewis acid sites as a result of the modification changes.

- Metal or metal oxide nanoparticles localize on the outer surface and pores of zeolite and form hydro-dehydrogenation centers, as well as the reduction of the volume of entrance windows and pores of zeolite; there is an increase in the share of micro- and mesopores, which leads to an increase in the paraselectivity of the catalytic system.

It was determined that, as a result of the modification, phos-

phate groups of cations, in contact with the "bridging" hydroxyl groups of H-ZSM-5 zeolite, replace part of the protons, reducing the number of strong Brønsted acid sites on its surface and pores, creating new Lewis acid sites, metal or metal oxide nanoparticles localization on the surface and pores of the zeolite.

Several types of active centers (Brensted and Lewis acid sites, metal or metal oxide nanoparticles) are involved in the reactions of disproportionation, isomerization, conversion of methanol and ethanol into hydrocarbons, and the number and ratio of these centers depends on the nature and amount of the modifier.

**Theoretical and practical significance of the research.** The results obtained in the presented work have created the basis for determining the principles of selection of new effective catalytic composition systems of ZSM-5 zeolite with transition Ln metals,  $Ce_xMg_{1-x}Al_2O_4$  and  $Ho_xMg_{1-x}Al_2O_4$  nanopowders for the processes of disproportionation, isomerization, and conversion of methanol and bioethanol into olefin, isoparaffin and aromatic hydrocarbons.

Low-temperature adsorption of catalytic compositions of nitrogen, chemisorption of ammonia, X-ray phase, IR spectroscopy, physico-chemical studies conducted with SEM methods, formation of active centers in catalysts, detection of factors affecting paraselectivity, development of paraselective catalytic compositions, allow the development this type of new systems in the future.

The results of the dissertation can be used by specialists engaged in research in the direction of disproportionation, isomerization of aromatic hydrocarbons and transformation of saturated diatomic alcohols, which are alternative raw materials, into olefin, high-octane components.

**Publishing and approbation of the work.** Overall, 56 scientific works related to the subject of the dissertation, including 23 articles (11 in indexed journals), 33 theses (18 international) have been published. The most important achievements of this dissertation have been presented at local and international conferences: Materials of IX, X, XI, XII scientific conferences of postgraduates, masters and young researchers on "Actual problems of chemistry" dedicated to 85, 87, 88, 89, 90, 91, 93, 94, 95, 96<sup>th</sup> anniversaries of National Lider Heydar Aliyev, (Baku, 2007, 2010, 2011, 2012, 2013, 2014, 2016,



2017, 2018, 2019); «Нагиевские чтения» посвященной 110 летию академика М.Нагиева (Баку, 2018); «Цеолиты и мезопористые материалы-достижения и перспективы» Тезисы и докладов 5-ой всероссийской цеолитной конференции - Звенигород (2008), Bakı Dövlət Universitetinin 90 illik yubileyinə həsr olunmuş Respublika Elmi Konfransının materialları - Bakı (2009), «Monomerlər və polimerlər kimyasının müasir problemləri» Respublika elmi konfransının materialları - Sumqayıt (2009), Отраслевой научно-производственной конференции «Интеграция науки и производства» -Салават (2013), «Цеолиты и мезопористые материалы-достижения и перспективы» Тезисы и докладов 7-ая всероссийской цеолитной конференции - Звенигород (2015), Химия и химическое образование XXI века - Санкт-Петербург (2017), Материалы II Всероссийской научной конференции (с международным участием) «Актуальные проблемы адсорбции и катализа» - Плес, Иванова (2017), II международная конференция «Современные решения научных и производственных задач в химия и нефтехимии» -Казан (2017), XII Международная конференция молодых ученых по нефтехимия -Звенигород (2018), Химия, химические технологии и экология: наука, производство, образования -Махачкала (2018), Материалы научной конференции «Нагиевские чтения», посвященной 110-летию академика М.Нагиева -Баку (2018), III всероссийской научной конференции с международным участием. Актуальные проблемы теории и практики гетерогенных катализаторов и адсорбентов -Иваново «Серебряный плес» (2018), III International (XIII Ukrainian) scientific conference for students and young scientists -Vinnytsia (2020), Актуальные вопросы химической технологии и защиты окружающей среды, Сборник материалов VIII Всероссийской конференции -Чебоксары (2020), Ümummilli lider Heydər Əliyevin anadan olmasının 98-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" XIV Beynəlxalq Elmi Konfransının materialları-Bakı (2021), Сборник тезисов докладов XII Российской конференции «Актуальные проблемы нефтехимии» (с международным участием) -Грозный (2021), XIII Всеукраїнська наукова

конференція студентів та аспірантів "Хімічні Каразінські читання - 2021" -Харків (2021), XI Международная научная конференция "Кинетика и механизм кристаллизации. Кристаллизация и материалы нового поколения" -Иваново (2021), Current chemical problems V International (XV Ukrainian) scientific conference for students and young scientists -Vinnytsia (2022), Ümummilli lider Heydər Əliyevin anadan olmasının 99-cü ildönümünə həsr olunmuş doktorant, magistrant və gənc tədqiqatçıların «Kimya və kimya texnologiyası» mövzusunda Respublika Elmi Konfrans -Bakı (2022), VII Всероссийская конференция с международным участием, посвященная 50-летию академической науки на Урале Техническая химия. От теории к практике -Пермь (2022), International Conference: Modern Problems of Theoretical & Experimental Chemistry -Baku (2022).

**Affiliation.** The research was performed at Baku State University, the department of Physical and Colloid Chemistry according to the topic of the department (State registration #0103Az00160).

**The scope and structure of the work.** The dissertation consists of an introduction (18075 symbols) and six chapters (1st chapter 119270 symbols, 2nd chapter 24234 symbols, 3rd chapter 47525 symbols, 4th chapter 41667 symbols, 5th chapter 31150 symbols, 6th chapter 46588 symbols), main results (5420 symbols), 270 cited references, in total has 292 pages, where, graphs (94) and tables (59) are shown.

**Personal contribution of the author.** The author's contribution includes the planning and organization of the thesis work and the achievement of the main results. The applicant carried out all theoretical and experimental research, as well as the interpretation and synthesis of the results. The analysis and systematization of the research results were prepared and formalized 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, published works and approbation of the work, affiliation, and personal contribution of the author.

The analysis of the literature review is reflected in the first chapter. In this chapter, the analysis of the structure, physico-chemical properties and catalytic properties of zeolites in the conversion reactions of aromatic hydrocarbons and alcohols is given. Based on the results of the literature analysis, the possibility of the synthesis of new, perspective and paraselective zeolite catalysts and the importance of preparing the scientific basis for studying their physico-chemical properties in the direction of obtaining the para isomers of alkylaromatic hydrocarbons, which are mainly valuable products, was formed.

The experimental part is presented in the second chapter. The reagents and materials used here, the preparation methods of mono, bi and polymetalzeolite catalysts, the methods of studying the physico-chemical and acid properties of the synthesized catalysts, the methods of product analysis, and the description of the catalytic unit for carrying out conversion reactions of toluene, ethylbenzene, C<sub>8</sub> fraction, methanol, bioethanol were described.

The third chapter the study of the physico-chemical and catalytic properties of the catalysts synthesized based on modified zeolites in the disproportionation reaction of toluene is described.

**The effect of modification with gallium on the physicochemical and catalytic properties of ZSM-5 zeolite in the disproportionation reaction of toluene.** As a result of extensive studies, it was found that catalysts based on ZSM-5 were more selective in the disproportionation reaction of toluene. The disproportionation of toluene is observed by the transalkylation reaction.

Table 1 shows the results disproportionation reaction in the presence of unmodified HZSM-5 zeolite obtained from the temperature-dependent toluene.

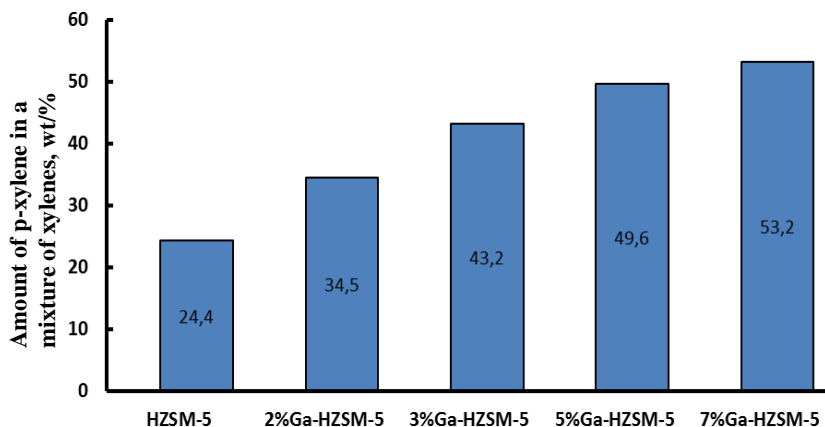
When the temperature of the reaction is raised from 450°C to 550°C, the conversion rate of toluene increases from 31.8% to 49.8%,

and the content of benzene+xylenes in the products increases from 29.5% to 43.9%.

**Table 1**  
**Effect of temperature on toluene conversion and distribution of toluene disproportionation reaction products in the presence of HZSM-5 zeolite**

T, °C	Conversion, %	Amount of reaction yields, wt. %			Selectivity to benzene + xylene, %	Amount of p-xylene in xylene mixture, %
		Benzene	Xylenes	TMB		
450	31,8	15,2	14,3	2,3	92,7	26,2
500	40,7	19,8	17,1	3,8	90,7	24,4
550	49,8	25,0	18,9	5,9	88,2	24,1

However, as the TMB content increases from 2.3% to 5.9% when the reaction temperature is increased, the selectivity for benzene+xylenes decreases from 92.7% to 88.2%. The reaction temperature has little effect on the amount of p-xylene in the mixture of xylenes and is close to thermodynamic equilibrium (24-26.2%).

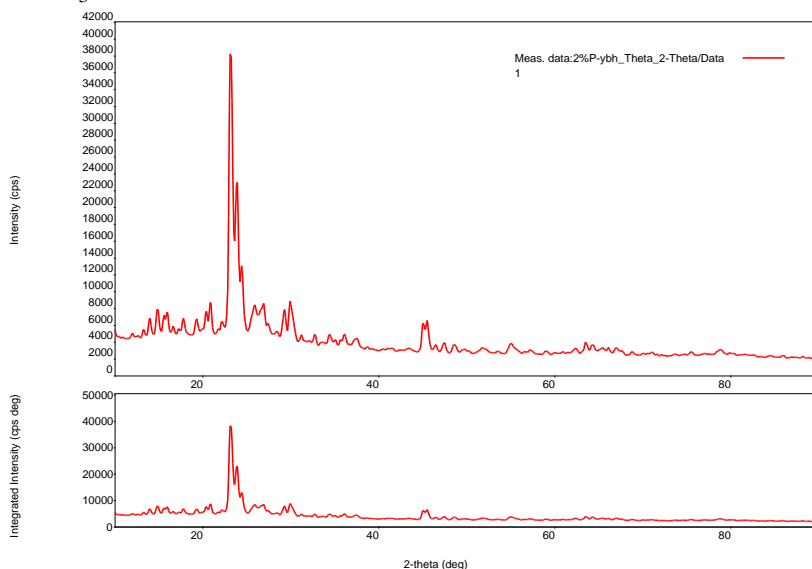


**Figure 1. Dependence of the amount of gallium in zeolite HZSM-5 on the amount of p-xylene in the xylene mixture**

As the amount of gallium in the HZSM-5 catalyst increases, the

amount of p-xylene in the mixture of xylenes increases (Figure 1). When HZSM-5 zeolite contains gallium in the amount of 2.0 wt.% the selectivity for p-xylene increases from 24.4% to 34.5%. A significant increase in the selectivity for p-xylene occurs in catalysts modified with 5.0-7.0 wt.% gallium, and the selectivity for p-xylene is 49.6%-53.2%. Thus, in the disproportionation reaction of toluene, gallium has a promoting effect in the content of HZSM-5 zeolite due to its benzene + xylene selectivity and para-selectivity.

**The effect of the amount of phosphorus in the disproportionation reaction of toluene on the properties of HZSM-5 zeolite.** To study the effect of phosphorus modification on the properties of HZSM-5 zeolite, HZSM-5 zeolite was modified with a solution of ammonium hydrogen phosphate salt using the impregnation method. Samples modified with different amounts (1.0-8.0 wt.%) of phosphorus were studied by XRD, BET, TPD methods of  $\text{NH}_3$ .



**Figure 2. XRD patterns of 2%P-HZSM-5 catalysts**

X-ray diffractograms (Figure 2) show that ZSM-5 zeolite does not include phosphorus in its crystalline structure. Phosphorus oxide peaks were not observed on the surface. In comparison with the

original HZSM-5 zeolite, the intensity of the peaks gradually decreases in the modified samples. This may be due to the ability of the PO<sub>4</sub> group to interact with crucial acidic OH groups.

Table 2 shows the textural properties of the modified catalysts. The obtained results show that as the content of phosphorus in zeolite increases, the specific surface area and the volume of pores decrease according to BET. These results confirm partial modifier blocking of ZSM-5 channels.

The combination of IR spectroscopy, XRD and low-temperature nitrogen desorption methods shows that various forms of phosphorus enter the ZSM-5 zeolite channels as a result of absorption and incandescence, some of them are localized on the surface of the channels, and therefore the specific surface area and pore volume of the modified samples decrease.

**Table 2**  
**Effect of the amount of phosphorus on the structural parameter of ZSM-5 zeolite pores**

Parametrs	HZSM-5	1%P HZSM-5	3%P HZSM-5	5%P HZSM-5	8%P HZSM-5
S <sub>BET</sub> (m <sup>2</sup> /g)	266,3	254,5	233,7	183,6	160,2
V <sub>pores</sub> (cm <sup>3</sup> /g)	0,266	0,221	0,178	0,167	0,155

It was determined by the TPD method of ammonia that the amount of weak and strong acid sites decreases as the amount of phosphorus in HZSM-5 zeolite increases.

**Table 3**  
**Effect of phosphorus amount on acid properties of HZSM-5 zeolite**

Phosphorus amount, wt. %	Desorption of NH <sub>3</sub> T <sub>max</sub> °C		Concentration of acid sites, μmol/g	
	form I	form II	form I	form II
0	198	418	618	544
1	197	368	472	438
3	190	302	314	197
5	184	253	198	112
8	178	-	186	-

When the amount of phosphorus in HZSM-5 zeolite is

enhanced to 3.0 wt.%, the amount of strong Brønsted acid site is reduced from 544  $\mu\text{mol/g}$  to 197  $\mu\text{mol/g}$ . When the amount of phosphorus is increased to 5.0 wt.%, the amount of strong Brønsted acid centers decreases by 4.9 times (112  $\mu\text{mol/g}$ ). The subsequent increase in the amount of phosphorus in HZSM-5 (8.0 wt.%) leads to the complete disappearance of strong acid sites (Table 3). Due to a 2.7-fold reduction in the number of strong Brønsted acid sites involved in disproportionation and transalkylation reactions, the modification leads to a dramatically decreased in toluene conversion rate (24.7-34.2%) and TMB selectivity (1.9-2.3%). By increasing the amount of phosphorus to 5.0 wt.%, the paraselectivity rises from 25.2% to 46.7%.

When HZSM-5 zeolite contains a phosphorus content of 8.0 wt.%, strong acid centers completely disappear and only weak acid centers (186  $\mu\text{mol/g}$ ) are present. Therefore, the 8%P-HZSM-5 catalyst does not show activity in the disproportionation reaction of toluene.

**Physicochemical and catalytic properties of TsVN zeolite modified with gallium and phosphorus in the disproportionation reaction of toluene.**

**Table 4**

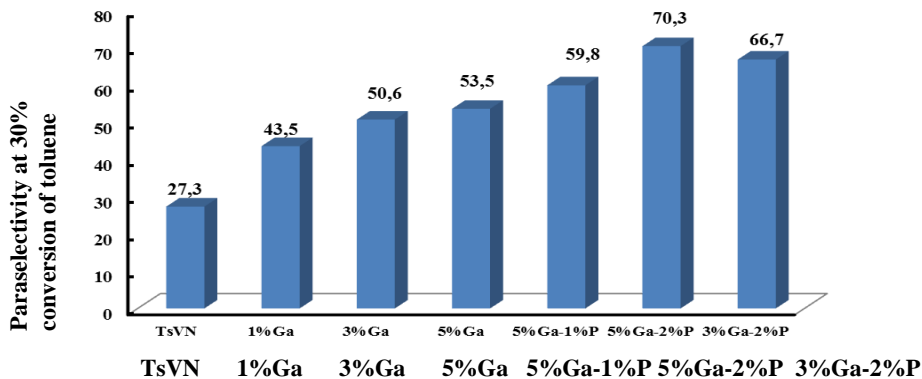
**Effect of phosphorus amount on catalytic properties of 5%Ga-TsVN catalyst in toluene disproportionation**

Catalyst	T, °C	Conversion, %	Selectivity, %			Sum of benzene and xylenes, %
			Benzene	Xylenes	TMB	
5%Ga-1%P-TsVN	500	28,7	49,8	49,5	0,7	64,8
	525	31,8	50,2	48,9	0,9	59,2
	550	37,3	50,6	48,1	1,3	55,3
5%Ga-2%P-TsVN	500	25,8	50,0	49,8	0,2	75,1
	525	30,4	50,2	49,5	0,3	70,3
	550	35,2	50,5	48,9	0,6	61,7
5%Ga-3%P-TsVN	500	20,4	50,0	50,0	-	77,8
	525	24,7	50,3	49,7	0,1	72,1
	550	29,6	50,6	49,1	0,3	66,7

It can be seen from Table 4 that when 1.0 wt.% phosphorus is

included in the composition of 5%Ga-TsVN catalyst, the selectivity of the formation of byproducts (TMB) decreases, it is only 0.7-1.3 wt.%.

When adding 3.0 wt.% phosphorus to the gallium-containing catalyst, the conversion rate of toluene at 500<sup>0</sup>C decreases from 28.7% to 20.4%.



**Figure 3. Effect of modification at 30% toluene conversion on the paraselectivity of TsVN based catalysts**

In addition, as a result of modification with phosphorus, the selectivity for p-xylene increases significantly. Among the studied catalysts, 5%Ga-2%P-TsVN catalysts show higher paraselectivity to benzene and xylenes (Figure 3).

**Table 5  
Distribution of the number of acid centers by activation energy in modified TsVN**

Catalyst	E<95, kJ/mol	95≤E<130 kJ/mol	E>130 kJ/mol	High temperature arm (>175°C)	130<E<(160-175°C) kJ/mol
H-TsVN	632	218	316	-	-
3%Ga- TsVN	248,6	265,6	136,8	39,4	97,4
5%Ga-TsVN	267,4	286,2	114,7	45,7	69,6
5%Ga-1%P-TsVN	281,8	314,3	96,4	41,2	55,2
5%Ga-2%P-TsVN	294,5	338,7	78,5	31,6	46,9



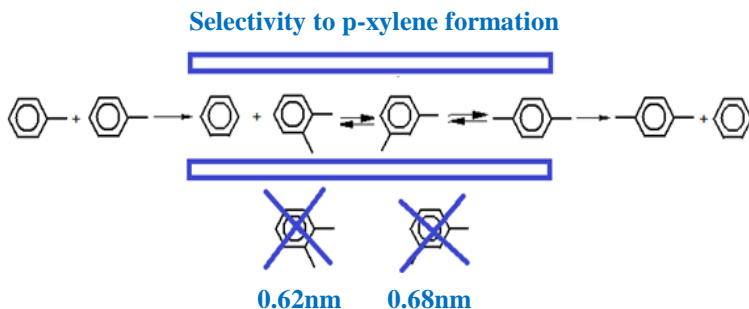
Additional modification of gallium-containing zeolite with phosphorus significantly increases the number of medium acid sites (314.3-338.7  $\mu\text{mol/g}$ ) and slightly decreases the number of strong Lewis acid sites (55.2-46.9  $\mu\text{mol/g}$ ) and B/L ratio decreases (Table 5).

