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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

ACTIVITY AND PARASELECTIVITY OF MODIFIED ZSM-5 ZEOLITES IN THE REACTION OF TOLUENE ALKYLATION WITH ISOPROPANOL

Specialty:	2316.01- Chemical kinetics and catalysis
Field of science:	Chemistry

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BAKU- 2025

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GENERAL CHARACTERISTICS OF THE WORK

Relevance and level of development of the topic.

Para-substituted alkyl aromatic hydrocarbons are of great industrial importance. Every year the demand for p-xylene, p-diethylbenzene, p-ethyltoluene and p-isopropylbenzene, which are used as raw materials in the production of terephthalic acid, synthetic rubbers, plastics, plasticizers, ion exchange resins, cresols, fungicides, pesticides, perfumery. A promising direction in the development of the production of dialkylbenzenes on solid acid catalysts is the use of zeolites, which eliminates the toxic and aggressive liquid and volatile components inherent in homogeneous Friedel-Crafts catalysts.

Zeolite catalysts have a low level of production waste, are highly environmentally friendly, active, selective and regenerable. Industrially used complexes based on $AlCl_3$, BF_3, $TiCl_4$ and phosphoric acid on kieselguhr do not provide a high yield of isopropyltoluenes (IPT), and for the para-substituted isomer (4-IPT) they have significant disadvantages associated with a rapid loss of activity and a high level of aggressive waste inherent in Friedel-Crafts catalysts[1].

Thus, it is necessary to develop approaches to solve the problem of synthesizing para-selective catalysts for the process of toluene alkylation with isopropanol, eliminating environmental pollution by waste, through the implementation of innovative technologies. Against this background, wide attention of researchers is attracted to the search for new highly efficient catalytic systems, their formation into a specific structure and ensuring maximum para-selectivity and stability.

Among the new catalytic systems, a special place belongs to synthetic zeolites, which have specific properties such as a unique crystalline and porous structure, the ability to ion exchange and molecular sieve selectivity, high thermal stability and acidity.

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[1] Lachter, E.L Fridel Crafts reactions revisited: some applications in heterogeneous catalysis/ E.L Lachter, Gil R.A, Valdivieso L.G // Current organic chemistry.- 2024, -v.28, -iss.14, -p.1060-1068.

Many results have been obtained in studies of the efficiency of alkylation of aromatic hydrocarbons with olefins and monohydric alcohols on various zeolite catalysts, mainly on wide-pore (X, Y, β, mordenite) and medium-pore with an MFI structure (ZSM-5, ZSM-11).On zeolites of the X, Y, β type and mordenite with large pores, the formation of all three branched isomers was observed, with the predominant formation of the m-isomer (3-IPT).Catalysts based on these zeolites do not exhibit the high selectivity necessary for the synthesis of 4-IPT.In addition, the strong Brønsted acidity of these zeolites promotes the occurrence of side reactions and rapid deactivation.

Catalysts based on ZSM-5 zeolite with a three-dimensional structure, possessing intersecting sinusoidal (0.51x0.53 nm) and straight (0.53x0.55 nm) channels have proven promising in the processes of converting various classes of hydrocarbons.

Among the new catalytic systems that have found application today in the processes of benzene alkylation with ethylene, disproportionation of toluene, ethylbenzene, MTO, MTG, M-2 reforming, CYCLAR, Alpha-process, Arkon and Aromax processes, a special place belongs to ZSM-5 zeolites.Catalysts based on ZSM-5 zeolites proved to be more promising in the processes of toluene alkylation with methanol, ethanol and isopropanol. Modification of ZSM-5 zeolite allowed to increase the selectivity of the catalyst for para-substituted isomers[2],[3].

In this regard, a comprehensive solution to the issue of synthesizing active and para-selective catalytic systems, achieving optimal distribution of applied modifiers in the structure of zeolite ZSM-5, optimizing the chemical composition of the catalyst, its acid sites and porous structure will allow obtaining new data on the

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[2] Han, H. Coke-resistant (Pt+Ni)-ZSM-5 catalyst for shape-selective alkylation of toluene with methanol to para-xylene/ H.Han, A.Zhang,L.Ren [et.al]//Chem. Eng.Science, - 2022,-v.252,- p. 11752-11758.

[3] Mamedov E.S., Gakhramanov T.O., Akhmedova N.F., Mamedov S.E., Mamedova A.Z. Effects of the type and loading of rare-earth metals (Pr, Yb, Ho) on the para-selectivity of HTsVM-5 zeolite toluene ethylation //Petroleum Chemistry, -2024, -v.64(2), p.258-266.

patterns and features of the catalytic action of the catalytic composition of
zeolite ZSM-5 with modifiers in the process of toluene alkylation with isopropanol.

Object and subject of study. The object of study is toluene, isopropanol, their alkylation products (m-isopropyltoluene, o-isopropyl-toluene and p-isopropyltoluene). Catalysts based on zeolite of the ZSM-5 type, modified with compounds of Mg, Sr, Ba, Sc, Y, REE (La, Yb, Ho, Gd) and phosphorus.

The purpose and objectives of the study. The main purpose of this work is to study the patterns of toluene alkylation with isopropanol in the presence of modified metal zeolite catalysts, to study the interaction of physicochemical, acidic, textural properties of zeolite catalysts of the MFI structural type (ZSM-5) and their catalytic activity, selectivity and stability, as well as the selection of an optimally effective catalyst for the alkylation process.

To achieve the goal, the following problems were solved:

- obtaining modified forms of ZSM-5 zeolites;
- the influence of the nature and concentration of modifiers in the reaction of toluene alkylation with isopropanol on the catalytic properties of zeolite catalysts, their selectivity for 4-isopropyltoluene and operational stability;
- study of the physicochemical, acidic and textural properties of modified zeolites and determination of the relationship of these properties with the selectivity for 4-isopropyltoluene;
- study of the regularities of the reaction of alkylation of toluene with isopropanol in the presence of modified catalysts based on zeolite ZSM-5;
- selection of an optimal catalyst with high selectivity and stability for the process of alkylation of toluene with isopropanol.

Research methods. The following physical and chemical methods were used in the dissertation: X-ray phase analysis, gas-liquid chromatography, low-temperature nitrogen adsorption, IR spectroscopy, temperature-programmed desorption of ammonia and a flow-through ideal displacement unit at atmospheric pressure, determining the activity of the synthesized catalysts.

The main provisions to be defended:

- the influence of the nature and amount of the modifier on the activity and selectivity of the catalyst based on ZSM-5 in the reaction of toluene alkylation with isopropanol.
- the influence of modification on the physicochemical, acidic and textural properties of the catalyst;
- results confirming the relationship between the acidic, textural and catalytic properties of catalysts modified based on ZSM-5;
- a study of the patterns of the reaction of toluene alkylation with isopropanol in the presence of catalysts based on modified zeolite ZSM-5.

Scientific novelty of the study.

A comprehensive study was conducted aimed at creating para-selective catalytic systems based on zeolites with the MFI structure modified with multi-charged cations and metals (Mg, Sr, Ba, Zn, Ni, La, Ho, Gd, Yb, Lu) and phosphorus for the process of toluene isopropylation. New data were obtained on the influence of the nature and concentration of modifiers on the stability of the catalyst and its para-selectivity with respect to the formation of p-isopropyltoluene (4-IPT).

