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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**SELECTIVE ALKYLATION OF BENZENE WITH  
ETHANOL IN THE PRESENCE OF MODIFIED HZSM-5  
ZEOLITE CATALYSTS**

Speciality: 2316.01 – Chemical kinetics and catalysis

Field of science: Chemistry

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## GENERAL CHARACTERISTICS OF WORK

### **Relevance of the topic and degree of development.**

Alkylation of aromatic hydrocarbons is a multiton process of chemical synthesis. One of the main industrial alkylation processes is the synthesis of ethylbenzene, which is the primary raw material for the production of styrene used in the production of synthetic resins and plastic masses. Industrially, ethylbenzene is produced by the process of alkylation of benzene with ethylene in the liquid phase in the presence of a Friedel-Crafts catalyst, and in the liquid and gas phase over zeolite-containing catalysts. Processes based on the Friedel-Crafts catalyst have a number of disadvantages: quick catalyst deactivation, being soluble in the reaction products and therefore unable to regenerate, accumulation of sour sludge in catalyst utilization, generation large amounts of wastewater, equipment corrosion. Zeolite catalysts are gradually replacing currently used homogeneous aggressive Friedel-Crafts acid catalysts due to their inherent disadvantages.

Application of heterogeneous zeolite catalysts can be a prospective solution to overcome the current technological problems and shortcomings of alkylation processes of aromatic hydrocarbons. Nowadays, in 8 out of 70 plants operating in the production of ethylbenzene, the alkylation reaction of benzene with ethylene is carried out in the gas phase mode over zeolite catalysts. Catalysts based on high-silica ZSM-5 zeolite are used in the process of alkylation of benzene with ethylene in the gas phase. Probably ten percentage of the valuable ethylene produced over the world is used for the alkylation of benzene. However, in recent years, the use in petrochemical synthesis of non-oil feedstock, such as, natural gas, syngas, methanol and bioethanol obtained from biomass, which is an alternative to traditional hydrocarbon feedstock, is considered economically and environmentally feasible. Currently, catalytic conversion of bioethanol produces high-octane motor fuel and a significant amount of valuable organic substances. For this reason, replacement of ethylene used as an alkylating agent in ethylbenzene production with bioethanol and development of efficient catalysts

for this process is one of the priority areas. Therefore, the study of physicochemical and catalytic properties of modified catalysts with three-dimensional structure and nanoscale channels for benzene alkylation reaction with ethanol and regularities of the alkylation process with their participation, as well as the development of highly efficient catalytic systems are very relevant at present and in the perspective of further development of science.

**The objects and scope of research.** The objects of research are benzene, ethanol and their alkylation products (ethylbenzene, xylenes, diethylbenzenes and trimethylbenzenes), and the subject is catalysts, which based on ZSM-5 zeolite modified with combinations of Sc, Y, lanthanides (La, Yb, Ho, Gd), B and P.

**The aims and objectives of the study.** The main purpose of this research is to study the patterns of benzene alkylation with ethanol in the presence of modified metal zeolite catalysts, to study the interaction of physicochemical, acidic, textural properties of zeolite catalysts of structural type MFI (ZSM-5) and their catalytic activity, selectivity and stability, and to select optimally effective catalysts for the alkylation process.

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

- Development of modified forms of ZSM-5 zeolites;
  - The effect of the nature and concentration of modifiers on the catalytic properties of zeolite catalysts, their selectivity to ethylbenzene and their stability in the alkylation reaction of benzene with ethanol;
  - Study of physicochemical, acid and textural properties of modified zeolites and determination of the correlation between these properties and the selectivity of ethylbenzene formation;
  - Study of the regularities of benzene alkylation reaction with ethanol in the presence of catalysts based on modified zeolite ZSM-5;
  - Selection of the best catalysts with high selectivity and stability for benzene alkylation with ethanol.

**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. The following physicochemical

methods were used in the thesis: X-ray phase analysis, gas-liquid chromatography, low-temperature nitrogen adsorption, thermo-programmed ammonia desorption, and IR spectroscopy.