Indeed, as can be seen from the data in Table 6, when TsVN is modified with phosphorus and gallium compounds, its pore volume, specific surface area, and micropore volume decrease. The volume of micropores in the total pore increases up to 64%.

**Table 6**  
**Effect of modification on texture characteristics of TsVN zeolite**

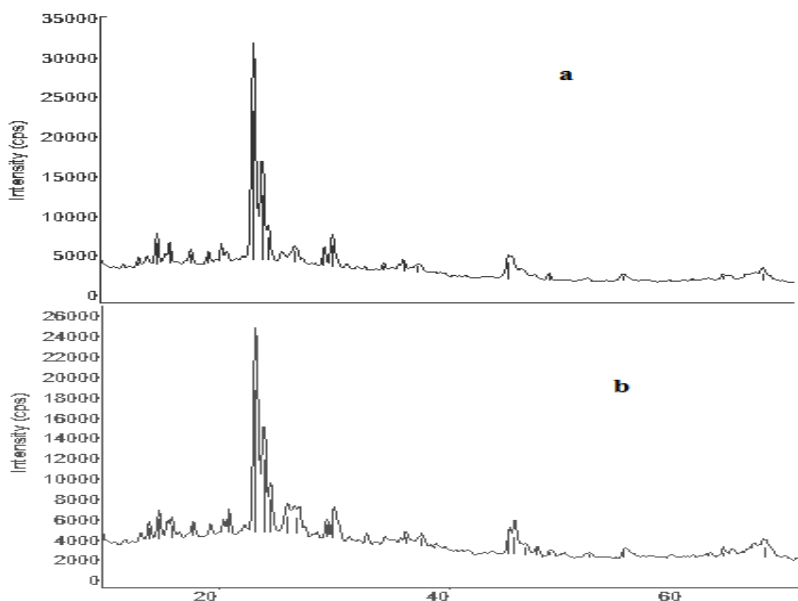
Catalyst	$S_{\text{BET}}$ , $\text{m}^2/\text{g}$	$V_{\text{pores}}$ , $\text{cm}^3/\text{g}$	$V_{\text{micro}}$ , $\text{cm}^3/\text{g}$	$V_{\text{micro}}/V_{\text{pores}}$ , %
TsVN	288	0,21	0,102	48,5
1%Ga-TsVN	274	0,20	0,098	49,1
3%Ga-TsVN	256	0,18	0,094	52,2
5%Ga-TsVN	232	0,16	0,091	56,8
5%Ga-2%P-TsVN	214	0,14	0,088	62,8
5%Ga-3%P-TsVN	196	0,13	0,084	64,0

In the bi-modified catalysts, the specific surface area and total pore volume decrease to 196-214  $\text{m}^2/\text{g}$  and 0.13-0.14  $\text{cm}^3/\text{g}$ , respectively. Along with acid sites, the porous structure of the catalyst also affects its paraselectivity. Product selectivity is observed in the toluene disproportionation reaction in the presence of TsVN zeolite-based modified catalysts.



**Figure 4. Scheme of toluene conversion in the presence of TsVN zeolite**

Figure 4 illustrates the molecular sieve property of TsVN zeolite. Since the diameter of the toluene molecule is smaller than the size of the entrance windows of TsVN zeolite, their diffusion into the channels of the zeolite occurs very easily, and as a result of disproportionation in the Brønsted acid centers located there, benzene and xylenes in thermodynamic equilibrium are formed. Since the kinetic diameters of the molecules of m- and o-xylenes are large (0.62-0.68 nm), they create steric barriers to their diffusion through the zeolite channels. On the contrary, since the kinetic diameter of the molecules of benzene and p-xylene corresponds to the dimensions of the zeolite channels and exit windows (~0.55 nm), they easily pass from the channels to the gas phase, and the gas phase is rich in p-xylene.



**Figure 5. XRD patterns of 3%Ga-TsVN (a) and 5%Ga-2%P-TsVN (b) catalysts**

Figure 5 shows the radiographs of 3%Ga-TsVN and 5%Ga-2%P-TsVN catalysts. It can be seen from the picture that the characteristic peaks in the structure of HZSM-5 zeolite do not change

as a result of modification. Thus, the structure of zeolite does not change as a result of modification. Because gallium oxide is localized on the surface and channels in a highly dispersed manner, the intensity of the peak becomes lighter.

Probably, as the amount of phosphorus decreases, the intensity of the peaks characteristic of HZSM-5 decreases. This is due to the fact that phosphorus is in contact with aluminum in the framework of zeolite and dealumination occurs.

**Effect of modification method of ZSM-5 on physico-chemical and catalytic properties of zeolite in toluene disproportionation.** ZSM-5 zeolite with silicate module 33 was used for the research, its modification was carried out by ion exchange and impregnation methods. H- and cation forms (La, Yb, Ho) of ZSM-5 zeolite were synthesized by the ion exchange method, and catalysts modified with phosphorus and lanthanum with different contents were synthesized by the impregnation method (Table 7). Since the specific surface area and pore volume of cationic forms change very little, when ZSM-5 zeolite is modified by the ion exchange method, the dimensions of its channels also change very little.

**Table 7**  
**Textural properties of catalysts modified by ion exchange and impregnation methods**

<b>Catalyst, Ion exchange</b>	<b>S<sub>spec.</sub> (m<sup>2</sup>/g)</b>	<b>V<sub>pores</sub> (cm<sup>3</sup>/g)</b>	<b>Catalyst (Impregnation)</b>	<b>S<sub>spec.</sub> (m<sup>2</sup>/g)</b>	<b>V<sub>pores</sub> (cm<sup>3</sup>/g)</b>
0.85 H-ZSM-5	266,3	0,226	3% P-ZSM-5	222,6	0,177
0.73La-ZSM-5	258,8	0,213	10% La-ZSM-5	213,5	0,157
0.68Yb-ZSM-5	257,7	0,217	6% La-3% P-ZSM-5	216,3	0,161
0.73Ho-ZSM-5	259,1	0,223	10% La-3% P-ZSM-5	211,2	0,152

The effect of the modification of HZSM-5 zeolite with phosphorus and lanthanides (La, Yb, Ho) on its catalytic properties by impregnation method was studied (Table 8) and it was determined that modification of HZSM-5 zeolite with 3.0 wt.% phosphorus increases the paraselectivity.

Phosphorus modification leads to the conversion rate of toluene decrease to 28.4%, and the paraselectivity increases to 38.1%, as compared to H-form catalyst at 500°C temperature (Table1). When HZSM-5 zeolite is modified with 3.0 wt.% lanthanum, its paraselectivity is more higher (41.3%).

**Table 8**

**Effect of modifier amount in toluene disproportionation reaction on catalytic properties of HZSM-5 zeolite**

Catalyst	T, °C	Toluene conversion, wt. %	Selectivity %		Amount of p-xylene in xylene mixture, %
			Benzene	Xylenes	
3% P-HZSM-5	500	28,4	51,5	47,5	38,1
	550	37,6	53,4	44,6	32,3
3% La-HZSM-5	500	24,7	51,2	47,8	41,3
	550	34,2	52,2	45,8	34,1
6% La-HZSM-5	500	15,9	50,6	48,9	50,4
	550	24,2	51,2	47,8	40,1
10% La-HZSM-5	500	9,6	50,3	49,4	70,3
	550	16,7	50,9	48,5	56,2
6% La-3%P-HZSM-5	500	13,8	50,8	48,6	71,3
	550	15,8	51,1	48,0	59,2
6% Yb-3%P-HZSM-5	500	17,6	50,9	48,2	66,6
	550	27,4	51,6	47,3	54,3
10% Yb-3%P-HZSM-5	500	10,3	50,4	49,0	81,3
	550	19,4	51,1	47,9	64,7
6% Ho-3%P-HZSM-5	500	16,2	50,9	48,3	68,6
	550	25,7	51,3	47,8	57,8
10%Ho-3%P-HZSM-5	500	9,1	50,4	49,2	83,4
	550	18,2	51,9	48,1	66,6
10%La-3%P-HZSM-5	500	7,8	50,4	49,4	85,1
	550	14,1	50,7	48,6	68,4

As a result of phosphorus modification, the conversion rate of toluene decreases to 28.4%, and the paraselectivity increases to 38.1%, as compared to the H-form catalyst at 500°C temperature (Table 1). When HZSM-5 zeolite is modified with 3.0 wt.% lanthanum, its paraselectivity is more higher (41.3%). When the

content of lanthanum in HZSM-5 zeolite is increased to 10.0 wt.%, the paraselectivity increases significantly and reaches 70.3%. However, at this time, the conversion rate of toluene decreases dramatically. The paraselectivity of the 10%La-3%P-HZSM-5 catalyst is higher at this temperature (85.1%).

Among these catalysts, higher paraselectivity is achieved in the presence of 6% La-3%P-HZSM-5 catalyst (71.3-59.2%) during the conversion of 13.8-15.8% of toluene in the temperature range of 500-550°C. Based on the results of physical and chemical studies, it was determined that as the amount of modifier in HZSM-5 zeolite increases, strong Brønsted acid sites ( $E > 130$  kJ/mol) decrease, and the amount of moderate acid sites ( $E \leq 95 < 130$  kJ/mol) increases. When HZSM-5 zeolite is co-modified with phosphorus and lanthanum, the amount of strong Lewis acid sites is slightly reduced.

Thus, in the presence of 6% La-3%-P-ZSM-5 and 10% La-3%-P-ZSM-5 catalysts, the conversion of toluene by disproportionation of toluene was 14.1-15.8%, and at this time, para-xylene selectivity was 59.2-68.4%.

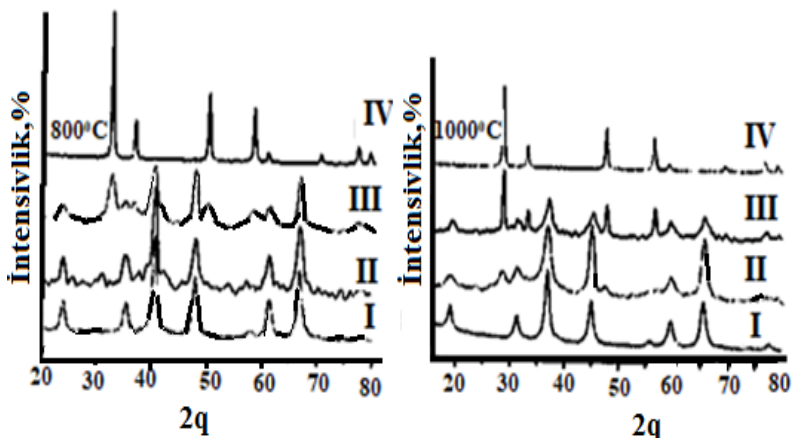
**Physico-chemical properties of catalytic composition of spinel-type nanoparticles with ZSM-5 zeolite and activity in disproportionation reactions of toluene.** Nanocomposites were prepared based on HZSM-5 zeolite with nanostructured pores (0.51x0.53 nm) modified with Ce and Ho doped spinel structured  $Ce_xMg_{1-x}Al_2O_4$  and  $Ho_xMg_{1-x}Al_2O_4$  nanopowders<sup>5</sup>.

It was determined that after thermal treatment, along with spinel phases ( $Ho_{0,10}Mg_{0,90}Al_2O_4$ ,  $Ho_{0,05}Mg_{0,95}Al_2O_4$ ,  $Ce_{0,05}Mg_{0,95}Al_2O_4$ ,  $Ce_{0,1}Mg_{0,90}Al_2O_4$ ),  $CeO_2$ ,  $Ho_2O_3$  phases are also formed (Figure 6).

During the synthesis, cerium and holmium replace magnesium ions at the nodes of the lattice and enter the lattice of magnesium-aluminum spinel.

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<sup>5</sup> Махмудова Н.И. Синтез наночастиц  $Ce_xMg_{1-x}Al_2O_4$  и исследование их физико-химических и каталитических свойств в композиции с цеолитом ZSM-5 в превращении метанола в п-ксилол // Махмудова Н.И., Вердиева Л.Р., Ильяслы Т.М. [и др.]. Журнал Фундаментальные исследования, – 2017, – № 10 (часть 3) – с. 483-491.



**Figure 6. X-ray diffractograms of powders of  $\text{MgAl}_2\text{O}_4$  (I),  $\text{Ce}_{0.05}\text{Mg}_{0.95}\text{Al}_2\text{O}_4$  (II),  $\text{Ce}_{0.1}\text{Mg}_{0.90}\text{Al}_2\text{O}_4$  (III) and  $\text{CeO}_2$  (IV) obtained by combustion at  $800^\circ\text{C}$  and  $1000^\circ\text{C}$**

The dependence of the particle sizes on the thermal treatment temperature was determined (Table 9).

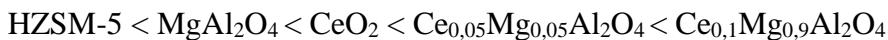
**Table 9  
Heat-treated particles size (nm)**

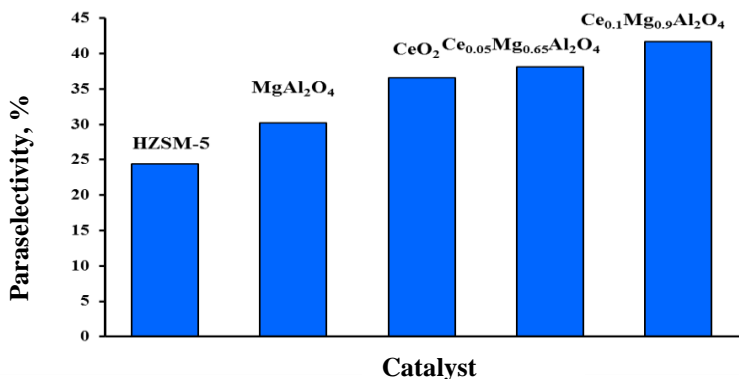
Composition of phase	Particle size (nm) at different temperatures	
	$800^\circ\text{C}$	$1000^\circ\text{C}$
$\text{MgAl}_2\text{O}_4$	9,98	10,65
$\text{Ce}_{0.05}\text{Mg}_{0.95}\text{Al}_2\text{O}_4$	10,25	15,45
$\text{Ce}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$	10,70	16,54
$\text{CeO}_2$	20,60	33,0

Figure 7 shows the catalytic properties of nanocomposite catalysts modified with 3.0 wt.%  $\text{MgAl}_2\text{O}_4$ ,  $\text{CeO}_2$ ,  $\text{Ce}_{0.05}\text{Mg}_{0.95}\text{Al}_2\text{O}_4$ ,  $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$  nanodust.

Compared to unmodified HZSM-5 zeolite, the inclusion of 3.0 wt.% spinel-structured nanopowders in HZSM-5 zeolite increases its paraselectivity from 24.4% to 41.7%.

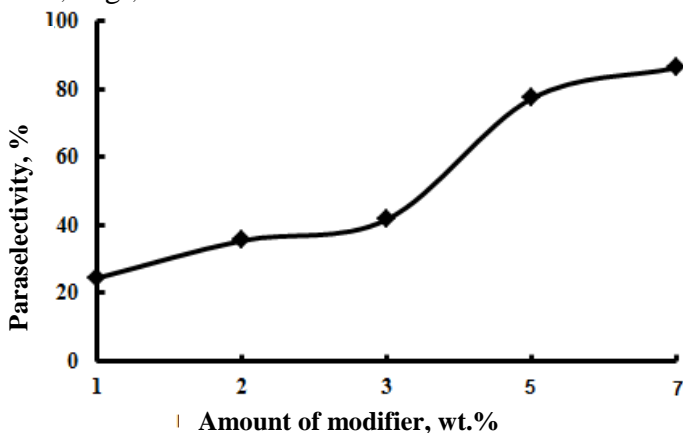
When HZSM-5 zeolite is modified with modifiers, the selectivity of the catalysts for p-xylene is arranged in the following order:





**Figure 7. Effect of modifier nature on catalyst para-selectivity in toluene disproportionation (T=500°C, V=1,0 h<sup>-1</sup>)**

A higher selectivity for p-xylene is 41.7% among the studied samples. This is demonstrated by the catalytic composition modified with 3% Ce<sub>0.1</sub>Mg<sub>0.9</sub>Al<sub>2</sub>O<sub>4</sub> nanodust.



**Figure 8. Effect of the amount of nanopowder in the Ce<sub>0.1</sub>Mg<sub>0.9</sub>Al<sub>2</sub>O<sub>4</sub> catalytic composition on its para-selectivity (500°C)**

The effect of the amount of Ce<sub>0.1</sub>Mg<sub>0.9</sub>Al<sub>2</sub>O<sub>4</sub> nanodust on the catalytic properties of HZSM-5 zeolite in the disproportionation reaction of toluene is given in Figure 8.

Table 10 shows the concentration and distribution of Brønsted and Lewis acid sites in the modified catalysts. By increasing the amount of Ce<sub>0.1</sub>Mg<sub>0.9</sub>Al<sub>2</sub>O<sub>4</sub> nanodust in the catalytic system, the

density of Brønsted acid sites decreases, which leads to an increase in the density of weak and medium sites. In addition, as a result of the modification, the concentration of stronger Lewis acid sites decreases. As a result of the redistribution of B- and L-acid sites, the ratio of B/L-sites in the catalyst significantly decreases (from 3.53 to 0.24).

**Table 10**  
**Concentration and distribution of B- and L-acid centers in the catalytic system of Ce<sub>0,1</sub>Mg<sub>0,9</sub>Al<sub>2</sub>O<sub>4</sub> nanopowder with HZSM-5 zeolite**

Amount of modifier, wt%	Concentration of B-sites, $\mu\text{mol/g}$			Concentration of L-sites, $\mu\text{mol/g}$			B/L
	Weak and medium (200°C)	Strong (300°C)	Total	Weak and medium (200°C)	Strong (300°C)	Total	
0	542	360	902	145	110	255	3,53
1	95	200	295	210	80	290	1,02
3	80	170	250	460	70	530	0,47
5	65	160	225	720	60	780	0,29
7	60	150	210	830	50	880	0,24

The specific surface area decreases from 266 m<sup>2</sup>/g to 262 m<sup>2</sup>/g, and the pore volume decreases from 0.24 cm<sup>3</sup>/g to 0.23 cm<sup>3</sup>/g. When the amount of modifier in the catalyst content is increased up to 3.0 wt.%, the specific surface area and the pore volume decrease (Table 11).

**Table 11**  
**Dependence between the amount of Ce<sub>0,1</sub>Mg<sub>0,9</sub>Al<sub>2</sub>O<sub>4</sub> nanopowder on the specific surface area and pore volume of the catalyst**

Catalyst	Amount of modifier, wt. %	S <sub>BET</sub> , m <sup>2</sup> /g	V <sub>pores</sub> , cm <sup>3</sup> /g
HZSM-5	0	266	0,24
Ce <sub>0,1</sub> Mg <sub>0,9</sub> Al <sub>2</sub> O <sub>4</sub>	1	262	0,23
Ce <sub>0,1</sub> Mg <sub>0,9</sub> Al <sub>2</sub> O <sub>4</sub>	3	239	0,18
Ce <sub>0,1</sub> Mg <sub>0,9</sub> Al <sub>2</sub> O <sub>4</sub>	5	221	0,16
Ce <sub>0,1</sub> Mg <sub>0,9</sub> Al <sub>2</sub> O <sub>4</sub>	7	214	0,15



**Effect of silicate modulus on acidic and catalytic properties of high-silica ultrasilic zeolite in the disproportionation reaction of ethylbenzene.** In order to study the effect of silicate module ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) on acid and catalytic properties of zeolite, ultrasilic zeolite with modulus ratio of 24, 61, 103 and 200 was studied (Table 12).