Inactivation of the outer surface of the zeolite with rare earth metals and phosphorus, the concentration of Brønsted and Lewis acid sites, their ratios, as well as the pore structure have a decisive effect on the para-selectivity of the catalyst.

The pattern of alkylation of toluene with isopropanol depending on the composition of the catalyst was revealed, the conditions of their synthesis, chemical composition, B/L ratio of acid centers and porous structure were optimized.

For the first time, new bimetallic catalysts Ni-La-P-HZSM-5 and Ni-Yb-P-HZSM-5 have been developed for the toluene isopropylation reaction. They exhibit high operational stability (30 h) and provide high selectivity for 4-IPT (74.1-76.6%).

Theoretical and practical significance of the work.

The theoretical significance of the work lies in the scientific substantiation of the possibility of modifying zeolite ZSM-5 for targeted change of its catalytic, acidic and textural properties. Modification allows to regulate catalytic and physicochemical properties for increase of stability and para-selectivity of the catalyst in the process of alkylation of toluene with isopropanol.

The practical significance of the work lies in the following:

1. As a result of the conducted research, para-selective bimetallic catalysts based on zeolite ZSM-5 were developed, providing high selectivity for p-isopropyltoluene.
2. The experimental results of studies of modification of zeolite ZSM-5 can be used as a basis for synthesis of effective catalysts for alkylation of alkylaromatic hydrocarbons with monohydric alcohols.

Validation and application. The main results of the work were discussed and presented at international scientific conferences: XII International Conference of Young Scientists on Petrochemistry. Collection of Abstracts, Zvenigorod, 2018; XXI Mendeleev Congress on General and Applied Chemistry Volume 4. Collection of Abstracts in 6 volumes, St. Petersburg, 2019; VI All-Russian Conference with International Participation "Technical Chemistry. From Theory to Practice, Perm, 2019; XIV International Scientific and Practical Conference "Actual Problems of Chemistry" for doctoral students, undergraduates and young scientists dedicated to the 98th anniversary of the national leader HEYDAR ALIYEV, 2021; XIII All-Ukrainian Scientific Conference of Students and Postgraduate Students "Kharazin Chemistry Readings - 2021" (KCH’21). Theses of Confessions, Kharkiv, 2021; XII Russian Conference “Current Problems of Petrochemistry”, 2021; Modern problems of theoretical and experimental chemistry devoted to the 90th anniversary of academician Rafiqa Aliyeva, BSU, 2022; XXI Mendeleev Congress on General and Applied Chemistry, dedicated to the 190th anniversary of D.I. Mendeleev and the 300th anniversary of the founding of the Russian Academy of Sciences, Sirius, Russia, 2024; Materials of the Republican scientific conference of doctoral students, masters and young researchers

"Modern approaches in chemistry and chemical technology" dedicated to the 80th anniversary of the Department of Petrochemistry and Chemical Technology, 2023; International conference on actual problems of chemical engineering, dedicated to the 100th anniversary of the Azerbaijan State Oil and Industry University, Baku, Azerbaijan, 2020; V International (XV Ukrainian) Scientific Conference For Students And Young Scientists. Current chemical problems, Vinnitsia, 2022; Actual issues of chemical technology and environmental protection: collection of materials of the VIII All-Russian conference dedicated to the 60th anniversary of PJSC "Khimprom". Cheboksary, 2020; The authors of the 1995 and 1999 scientific conferences devoted to the development of the Republic of Elmi Materials Conference, Baku, 2018, 2022.

Place of dissertation work. The dissertation work was carried out according to the plan of scientific research conducted in this direction at the Department of "Physical and Colloidal Chemistry" of Baku State University.

The structure and scope of the dissertation. The dissertation consists of an introduction (11246 characters), 4 chapters (182881 characters), conclusions (3625 characters), 144 cited literature sources (34411 characters), 30 tables and 35 figures. Total 237081 characters. According to the results of the dissertation, the author has 24 scientific publications, including 7 articles in journals, included in the list of AK (2 of them single-authored), 14 reports and conference materials at international and republican conferences.

Personal contribution of the author. The personal contribution of the author consists in planning and organizing the dissertation work, in obtaining the main results. All theoretical and experimental studies, as well as interpretation and generalization of the obtained results were implemented by the applicant himself. Analysis and systematization of the research results were prepared and designed as scientific reports and articles with the active participation of the applicant.

MAIN CONTENT OF THE WORK

The **introduction** (11246 characters) assessed the degree of development of the topic, its relevance, the purpose of the study, its scientific novelty, and practical significance.

The **first chapter** (83327 characters) considered the synthesis, structure, physicochemical properties of high-silica zeolites, the current state of research in the field of toluene alkylation with monohydric alcohols C_1-C_3 in the presence of acid catalysts of the Friedel-Crafts type and zeolite catalysts. It was shown that more promising is the alkylation of toluene with isopropanol in the presence of zeolite catalysts in the presence of catalysts based on ZSM-5 in the vapor phase.

The **second chapter** (10055 characters) - methods of preparation of catalysts based on zeolites of the ZSM-5 type, physicochemical methods of studying the synthesized catalysts, describes the laboratory experimental flow-type setup on which alkylation was carried out and provides a method for analyzing the reaction products.

The **third chapter** (74703 characters) - presents the results of the study of the catalytic and acidic properties of multi-charged cationic forms of high-silica zeolites of the ZSM-5 type in the alkylation of toluene with isopropanol.

The **fourth chapter** (21456 characters) is devoted to the study of the catalytic and physicochemical properties of bimetallic and metal-non-metallic catalysts based on zeolite ZSM-5 in the alkylation of toluene with isopropanol.

The dissertation ends with conclusions, a list of references and a list of abbreviations.

Summary of the third chapter

Catalytic properties of multi-charged cationic forms of zeolite TsVM in the alkylation of toluene with isopropanol

The H-form of zeolite with a silicate module equal to 33 has a fairly high activity. At the ZSM, with an increase in the reaction temperature from 300 °C to 350 °C, the toluene conversion increases from 24.5% to 37.2%, and the alcohol conversion is

98.5-99.8%. The reaction products consist of the following hydrocarbons: benzene, isopropyl toluenes (IPT), propyl toluenes (PT), C_{5+} aliphatic hydrocarbons and C_{8+} aromatic hydrocarbons. With an increase in the reaction temperature, there is an increase in selectivity for IPT (from 53.2 to 55.9%) and C_{8+} aromatic hydrocarbons (from 4.9 to 6.4%) and a decrease in selectivity for PT (from 31.1 to 29.6%) and C_{5+} aliphatic hydrocarbons (8.4 to 6.5%). Cationic forms of Me^{n+}-ZSM zeolite also exhibit high activity in the alkylation of toluene with isopropanol. However, the conversion of toluene on cationic forms of ZSM zeolite is lower than on the H-form of the zeolite. The nature of the multicharged cation significantly affects the conversion of toluene (Figure 1).