### **The main provisions of the defense.**

- Effect of nature and amount of modifier on the activity and selectivity of the catalysts zeolite based on ZSM-5 in the reaction of benzene alkylation with ethanol;

- Effect of modification on physicochemical, acid and textural properties of the catalyst;

- Results validating the correlation between acidic, textural and catalytic properties of modified ZSM-5 zeolite-based catalysts;

- Study of the regularities of benzene alkylation reaction with ethanol in the presence of modified zeolite catalysts ZSM-5.

**Scientific innovation of the research.** The properties of catalysts based on zeolites of structural type MFI modified with Mg, Sc, Y, La, Gd, Ho, Yb compounds in the reaction of gas-phase alkylation of benzene with ethanol have been systematically studied for the first time. The effect of modification on the catalysts' ethylbenzene selectivity, texture, acidic and catalytic properties was studied and the interaction between them was revealed.

By methods of X-ray phase analysis, X-ray structural analysis, low-temperature nitrogen adsorption and IR spectroscopy the texture and acid properties of the synthesized catalysts were determined. It has been established that with the increase for modifiers the specific surface area and pore volume decrease, the distribution of acid centers changes, the number of acid sites of medium strength increases, and these changes provide high selectivity and stability of the catalysts to ethylbenzene. Catalytic systems Me-B-ZSM-5 and Me-P-ZSM-5 with high selectivity (69-75%) to ethylbenzene, avoiding the formation of undesirable o- and m-xylenes for the process of benzene alkylation with ethanol in the gas phase, were also developed for the first time.

### **Theoretical and practical significance of the research.**

Theoretical relevance of the study includes scientific validation of selective production of ethylbenzene by alkylation of benzene with ethanol in the presence of modified zeolite catalysts

ZSM-5. Loading of modifiers into zeolite ZSM-5: phosphorus and boron, elements of group III B (Sc, Y, La, Gd, Ho, and Yb) allows increasing the activity of catalysts in the reaction of benzene alkylation with ethanol and selectivity for ethylbenzene. The nature and amount of modifier were found to have influence on the stability, selectivity and regenerability of the catalysts, which are important practical properties. The patterns revealed in the synthesis of catalysts can be used in the purposeful synthesis of highly selective metal zeolite catalysts for the alkylation of alkylaromatic hydrocarbons with olefins and alcohols. Me-B-ZSM-5 and Me-P-ZSM-5 catalytic systems with high selectivity and stability for ethylbenzene were proposed for the benzene alkylation reaction with ethanol.

### **Published works and approbation of the work.**

The main results of the work were discussed and reported at international scientific conferences: Сборник материалов IV Всероссийской студенческой конференции с международным участием, Санкт-Петербург, 2017 (Ru); XII Международная конференция Молодых ученых по нефтехимии. Сборник тезисов, г. Звенигород, 2018 (Ru); II International (XII Ukrainian) scientific conference for students and young scientists, Vinnytsia, 2019; XXI Менделеевский Съезд по общей и прикладной химии Том 4. Сборник тезисов в 6 томах, Санкт-Петербург, 2019 (Ru); VI Всероссийская конференции с международным участием, посвященная 85-летию со дня рождения чл-корр. РАН Ю.С. Клячкина (1934-2000). Сборник тезисов докладов, Пермь, 2019(Ru); Актуальные вопросы химической технологии и защиты окружающей среды. Сборник материалов VIII Всероссийской конференции, Чебоксары, 2020(Ru); XIII Всеукраїнська наукова конференція студентів та аспірантів "Хімічні Каразінські читання - 2021" (ХКЧ'21). Тези доповідей, Харків, 2021 (UA); 9-ая Всероссийская цеолитная конференция. Цеолиты и мезопористые материалы: достижения и перспективы. Тезисы докладов, Грозный, 2021(Ru); Кластер Конференций. Тезисы докладов, Иваново, Россия, 2021; XXV Всероссийская конференция молодых ученых-химиков (с

Международным участием). Тезисы докладов, Нижний Новгород, 2022(Ru); Ümummilli Lider Heydər Əliyevin 93-cü, 94-cü, 95-ci və 96-cı ildönümünə həsr olunmuş Respublika Elmi Konfranslarının materialları, Bakı, 2016, 2017, 2018, 2019 (AZE).