**Table 12**

**Effect of silicate modulus on the concentration of acid sites of zeolite H-ultrasil**

Molar ratio of silicate modulus	$T_{\max}$ °C		Concentration of acid sites, $\mu\text{mol/g}$		L/B
	form I	form II	form I	form II	
24	200	421	634	554	1,14
61	195	408	625	528	1,18
103	192	372	597	374	1,60
200	188	358	585	321	1,82

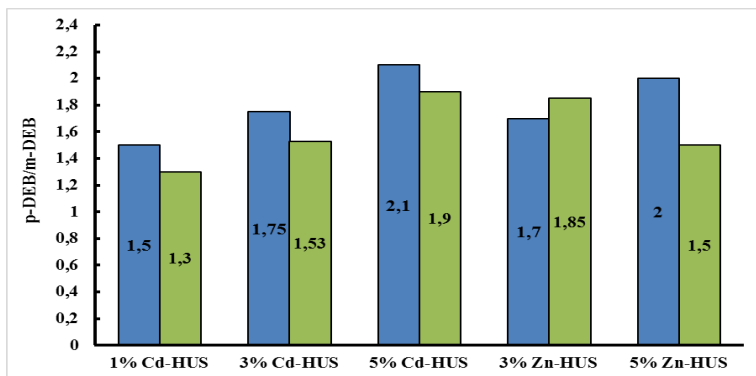
As the silicate modulus increases in ultrasil, the density of weak Lewis sites changes less than the density of Brønsted acid sites.

Since H-ultrasils with a silicate module of 103 and 200 have 1.5-1.7 times less Brønsted acid sites, the rate of external reactions decreases sharply and the disproportionation selectivity increases.

**The effect of the amount of Zn and Cd on the catalytic properties of ZSM-5 zeolite in the disproportionation reaction of ethylbenzene.** In order to reveal the effect of modifiers on the catalytic properties of zeolite, ultrasil zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3=61$ ), an analog of ZSM-5 zeolite, was modified with 1.0-5.0 wt.% Zn and Cd by impregnation and their H-ultrasil zeolite its effect on catalytic properties was studied (Figure 9). Higher para selectivity is shown by samples modified with 5.0 wt.% modifiers (2.0-2.1).

The effect of the modifier on the catalytic properties of H-ultrasil zeolite in the disproportionation of ethylbenzene is to prevent the formation of byproducts (toluene, TMB) and o-DEB and to increase the amount or paraselectivity of p-DEB in the DEB mixture.

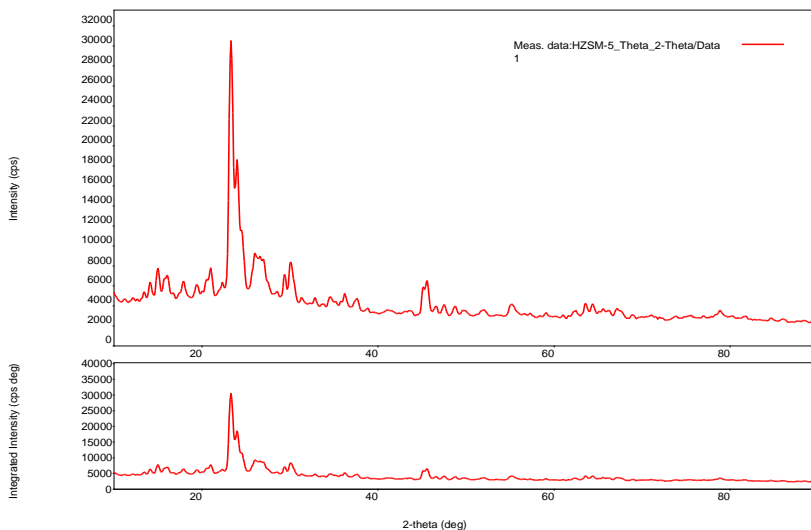
The effect of the modifier on the catalytic properties of H-ultrasil zeolite in the disproportionation of ethylbenzene is to prevent the formation of byproducts (toluene, TMB) and o-DEB and to increase the amount or paraselectivity of p-DEB in the DEB mixture.



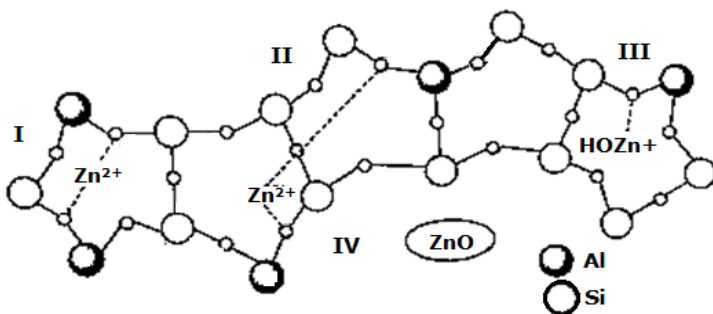
**Figure 9. Dependence of p-DEB/m-DEB ratio on the amount of modifier**

■ -300 °C    ■ -400 °C

**Physicochemical, textural properties of modified ultrasilic zeolite and their correlation with catalyst paraselectivity.** It can be seen from the picture that peaks ( $2\theta=7.96^{\circ}$ ,  $8.88^{\circ}$ ,  $23.2^{\circ}$ ,  $23.3^{\circ}$  and  $24.0^{\circ}$ ) characteristic of ZSM-5 (ICDD No. 01-086-1722) zeolite are observed in H-ultrasil zeolite (Figure 10).

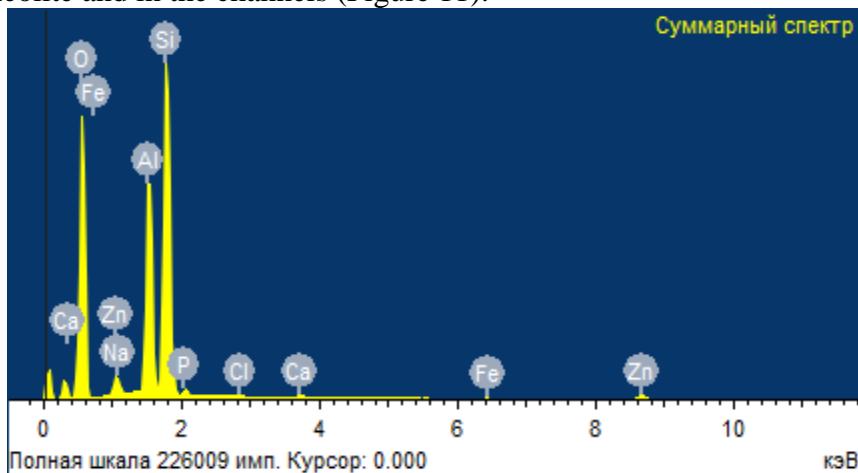


**Figure 10. XRD pattern of H-ultrasil**



**Figure 11. Description of active sites in modified zeolite**

Thus, it was determined that several active centers are formed in zeolite as a result of modification with zinc or cadmium: cations isolated outside the framework ( $Zn^{2+}$ ,  $Cd^{2+}$ ;  $ZnOH^+$  or  $CdOH^+$ ) are nanosized ZnO or CdO oxides localized on the outer surface of zeolite and in the channels (Figure 11).



**Figure 12. EDS spectrum of zeolite 3% Zn-H-ultrasil**

It can be seen from Table 13 that when the amount of Zn in H-ultrasilin is increased to 5.0 wt.%, its specific surface area decreases to 222  $m^2/g$  and the pore volume decreases to 0.19  $cm^3/g$ . The reduction in pore volume leads to a decrease in micropore volume as

a result of the modification.

**Table 13**  
**Effect of modification with zinc on specific surface area and pore volume of H-ultrasil**

Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>pores</sub> (cm <sup>3</sup> /g)
H-ultrasil	266	0,24
1,0 % Zn/H-ultrasil	265	0,23
2,0 % Zn/H-ultrasil	264	0,22
3,0 % Zn/H-ultrasil	240	0,20
5,0 % Zn/H-ultrasil	222	0,19
7,0 % Zn/H-ultrasil	211	0,17

**Effect of the nature and quantity of rare earth elements (NTE) on the physicochemical and catalytic properties of H-TsVM zeolite in the disproportionation reaction of ethylbenzene.** Table 14 shows that at 300°C, HZSM-5 shows sufficient activity. At that temperature, the degree of conversion of ethylbenzene reaches 20.2wt.%. The selectivity (PS) for p-DEB in a mixture of DEBs is 42.6 %. When the temperature of the reaction is raised to 400°C, the degree of conversion of ethylbenzene increases to 62.4 wt.%, the amount of m-DEB increases and is 9.7 wt.%.

**Table 14**  
**The composition of ethylbenzene disproportionation products**

T, °C	Conversion of EBs, %	Yields, wt. %								
		Benzene	Toluene	Xylenes	TEB	m-DEB	p-DEB	o-DEB	PS*, %	S <sub>dis.</sub> ** , %
250	5,1	1,3	0,1	-	-	2,0	1,7	-	45,9	98,1
300	20,2	6,1	0,1	-	0,4	7,8	5,8	-	42,6	97,5
350	40,0	13,5	0,2	0,5	1,7	14,3	9,6	0,2	40,1	92,7
400	62,4	25,5	0,7	2,8	4,8	9,7	6,0	3,5	38,2	70,8

PS\* - paraselectivity; S<sub>dis.</sub>\*\* - disproportionation selectivity

In addition, an increase in the amount of toluene, xylene, triethylbenzenes and o-DEB in the products is observed. For this reason, the paraselectivity (PS) of the catalyst and disproportionation decrease the selectivity. When increasing the reaction temperature from 300°C to 400°C, the PS decreases from 42.6% to 38.2%, and the disproportionation selectivity reduces from 98.1% to 70.8%.

The disproportionation selectivity and paraselectivity of the catalyst is significantly affected by the nature and amount of its modifying metals. The modified catalysts are ranked in order of decreasing paraselectivity as follows.

La- H-TsVM > Ho- H-TsVM > Pr- H-TsVM > H-TsVM

Figures 12, 13, and 14 show comparative radiographs of samples modified with forms H, La, and Pr. It has been determined that as a result of modification, no changes occur in the structure of HZSM-5 zeolite, peaks related to lanthanum oxide are not detected. It is assumed that metal oxide species are dispersed on the surface of the catalyst.

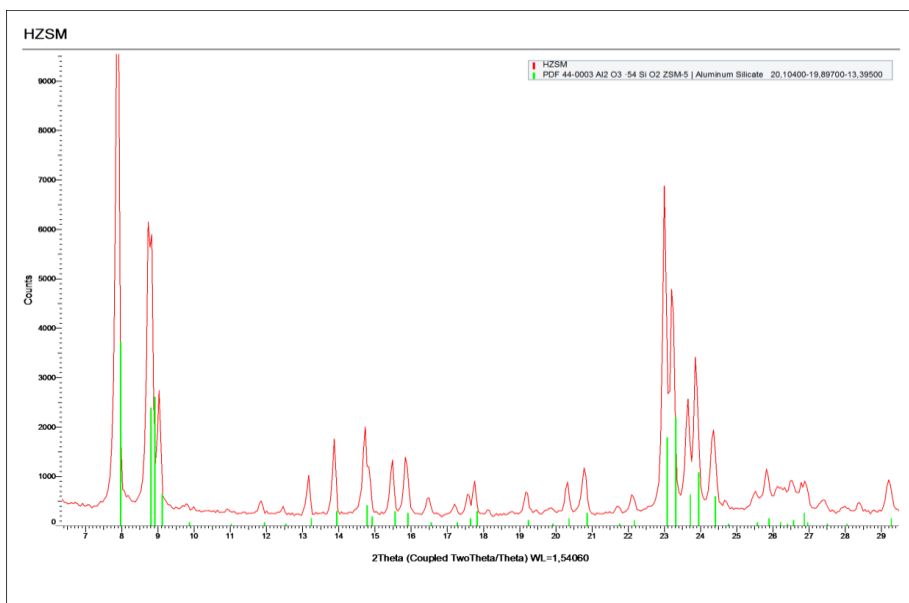


Figure 12. XRD pattern of HZSM-5 catalyst ( $2\theta=0-30^\circ$ )

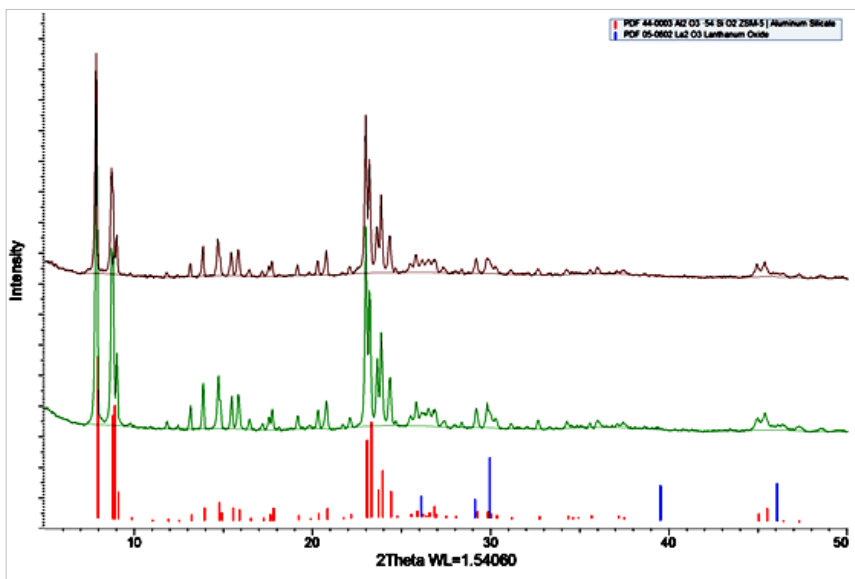


Figure 13. XRD patterns of HZSM-5 and 3%La-H-ZSM-5 catalyst

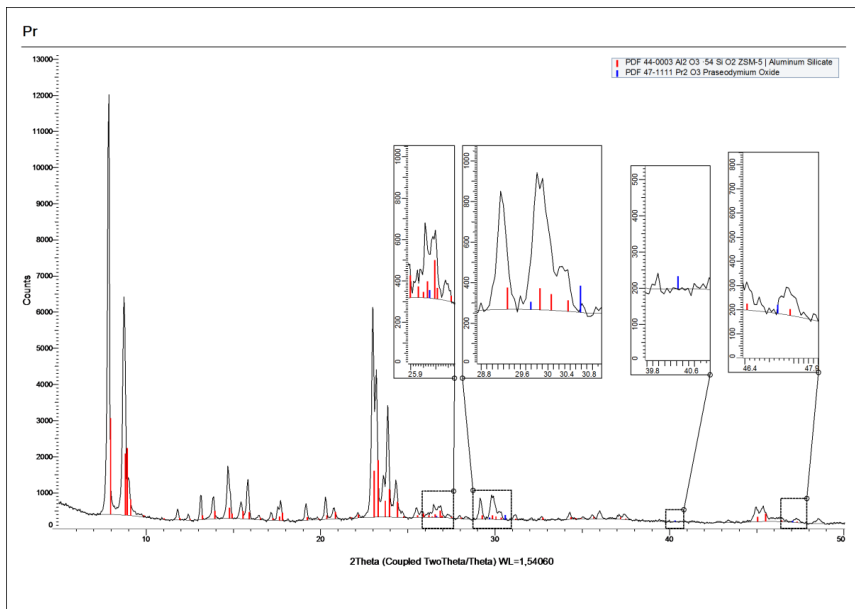


Figure 14. XRD patterns of Pr-HZSM-5 catalyst

Table 15

**Effect of modification on specific surface area and total pore volume of the catalyst**

<b>Catalyst</b>	<b>Amount of rare-earth elements (REE), %</b>	<b>Amount of REE by AAS method, %</b>	<b>S<sub>BET</sub> (m<sup>2</sup>/g)</b>	<b>V<sub>pores</sub> (cm<sup>3</sup>/g)</b>
H-TsVM	-		266,3	0,22
La/ H-TsVM	1,0	0,89	264,5	0,21
La/ H-TsVM	3,0	2,87	236,2	0,17
La/ H-TsVM	5,0	4,83	224,3	0,16
La/ H-TsVM	10,0	9,71	212,4	0,15
Pr/ H-TsVM	3,0	2,89	255,8	0,19
Ho/ H-TsVM	3,0	2,91	247,7	0,18

The high paraselectivity of NTE-containing zeolites may be related to the reduction of the strength of Brønsted and Lewis acid sites of zeolite and the change of its pore structure as a result of modification (Table 15).

The increase in paraselectivity of H-TsVM zeolite can be caused by the redistribution and change of its acid sites as a result of modification (Table 16).

**Table 16**  
**Distribution of acid sites by E value**

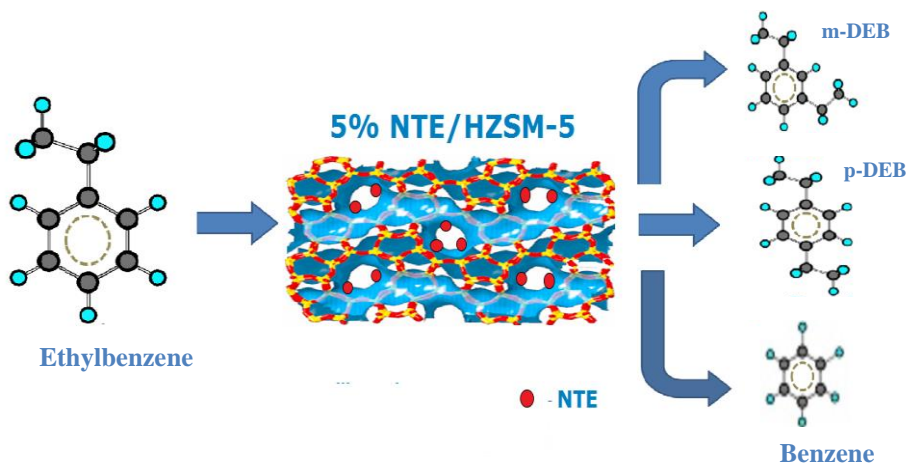
<b>Catalyst</b>	<b>E&lt;95</b>	<b>E&lt;95&lt;130</b>	<b>E&gt;130 (160-175)</b>	<b>130&lt;E&lt;(160-175)</b>
H-TsVM	618	216	326	-
3%La- H-TsVM	324	247	120	40
5%La- H-TsVM	286	268	52	45
10%La- H-TsVM	252	297	68	22
5%Ho- H-TsVM	285	260	59	54
5%Pr- H-TsVM	292	254	70	62
10%Pr- H-TsVM	267	282	28	30

The effect of lanthanum modification on the hardness of B- and L-centers in zeolite is shown in table 17.

**Table 17**  
**Concentration and distribution of Brsted and Lewis acid sites**

Catalyst	Concentration of B-sites, $\mu\text{mol/g}$			Concentration of L-sites, $\mu\text{mol/g}$			
	Weak and medium 200 $^{\circ}\text{C}$	Strong 350 $^{\circ}\text{C}$	Total	Weak and medium 200 $^{\circ}\text{C}$	Strong 350 $^{\circ}\text{C}$	Total	B/L
HZSM-5	530	350	880	150	110	260	3,42
1,0%La/HZSM-5	75	180	255	220	75	295	0,86
3,0%La/HZSM-5	60	165	225	400	55	455	0,49
5,0%La/HZSM-5	50	160	210	770	40	810	0,26
7,0%La/HZSM-5	60	150	210	860	40	900	0,23

It can be seen that with increasing an amount of lanthanum in the zeolite, the hardness of both acid sites decreases, which leads to an increase in the amount of weaker Lewis acid sites. Also, decreasing the density of stronger Lewis acid centers leads to a significant decrease in the ratio of B/L centers from 3.42 to 0.23. This factor is the reason for the change in activity and paraselectivity of modified catalysts.