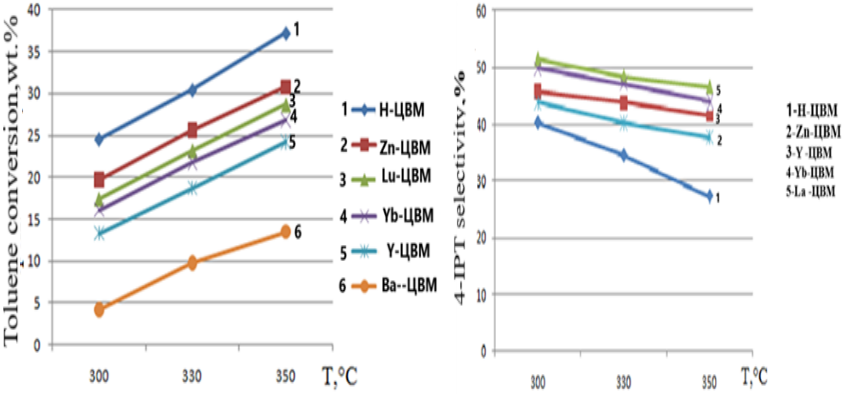

Figure 1. Dependence of toluene conversion and 4-IPT selectivity on temperature on cationic forms of zeolite ZSM [17]

The zinc form of zeolite ZSM (0.76-Zn- ZSM) exhibits the highest activity with respect to toluene conversion (19.7-31.8%). 0.74 Lu-ZSM and 0.72 Yb- ZSM are slightly inferior in activity to zeolite 0.76-Zn-TsVM. However, when switching to the Ba-form of zeolite, a significant decrease in toluene conversion is observed (4.9-13.5%).

Therefore, zeolites with triply charged cationic forms (Me^{3+}CVM) exhibit higher activity with respect to toluene conversion compared to the divalent cationic form (Ba-TsVM). The smaller the cation size, the higher the toluene conversion. In order of increasing toluene conversion, multi-charged cationic forms of the TsVM zeolite are arranged in the following row:

Ba-TsVM < Y-TsVM < Yb-TsVM < Lu-TsVM < Zn-TsVM.

affects the selectivity of the formation of the target product, i.e.: the content of 4-isopropyltoluene (4-IPT) in the mixture of isopropyltoluenes. The lowest selectivity for 4-IPT is exhibited by the H-form of zeolite (29.6-40.1%). Zeolites containing larger It is important to note that the nature of the multicharged cation significantly cations exhibit higher selectivity for 4-IPT (Figure 1). The highest selectivity for 4-IPT is achieved on the Ba-form of zeolite and is 61.3% at a temperature of 300°C, at which a very low conversion of toluene (4.8%) is achieved. Among the triply charged cationic forms at a temperature of 300°C, higher selectivity for 4-IPT (51.5%) is achieved on the La form of TsVM. In order of increasing paraselectivity, the multiply charged cationic forms of zeolite are arranged in the following sequence.

Ba-TsVM> La -TsVM> Y-TsVM> Yb-TsVM> Zn -TsVM

The same pattern is observed in the presence of multi-charged cationic forms of zeolites of the Ultrasil type.

The change in the activity and selectivity of cationic forms of zeolites can be explained by the change in their acidity as a result of modification. The H-forms of zeolites of the ЦВМ and H-Ultrasil types have a high concentration of strong Brønsted acid centers: 328.1 and 314.5 μmol/g, respectively. The concentration of strong acid centers on zeolites containing multi-charged cations (Zn^{2+}, Y^{3+}, REE^{3+}) is 1.8-2.0 times less than in the H-form of zeolite. However, as a result of modification, new strong cationic Lewis's acid centers are also formed (160.20-190.60 μmol/g-1). Sr and Ba forms of zeolites have a low concentration of strong Brønsted acid sites (12.1-17.5 μmol/g-1). As a result, modification with multi-charged cations also results in a noticeable increase in the number of average acidic centers (from 206.4-210.5 to 238.8-247.4 μmol/g-1). Among the largest number of samples studied protic and aprotic acid centers are possessed by samples with trivalent cationic (Y^{3+}, REE^{3+}) forms.

Consequently, in the alkylation reaction, along with the Brønsted acid centers, L-centers formed as a result of modification of the zeolite with multiply charged cations also participate. On the H-forms of zeolites, which have a high concentration of strong Brønsted acid centers, alkylation occurs non-selectively. Sr and Ba-forms of zeolites, which have mainly weak and medium acid centers, exhibit low activity. High activity in the alkylation of toluene with isopropanol is exhibited by zeolites with trivalent cationic forms, which have a sufficient concentration of medium and strong B and L-centers. Among the studied samples, the highest selectivity for 4-IPT is exhibited by the sample (La zeolite) with a larger ionic radius. Thus, the activity and selectivity for 4-IPT on the cationic forms of TsVM and Ultrasil depend on the nature, charge, size of the cation and the distribution of acid sites in zeolites. The nature of the cation significantly changes the distribution of acid sites by strength, the ratio of B/L acid sites. The maximum selectivity (51.5-52.7%) for 4-IPT is exhibited by the catalysts La-TsVM and La-Ultrasil, which have a more optimal combination of medium and strong Brønsted and Lewis acid centers [1,4,17].

Regularities of toluene alkylation with isopropanol on high-silica zeolites modified with rare earth metals

One of the effective methods for obtaining paraselective catalysts is chemical modification of high-silica zeolites with rare earth metals (REM). In this regard, this paper presents the results of a systematic study of the concentration and nature of REM on the properties of ZSM-5 type zeolite in the alkylation reaction with isopropanol.

It is evident that for the initial HZSM-5 sample, the X-ray diffraction pattern shows diffraction peaks at $2\theta=7{,}96°$, $8{,}88°$, $23{,}2°$, $23{,}3°$ and $24{,}0°$ and two obvious peaks at $2\theta=44\text{-}48^{O}C$, characteristic of MFI type zeolites.

After modification, the characteristic peaks for the HZSM zeolite are preserved. This indicates that the zeolite framework is well preserved after modification. After modification, no diffraction peaks belonging to lanthanum oxide were detected. Apparently, this is due to the localization of lanthanum oxide particles in a highly dispersed state on the external and intrazeolite structure of the zeolite. As a result of modifying the zeolite with lanthanum, the zeolite structure remains virtually unchanged.

Indeed, when zeolite HZSM-5 is modified with lanthanum, its surface area and total pore volume change. The most significant changes occur with a lanthanum content of more than 2.0 wt.% in the catalyst. An increase in the lanthanum content to 5.0 wt.% leads to a decrease in the specific surface area from 266 m^2 /g to 223 m^2 /g, and the total pore volume from 0.24cm^3/g to 0.17 cm^3/g.