The disproportionation selectivity of ethylbenzene and the probability of formation of DEB isomers (Scheme) depend on the pore size, molecular configuration, and B/L acid sites in the zeolite.

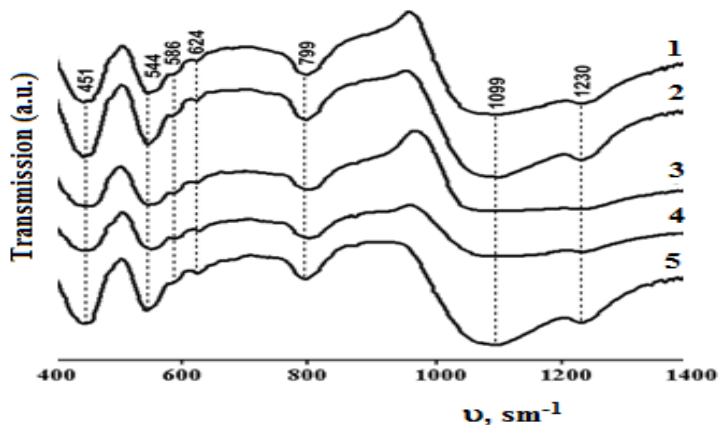


The effect of modification with lanthanides on the properties of ZSM-5 (TsVM) zeolite in the disproportionation reaction of ethylbenzene. Catalysts were prepared by the impregnation method using nitrate salts of lanthanides, their amount in the catalyst was changed in the range of 1.0-7.0 wt.%. After modification, the actual amount of modifiers in the catalyst was determined by atomic adsorption method (AAS) and the obtained results are given in Table 18.

**Table 18**  
Actual amount of Ln in Ln/HZSM-5 catalysts by AAS method

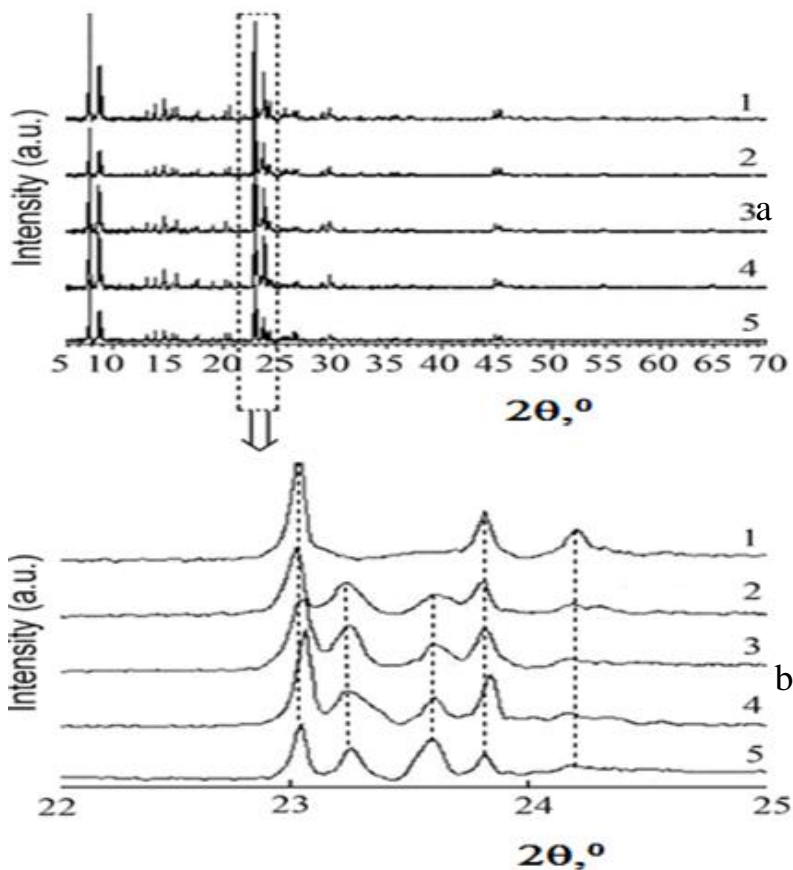
Calculated amount of lanthanide	Defined amount of Ln, wt.%			
	Pr-HZSM-5	Gd-HZSM-5	Ho-HZSM-5	Yb-HZSM-5
1	0,56	0,60	0,63	0,65
3	2,69	2,72	2,77	2,80
5	4,77	4,81	4,84	4,87
7	6,81	6,85	6,87	6,89

The obtained results confirm that the lanthanides were successfully incorporated into the zeolite. TO simplify the zeolite modification, Ln/HZSM-5 samples had modifier amounts of 1, 3, 5, and 7 wt%.



**Figure 15.** IR spectra of catalysts: HZSM-5 (1), Pr/HZSM-5 (2), Gd/HZSM-5 (3), Ho/HZSM-5 (4), Yb/HZSM-5 (5) (5 wt.% Ln)

As a result of the modification, IR-spectra in the region of 400-1400 $\text{cm}^{-1}$  also confirm that the framework of HZSM-5 zeolite does not change (Figure 15). The introduction of the modifier into the zeolite by the impregnation method does not affect the characteristic absorption bands for the Si-O-Si and Si-O-Al fragments. In the catalysts, characteristic IR oscillations ( $\sim 799\text{ cm}^{-1}$ ) belonging to the  $\text{TO}_4$  tetrahedron and asymmetric and symmetric oscillations ( $\sim 624, 586, 544$  and  $451\text{ cm}^{-1}$ ) connecting TO double rings are observed. In La/HZSM-5 samples, the IR spectra related to La-O fragments are not clearly observed, but the bathochromic shift of the bands connecting TO double rings ( $\sim 624, 544$  and  $451\text{ cm}^{-1}$ ) occurs with decreasing intensity.



**Figure 16.** XRD patterns of catalysts: (1) HZSM-5, (2) Pr/HZSM-5, (3) Gd/HZSM-5, (4) Ho/HZSM-5, (5) Yb/HZSM-5 (5 wt.% Ln)

Peaks ( $7,8^\circ$ ,  $8,7^\circ$ ,  $23,0^\circ$ ,  $23,8^\circ$ ,  $24,2^\circ$ ) characterizing the structure of ZSM-5 zeolite in Figure 16a ( $2\Theta=5-70^\circ$ ) and Figure 16b ( $2\Theta=5-70^\circ$ ) seem obvious.

XRD analysis of Ln/HZSM-5 and HZSM-5 catalysts shows that no changes occur in the general structure of zeolite after modification. The diffraction peaks of those catalysts correspond to the peaks of HZSM-5 zeolite. On the other hand, new peaks ( $2\Theta=23,6^\circ$ ,  $30,2^\circ$ ,  $44,9^\circ$  v $\grave{a}$   $45,5^\circ$ ) appear in Ln/HZSM-5 catalysts with very weak intensity. The intensity of the peak at  $23,6^\circ$  increases with decreasing lanthanide ionic radius ( $\text{Pr}>\text{Gd}>\text{Ho}>\text{Yb}$ ). This effect indicates the interaction of lanthanides with the zeolite framework. The peaks characteristic of  $\text{NTE}_2\text{O}_3$  oxides are not clear. It is likely that nanoscale oxides of lanthanides are dispersed on the surface and pores of zeolite. Thus, various types of lanthanides are highly dispersed on the surface of HZSM-5 zeolite.

**Catalytic properties of ZSM-5 zeolite-based catalysts in the isomerization of m-xylene.** The degree of conversion of m-xylene in the presence of H ultrasil is 34.8-49.4 wt.% (Table 19). However, as the reaction temperature increases, the selectivity according to PK and OK decreases (from 90.8 % to 84.8 %) due to the increase of by-products. Under these conditions, the selectivity of unwanted products (TMB+other ArH) increases from 9.2% to 15.2%. When the amount of Zn in the catalyst content is increased to 3.0 wt.%, its activity decreases considerably. The decrease in activity is more pronounced at lower temperatures. For example, the conversion rate of m-xylene drops from 34.8% to 25% at  $300^\circ\text{C}$ . However, as a result of the modification, the selectivity of the sum of PK and OK increases quite a bit (91.7-93.8%), the selectivity due to by-products decreases (9.2-7.0%). When the content of Zn in H-ultrasilin is increased to 5.0 wt.%, the activity of the catalyst decreases significantly.

However, in this case, the sum of the selectivity of PK and OK increases to 93.8-94.9%, and the selectivity of by-products decreases to 5.1-6.8%. When the amount of Zn in H-ultrasil is increased to 7.0 wt.%, its activity drops sharply. In the presence of this sample, at  $330^\circ\text{C}$ , the sum of the selectivity of PK and OK increases to 95.4%, while the selectivity of byproducts decreases to 4.6%.

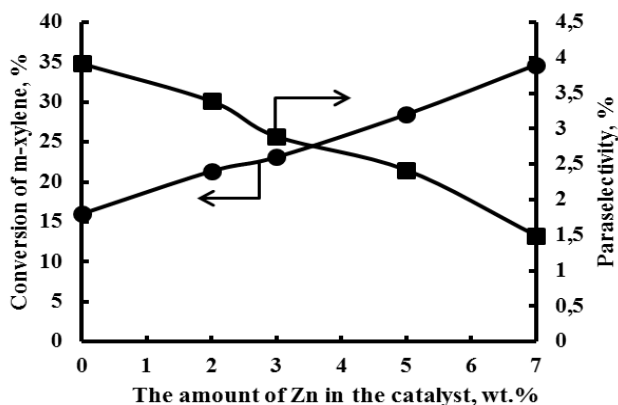
**Table 19**

**Effect of zinc content on catalytic properties of H-ultrasil in the reaction of m-xylene isomerization**

Amount of Zn, wt.%	T, °C	Conversion %	Product selectivity, %			
			PK+OK	PK	TMB	Other ArH
0	300	34,8	90,8	58,3	6,1	3,1
	330	43,2	87,1	56,5	8,6	4,4
	350	49,4	84,8	54,5	10,3	4,9
2	300	30,1	91,7	64,3	5,6	2,7
	330	38,8	88,6	63,0	7,5	3,9
	350	45,1	86,9	61,5	8,9	4,2
3	300	25,7	93,8	67,2	4,3	2,7
	330	33,1	92,9	66,8	7,5	3,9
	350	39,3	91,8	65,5	8,9	4,2
5	330	21,5	94,9	72,2	3,2	1,9
	350	26,8	93,8	70,1	4,3	2,5
7	330	13,3	95,4	76,2	3,0	1,6
	350	17,1	93,2	75,0	4,1	2,7

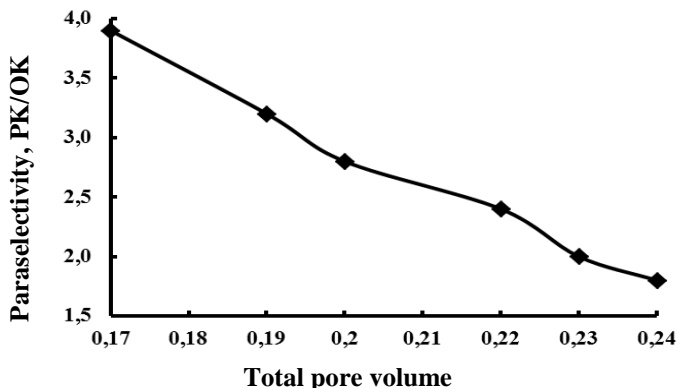
PK vø OK – p- vø o- xylenes; TMB - trimethylbenzenes; other ArH- benzene, toluene, ethylbenzene

Figure 17 shows that as the amount of zinc in the catalyst increases, the activity of the catalyst decreases and the parasitelectivity increases.



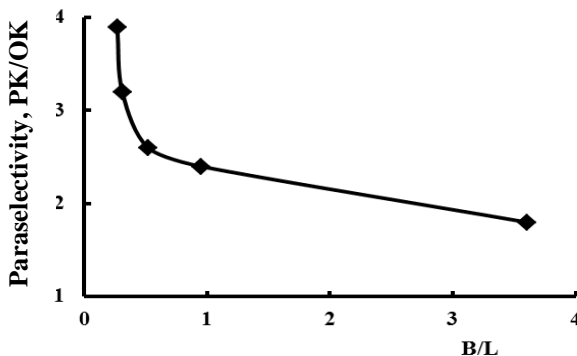
**Figure 17. Dependence of m-xylene conversion and PK/OK ratio (parasectivity) on the amount of zinc in the catalyst (T=330°C)**

When the amount of zinc in H-ultrasilin is increased to 5.0 wt.%, the conversion of m-xylene is almost doubled from 43.2% to 21.5%. However, the paraselectivity increases significantly (from 2.4 to 3.2). When the amount of zinc in the catalyst is increased to 7.0 wt.%, the paraselectivity increases to 3.9%. However, in this case, the m-xylene conversion rate is very low (13.3%). Taking this into account, the optimal amount of zinc in the catalyst can be considered to be 5% by mass.



**Figure 18. Dependence between catalyst paraselectivity and pore volume**

It can be seen from Figure 18 that the pore volume of the catalyst also affects the paraselectivity. As the pore volume decreases, the paraselectivity of the catalyst increases.

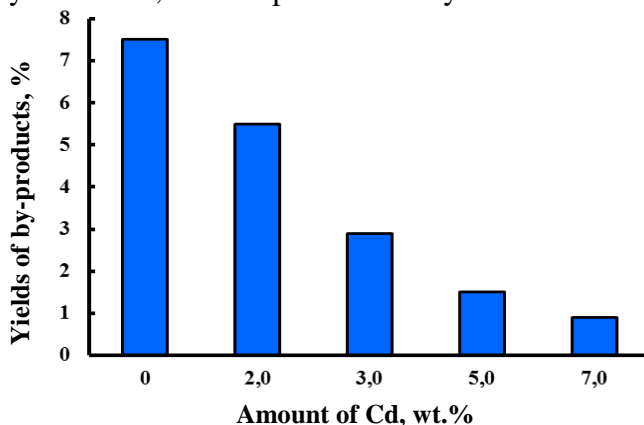


**Figure 19. Dependence between the paraselectivity of the catalyst and the ratio of B/L acid sites**

Indeed, it can be seen from Figure 19 that as a result of the modification, the density of stronger Brønsted acid sites decreases, and the density of moderate Lewis acid sites increases. As a result of these changes, the ratio of B/L acid sites decreases from 3.6 to 0.27.

Paraselectivity increases as the ratio of B/L acid sites decreases. Higher paraselectivity is achieved with B/L acid site ratios of 0.27-0.31. It is clear from this that both acid sites are involved in the conversion of m-xylene. However, in order to target m-xylene preferentially towards isomerization, the density of medium-strength Lewis acid sites must be 3.2-3.6 times higher than that of the Brønsted acid sites. A small amount of strong Brønsted acid centers (170-180  $\mu\text{mol/g}$ ) is required for the isomerization of m-Xylene.

**Catalytic properties of cadmium-modified ultrasil zeolite in the isomerization of m-xylene.** The effect of cadmium, another metal of the II B group of the periodic system, as a modifier on the catalytic properties of H-ultrasiline in the isomerization of m-xylene was studied. It was determined that when the amount of cadmium in H-ultrasilin exceeds 3.0 wt.%, the degree of conversion of m-xylene significantly decreases, and the paraselectivity increases.



**Figure 20. Dependence of the amount of cadmium in the catalyst on the yield of by-products (T=330°C)**

It can be seen from Figure 20 that the amount of cadmium significantly affects the yield of byproducts. As the amount of cadmium in the catalyst increases, the release of byproducts

decreases. When the content of cadmium in the catalyst is 5.0-7.0wt.%, the yield of by-products decreases by 5.0-9.0 times and is only 0.9-1.5wt.%.

Thus, in the presence of an H-ultrasilic catalyst containing 5.0-7.0% zinc or cadmium, m-xylene undergoes mainly isomerization and the formation of byproducts is avoided. Comparing 5% Zn-H-ultrasil and 5% Cd-ultrasil catalysts (330oC), it is found that m-xylene conversion rate is slightly higher (2.2 kw.%) in zinc modified sample, but the paraselectivity in cadmium modified sample becomes higher.

**The effect of lanthanides on the physicochemical and catalytic properties of HTsVM zeolite in the isomerization reaction of m-xylene.** Table 20 shows the distribution of the amount of acidic sites ( $\mu\text{mol/g}$ ) based on the value of activation energy ( $E$ , kJ/mol) of catalysts based on HTsVM modified with lanthanoids.

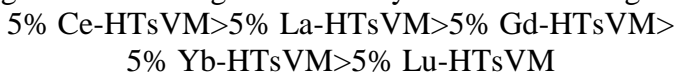
**Table 20**  
**Distribution of the number of acid sites by activation energy in lanthanide-modified pentasils**

Catalyst	$E < 95$ kJ/mol	$95 \leq E < 130$ kJ/mol	$E > 130$ kJ/mol	High temperature arm	$130 < E <$ (160- 175), kJ/mol
HTsVM	620	215,7	316,3	-	-
H-ultrasil	625	213,5	314,5	-	-
1% Yb-HTsVM	396,4	228,6	178,7	60,3(>160°C)	118,4
5% Yb-HTsVM	264,3	253,7	92,4	46,1(170°C)	46,3
10% Yb-HTsVM	275,6	274,6	54,2	31,6(>165°C)	22,6
5% La-HTsVM	286,0	268,0	52,0	40,6(>170°C)	45,0
10% La-HTsVM	252,0	297,0	46,1	23,4(>165 °C)	22,0
5% Ce-HTsVM	280,2	275,7	84,6	41,6(>170 °C)	43,0
5% Gd-HTsVM	278,3	256,3	89,5	43,7(>170 °C)	45,8
5% Lu-HTsVM	280,2	247,2	94,6	50,8(>170 °C)	43,8
5% La-H-ultrasil	282,5	276,6	86,3	38,8(>170 °C)	70,9
5% Yb-H-ultrasil	274,6	263,3	87,5	42,2(>170 °C)	45,3
5% Lu-H-ultrasil	272,7	252,6	91,2	48,4(>170 °C)	42,8

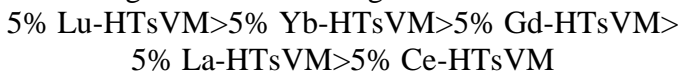
As the amount of lanthanoid metals in the samples increases, the density of strong Brønsted acid sites ( $E > 130$  kJ/mol) decreases

and the density of moderate Lewis and Brønsted acid sites ( $95 \leq E < 130$  kJ/mol) increases.

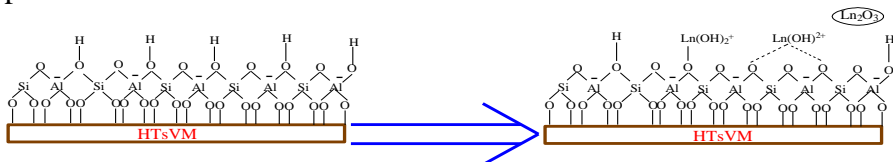
The modification also leads to the formation of centers that hold ammonia tightly. When adding lanthanoid metals to HTsVM and H-ultrasil zeolites, new stronger ( $130 < E < (160-175)$  kC/mol) Lewis acid centers are formed. A comparison of lanthanoid metals according to their nature shows that catalysts are arranged in the following order according to the density of medium strength centers:



According to the concentration of strong Brønsted acid sites, catalysts are arranged in the following order:



The change in acid properties of pentasils after modification can be explained as follows: in the impregnation process, a part of  $\text{H}^+$  ions in H-pentasil is replaced by  $\text{Ln}^{3+}$ ,  $\text{Ln}(\text{OH})_2^+$  and  $\text{Ln}(\text{OH})_2^{2+}$  ions. Since  $\text{Ln}^{3+}$ ,  $\text{Ln}(\text{OH})_2^+$  and  $\text{Ln}(\text{OH})_2^{2+}$  are electron acceptor particles, they act as Lewis acid sites. In this case, some of the Brønsted acid sites are converted into Lewis acid sites, and this process is shown in the scheme below.



A part of the  $\text{Ln}_2\text{O}_3$  (or  $\text{CeO}_2$ ) nanoparticles formed after the thermal treatment of the modified sample in air is located in the channels and on the outer surface of the zeolite. For this reason, during the modification process, the density and strength of strong Brønsted acid sites of zeolite decrease, the density of medium-strength centers increases, new Lewis acid sites are formed, and the volume of zeolite pores decreases.

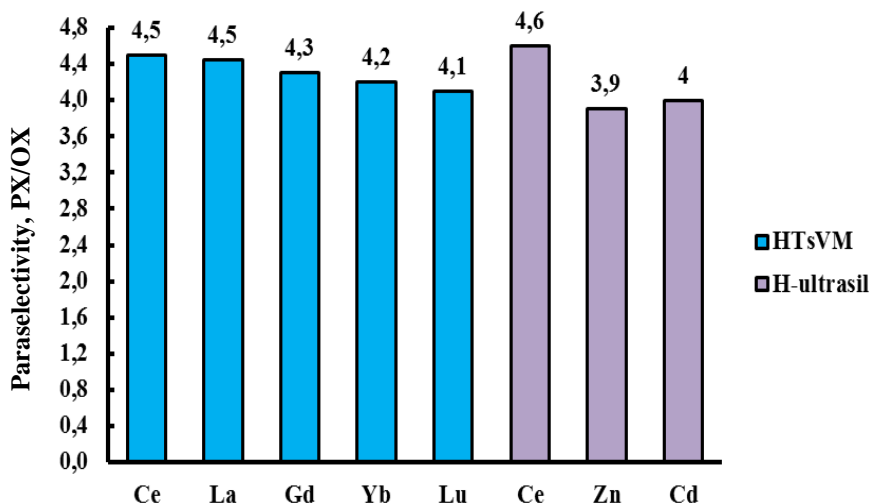
It can be seen from Table 21 that as the amount of lanthanide metal in H-TsVM content increases, the specific surface area and pore volume decrease. When the content of Ln in the catalyst is 1.0 wt.%, the change is negligible. The specific surface area decreases



from 266.3 to 265.1 m<sup>2</sup>/g, and the pore volume decreases from 0.223 to 0.216 cm<sup>3</sup>/g. A change in these characteristics of zeolite occurs when it contains 3.0 wt.% lanthanides. In this case, the specific surface area of the catalyst decreases to 241.2 m<sup>2</sup>/g, and the volume of pores decreases to 0.167 cm<sup>3</sup>/g. Increasing the amount of modifier up to 10.0 wt.% shows more sharp changes. The specific surface area decreases to 213.4 m<sup>2</sup>/g, and the pore volume decreases to 0.148 cm<sup>3</sup>/g.

**Table 21**  
**Textural properties of lanthanide-modified catalysts**

Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>pores</sub> (cm <sup>3</sup> /g)
H-TsVM	266,3	0,223
1%Ce-H-TsVM	265,1	0,216
3%Ce-H-TsVM	241,2	0,167
5%Ce-H-TsVM	228,3	0,155
10%Ce-H-TsVM	213,4	0,148
5%La-H-TsVM	224,3	0,162
5%Ln-H-TsVM	232,4	0,173



**Figure 21. Effect of metal nature on paraselectivity (T=300 °C)**

Figure 21 shows that catalysts modified with 5%Ce and 5%La show higher paraselectivity. Thus, when H-pentasils are modified

with lanthanides, a redistribution of acid sites occurs. The density of strong Brønsted acid sites significantly decreases due to the fact that the modifier does not interact with the crystalline framework of zeolite, the density of medium-strength acid sites increases, new Lewis acid sites are formed, and the volume of zeolite pores decreases. As a result, the paraselectivity of the m-xylene isomerization of catalysts modified with lanthanum increases.

**Physico-chemical and catalytic properties of catalysts based on platinum and palladium-modified ZSM-5 zeolite in the conversion of m-xylene.** It can be seen from Table 22 that when HZSM-5 zeolite is modified with Pt by impregnation, the conversion of m-xylene is quite low and is 39.8-44.3%. As a result of the modification, a decrease in the yields of by-products is observed.

**Table 22**  
**Effect of Pt and Pd addition method to HZSM-5 zeolite at conversion of m-xylene on its activity and product yields**

Catalyst	T°C	Conversion of m-xylene, %	Product yields, wt. %			
			PK	OK	TMB	Others
HZSM-5	350	48,1	20,8	21,1	3,4	2,3
	380	53,4	21,3	23,5	5,2	3,4
0,5% Pt/ HZSM-5 (Impregnation)	350	39,8	19,5	17,0	2,1	1,2
	380	44,3	20,6	19,4	2,7	1,6
0,5 %Pt/ HZSM-5 [Pt(NH <sub>3</sub> ) <sub>4</sub> ]Cl <sub>2</sub> (Ion exchange)	350	26,2	15,3	10,2	1	0,6
	380	34,0	18,2	14,0	0,8	1,0
	400	41,3	20,3	18,4	1,4	1,2
0,5% Pd/ HZSM-5 [Pd(NH <sub>3</sub> ) <sub>4</sub> ]Cl <sub>2</sub> (Ion exchange)	350	27,4	15,7	10,6	0,3	0,8
	380	36,2	19,4	14,6	1,0	1,2

The effect of Pt and Pd introduction into ZSM-5 zeolite, which has a silicate modulus equal to 61, on its catalytic properties in the isomerization reaction of acid and m-xylene was studied (Table 23). Modification of HZSM-5 zeolite with platinum and palladium by the ion exchange method leads to a significant decrease in the yield of TMB and other products (heavy aromatic hydrocarbons). For example, at 380°C, the yield of TMB and other ArH decreases to 0.8-1.0%

and 1.0-1.2%, respectively. Because of the modification, the amount of p-xylene in the products is significantly higher than that of o-xylene.

**Table 23**

**Effect of modification method on acidic properties of HZSM-5 zeolite**

Catalyst	T <sub>max</sub> , °C		Concentration of acid sites, μmol/g	
	form I	form II	form I	form II
HZSM-5	195	408	625	528
0,5 %Pt-HZSM-5 (Impregnation)	194	362	429	447
0,5 %Pt-HZSM-5 (Ion exchange)	192	305	354	103
0,5 %Pd-HZSM-5 (Ion exchange)	194	310	362	112

When adding platinum to the catalyst by impregnation, the amount of strong Brønsted acid sites is reduced enough (447 μmol/g). When HZSM-5 zeolite is modified by ion exchange with platinum or palladium, it causes a sharp decrease in strong Brønsted acid sites (103-112 μmol/g), and along with a decrease in the density of strong Brønsted acid sites, the strength of these centers weakens (Table 23).

Thus, when HZSM-5 zeolite is modified by ion exchange with Pt and Pd, its isomerization selectivity increases to 97%.

**Effect of lanthanum modification on catalytic properties of zeolite H-TsVN in the process of isomerization of C<sub>8</sub> aromatic hydrocarbon mixture.** The results of the effect on the catalytic properties of HTsVN zeolite in the conversion of a mixture of xylene and ethylbenzene are shown in Table 24. It can be seen that as a result of significant disproportionation and transalkylation reactions of xylene and ethylbenzene in the presence of zeolite TsVN in the reaction products the formation of benzene, toluene, trimethyl-, methyl-, methylethyl- and diethylbenzene is observed.

However, the isomerization of m-xylene and ethylbenzene is negligible. Although the increase of p-xylene in the catalyst at 350°C is 3.2 wt.%, the amount of by-products (C<sub>9</sub>-C<sub>10</sub> aromatic hydrocarbons) reaches 7.9 wt.%.

**Table 24**

**Effect of the amount of lanthanum on the isomerization activity of zeolite TsVN at different temperatures**

Composition of raw material	Amount in raw material %	TsVN		1% La/TsVN		3% La/TsVN		5% La/TsVN	
		350°C	380°C	350°C	380°C	350°C	380°C	350°C	380°C
C <sub>6</sub> -C <sub>8</sub> non-ArH, benzene	1,6	5,7	6,3	4,4	4,9	3,4	3,7	2,9	3,2
Toluene	1,8	3,2	3,5	3,1	3,3	2,9	3,1	2,6	2,8
Ethylbenzene	18,7	11,9	11,2	13,0	11,8	12,8	12,0	13,3	12,6
m- Xylene	55,9	39,9	37,8	39,5	38	41,9	40,7	42,7	41,4
p- Xylene	10,7	14,2	15,1	16,9	16,3	18,0	17,6	17,8	17,4
o- Xylene	11,3	17,2	16,8	17,4	17,8	17,0	17,7	17,1	18,0
C <sub>9</sub> -C <sub>10</sub> ArH	-	7,9	9,3	5,7	7,9	4,0	5,2	3,6	4,6

Increasing the amount of lanthanum in the zeolite up to 5.0 wt.% does not increase its isomerizing activity. The amount of p- and o-xylenes in the catalyst is 17.8-17.4 wt.% and 17.1-18.0 wt.%, respectively. However, at this time a slight decrease in the amount of non-aromatic hydrocarbons C<sub>6</sub>-C<sub>8</sub> (2.9-3.2 wt.%) and aromatic hydrocarbons C<sub>9</sub>-C<sub>10</sub> (3.6-4.6 wt.%) is observed. As a result of modification, an increase in the selectivity of the isomerization reaction is observed due to a decrease in the yield of extraneous products. The results show that the selectivity of the isomerization of the catalyst depends largely on the amount of modifier. Higher selectivity of isomerization (92.4-93.6%) is achieved in the presence of TsVN zeolite modified with 3.0-5.0 wt.% lanthanum.

**Investigation of the catalytic properties of bi- and polymetallic catalysts based on zeolite TsVN at the conversion of xylene and ethylbenzene mixtures.** In order to increase the isomerization property of the monometallic catalyst 3%La/TsVN (CT-3), this catalyst was additionally modified with platinum and cobalt and the catalytic properties of the catalysts prepared on their basis were studied.

Table 25 shows the results of the modifying effect of platinum

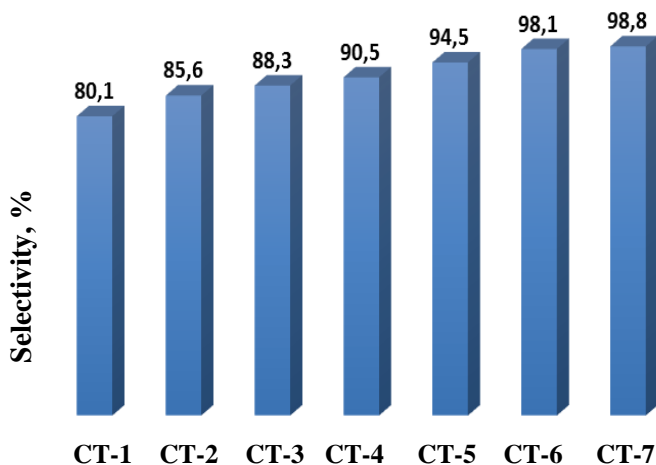
and cobalt on the isomerization properties of 3%La/TsVN catalyst. The addition of 0.5 wt.% platinum to the composition of 3% La/TsVN catalyst (CT-3) increases its isomerization ability and reduces the amount of by-products.

At an increase of reaction temperature up to 380°C modification of the bimetallic catalyst 0.5% Pt 3%La-TsVN (CT-5) with cobalt in the amount of 0.2-0.3 wt.% leads to increase of its isomerization ability.

**Table 25**  
**Effect of modification of 3% La/TsVN catalyst with platinum and cobalt on its isomerization activity**

Composition of the catalyst, wt.%	0,5%Pt 3%La/ TsVN		0,5%Pt 0,2%Co 3%La/ TsVN		0,5%Pt 0,3%Co 3%La/ TsVN	
	350°C	380°C	350°C	380°C	350°C	380°C
Non-ArH, C <sub>6</sub> -C <sub>8</sub> , benzene	2,6	3,2	1,9	2,4	1,8	2,3
Toluene	2,7	2,9	2,1	2,6	2,0	2,4
Ethylbenzene	11,8	10,6	1,8	9,3	11,0	9,7
m- Xylene	43,5	42,6	42,1	42,8	43,3	43,1
p- Xylene	18,5	18,7	21,8	21,6	21,2	20,9
o- Xylene	18,4	18,8	20,4	20,6	20,7	21,4
ArH C <sub>9</sub> -C <sub>10</sub>	2,4	3,2	0,9	1,2	1,1	1,4

In the presence of platinum-modified catalyst (CT-5) at 350°C, the amount of p- and o-xylenes in the catalyst increases to 18.5 and 18.4 wt.%, respectively, and the amount of by-products (non-aromatic C<sub>6</sub>-C<sub>8</sub>, benzene and ArH C<sub>9</sub>-C<sub>10</sub>) decreases to 5.0 wt.% and the isomerization selectivity increases from 88.3% to 94.5% (Figure 22). Modification of bimetallic catalyst CT-5 with cobalt in the amount of 0.2 wt.% leads to an increase in the amount of p- and o-xylenes in the catalyst to 21.8 and 20.4 wt.%, respectively at 350°C, a decrease in the amount of by-products to 2.8 wt.% and an increase in the isomerization selectivity to 98.1% (CT-6). When increasing the amount of cobalt in the composition of polymetallic catalyst up to 0.3 wt.% (CT-7), its isomerization ability slightly decreases, but the selectivity slightly increases up to 98.8%. Increasing the amount of lanthanum in TsVN zeolite to 3.0 wt.% increases its isomerization selectivity from 80.1% to 88.3%.



**Figure 22. Dependence of isomerization selectivity on the nature of the catalyst: T=350°C. CT-1 – TsVN; CT-2 – 1%La/ TsVN; CT-3 – 3%La/ TsVN; CT-4 – 5%La/ TsVN; CT-5 – 0,5%Pt 3%La/ TsVN; CT-6 – 0,5%Pt 3%La 0,2%Co/ TsVN; CT-7 – 0,5%Pt 3%La 0,3%Co/ TsVN**

Modification of the La-containing catalyst (CT-3) with platinum (CT-5) increases its isomerization selectivity up to 94.5%. Additional modification of the bimetallic (CT-5) catalyst with cobalt (CT-6, CT-7) in the amount of 0.2-0.3 wt.% increases the selectivity of its isomerization up to 98.1-98.8%. In the process of isomerization of a mixture of aromatic hydrocarbons C<sub>8</sub>, the use of polymetallic catalysts based on high-silica (TsVN) zeolite can be considered more appropriate (Figure 22).

**Physicochemical properties of catalytic composite systems based on high-silica zeolite of ZSM-5 type and Ln(lanthonoid)-oxides in the process of conversion of methanol into hydrocarbons.** Table 26 shows the effect of catalytic composition of HZSM-5 zeolite with Ho<sub>2</sub>O<sub>3</sub> oxide on the composition of methanol conversion products.

In the presence of unmodified HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=33), the content of C<sub>1</sub>-C<sub>4</sub> alkanes and aromatic hydrocarbons in the products is higher at 42.7% and 42.3%, respectively.

**Table 26**

**The effect of the amount of Ho<sub>2</sub>O<sub>3</sub> on the composition of the conversion products of methanol in the presence of HZSM-5-modifier catalyst system**

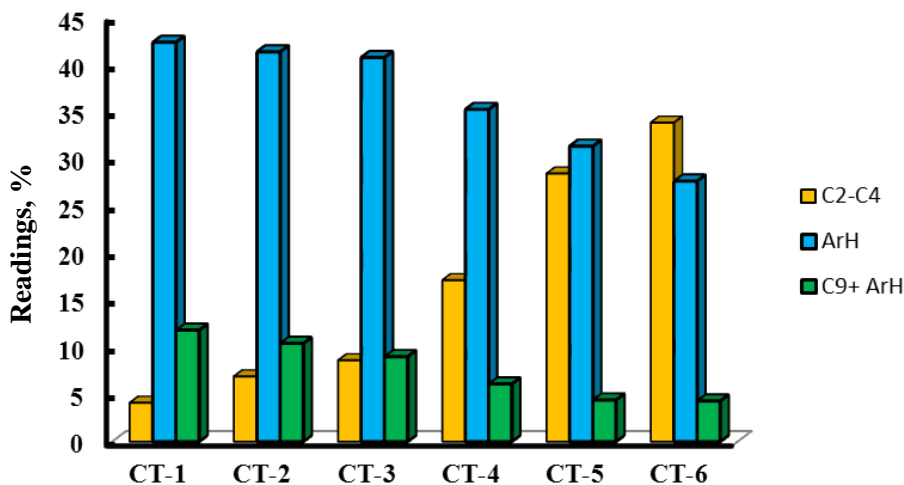
Products	Catalyst					
	CT-1 (0)	CT-2* (0,6)	CT-3 (1,0)	CT-4 (3,0)	CT-5 (5,0)	CT-6 (6,0)
Alkanes C <sub>1</sub> -C <sub>4</sub>	42,7	41,9	38,7	33,7	21,6	18,6
Alkenes C <sub>2</sub> -C <sub>4</sub>	4,1	6,9	8,6	17,1	28,4	33,8
Total Σ C <sub>1</sub> -C <sub>4</sub>	46,8	48,8	47,3	50,8	50,0	52,4
Alkanes C <sub>5+</sub>	0,8	0,7	0,9	1,0	1,2	1,3
Alkenes C <sub>5+</sub>	0,6	0,5	0,4	0,7	1,0	1,2
İsoalkanes and cycloalkanes C <sub>5+</sub>	8,5	8,8	10,7	12,3	16,5	17,4
Aromatic hydrocarbons (ArH)	43,3	41,2	40,7	35,2	31,3	27,6
Benzene	2,4	1,9	1,7	1,2	0,9	0,7
Toluene	11,2	9,8	9,2	5,8	4,3	3,7
Xylenes	17,9	19,1	20,8	22,1	21,2	19,1
ArH C <sub>9+</sub>	11,8	10,4	9,0	6,1	4,9	4,3
Total Σ C <sub>5+</sub> +Ar	53,2	54,2	52,7	49,2	50,0	47,6

\*Kt-2- holmium was loaded into the zeolite by the ion exchange method.

Due to the fact that HZSM-5 zeolite has strong Brønsted acid sites, the unsaturated intermediates obtained from the conversion of methanol undergo faster hydrogenation, oligomerization and cyclization, and are mainly converted into saturated C<sub>1</sub>-C<sub>4</sub> alkanes and aromatic hydrocarbons. For this reason, the amount of C<sub>2</sub>-C<sub>4</sub> and C<sub>5+</sub> alkenes in the reaction products is significantly small. The amount of C<sub>2</sub>-C<sub>4</sub> alkenes is 4.1%, and the amount of C<sub>5+</sub> is insignificant (0.6%). Aromatic hydrocarbons consist of benzene, toluene, xylene and C<sub>9+</sub> aromatic hydrocarbons. Among them, xylenes are the most abundant (17.9%). However, as a result of condensation of unsaturated hydrocarbons in the presence of zeolite HZSM-5, a significant amount (11.8%) of C<sub>9+</sub> aromatic hydrocarbons is formed.