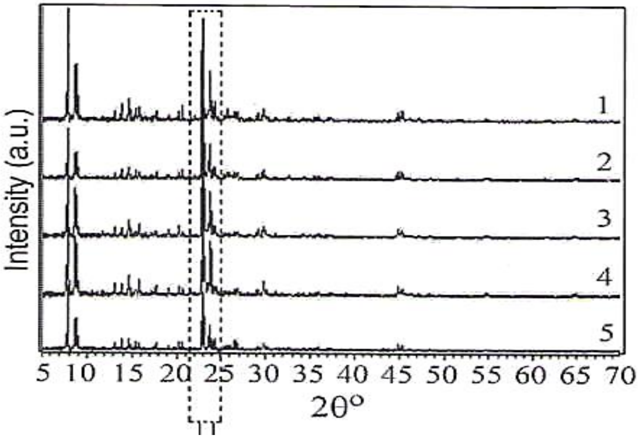

Figure 2. X-ray diffraction patterns of the original HZSM-5 and lanthanum-modified catalysts. 1-HZSM-5; 2-1.0%La-HZSM-5; 3-2.0%La-HZSM-5; 4-3.0%La-HZSM-5; 5-5.0%La-HZSM-5 [10]

Lanthanum concentration significantly affects the distribution of the concentration of Brønsted (B) and Lewis (L) centers and their ratio. With an increase in the lanthanum content in the catalyst to 7.0 wt.%, both a decrease in weak, medium Brønsted acid centers (from 542 to 50 µmol/g) and a decrease in strong Brønsted acid centers occur. centers (from 360 to 150 µmol/g). The concentration of strong Brønsted acid centers decreases by 2.4 times. The total concentration of Brønsted acid centers decreases by 4.5 times.

Increasing the lanthanum concentration in the catalyst to 7.0 wt.% leads to an increase in the concentration of weak and medium Lewis's acid sites from 145 to 880 µmol/g and a decrease in strong

Lewis's acid sites from 110 to 40 μmol/g. The total concentration of Lewis acid sites increases from 255 to 920 μmol/g, i.e. by 3.6 times.

The changes that occur as a result of modification lead to a significant decrease in the B/L acid site ratio. The original HZSM-5 has the highest B/L acid site ratio (3.53). Increasing the lanthanum content in the zeolite to 7.0 wt.% helps to decrease the B/L acid site ratio to 0.22.

Table 1.
Effect of Lanthanum Content in HZSM-5 on the Concentration and Distribution of Brensted and Lewis Acid Sites [10]

La, wt. %	Concentration B (μmol/g)			Concentration L (μmol/g)			
	weak and medium (200°C)	Strong (350 °)	Total	weak and medium (200°C)	Strong (350°)	Total	*B/L*
-	542	360	902	145	110	255	3,53
1,0	75	180	255	200	70	270	0,94
3,0	65	170	235	480	60	540	0,44
5,0	55	160	216	790	50	840	0,25
7,0	50	150	200	880	40	920	0,22

Based on the obtained data, it can be concluded that the lanthanum-modified HZSM-5 zeolite has acidic centers of varying strength, which is associated with induction effects during the interaction of Brønsted centers with neighboring Lewis centers, i.e. lanthanum cations. In the general case, when modifying the HZSM-5 zeolite with REE cations, the formation of cationic Lewis acidic centers can be shown in Figure 4.

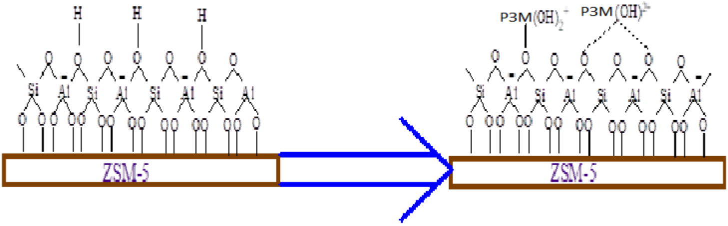

Figure 3. The process of Lewis acid site formation during modification of HZSM-5 with REE [10]

The reaction temperature and La content in the zeolite affect the composition of the products of toluene alkylation with isopropanol. Increasing the reaction temperature and the La content in the zeolite to 5.0 wt.% leads to an increase in the selectivity for IPT and decrease in selectivity for propyltoluenes (PT). Modification helps to decrease selectivity for by-products. The La content has a decisive influence on the selectivity of the reaction products and the distribution of is opropyltoluenes in the catalysate.

Table 2.

The effect of temperature and lanthanum concentration in the HZSM-5 zeolite on the composition of the alkylation products

La, wt.%	T,^{O}C	Conversion, %		Selectivity by products in the catalyst, %				
		Toluene	Alcohol	Benzene	IPT	PT	C_{5+} alif.c/h	АРУ C_8 and higher
0	250	9,2	94,5	0,4	52,4	33,6	12,2	1,4
	300	19,8	99,4	2,2	54,0	30,4	8,6	4,8
	330	27,7	99,9	2,7	55,8	29,8	6,1	5,6
1,0	280	12,8	95,8	0,4	57,6	30,0	10,7	1,3
	300	18,1	97,7	1,9	58,7	28,8	8,3	2,3
	330	25,9	98,3	2,6	59,6	28,1	6,1	3,6
2,0	330	25,4	98,2	2,2	60,2	28,2	6,0	3,4
	350	30,1	98,9	2,4	61,4	27,1	5,4	3,7
3,0	300	16,4	94,7	1,5	62,0	27,8	6,7	2,0
	330	24,6	97,5	1,8	63,8	26,1	5,7	3,2
	350	28,8	98,8	2,0	64,6	24,9	5,2	3,5
5,0	300	15,3	93,9	1,3	67,4	23,1	6,5	1,7
	330	22,1	97,3	1,6	68,3	21,7	5,4	3,0
	350	24,9	98,4	1,9	70,3	19,6	5,1	3,2

It is evident that with an increase in the La content in the catalyst to 5.0 wt.%, an increase in paraselectivity is observed. The maximum selectivity for 4-IPT (72.4%) is observed on the 5% La-HZSM-5 catalyst at a temperature of 300°C. An increase in the reaction temperature to 330 °C reduces the selectivity for 4-IPT to 69.1%. The same pattern is observed in the zeolite TsVN modifying with ytterbium. The maximum selectivity for 4-IPT (68.8%) is achieved on a sample containing 4.0 wt.% Yb.

An increase in paraselectivity with an increase in the La content in the catalysts can be due to the redistribution of acid sites, as well as a change in the specific surface area from the total pore volume as a result of modification.

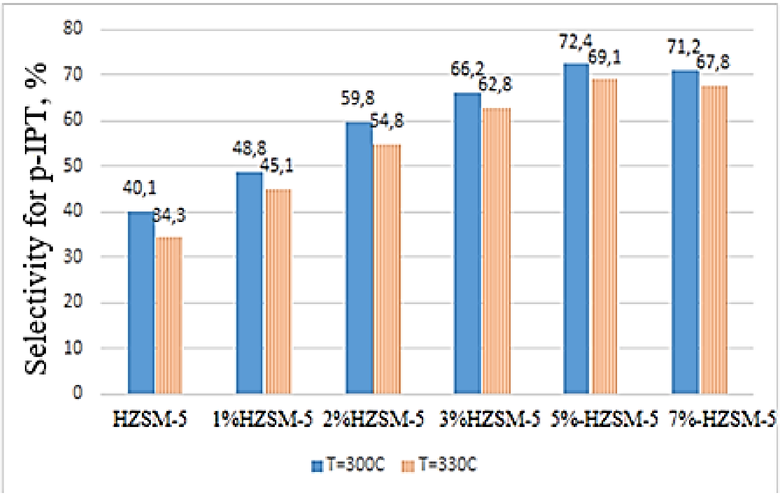

Figure 4. Dependence of selectivity for p-IPT on the concentration of La in the catalyst

The changes that occur are obviously associated with the fact that during the modification process, part of the La $^{+}$ ions in the zeolite are exchanged for La^{3+}, La $(OH)_2^{+}$ or La $(OH)^{2+}$ ions, which are formed during the hydrolysis of lanthanum nitrate. After heat treatment, the modified catalyst undergoes formation of lanthanum oxide, which interacts with the H+ zeolite according to the scheme:

$$La_2O_3 + 3H^{+}\text{ zeolite} \longrightarrow 2La^{3+}\text{ zeolite} + 3H_2O$$

The part of the lanthanum oxide formed as a result of calcination in the form of nanoparticles is distributed on the outer surface, in the mouths of the inlet windows and in the channels of the zeolite, which is the reason for the change in their sizes.