The addition of 0.6 wt.% holmium to the composition of zeolite

HZSM-5 by the ion exchange has little effect on its catalytic properties. Considering that zeolite ZSM-5 contains a limited amount of metal (<1.0 wt.%) by ion exchange method, catalytic compositions of zeolite HZSM-5 with  $\text{H}_2\text{O}_3$  oxide were prepared by mechanical mixing. The amount of  $\text{H}_2\text{O}_3$  nanopowder in the catalytic composition varied in the range of 1.0-6.0 wt.%. In the presence of samples containing 5.0-6.0 wt.% of modifier, the amount of  $\text{C}_1$ - $\text{C}_4$  alkanes decreases to 18.6-21.6% and the amount of  $\text{C}_2$ - $\text{C}_4$  alkenes increases to 28.4-33.8% . In the presence of these samples, the amount of aromatic hydrocarbons decreases to 27.6-31.3%. The amount of  $\text{C}_{9+}$  aromatic hydrocarbons decreases 2.4-2.7 times compared to the unmodified sample. In the sample containing 5.0 wt.%, the amount of xylene is high and makes 21.2%. Increasing the amount of modifier up to 6.0 wt.% leads to a significant decrease in the amount of xylenes (19.1%).



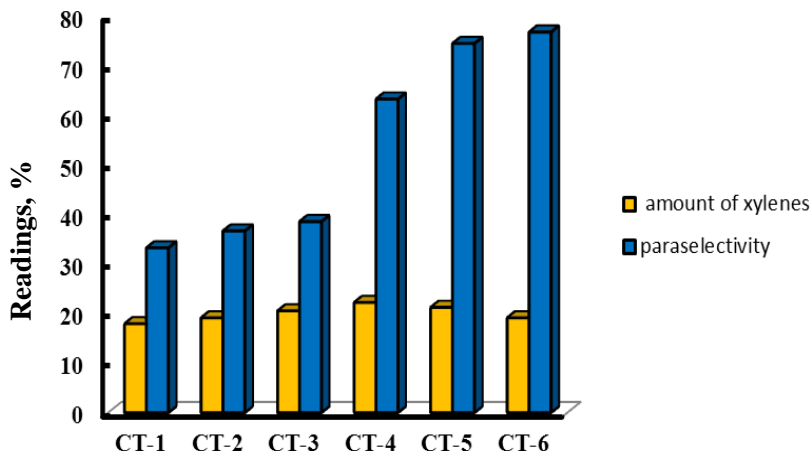
**Figure 23. Effect of modifier concentration in the catalytic composition on the amount of  $\text{C}_2$ - $\text{C}_4$ , ArH and  $\text{C}_{9+}$  ArH**

Figure 23 shows the effect of the amount of  $\text{H}_2\text{O}_3$  nanopowder in the catalytic composition on the amount of  $\text{C}_2$ - $\text{C}_4$  alkenes, aromatic hydrocarbons and  $\text{C}_{9+}$  ArH obtained during the conversion of methanol. As a result of increasing the amount of modifier in the



catalytic composition, an increase in the content of C<sub>2</sub>-C<sub>4</sub> alkenes, a decrease in the amount of aromatic hydrocarbons and C<sub>9+</sub> aromatic hydrocarbons can be clearly seen.

Figure 24 shows the effect of modifier concentration in the catalytic composition on the amount of xylene and the selectivity of p-xylene in the xylene mixture.



**Figure 24. Effect of modifier concentration on the amount of xylene in the catalytic composition and selectivity for p-xylene in the xylene mixture**

When the modifier concentration in the catalytic composition is increased up to 5.0 wt.%, the amount of xylenes decreases insignificantly (21.2%), and the p-xylene selectivity increases up to 71.4%. When the modifier concentration in the catalyst is increased to 6.0 wt.%, the amount of xylenes decreases significantly (19.1%), and the para selectivity increases more sharply (76.7%).

Thus, the catalytic composition containing 5.0-6.0 wt.% of modifier shows higher activity on the amount of C<sub>2</sub>-C<sub>4</sub> alkenes, xylenes and shows high selectivity for p-xylene.

**Catalytic properties of catalytic composition of zeolite HZSM-5 with nanopowders of spinel structure Ln-oxides in the conversion of methanol into hydrocarbons.** Catalytic compositions were obtained by mechanical displacement of H-form zeolite and

$\text{Ln}_2\text{O}_3$  nanopowders. In all samples the amount of  $\text{Ln}_2\text{O}_3$  nanopowders was kept at 5.0 wt.%.

**Table 27**

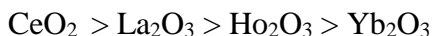
**Effect of the nature of  $\text{Ln}_2\text{O}_3$  spinel nanopowders in the catalytic composition on the composition and distribution of methanol conversion products ( $T=400^\circ\text{C}$ ,  $\text{N}_2/\text{CH}_3\text{OH}=0,33$ ,  $v=2,0 \text{ h}^{-1}$ )**

Products	Catalytic composition ( $\text{HZSM}+\text{Ln}_2\text{O}_3$ )			
	$\text{La}_2\text{O}_3$	$\text{CeO}_2$	$\text{Ho}_2\text{O}_3$	$\text{Yb}_2\text{O}_3$
Alkanes $\text{C}_1\text{-C}_4$	17,1	17,3	20,3	21,5
Alkenes $\text{C}_2\text{-C}_4$	33,8	36,4	31,6	29,4
Total $\sum \text{C}_1\text{-C}_4$	50,9	53,7	51,5	50,9
Alkanes $\text{C}_{5+}$	1,1	0,9	1,2	1,3
Alkenes $\text{C}_{5+}$	1,2	1,0	1,3	1,4
isoalkanes and cycloalkanes $\text{C}_{5+}$	18,8	19,7	17,9	16,2
Aromatic hydrocarbons (ArH)	28,0	24,7	27,7	30,2
Benzene	0,8	0,5	0,6	1,0
Toluene	4,1	3,4	3,8	5,0
Xylenes	19,7	17,7	18,8	19,1
ArH $\text{C}_{9+}$	3,4	3,1	4,5	5,1
Total $\sum \text{C}_{5+}$	49,1	46,3	48,1	49,1

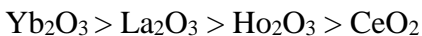
The composition of the products obtained during methanol conversion in the presence of the prepared catalytic compositions is shown in Table 27.

The largest amount of  $\text{C}_2\text{-C}_4$  alkenes in the composition of the products (36.4%) was obtained in the catalytic composition modified with  $\text{CeO}_2$  nanopowders (Figure 25).

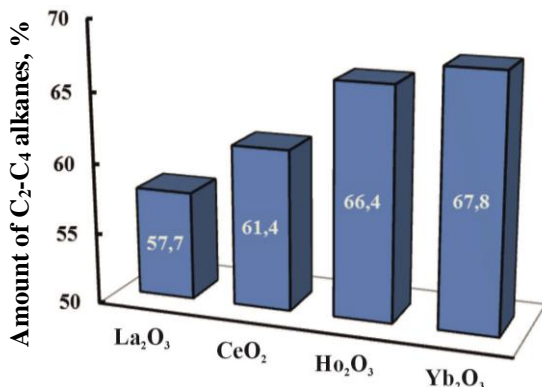
According to the nature of the modifiers in the catalytic composite, they are arranged according to the decreasing amount of  $\text{C}_2\text{-C}_4$  alkenes:



The higher amount of aromatic hydrocarbons (30.2%) is observed in the catalytic composition modified with  $\text{Yb}_2\text{O}_3$  nanopowders. According to the nature of the modifier, the decrease in the amount of aromatic hydrocarbons is in the following order:

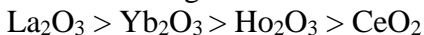


In the presence of the catalytic composition modified with  $\text{CeO}_2$ , the amount of xylenes (17.7%) is relatively low.



**Figure 25. Effect of the nature of the modifier in the catalytic composition on the amount of C<sub>2</sub>-C<sub>4</sub> olefins in the gas phase**

The amount of xylenes (19.7 %) is higher in the catalytic composition modified with  $\text{La}_2\text{O}_3$  nanopowders. According to the nature of the modifier, the decrease in the amount of xylenes in the products is arranged in the following order :



**Properties of catalytic compositions of spinel structure nanopowders with HZSM-5 zeolite in the process of conversion of methanol into hydrocarbons.** The properties of spinel structure catalytic systems in the process of methanol conversion to C<sub>2</sub>-C<sub>4</sub> olefins and p-xylene have been studied.

Table 28 shows the results of methanol conversion to hydrocarbons in the presence of unmodified HZSM-5 (CT-1) and catalytic systems modified with  $\text{Ho}_2\text{O}_3$  (CT-2),  $\text{Ho}_{0.05}\text{Mg}_{0.05}\text{Al}_2\text{O}_4$  (CT-3) and  $\text{Ho}_{0.1}\text{Mg}_{0.1}\text{Al}_2\text{O}_4$  (CT-4) nanopowders (1.0 wt.%).

It can be seen that in the presence of zeolite HZSM-5 in the result of methanol conversion alkanes and alkenes C<sub>1</sub>-C<sub>4</sub>, aliphatic and aromatic hydrocarbons C<sub>5+</sub> are obtained. Aromatic hydrocarbons

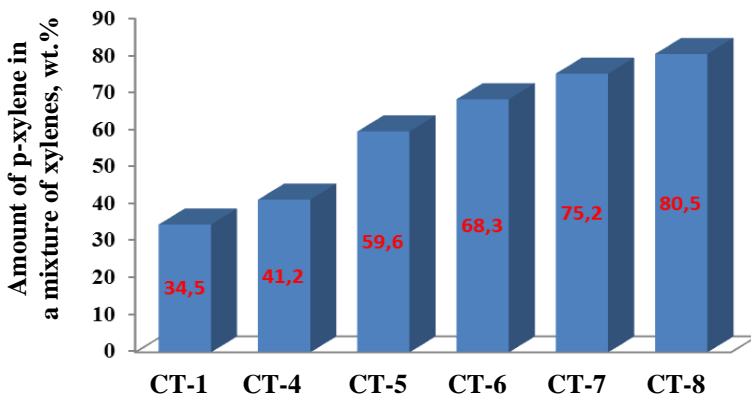
C<sub>6</sub>-C<sub>8</sub> consist of benzene, toluene and xylenes. The amount of C<sub>9+</sub> aromatic hydrocarbons is 10.1 wt.%.

**Table 28**

**Effect of the amount of nanopowders in the catalytic composition on the content of methanol conversion products**

Products	Products yield, %			
	CT-1	CT-2	CT-3	CT-4
Alkanes C <sub>1</sub> -C <sub>4</sub>	41,8	38,8	34,4	32,6
Alkenes C <sub>2</sub> -C <sub>4</sub>	5,40	8,20	12,1	14,7
ΣC <sub>1</sub> -C <sub>4</sub>	47,2	47,0	46,5	47,3
Alkanes C <sub>5+</sub>	1,20	1,00	0,80	1,10
Alkenes C <sub>5+</sub>	0,70	0,50	0,30	0,60
Isoalkanes and cycloalkanes C <sub>5+</sub>	9,70	11,4	13,3	14,1
Aromatic hydrocarbons	41,2	40,1	39,1	36,9
Benzene	2,10	1,80	1,50	0,90
Toluene	10,2	8,70	7,60	5,10
Xylenes	18,8	21,1	23,7	25,2
Aromatic hydrocarbons C <sub>9+</sub>	10,1	8,50	6,30	5,70
ΣC <sub>5+</sub>	52,8	53,0	53,5	52,7

The total amount of aromatic hydrocarbons reaches 41.2 wt.%. Among them xylenes prevail (18.8 wt.%). When zeolite HZSM-5 is modified with Ho<sub>0.05</sub>Mg<sub>0.05</sub>Al<sub>2</sub>O<sub>4</sub> nanopowders of spinel structure (CT-3), the amount of C<sub>2</sub>-C<sub>4</sub> alkenes increases up to 12.1 %, and the amount of C<sub>5+</sub>-isoalkanes, C<sub>5+</sub>-cycloalkanes increases up to 13.3 %. The amount of xylenes in the products increases up to 23.7%. Modification leads to a significant reduction of aromatic hydrocarbons C<sub>9+</sub> (from 8.5% to 6.3%). In the presence of catalytic composition HZSM-5 Ho<sub>0.1</sub>Mg<sub>0.9</sub>Al<sub>2</sub>O<sub>4</sub> (CT-4) the amount of C<sub>2</sub>-C<sub>4</sub> alkenes in methanol conversion products increases up to 14.7%. As a result of modification, the total amount of aromatic hydrocarbons decreases significantly (up to 36.9%), but the amount of xylenes increases up to 25.2%. There is a decrease in the amount of aromatic hydrocarbons C<sub>9+</sub> in the products up to 5.7%.



**Figure 26. Dependence of the amount of modifier in the catalytic composition on the amount of p-xylene in the xylene mixture**

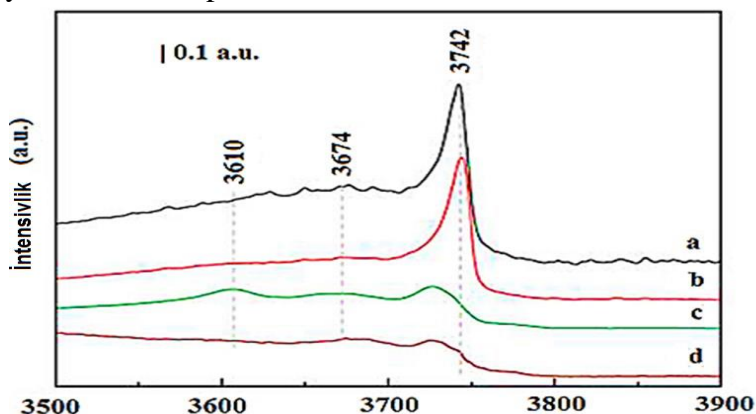
With increasing the amount of modifier in the catalytic composition, the selectivity for para-xylene increases. Figure 26 shows the amount of p-xylene (paraselectivity) in the xylene mixture depending on the amount of modifier in the catalytic composition: CT-5 (2 wt.%), CT-6 (3 wt.%), CT-7 (4 wt.%), CT-8 (5 wt.%). The catalytic composition containing 4.0-5.0 wt.% of modifier shows higher selectivity for p-xylene (75.2-80.5%).

The increase in the yield of C<sub>2</sub>-C<sub>4</sub> alkenes and the increase in the selectivity for p-xylene can be attributed to changes in the acid and textural properties of the catalysts as a result of the modification.

The IR spectra of unmodified and modified catalysts degassed at 200°C were recorded in the absorption band range of 3500-3900 cm<sup>-1</sup> (Figure 27). It is evident from the spectra that these catalysts exhibit absorption bands at 3742, 3674, 3610 cm<sup>-1</sup>. These absorption bands characterize the vibrations of OH-groups in Si-OH (3742 cm<sup>-1</sup>) and Si(OH)Al (3674 and 3610 cm<sup>-1</sup>). The OH groups in Si(OH) and Si(OH)Al are known to provide Brønsted acid sites for catalysis.

Compared to HZSM-5 zeolite, the OH-bands belonging to the Brønsted acid sites are shifted toward lower frequencies for Ho<sub>0.1</sub>Mg<sub>0.9</sub>Al<sub>2</sub>O<sub>4</sub>/HZSM-5 catalysts. With increasing the amount of

$\text{H}_{0,1}\text{Mg}_{0,9}\text{Al}_2\text{O}_4$  nanopowders in the catalytic composition, the intensity of these absorption bands decreases.



**Figure 27. IR spectra of degassed catalysts at 200 °C: a-HZSM-5, b-2,wt.%  $\text{H}_{0,1}\text{Mg}_{0,9}\text{Al}_2\text{O}_3/\text{HZSM-5}$ , c-3,0 wt.%  $\text{H}_{0,1}\text{Mg}_{0,9}\text{Al}_2\text{O}_4/\text{HZSM-5}$ , d-5,0 wt.%  $\text{H}_{0,1}\text{Mg}_{0,9}\text{Al}_2\text{O}_4/\text{HZSM-5}$**

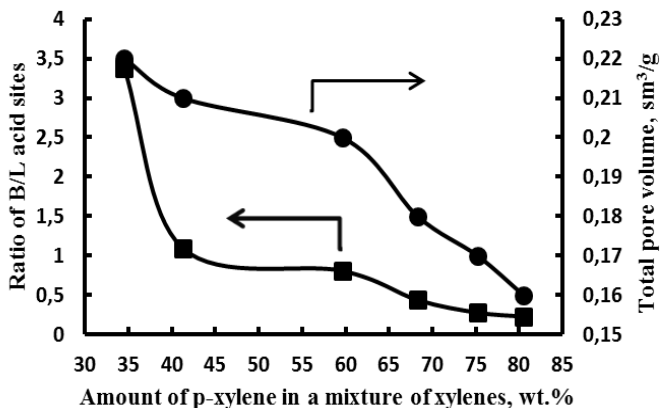
The obtained results confirm that the modifier interacts with hydroxyl groups localized on the zeolite surface. Modification of HZSM-5 zeolite with  $\text{H}_{0,1}\text{Mg}_{0,9}\text{Al}_2\text{O}_4$  nanopowders leads to a decrease in the concentration of acidic OH-groups.

**Table 29**  
**Effect of modifier amount on textural properties of catalytic composition**

Cataysts	Amount of modifier $\text{H}_{0,1}\text{Mg}_{0,9}\text{Al}_2\text{O}_4$ , wt.%	S, m <sup>2</sup> /g	V <sub>por</sub> , cm <sup>3</sup> /g
CT-1	0	288	0,22
CT-4	1	282	0,21
CT-5	2	269	0,20
CT-6	3	258	0,18
CT-7	4	241	0,17
CT-8	5	230	0,16

The results obtained show (Table 29) that the amount of modifier leads to a change in the textural properties of the catalyst. When the amount of modifier in the catalyst is 4.0-5.0 wt.%, its

specific surface area and pore volume decrease significantly. The specific surface area of the catalyst decreases to 230-241 m<sup>2</sup>/g, and the pore volume decreases to 0.16-0.17 cm<sup>3</sup>/g.



**Figure 28. Dependence of catalyst selectivity for p-xylene on the ratio of acid centers B/L and pore volume**

Figure 28 shows the dependence of the catalyst selectivity for p-xylene on the ratio of acid sites B/L and pores.

It can be seen that the selectivity of the catalyst for p-xylene and the yield for C<sub>2</sub>-C<sub>4</sub> alkenes increase with the decrease in the ratio of acid sites B/L and pore volume.

**Bioethanol conversion in the presence of a zinc-modified catalyst based on ZSM-5.** The distribution of products obtained during bioethanol conversion in the presence of HZSM-5 zeolite at different temperatures is shown in Table 30. With increasing temperature, the yield of alkenes decreases, while the yield of C<sub>3</sub> and aromatic hydrocarbons increases. At 300°C, the main part of the products are propane+propylene (12.2%), C<sub>4</sub>-C<sub>6</sub> isoalkanes (11.7%) and C<sub>6</sub>-C<sub>8</sub> aromatic hydrocarbons (10.5%).

When the reaction temperature increases from 300°C to 400°C, the amount of C<sub>1</sub>-C<sub>2</sub> cracking products increases from 0.2% to 2.9%, the amount of ethylene decreases from 5.1% to 0.9%, and the amount of propane+propylene increases from 12.2% to 17.3%. In the temperature range studied, the amount of n-C<sub>4</sub>-C<sub>5</sub> and n-C<sub>7</sub>-C<sub>14</sub>

hydrocarbons is small and is respectively 0.5-0.8% and 0.1-0.6%.

**Table 30**  
**Products of bioethanol conversion in the presence of HZSM-5**

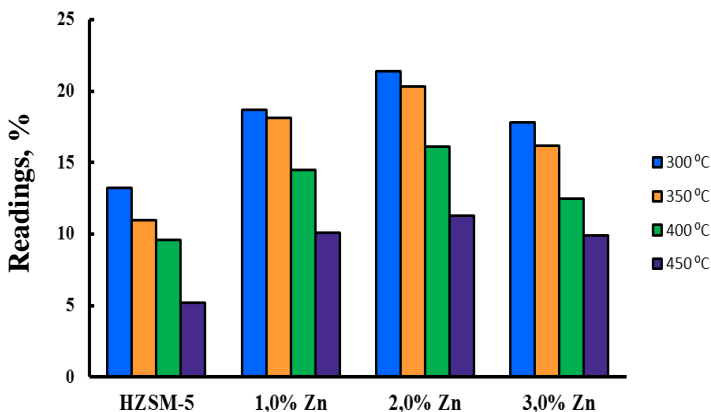
Product	HZSM-5			
	300 °C	350 °C	400 °C	450 °C
H <sub>2</sub>	-	-	0,1	0,1
C <sub>1</sub> -C <sub>2</sub>	0,2	0,6	1,9	2,9
C <sub>2</sub> H <sub>5</sub> OH	1,8	1,2	-	-
C <sub>2</sub> H <sub>4</sub>	5,1	6,1	1,5	0,9
C <sub>3</sub> H <sub>8</sub> +C <sub>3</sub> H <sub>6</sub>	12,2	13,8	15,8	17,3
n-C <sub>4</sub> -C <sub>5</sub>	0,5	0,8	0,7	0,6
n-C <sub>6</sub> -C <sub>14</sub>	0,6	0,2	0,1	-
iso-C <sub>4</sub> -C <sub>6</sub>	11,7	9,9	8,8	4,7
iso-C <sub>7</sub> -C <sub>14</sub>	1,5	1,1	0,8	0,5
n-C <sub>7</sub> -C <sub>14</sub>	0,4	0,3	0,2	0,1
Alkene C <sub>4</sub> -C <sub>6</sub>	2,4	1,1	0,8	0,4
Alkene C <sub>7</sub> -C <sub>14</sub>	0,9	0,3	0,2	0,2
C <sub>6</sub> H <sub>6</sub> *	0,7	1,0	1,4	1,9
ArH C <sub>6</sub> -C <sub>8</sub>	10,5	13,5	15,3	17,8
ArH C <sub>9</sub> -C <sub>14</sub>	2,0	3,4	5,3	8,4
Naphthenes C <sub>5</sub> -C <sub>6</sub>	-	0,1	0,3	0,1
Naphthenes C <sub>7</sub> -C <sub>14</sub>	0,2	0,3	0,3	0,4
H <sub>2</sub> O	50,0	47,3	47,8	45,6

\* - The mass fraction of benzene is included in ArH C<sub>6</sub>-C<sub>8</sub>.

At 300°C the amount of iso-C<sub>4</sub>-C<sub>6</sub> hydrocarbons is rather high (11.7%). When the reaction temperature increases to 450°C, the amount of iso-C<sub>4</sub>-C<sub>6</sub> hydrocarbons decreases to 4.7%. Compared to iso-C<sub>4</sub>-C<sub>6</sub> hydrocarbons, the amount of iso-C<sub>7</sub>-C<sub>14</sub> hydrocarbons in isoproducts is very low (0.5-1.5%). The small amount of C<sub>4</sub>-C<sub>6</sub> and C<sub>7</sub>-C<sub>14</sub> alkenes (0.1-1.5%) can be explained by transformation of alkenes into aromatic hydrocarbons in strong acid sites of zeolite HZSM-5.

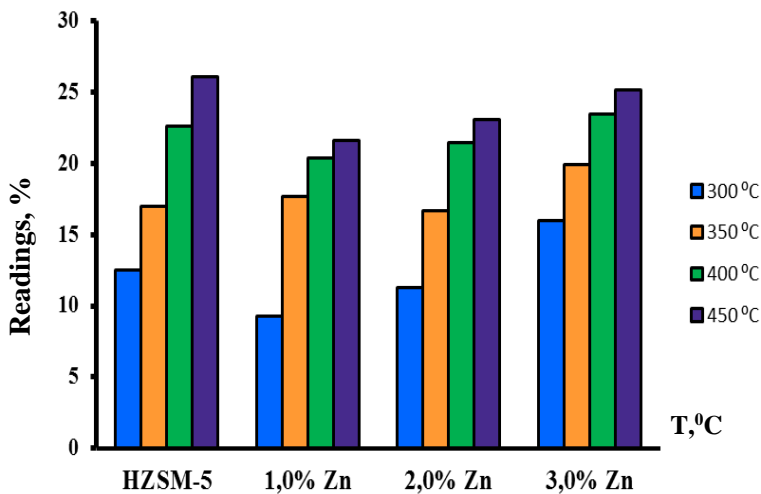
From the results obtained, it can be seen that zeolite HZSM-5 exhibits high cracking and aromatization activity in bioethanol conversion. Figure 29 shows the effect of Zn concentration on the total amount of iso-C<sub>4</sub>-C<sub>6</sub>+iso-C<sub>7</sub>-H<sub>16</sub> in HZSM-5 zeolite during bioethanol conversion.





**Figure 29. Effect of Zn concentration in HZSM-5 zeolite on the total amount of the  $\Sigma$  of iso-C<sub>4</sub>-C<sub>6</sub>+iso-C<sub>7</sub>-C<sub>14</sub> hydrocarbons at different temperatures**

Thus, the catalyst 2%Zn-HZSM-5 shows higher isomerization activity among similar samples in the temperature range of 300-350°C. The content of iso-C<sub>4</sub>-C<sub>6</sub>+iso-C<sub>7</sub>-C<sub>14</sub> hydrocarbons in the products increases to 20.3-21.4%.



**Figure 30. Effect of Zn concentration on ArH content  $\Sigma$ C<sub>6</sub>-C<sub>8</sub>+C<sub>9</sub>-C<sub>14</sub> in zeolite HZSM-5 at different temperatures**

Figure 30 shows that the amount of aromatic hydrocarbons in

the presence of samples modified with 1.0 wt.% and 2.0 wt.% zinc is 9.3-21.6% and 11.3-23.3%, respectively. Unlike isoparaffinic hydrocarbons, the amount of aromatic hydrocarbons increases when the reaction temperature increases from 300°C to 450°C. Increase of Zn concentration in zeolite HZSM-5 up to 3.0 wt.% has a promoting effect on its aromatization activity.

Table 31 shows the octane numbers of liquid hydrocarbon products (catalyst) obtained at different temperatures in the presence of 2%Zn-HZSM-5 catalyst.

**Table 31**  
**Temperature dependence of catalyst octane number**

<b>Temperature, °C</b>	<b>300°C</b>	<b>350°C</b>	<b>400°C</b>	<b>450°C</b>
octane number by RM*	100	115	117	119

\*RM- research method

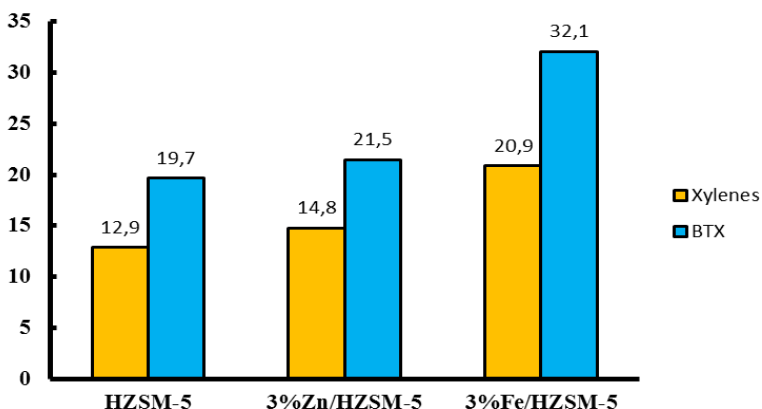
Liquid hydrocarbon products obtained in the temperature range of 300-350°C contain a large amount of high-octane components (isoparaffins 41.5-43.2%; aromatic hydrocarbons 22.1-28.6%). The amount of benzene in the catalyst does not exceed 1.0wt%. The content of aromatic hydrocarbons in the high-octane catalyst is less than 30%, and the benzene content is less than 1.0 wt. %, which means that it meets the requirements of Euro-5 motor fuels.

**Bioethanol conversion in the presence of iron and chromium modified ZSM-5 based catalysts.** The catalytic properties of ZSM-5-based catalysts modified with 2.0-3.0 wt.% iron and chromium were studied in order to study the effect of the nature of transition metals in ZSM-5 zeolite on the distribution and composition of products obtained from the bioethanol conversion process. The obtained results are presented in Table 32. Its clear that Fe/HZSM-5 catalysts have higher aromatizing activity in comparison with Zn-HZSM-5 catalysts. When iron is added to the composition of HZSM-5 zeolite, its isomerization activity decreases. When the amount of iron in the catalyst is increased to 3.0 wt.%, its isomerization activity decreases more sharply.

**Table 32**  
**Effect of the amount of iron in the presence of modified catalyst**  
**on the distribution and composition of bioethanol conversion**  
**products**

Products	Amount of products, wt. %					
	2%Fe/HZSM-5			3%Fe/HZSM-5		
	350 °C	400 °C	450 °C	350 °C	400 °C	450 °C
H <sub>2</sub>	0,2	0,9	1,1	0,3	1,3	1,5
C <sub>2</sub> H <sub>5</sub> OH	2,7	1,8	0,2	1,8	0,4	-
C <sub>2</sub> H <sub>4</sub>	1,9	1,2	0,4	1,4	0,2	0,1
C <sub>3</sub> H <sub>8</sub> +C <sub>3</sub> H <sub>6</sub>	13,1	11,7	9,8	11,9	10,1	8,4
n-C <sub>4</sub> -C <sub>14</sub>	1,6	1,3	0,6	1,4	0,9	0,4
İso-C <sub>4</sub> -C <sub>6</sub>	8,3	7,8	4,2	7,6	6,5	2,4
İso-C <sub>7</sub> -C <sub>14</sub>	1,6	1,2	0,9	1,2	1,0	0,3
C <sub>4</sub> -C <sub>14</sub> - alkenes	1,1	0,8	0,4	0,7	0,6	0,4
C <sub>6</sub> -C <sub>14</sub> -ArH	19,5	20,1	33,8	24,7	30,6	37,1
C <sub>5</sub> -C <sub>14</sub> naphthenes	0,8	0,7	0,4	0,6	0,5	0,4
H <sub>2</sub> O	49,2	47,5	48,6	48,4	47,9	49,0

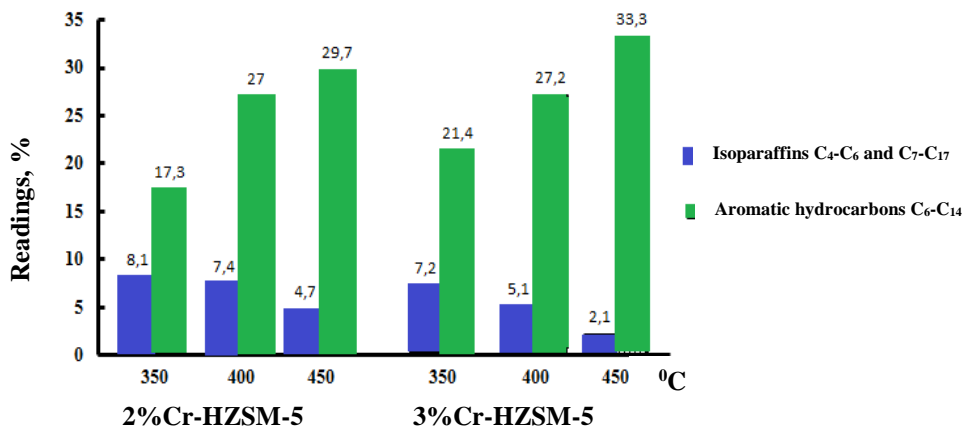
Figure 31 shows that the nature of the modifier in the catalyst has a significant effect on the amount of xylene and BTX fractions.



**Figure 31. Amount of xylene and BTX fraction in products of**  
**bioethanol conversion in the presence of catalysts modified with zinc**  
**and iron (T=450°C)**

When comparing the amount of xylene and BTX (benzene, toluene, xylene) fractions obtained from the conversion of bioethanol at 450°C with the presence of various catalysts, it is known that when HZSM-5 zeolite is modified with Fe and Zn, the amount of these fractions in the products increases. When 3.0 wt.% Zn was added to HZSM-5 zeolite, the amount of xylene and BTX fractions increased from 12.9 and 19.7% to 14.8 and 21.5%, respectively. A higher promotion effect is achieved on the catalyst modified with 3.0 wt.% iron. In the presence of 3%Fe-HZSM-5 catalyst, the amount of xylene and BTX fractions is 20.9 and 32.1%, respectively.

Figure 32 shows that when HZSM-5 zeolite is modified with chromium, the intermediates formed in the pores of the zeolite undergo dehydrocyclization and are converted into aromatic hydrocarbons. For this reason, the amount of aromatic hydrocarbons in the reaction products is high.



**Figure 32. Effect of temperature on the amount of C<sub>4</sub>-C<sub>6</sub>+C<sub>7</sub>-C<sub>14</sub> isoparaffins and C<sub>6</sub>-C<sub>14</sub> aromatic hydrocarbons in the products obtained by bioethanol conversion in the presence of chromium-modified catalyst**

When the amount of chromium in HZSM-5 zeolite increases, its aromatization activity increases. When the reaction temperature increases from 350°C to 450°C, the aromatization activity of the modified samples increases. When the temperature is increased from

350°C to 450°C in the presence of zeolite 2%Cr-HZSM-5, the content of aromatic hydrocarbons in the composition of products increases from 17.3% to 29.7%. When the amount of modifier in the catalyst is increased to 3.0 wt.%, the maximum amount of aromatic hydrocarbons is 33.3%.

Depending on the nature of the modifier, the order of change in aromatization activity is determined:



Moreover, depending on the nature of the modifier, the order of change in isomerization activity is determined:



Thus, in the process of bioethanol conversion in the temperature range of 300-350°C the isomerization activity of ZSM-5 type catalysts modified with zinc (2% Zn-HZSM-5) exceeds the aromatization activity. For bioethanol conversion in the temperature range of 350-450°C, catalysts modified with iron and chromium (2.0-3.0% Fe-HZSM-5; 2.0-3.0% Cr-HZSM-5) have very weak isomerizing and higher aromatization activity.

## Conclusions

1. As a result of fundamental and complex research, the main principles of the preparation of metalzeolite catalytic systems with high activity and selectivity for the processes of disproportionation, isomerization of C<sub>7</sub>-C<sub>8</sub> alkylaromatic hydrocarbons, conversion of methanol and ethanol into isoparaffins, as well as aromatic hydrocarbons were determined.
2. In order to increase the activity and paraselectivity of catalytic compositions in the conversion of alkylaromatic hydrocarbons, methanol and ethanol, the regularities of industrially produced ZSM-5 zeolite modification using various methods (ion exchange, wet impregnation, low-temperature combustion and mechanical shifting, etc.) have been studied.
3. It was determined that the polyfunctional nature of the catalytic composition is related to the localization of the modifier distributed in the micropores and surface of the zeolite. Thus, the nanoscale modifier interacts with the crystal lattice of zeolite and

reduces the amount of strong Brønsted acid sites by forming Lewis acid sites.

4. Catalysts obtained on the basis of ZSM-5 zeolite modified with gallium, lanthanide, other transition metals and phosphorus showed high activity and paraselectivity in disproportionation of toluene and ethylbenzene, isomerization of C8 aromatic hydrocarbons mixture. It was determined that 5%Ga2%P-HZSM-5 in toluene disproportionation and 5%La-HZSM-5 catalytic systems in ethylbenzene disproportionation have high paraselectivity (70.3-75.1% and 69.5-72.1%, respectively), and the 0,5%Pt0,3%Co3%La-TsVN polymetallic catalytic system exhibits high isomerizing selectivity (98.8%).
5. The study of the TsVN zeolite catalyst modified with La, Co, Pt and other transition metals in the isomerization of C8-aromatic hydrocarbons in the temperature range of 350-380°C showed that the yield of by-products decreases and the isomerization selectivity increases. It was determined that La, Co, Pt have a promoting effect in the process. Also, in the presence of a monometallic catalyst (3%La-TsVN), the isomerization selectivity increased to 92.4%, in bimetallic (0.5%Pt3%La-TsVN) to 94.5%, in polymetallic (0.5%Pt0.3% Co3%La-TsVN) was found to increase up to 98.4%.
6. The effect of the amount of metals (Zn, Cd, Ce, La, Gd, Yb, Lu) on the physical-chemical and catalytic properties of HZSM-5 zeolite (HTsVN, H-ultrasil) in the m-Xylene isomerization reaction in the temperature range of 300-350°C RFA, IR-spectroscopy, NH<sub>3</sub> was studied by TPD and nitrogen low-temperature adsorption (BET, BJH) methods, and it was found that when the amount of modifiers in the catalytic composition is increased from 1.0 wt.% to 7.0 wt.%, the maintenance of the zeolite structure, the specific surface area, decrease in the volume of pores and density of strong Brønsted acid sites, increase in density of moderate Lewis acid sites, B/L ratio decreases from 3.6 to 0.77. The maximum paraselectivity (PK/OK=3.9-4.5) is obtained at 5.0 wt.% of the modifier at 300°C.

7. In the course of research, higher paraselectivity was found in samples modified with lanthanides. The paraselectivity of the catalytic composition modified with 5.0 wt.% cerium in lanthanoids was equal to 4.5. As a result of research, the catalysts were arranged in the following order according to paraselectivity:

Ce/HZSM-5 > La/HZSM-5 > Gd/HZSM-5 > Yb/HZSM-5  
> Lu/HZSM-5 > Zn/HZSM-5 > Cd/HZSM-5

8. The study of zeolite ZSM-5 modified with nanosized (10-35 nm) spinel structured  $Ce_xMg_{1-x}Al_2O_4$ , and  $Ho_xMg_{1-x}Al_2O_4$  powders obtained from by high-temperature combustion showed that the physicochemical, textural and catalytic properties of the composition depend on the amount of the nanopowder (1.0-7.0 wt.%). It was determined that the modifier interacts with HZSM-5 to decrease the ratio of B/L acid sites from 3.61 to 0.23. This plays a decisive role in increasing the share of paraselective conversion reactions of C<sub>7</sub>-C<sub>8</sub> aromatic hydrocarbons.
9. High selectivity to p-xylene in the disproportionation reaction of toluene (65.7%, 29.7% conversion of toluene) occurs at 550°C on the catalytic composition of 5%Ce<sub>0.1</sub>Mg<sub>0.9</sub>Al<sub>2</sub>O<sub>4</sub>-HZSM-5 with a pore volume of 0.16 g/cm<sup>3</sup> and a B/L ratio of 0.29. Also, the maximum paraselectivity in the disproportionation reaction of ethylbenzene (67.5%, 42.4% conversion of ethylbenzene) at 400°C is obtained in the presence of a 5%Yb-HZSM-5 catalytic composition with 0.15 g/cm<sup>3</sup> pore volume and B/L ratio of 0.23.
10. Catalytic, acidic and textural properties of  $Ce_xMg_{1-x}Al_2O_4$  and  $Ho_xMg_{1-x}Al_2O_4$  nanopowders with HZSM-5 zeolite in the processes of conversion of methanol to C<sub>2</sub>-C<sub>4</sub> alkenes and p-xylene were investigated. Also, the dependence between the selectivity of C<sub>2</sub>-C<sub>4</sub> alkenes and p-xylene and the ratio of L- and B- acid sites, the volume of total pores and the amount of modifier was studied. It was determined that when the amount of  $Ce_xMg_{1-x}Al_2O_4$  and  $Ho_xMg_{1-x}Al_2O_4$  nanopowders in the catalytic composition increases, the B/L ratio and the volume of total pores decrease, while the volume of mesopores increases. These factors play a decisive role in increasing the selectivity for C<sub>2</sub>-C<sub>4</sub> alkenes and p-xylene, the maximum yield of alkenes (31.6 wt.%)

and p-xylene in the catalytic composition containing 5.0 wt.%  $\text{Ho}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$  selectivity (80.5%) is achieved.