Based on the data obtained using X-ray structural analysis, BET and IR spectroscopy, it was shown that with an increase in the concentration of lanthanum and also ytterbium in HZSM-5 from 1.0 wt.% to 7.0 wt.%, the specific surface area, the total pore volume decreases and a redistribution of acid sites occurs: a decrease in the concentration of strong Brønsted acid sites, an increase in the concentration of medium-strength Lewis acid sites, which leads to a decrease in the B/L ratio of acid sites from 3.53 to 0.20. The concentration of lanthanum in the zeolite, the pore size and the B/L ratio of sites have a decisive effect on the selectivity of the reaction products and the selectivity for p-isopropyltoluene (p-IPT). The maximum selectivity for p-IPT (72.4%) is achieved on a zeolite containing 5.0 wt.% lanthanum, where the B/L center ratio is 0.25 [10,12,21].

Effect of modification of zeolite ZSM-5 with rare earth metals in the reaction of toluene alkylation with isopropanol

The effect of the nature of REE (La, Ho, Yb, Pr) on the acidic, textural, and catalytic properties of ZSM-5 type high-silica zeolite in the temperature range of 250-350°C was studied. It was found that the nature of the rare earth metal in ZSM-5 zeolites plays a decisive role in its para-selectivity and catalytic activity. The maximum activity with respect to toluene conversion is observed on Yb-HZSM-5, and the highest para-selectivity (72.4%) on La-HZSM-5.

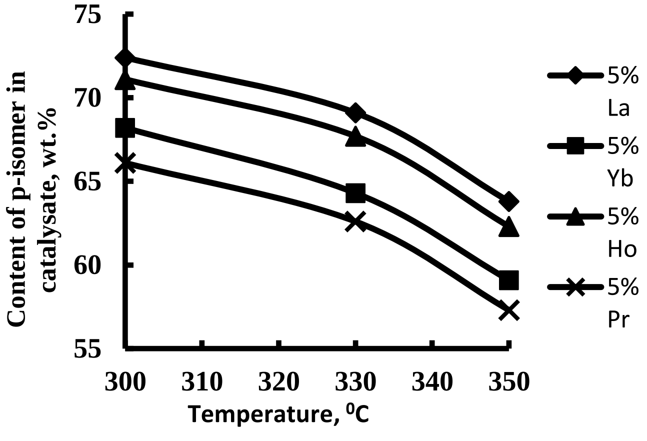

Figure 5. Effect of the nature of REE in the catalytic composition with zeolite HZSM-5 on the selectivity of 4-IPT formation at different temperatures [7]

The lowest selectivity for IPT is observed on Pr-HZSM-5 (62.5%). The difference in selectivity for 4-IPT from the nature of REE is explained by their different effects on the distribution of acid sites and the pore volume of the catalyst. Pr-HZSM-5 has the highest concentration of strong acid sites (242 μmol/g), and La-HZSM-5 has the lowest (103 μmol/g). In addition, with the same modifier content (5 wt.%), the total pore volume of La-HZSM-5 and Pr-HZSM-5 is 0.17 and 0.20 cm3/g, respectively. Therefore, when HZSM-5 is modified with lanthanum, more significant steric hindrances are created for the diffusion of m- and o-isomers from the zeolite channels, and the isomerization of 4-IPT on its surface is significantly reduced. For these reasons,La-HZSM-5 exhibits higher paraselectivity [5,9,16,20,21,24].

The influence of double modification (REM, Sc, Mg and P) on the para-selectivity of catalysts based on ZSM-5 zeolites

To improve the paraselectivity of the catalyst, double modification of the ZSM-5 zeolite with REE, Sc, Mg and P was carried out.

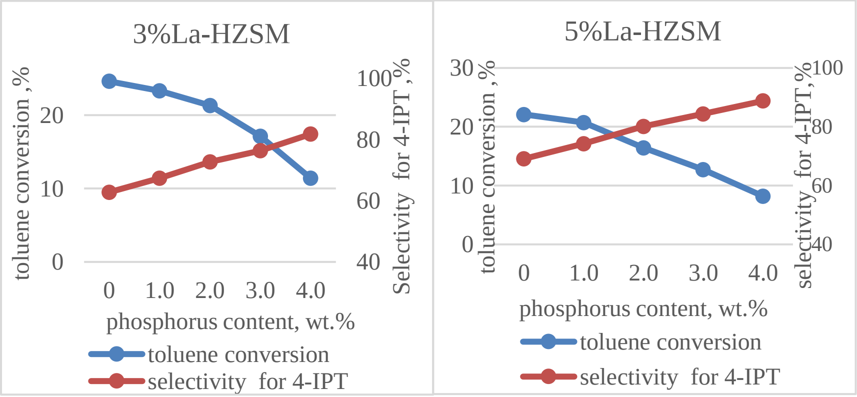

Figure 6. Dependence of toluene conversion and selectivity for 4-IPT on the phosphorus content in the catalysts: 3%La- HZSM; 5%La- HZSM [15]

To identify the effect of the phosphorus concentration in the composition of 3.0-5.0 REE-HZSM-5 on the conversion of toluene and selectivity for 4-IPT, alkylation was carried out at 330^{O}C.

It is evident that with an increase in the phosphorus content in the catalysts 3% La-HZSM and 5%La- HZSM, there is an increase in selectivity for 4-IPT and a decrease in toluene conversion on the catalyst 4%P-3% La- HZSM, the highest selectivity for IPT (81.8%) is achieved at a toluene conversion of 11.4%. On the catalysts 3.0-4.0%P-5% La- HZSM, a higher selectivity for IPT (84.4-88.8%) is achieved at a toluene conversion of 8.2-12.7%. The most optimal catalysts can be considered to be those with the compositions 2.0-3.0% P-3% La- HZSM and 2.0% P-5% La- HZSM.

On the 3% La- HZSM catalyst modified with 2.0-3.0 wt.% phosphorus, high selectivity for IPT (72.4-76.4%) is achieved with a toluene conversion of 17.1-21.3%, and on the 5% La- HZSM catalyst modified with 2.0 wt.% phosphorus, high selectivity for IPT (80.1%) is achieved with a toluene conversion of 16.4%. The same pattern is observed when modifying HZSM-5 zeolite Gd and phosphorus: 5% Gd-4%P-HZSM-5 and Yb phosphorus:3% Yb-HZSM-5 and 3% Yb-H-US**.** High selectivity for 4-IPT (67.8%) is observed on the ZSM-5 catalyst modified with 5.0 wt.% Mg and 3.0 wt.% P [3,6,11,13,14,15,19,23].

Catalytic properties of bimetallic catalysts based on ZSM-5 zeolite

To improve the selectivity for IPT, reduce the selectivity of by-products and increase the stability of the REE-HZSM-5 and REE-P-HZSM-5 catalysts, additional modification with nickel was carried out.

It is evident that the introduction of nickel in the amount of 1 wt.% into the composition of the Yb-containing catalyst leads to an increase in selectivity for IPT (up to 71.2%), a decrease in selectivity for C_{5+} aliphatic (up to 1.6%) and C_{8+} aromatic hydrocarbons (up to 1.9%). The same pattern is observed when modifying the 3%-La-HZSM-5 and 3%-La-P-HZSM-5 catalysts with nickel.

An increase in the nickel concentration in the catalyst composition to 1.0-1.5 wt.% prevents to the formation of 2-IPT and promotes an increase in the selectivity for the formation of 4-IPT to 73.8-76.4%.

Table 3. Effect of Ni concentration in the Ni-3%-Yb-HZSM-5 catalyst on product selectivity

Catalyst	Ni, wt. %	T,^{O}C	Conversion, %		Selectivity by products in the catalyst, %				
			Toluene	Alcohol	Benzene	IPT	PT	C_{5+} alif.c/h	ARH C_8 and higher
3%-Уb H-US	-	300	17,8	95,2	1,7	64,5	24,7	6,9	2,2
	-	330	25,8	98,1	1,9	67,1	22,2	5,5	3,3
3%-Уb H-US	0,5	300	17,1	95,7	1,3	67,8	28,8	5,3	1,8
		330	25,2	98,9	1,6	69,1	22,1	5,1	2,1
	1,0	300	16,4	95,1	1,0	71,2	21,3	4,9	1,6
		330	24,6	98,7	1,2	70,8	20,4	4,7	1,9
	1,5	300	14,6	94,3	0,8	70,4	22,0	4,5	1,5
		330	20,1	96,6	1,1	71,9	21,0	4,3	1,7

A bimetallic catalyst of the composition 1% Ni-3% Yb-2% P-H-ultrasil and 1% Ni-3% La-2% P-H-ultrasil, since in the presence of this catalyst the conversion of toluene compared to the catalyst containing 1.5 wt.% nickel is higher by 2.0-4.5% is more preferable.

Table 4.
IPT isomer composition on modified catalysts [23]

Catalyst	T,℃	Isomer composition IPT,%		
		3-IPT	4-IPT	2-IPT
3%-Уb-H-ultrasil	300	32,4	66,0	0,7
	330	35,1	63,8	1,1
0,5%Ni-3%Уb-H- ultrasil	300	30,6	69,1	0,3
	330	32,9	66,7	0,4
1%Ni-3%Уb-H- ultrasil	300	26,2	73,8	-
	330	28,5	71,5	-
1%Ni-3%Уb-2%-P-H- ultrasil	330	25,9	74,1	-
1%Ni-3%La-2%-P-H- ultrasil	330	23,6	76,4	-
1,5%Ni-3%Yb-2%-P-H- ultrasil	330	28,2	71,8	-

Figures 7 and 8 demonstrates the effect of phosphorus and nickel on toluene conversion and 4-IPT selectivity in the 3%La-H-ultrasil catalyst modified with lanthanum in an amount of 3.0 wt.%.

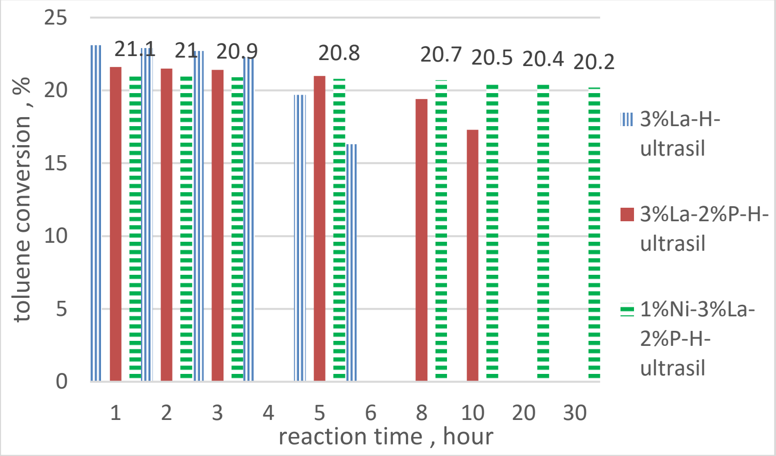

Figure 7. Dependence of toluene conversion on reaction time on modified catalysts

Conditions: T=330^{O}C, V=1.0 h^{-1}, toluene: alcohol =2:1 (molar)

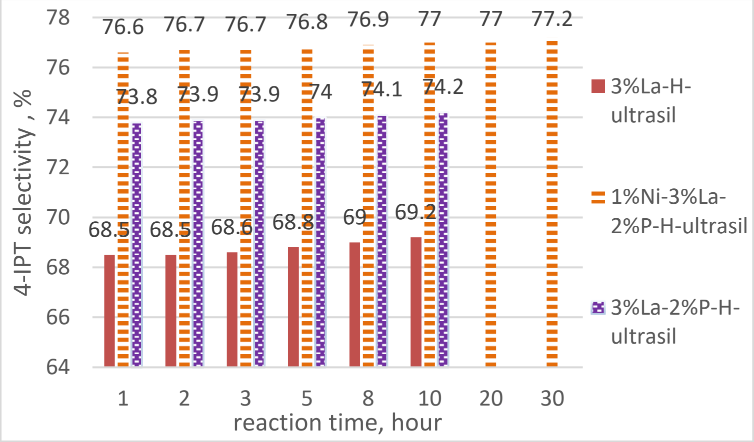

Figure 8. Dependence of 4-IPT selectivity on reaction time on modified catalysts

Conditions: T=330^{O}C, V=1.0 h^{-1}, toluene: alcohol = 2:1 (molar)

The 3%La-H-ultrasil catalyst operates stably for 5 hours. Modifying the catalyst with phosphorus improves its operating stability for up to 10 hours. Toluene conversion decreases slightly, by only 2.4%. After 10 hours of operation, a significant decrease in toluene conversion is observed (to 4.3%), and the 4-IPT selectivity increases slightly to 74.1%.

Modification of 3% La-2% P-H-ultrasil with nickel increases its operational stability up to 30 hours. During this time, toluene conversion does not decrease, and selectivity for IPT increases to 77.2%.

The catalysts practically retain their initial activity during 15-hour operation. In addition, modification of the catalyst with 3% La-2% P-H-ultrasil with nickel in an amount of 1.0 wt.% leads to an increase in selectivity for 4-IPT to 76.6% [18,22,23,24].

Patterns of toluene alkylation with isopropanol on unmodified and modified catalysts

Kinetic studies of the toluene alkylation patterns with isopropanol were studied on unmodified and modified catalysts in the temperature range of 200-300°C, a toluene/isopropanol molar ratio of 2-1, and a feedstock space velocity of 2.0-5.0 h^{-1}. It was preliminarily established that the 1%-Ni-3%Yb-2%P-H-ultrasil catalyst operates stably for 30 hours.