11. For the first time, the conversion of bioethanol into aromatic hydrocarbons and engine fuel components was studied by preparing catalytic compositions based on Zn, Fe, Cr salts with HZSM-5 zeolite. It was determined that the nature, amount, B/L ratio and temperature of the modifier have a decisive effect on the selectivity of isomerization and aromatization. Maximum selectivity for isoparaffins (43.9%) was achieved in the catalytic composition modified with 2.0 wt.% zinc. According to the research, the amount of benzene (<1.0% by mass), aromatic (<30.0% by mass) and olefin (<2.0% by mass) hydrocarbons of the catalyst obtained at 300-350°C is "Euro -5" standard.

### **Published references related to the dissertation:**

1. Azməmmədova, X.M., Kərimli, F.Ş., Musayeva, A.Ə. [və b.] Modifikasiya olunmuş pentasillər iştirakında ksilollar və etilbenzolun izomerləşməsi // Ümummilli lider Heydər Əliyevin anadan olmasının 90-cı ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" VII Respublika Elmi Konfransının materialları, Bakı: – 2013, – s.62-63.
2. Əzməmmədova, X.M., Kərimli, F.Ş., Məmmədov, S.E. və b. Pt və Pd pentasil katalizatorların fiziki-kimyəvi və m-ksilolun izomerləşmə reaksiyasında katalitik xassələri // Kimya problemləri, – 2013, №3, – s.372-375.
3. Азмамедова, X.M., Керимли, Ф.Ш., Мамедов, С.Э. Влияние содержания фосфора на каталитические свойства цеолита ZSM-5 в превращении ксилолов // Ümummilli lider Heydər Əliyevin 85 illik yubileyinə həsr olunmuş Respublika elmi konfransının materialları, – Bakı: –07-08 may, – 2008, – s.25.
4. Азмамедова, X.M. Керимли, Ф.Ш., Мамедов, С.Э. [и др.] Изомеризация м-ксилола на цеолитах типа ультрасила, модифицированных кадмием и цинком // Журнал химических проблем, –2008, №2, –с.272-274.
5. Азмамедова, X.M., Мамедов, С.Э., Керимли, Ф.Ш. [и др.] Превращение смеси ароматических углеводородов  $\text{C}_8$  на La-



- содержащих пентасилах, модифицированных платиной // Akademik M.F.Nağıyevin 100-illik yubileyinə həsr olunmuş elmi konfransın məruzələrinin tezisləri, – Bakı:– 2008, – s.260.
6. Ахмедов, Э.И., Алиев, И.И., Керимли, Ф.Ш. [и др.] Влияния концентрации лантана на кислотные и каталитические свойства н-пентасила в реакции изомеризации м-ксилола // Журнал прикладной химии, – 2009, т.82, вып.5, – с.862-863.
  7. Бабаева, Т.А., Керимли, Ф.Ш., Мустафаева, А.Л., [и др.] Каталитические свойства РЗЭ-содержащих пентасила в превращении метанола в ароматические и низкомолекулярные углеводороды C<sub>2</sub> -C<sub>4</sub> // Ümummilli lider Heydər Əliyevin anadan olmasının 94-cü ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" XI Respublika Elmi Konfransının materialları, –Bakı, –2017, – s.22-23
  8. Гахраманов, Т.О., Ахмедов Э.И., Керимли, Ф.Ш. [и др.] Влияние способа модифицирования на физико-химические и каталитические свойства цеолита ZSM-5 в превращении насыщенных и алкилароматических углеводородов // «Цеолиты и мезопористые материалы-достижения и перспективы» Тезисы докладов: 5-ая Всероссийская цеолитная конференция, – Звенигород: –8-11 июня, – 2008, – с.172-173.
  9. Гахраманов, Т.О., Мамедов, С.Э., Керимли, Ф.Ш. [и др.] Алкилирование ароматических углеводородов метанолом и этанолом на модифицированных цеолитах типа ZSM-5 // Ümummilli lider Heydər Əliyevin anadan olmasının 98-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" XIV Beynəlxalq Elmi Konfransının materialları, – Bakı: – 2021, – s.402-403.
  10. Гахраманов, Т.О., Мамедов, С.Э., Керимли, Ф.Ш. [и др.] Алкилирование ароматических углеводородов на модифицированных цеолитах типа пентасила // XI Международная научная конференция "Кинетика и механизм кристаллизации. Кристаллизация и материалы нового поколения", – Иваново: –20–24 сентября, – 2021, – с.297.
  11. Исмайлова, С.Б., Ахмедова, Н.Ф., Керимли, Ф.Ш. [и др.] Селективное диспропорционирование толуола на пентаси-

- лах, модифицированных редкоземельными элементами // Ümummilli lider Heydər Əliyevin anadan olmasının 89-cu ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" VI Respublika Elmi Konfransının materialları, Bakı: – 2012, – с.5.
12. Керимли, Ф.Ш. Влияние концентрации кадмия на физико-химические и каталитические свойства пентасилов в реакции диспропорционирования толуола // Журнал химических проблем, –2019, №1, –с.129-134.
  13. Керимли, Ф.Ш. Влияние модифицирования на каталитические свойства цеолита НЦВН в процессе изомеризации смеси ароматических углеводородов  $C_8$  // Башкирский химический журнал, – 2021, т.28, №3, – с.44-48.
  14. Керимли, Ф.Ш. Диспропорционирование толуола на цеолите ZSM-5 модифицированном галлием // Вестник Бакинского Университета, –2022, №2, –с.5-9
  15. Керимли, Ф.Ш. Диспропорционирование этилбензола на цеолите типа ZSM-5 модифицированном лантаном // Вестник Бакинского Университета, –2021, №1, –с.14-24
  16. Керимли, Ф.Ш. Селективное диспропорционирование этилбензола на модифицированных цеолитах типа ZSM-5 // Ümummilli lider Heydər Əliyevin anadan olmasının 99-cu ildönümünə həsr olunmuş doktorant, magistrant və gənc tədqiqatçıların «kimya və kimya texnologiyası» mövzusunda Respublika Elmi Konfrans, – Bakı: – 18-19 may, – 2022, – s.8
  17. Керимли, Ф.Ш., Азмамедова, Х.М., Мамедов, С.Э. [и др.] Каталитические свойства биметаллцеолитных катализаторов в реакции изомеризации м-силолов // Ümummilli lider Heydər Əliyevin anadan olmasının 91-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" VIII Respublika Elmi Konfransının materialları, Bakı: – 2014, – с.7-8.
  18. Керимли, Ф.Ш., Азмамедова, Х.М., Мамедов, С.Э. Изомеризация м-силола на биметаллических цеолитных катализаторах // Журнал химических проблем, –2014, №1, –с.87-89.
  19. Керимли, Ф.Ш., Азмамедова, Х.М., Мусаева, Н.Дж. [и др.] Ізомерізація суміші ароматичних вуглеводнів  $C_8$  на модифі-

- кованих катализаторах на основі цеоліту типу ZSM-5 // Current chemical problems V International (XV Ukrainian) scientific conference for students and young scientists, – Vinnytsia: – March 22–24, – 2022, – p.91.
20. Керимли, Ф.Ш., Ахмедов, Э.И. Влияние способа модифицирования на физико-химические и каталитические свойства цеолита типа пентасила в реакции изомеризации м-ксилола // Ümummilli lider Heydər Əliyevin anadan olmasının 87-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların IV, Respublika Elmi Konfransının materialları, Bakı: – 2010, – с.14.
  21. Керимли, Ф.Ш., Ахмедов, Э.И., Азмамедова, Х.М. [и др.] Влияние концентрации цинка на кислотные свойства Н-пентасила в реакции изомеризации м-ксилола // II Отраслевая научно-производственная конференция «Интеграция науки и производства», – Салават: –30 ноября, – 2013, – с.12.
  22. Керимли, Ф.Ш., Ахмедов, Э.И., Искандарова, К.А. [и др.] Влияние способа модифицирования на физико-химические и каталитические свойства цеолита типа ультрасила в реакции изомеризации м-ксилола // Ümummilli lider Heydər Əliyevin anadan olmasının 88-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların V Respublika Elmi Konfransının materialları, Bakı: – 2011, – с.5.
  23. Керимли, Ф.Ш., Магеррамов, А.М., Азмамедова, Х.М. [и др.] Изомеризация м-ксилола на полиметаллических цеолитных катализаторах // Журнал химических проблем, – 2016. №4, –с.390-393.
  24. Керимли, Ф.Ш., Магеррамов, А.М., Мамедов, С.Э. [и др.] Изомеризация смеси ксилолов и этилбензола на полиметаллическом катализаторе // Нефтепереработка и нефтехимия, –2017, №9, –с.21-22.
  25. Керимли, Ф.Ш., Магеррамов, А.М., Мамедов, С.Э. Влияние концентрации кадмия на физико-химические и каталитические свойства Н-ультрасила в реакции диспропорционирования этилбензола // III Всероссийская научная конференция с международным участием. Актуальные проблемы теории и практики гетерогенных катализаторов и адсорбен-

- тов, – Иваново: – 2018, – с.184.
26. Керимли, Ф.Ш., Магеррамов, А.М., Мамедов, С.Э. Влияние природы и концентрации редкоземельных элементов на физико-химические и каталитические свойства H-пентасила в реакции диспропорционирования этилбензола // Журнал химических проблем, – 2017, №4, – с.425-430.
  27. Керимли, Ф.Ш., Магеррамов, А.М., Мамедов, С.Э. Диспропорционирование этилбензола на H-пентасилах модифицированных редкоземельными элементами // XII Международная конференция молодых ученых по нефтехимии, – Звенигород: – 2018, – с.459-460.
  28. Керимли, Ф.Ш., Магеррамов, А.М., Мамедов, С.Э. Изомеризация ароматических углеводородов C<sub>8</sub> на биметаллических цеолитных катализаторах // «Цеолиты и мезопористые материалы-достижения и перспективы» Тезисы докладов: 7-ая всероссийская цеолитная конференция, – Звенигород: –16-18 июня, – 2015, – с.204-205.
  29. Керимли, Ф.Ш., Магеррамов, А.М., Мамедов, С.Э. Изомеризация смеси ароматических углеводородов C<sub>8</sub> на полиметаллических цеолитных катализаторах // Материалы II Всероссийской научной конференции (с международным участием) «Актуальные проблемы адсорбции и катализа», – Плес, Иванова: – 2017, – с.252-253.
  30. Керимли, Ф.Ш., Мамедов, С.Э. Влияние модифицирования и термопаровой обработки на свойства цеолита ZSM-5 в диспропорционировании толуола // Актуальные вопросы химической технологии и защиты окружающей среды, Сборник материалов VIII Всероссийской конференции, – Чебоксары: –16-17 апреля, – 2020, – с.193.
  31. Керимли, Ф.Ш., Мамедов, С.Э. Влияние мольного соотношения SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> на кислотные и каталитические свойства цеолита HZSM-5 в реакции диспропорционирования этилбензола // Молодой ученый, – 2017, №27(161),– с.12-14.
  32. Керимли, Ф.Ш., Мамедов, С.Э. Диспропорционирование толуола на пентасилах модифицированных редкоземельными элементами // Молодой ученый, – 2018, №47, – с.233.
  33. Керимли, Ф.Ш., Мамедов, С.Э. Изомеризация фракции C<sub>8</sub>

- ароматических углеводородов на модифицированных цеолитах типа ZSM-5 // VII Всероссийская конференция с международным участием, посвященная 50-летию академической науки на Урале Техническая химия. От теории к практике, – Пермь: –5-9 сентября, – 2022, – с.167.
34. Керимли, Ф.Ш., Мамедов, С.Э. Селективное диспропорционирование этилбензола на модифицированных пентасилах //III International (XIII Ukrainian) scientific conference for students and young scientists, – Vinnytsia: –25-27 march, – 2020, – с.112.
  35. Керимли, Ф.Ш., Мамедов, С.Э. Селективное диспропорционирование толуола на модифицированных пентасилах // Башкирский химический журнал, – 2020, т.27, №2, –с.64-69.
  36. Керимли, Ф.Ш., Мамедов, С.Э., Ахмедов, Э.И. Влияние концентрации редкоземельных элементов на физико-химические и каталитические свойства пентасила в реакции этилирования толуола и этилбензола // Ümummilli lider Heydər Əliyevin anadan olmasının 95-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" XII Respublika Elmi Konfransının materialları, – Bakı: – 2018, – с.140-141.
  37. Керимли, Ф.Ш., Мамедов, С.Э., Магеррамов, А.М. Селективное диспропорционирование этилбензола на модифицированных цеолитах типа ZSM-5 // Ümummilli lider Heydər Əliyevin anadan olmasının 96-cı ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" XIII Respublika Elmi Konfransının materialları, – Bakı: – 2019, – с.6-8.
  38. Керимли, Ф.Ш., Мамедов, С.Э., Магеррамов, А.М. Синтез и свойства катализаторов на основе цеолитов типа Y модифицированных катионами цезия и фтором калия // Ümummilli lider Heydər Əliyevin anadan olmasının 93-cü ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların "Kimyanın aktual problemləri" X Respublika Elmi Konfransının materialları, –Bakı: – 2016, – с.6-7.
  39. Керимли, Ф.Ш., Мамедов, С.Э., Магеррамов, А.М. Эффект модифицирования Н-пентасила фосфором в реакции

- диспропорционировании этилбензола // Материалы научной конференции «Нагиевские чтения», посвященной 110-летию академика М.Нагиева, – Баку: – 2018, – с.199.
40. Керимли, Ф.Ш., Мамедов, С.Э., Мамедзаде, Х.А. [и др.] Исследование каталитических свойств биметаллических цеолитных катализаторов в процессе изомеризации смеси ароматических углеводородов  $C_8$  // XIII Всеукраїнська наукова конференція студентів та аспірантів "Хімічні Каразінські читання - 2021", – Харків: – 2021, – с.131-132.
41. Керимли, Ф.Ш., Мирзалиева С.Э., Эминова С.Ф. [и др.] Превращение парафиновых и ароматических углеводородов на би- и полиметаллических цеолитных катализаторах // II международная конференция «Современные решения научных и производственных задач в химия и нефтехимии», – Казан: – 2017, – с.83-86.
42. Магеррамов, А.М., Керимли, Ф.Ш., Мамедов, С.Э. Влияния концентрации редкоземельных элементов на физико-химические и каталитические свойства цеолита ZSM-5 в диспропорционировании этилбензола // Химия и химическое образование XXI века, –Санкт-Петербург: – 2017, – с.81-82.
43. Магеррамов, А.М., Мамедов, С.Э., Керимли, Ф.Ш. [и др.] Диспропорционирование этилбензола на Н-пентасиле, модифицированном кадмием // Химия, химические технологии и экология: наука, производство, образование, – Махачкала: – 2018, – с.77-78.
44. Мамедов, С.Э., Ахмедов, Э.И., Керимли, Ф.Ш. [и др.] Изомеризация смеси ксилолов и этилбензола на модифицированных // Нефтепереработка и нефтехимия, –2009, №2, – с.36.
45. Мамедов, С.Э., Ахмедов Э.И., Керимли, Ф.Ш. [и др.] Закономерности превращения ксилолов на модифицированном природном мордените // Химическая технология, – 2013, т.14, №3, с.134-137.
46. Мамедов, С.Э., Ахмедов Э.И., Керимли, Ф.Ш. [и др.] Природа активных центров La содержащих цеолитных катализатора изомеризации м-ксилола и алкилирования толуола

- метанолом // Материалы международной научной конференции, посвященной 90-летию Бакинского Государственного Университета, – Баку: – 2009, – с.330-331.
47. Мамедов, С.Э., Исмаилова, С.Б., Керимли, Ф.Ш. [и др.] Превращение смеси ксилолов и этилбензола на модифицированных ультрасилах // Журнал научных публикаций аспирантов и докторантов, –2009, №3, –с.116-117.
  48. Мамедов, С.Э., Керимли, Ф.Ш., Ахмедов, Э.И. Влияние способа модифицирования на физико-химические свойства цеолитов типа пентасил и на селективность алкилирования толуола этанолом // «Monomerlər və polimerlər kimyasının müasir problemləri» Respublika elmi konfransının materialları, – Sumqayıt: – 2009, – с.77.
  49. Babayeva, T., Mammadov, S., Karimli, F. [et al.] Methanol into C<sub>2</sub>-C<sub>3</sub> olefins and p-xylene conversion over ZSM-5 type zeolites modified with rare earth metals // International Conference: Modern Problems of Theoretical & Experimental Chemistry, – Baku, –2022, –p.13
  50. Babayeva, T.A., Akhmedov, E.I., Kerimli, F.Sh. [et al.] Catalytic performance of zeolites modified by Zr and W nanopowders for the conversion of the methanol to hydrocarbons // Сборник тезисов докладов XII Российской конференции «Актуальные проблемы нефтехимии» (с международным участием), – Грозный: –5–9 октября, – 2021, – с.164-165.
  51. Kerimli, F.Sh., Ilyasli, T.M., Mammadov, S.E. [et al.] Evaluation of the Properties of ZSM-5 Type Zeolites Modified with Ce<sub>x</sub>Mg<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> Nanopowders in the Toluene Disproportionation Reaction // Petroleum Chemistry, – 2021, vol.61, – p.895–900.
  52. Kerimli, F.Sh., Mammadov, E.S. Isomerization of m-xylene on ZSM-5 type zeolite Modified with zinc // Processes of Petrochemistry and oil Refining, – 2021, vol.22, №3, – p.363-370.
  53. Mahmudov, K.T., Kerimli, F.Sh., Mammadov, E.S. [et al.] Catalytic disproportionation of ethylbenzene over Ln-modified HZSM-5 zeolites // Petroleum Chemistry, – 2022, vol.62, – p.933–941.
  54. Makhmudova, N.I., Mammadov, E.S., Kerimli, F.Sh. [et al.] Study of catalytic properties of the Ho<sub>x</sub>Mg<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> modified

HZSM-5 zeolite in conversion of methanol to C<sub>2</sub>-C<sub>4</sub> alkenes and p-xylene // Bulletin of Chemical Reaction Engineering & Catalysis, – 2022, 17(4), – p.725–732.

55. Mamedov, E.S., Babaeva, B.A., Kerimli, F.Sh. [et al.] Production of High-Octane Gasolines from Bioethanol on Zn-Modified HZSM-5 Zeolite // Moscow University Chemistry Bulletin, – 2021, vol.77. №4, – p.222–229.
56. Mammadov, E.S., Karimli, F.Sh., Mammadova A.Z. [et al.] Effects Ga- and P-modified high-silica TsVN zeolite based catalysts on toluene disproportionation reaction // Processes of Petrochemistry and oil Refining, – 2023, vol.24, iss.1, – p.89-98.





The defense will be held on "14" february 2024 at 11<sup>00</sup> am 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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Electronic versions of dissertation and its abstract are available on the official website of the Supreme Attestation Commission under the President of the Republic of Azerbaijan.

Abstract was sent to the required addresses on "11" January 2024

Signed for print: 07.01.2024  
Paper format: 60×84 1/16  
Volume: 75370  
Number of hard copies: 30