To assess the effect of external diffusion in the presence of catalyst samples weighing 1.0 and 2.0 g, experiments were carried out at a constant effective contact time (W/F $g^{\bullet}$ h/mol) at a temperature of 250°C, a toluene to isopropanol molar ratio of 4. For both samples, the toluene conversion remained virtually unchanged (10.8 and 10.9%). It was found that at an effective contact time of 30-45 $g^{\bullet}$ h/mol, the toluene conversion remained constant. To test the effect of internal diffusion on the reaction rate, experiments were conducted with samples of different sizes (0.7; 1.0 and 1.5 mm). It was found that at a constant contact time, the toluene conversion does not depend on the catalyst size.

Table 5.
Catalytic conversion on zeolite H-ultrasil (toluene / isopropanol =4mol/mol, V=5.0 h^{-1}) [18]

Transformation parameters	**Temperature, °C**				
	200	**220**	**250**	**275**	**300**
Toluene conversion, wt.%	4,9	10,1	10,9	11,5	7,2
Selectivity for IPT,%[a]	84	64	55	49	33
Selectivity for n-PT,% [b]	0	15	26	34	54
Composition of IPT (%)					
4-IPT (28,2-27,6)[v]	75,7	67,8	55,1	44,2	36,7
3-IPT (56,4-55,2)	24,3	28,6	40,1	50,4	57,6
2-IPT (15,4-17,2)	0	3,6	4,8	5,4	5,7
Composition of n-PT (%)					
Para (28,3-27,7)[в]	0	22,5	19,6	15,8	12,4
Meta (56,6-55,1)	0	77,5	80,4	84,2	87,6
Orto (15,1-17,2)	0	0	0	0	0

It is evident from Table 5 that with an increase in the reaction temperature from 200°C to 275°C, an increase in toluene conversion is observed, and at temperatures above 275°C, a decrease in toluene conversion was observed, which can be explained by an increase in the dealkylating activity of the catalyst and an increase in the proportion of isopropanol consumed in side reactions.

In addition, with an increase in the reaction temperature, a decrease in the selectivity for isopropyltoluenes and para-selectivity of the catalyst was observed. With an increase in the reaction temperature from 200°C to 300°C, the selectivity for 4-IPT decreases from 75.7% to 36.7%. The tendency to decrease the para-selectivity of the catalyst with an increase in temperature can be explained by the thermodynamics of the reactions occurring. It should be noted that at a reaction temperature of 200°C, n-propyltoluenes were not detected in the catalyst. In the temperature range of 200-300°C, o-propyltoluene was absent in the reaction products.

At 200°C, the formation of the ortho-isomer of isopropyltoluene (2-IPT) did not occur. A noticeable amount of 2-IPT (3.6-5.7 wt.%) was formed in the temperature range of 220-

300°C, but its concentration was lower than the thermodynamically equilibrium mixture (15.34-17.18%).

Table 6.

Effect of the molar ratio of toluene to isopropanol in the feedstock on the catalytic characteristics of H-ultrasil (temperature 250°C, V=5.0 h^{-1}, τ=1 hour)

Transformation parameters	**toluene / isopropanol (mol/mol)**				
	2	**4**	**5**	**6**	**8**
Toluene conversion, wt.%	13,4	10,9	8,1	6,7	3,8
Selectivity for IPT,%	43	55	62	68	72
Selectivity for n-PT,%	28	25	22	20	17
Composition of IPT (%)					
4-IPT	56,8	55,4	54,9	54,7	55,8
3-IPT	38,6	40,2	41,1	41,5	41,7
2-IPT	4,6	4,4	4,0	3,8	3,5
Composition of n-PT (%)					
Para	14,1	19,6	19,8	20,2	19,4
Meta	80,9	80,4	80,2	79,8	80,6
Orto	0	0	0	0	0

It is evident that with an increase in the feed space velocity from 2.0 to 8.0 h-1, a decrease in toluene conversion is observed (from 13.4 to 3.8 wt.%), the selectivity for IPT increases (from 43 to 72%), and the selectivity for n-pripyltoluenes decreases (from 28% to 17%). An increase in the space velocity has little effect on the IPT distribution. The main part (more than 95%) is made up of p- and m-isomers. The content of 4-IPT in the IPT composition is 54.7-56.8%, and 2-IPT is only 3.5-4.6%.

Table 7 compares the results obtained on unmodified and modified catalysts. It is evident that as a result of modification there is a significant increase in selectivity for IPT (from 55 to 78%) and a decrease in selectivity for n-propyltoluenes (from 26 to 15.5%). In contrast to the unmodified sample at 250°C, a feedstock volumetric feed rate of 5 h-1 and a molar ratio toluene / isopropanol 4 mol/mol on modified samples, 2-IPT does not form.

Table 7.
Effect of modification of zeolite H-ultrasil on the catalytic characteristics of the catalyst (temperature 250°C, V = 5.0 h^{-1}, toluene / isopropanol = 4 mol/mol, reaction duration 1 hour)

Transformation parameters	**H-ultrasil**	**Yb- H-ultrasil**	**Ni- Yb-P-H-ultrasil**
Toluene conversion, wt.%	10,9	6,3	5,2
Selectivity for IPT,%	55	71	76
Selectivity for PT,%	26	18	15
Composition of IPT (%)			
4-IPT	55,1	77,8	100
3-IPT	50,4	22,1	-
2-IPT	5,4	-	-
Composition of n-PT (%)			
Para	19,6	49,2	69,4
Meta	80,4	50,8	30,6
Orto	-	-	-

Modification of H-ultrasil with ytterbium leads to an increase in selectivity for IPT from 55.1 to 77.8%, and additional modification of the Yb-containing catalyst with phosphorus and nickel completely prevents the formation of 3-IPT. Selectivity for 4-IPT at a toluene conversion of 5.2% is 100%.

Modification of the H-ultrasil zeolite also affects the composition of propyltoluenes. As a result of modification, there is an increase in p-propyltoluene and a decrease in the content of m-propyltoluene. Based on the data obtained, the reaction scheme for alkylation of toluene with isopropanol on modified ultrasils can be presented in the following scheme:

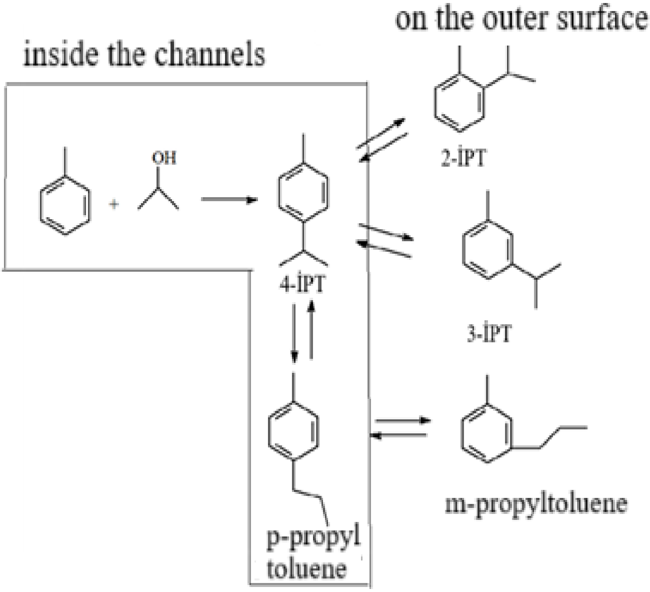

Figure 10. Scheme of the reaction of alkylation of toluene with isopropanol on modified ultrasils.

During alkylation of toluene, the methyl group present in the benzene ring activates the ortho and para positions. This means that the m-isomer present in the product can be formed as a result of isomerization of the p- and o-isomer. Inside the channels of the H-ultrasil zeolite, the formation and diffusion of the o-isomer from its channels is excluded due to spatial limitations. Therefore, 4-IPT (p-isomer) is the main product, which is confirmed by the results obtained with the modified samples. However, in the reaction products obtained on H-ultrasil, the formation of all three IPT isomers is observed. This is explained by the isomerization of the p-isomer on strong Brønsted acid sites localized on the outer surface of the zeolite crystals. The formation of p-isopropyltoluene can be explained by the isomerization of 4-IPT on acid sites localized in the zeolite channels. The formation of m-isopropyltoluene occurs as a result of isomerization of p-isopropyltoluene on the outer surface of the zeolite. Modification of H-ultrasil with ytterbium, phosphorus and nickel deactivates the strong Brønsted acid centers of the outer surface, which leads to a strong decrease in the degree of isomerization of the p-isomer of isopropyltoluene and propyltoluene.

Thus, the reaction mechanism shown schematically in Figure 10 indicates that the primary product is 4-IPT, which undergoes two types of isomerization: skeletal and positional, which leads to the formation of p-propyltoluene and m-isopropyltoluene [18,22,23,24].

CONCLUSION

1. To obtain paraselective catalysts for the alkylation of toluene with isopropanol, the properties of metal-containing catalysts based on ZSM-5 type zeolites were studied. It is shown that the catalytic properties of multiply charged cationic forms of pentasils depend on the nature, charge, size and polarizing action of the Men+ cation, as well as on the concentration and strength of the acid sites. On the cationic Mg2+, Zn2+ and REE3+ forms of pentasil, an increase in para-selectivity is accompanied by significant side reactions, while on the Ba and Sr forms, an increase in para-selectivity is accompanied by a sharp decrease in the catalyst activity. These patterns are due to the presence of strong Brønsted and Lewis acid sites in the REE, Mg and Zn forms of pentasils, and weak and medium acid sites in the Ba and Sr forms. Zeolites with larger cations demonstrate higher para-selectivity. Among the triply charged cationic forms, the La forms of pentasils exhibit higher selectivity for 4-IPT (51.5-52.7%) [1,17].

2. Using the methods of XRD, IR spectroscopy, TPD-ammonia and low-temperature nitrogen adsorption, the features of the formation of active centers on REE- and REE-P-containing pentasils were established. It was shown that the change in the strength, number of acid centers and textural characteristics of the catalysts occurs as a result of the interaction of modifiers with Brønsted acid centers localized on the outer surface and in the pores of the zeolite [9,10,11,16].

3. It was shown that when modifying the zeolite with modifiers (Mg, REE, P) in an amount of 3.0-7.0 wt.%, there is a decrease in the

specific surface area, micropore area, total pore volume, concentration and strength of Brønsted acid centers on the zeolite surface and the formation of new, stronger Lewis acid centers, which play an important role in increasing the para-selectivity of the catalysts [11,12].

4. The effect of the nature and concentration of Mg,Sc and REE (La, Yb, Ho, Gd, Pr) on the properties of decationized zeolite HZSM-5 was established. Modification improves the selectivity of alkylation and has a promoting effect on its para-selectivity with respect to 4-IPT. With sufficient toluene conversion (15.3-18.1%), the highest selectivity is achieved on catalysts containing 5.0 wt.% REE. Among the studied modifiers, the maximum para-selectivity is achieved on the La-modified (72.4%), and relatively low on the Pr-modified (62.5%) sample [5,7,19].

5. The effect of three-component Ni-La (Yb)-P modification of zeolite HZSM-5, consisting in an increase in the density of medium acid sites, an increase in the volume of mesopores and annihilation of side reactions of olefins by Ni nanoparticles, which provide high selectivity and stability of the bimetallic catalyst was established [22,23].

6. Kinetic studies of the alkylation reaction of toluene with isopropanol on unmodified (H-ultrasil) and modified (Yb-H-ultrasil, Ni-Yb-P-H-ultrasil) catalysts were carried out. It is shown that in the presence of H-ultrasil, which has strong Brønsted acid centers, all three IPT isomers are formed. Modification of H-ultrasil with modifiers (Ni, Yb, P) deactivates strong Brønsted acid centers localized on its outer surface and prevents isomerization of the p-isomer into m- and o-isomers of IPT, as well as into propyltoluenes. The results obtained on the modified samples confirm that the primary product is the p-isomer, which is formed on moderate acid centers localized in the zeolite channels. The formation of m-isomers of isopropyltoluene and propyltoluene occurs by skeletal and positional isomerization of 4-IPT on the outer surface of the zeolite crystal [18].

7. For the first time, new bimetallic catalysts of the composition 1% Ni3% La (Yb) - 2% P-HZSM-5 have been

developed for the reaction of toluene alkylation with isopropanol. They have an optimal combination of B/L acid sites, a moderate density of B-acid sites and a porous structure, which at 330 °C, a feedstock volumetric feed rate of 1.0 h^{-1} and a toluene/isopropanol molar ratio of 2 with a toluene conversion of 20.2-21.1% provide high paraselectivity (74.1-76.2%) with respect to 4-IPT and operational stability (30 h) [22,23].

THE MAIN CONTENT OF THE DISSERTATION IS PUBLISHED IN THE FOLLOWING WORKS:

1. Abdullayeva, N.M. Influence of modification on acidic and catalytic properties of high-silica zeolites in the reaction of alkylation of toluene with isopropanol / L.Q. Voskresenskiy, N.D.Musayeva, N.F.Akhmedova // Journal of Environmental Science, Computer Science and Engineering &Technology, India,-2018,- Vol.7.-No.4, p.528-534.
2. Абдуллаева, Н.М., Мамедов С.Э., Гахраманов Т.О., Азмамедова Х.М./ Алкилирование толуола изопропанолом на высококремнеземном цеолите типа ЦВМ, модифицированном магнием // Ümummilli Lider HEYDƏR ƏLİYEVİN anadan olmasının 95-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların “KİMYANIN AKTUAL PROBLEMLƏRİ” XII Beynəlxalq Elmi Konfransı, BDU, Bakı, Azərbaycan, -2018, -с 129-130.
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The defense will be held on 25 september 2025 at 10:00 at the meeting of the Dissertation council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Catalysis and Inorganic Chemistry named after Academician M. Nagiyev of Ministry of Science and Education of the Republic of Azerbaijan

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Abstract was sent to the required addresses on 20 august 2025

Signed for print: 12.06.2025

Paper format: 60x84$^{1/16}$

Volume: 39284

Number of hard copies:20