**Affiliation.** The research was performed at Baku State University, the department of Physical and Colloid Chemistry

**The scope and structure of the work.** The dissertation consists of an introduction (9592 symbols) and four chapters (1st chapter 57224 symbols, 2nd chapter 20095 symbols, 3rd chapter 36617 symbols, and 4th chapter 41285 symbols), main results (2622), 149 cited referances; in total has 145 pages, where, figures (39) and tables (34) are shown.

Nine (9) articles on the materials of the dissertation work (4 of them in periodical scientific journals included in the International databases with indexing criteria) and abstracts of 16 reports were published.

**Personal contribution of the author.** The author's personal contribution includes the statement of goal and target of the thesis work and the achievement of the main results. The applicant carried out all theoretical and experimental research, as well as synthesis and characterization of catalysts, analysis of the obtained chromatograms, physicochemical results, interpretation of the obtained results, presentation of the results at conferences of different levels, preparation of scientific articles for printing.

## CONTENT OF THE WORK

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

**The first chapter** the current state of research in the field of alkylation of benzene in the presence of acid and zeolite catalysts in the liquid phase was reviewed. Moreover, in parallel, an analysis was given based on the literature review devoted to the alkylation of benzene with methanol and ethanol in the presence of zeolite

catalysts in the vapor phase.

**The second chapter** outlines methods for the synthesis of the catalysts based on pentasil modified with transition and Ln elements, their physicochemical investigations, analysis of reaction products, the flow type the experimental catalytic unit on which the process is carried out, and the methodology of experiments.

**The third chapter** presents the results of the study of the physical-chemical and catalytic properties of ZSM-5 zeolites modified with metals (Mg, Sc, Y and Ln elements) and non-metals (boron and phosphorus) in the alkylation of benzene with ethanol.

**In the fourth chapter,** regularities of alkylation of benzene with ethanol in the presence of ZSM-5 zeolite (Me-B-ZSM-5, Me-P-ZSM-5) co-modified with metal, non-metal were studied, and the mechanism of the alkylation process was given.

The conclusion summarises the results of the research carried out.

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

### **Summary of chapter 3**

#### **Physicochemical and catalytic properties of ZSM-5 zeolite modified with boron and phosphorus in the alkylation reaction of benzene with ethanol**

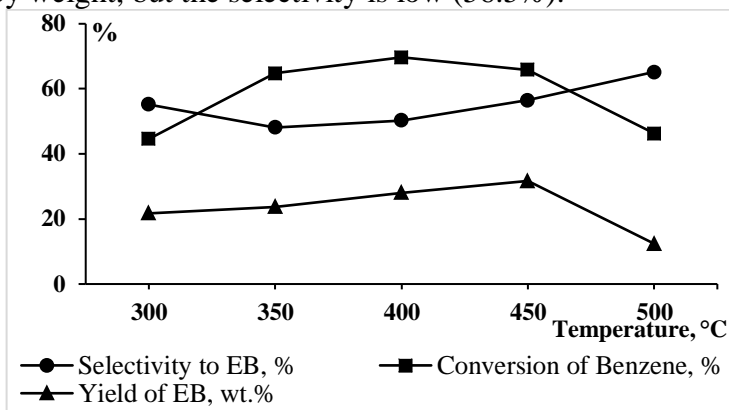
In order to study the effect of modification with boron and phosphorus on the catalytic and physicochemical properties of HZSM-5 zeolite, the H-form of ultrasil ( $\text{SiO}_2/\text{Al}_2\text{O}_3=38-200$ ) and TSVM ( $\text{SiO}_2/\text{Al}_2\text{O}_3=33$ ) zeolites, which are analogs of ZSM-5 zeolite, were obtained by ion exchange method. Simultaneously, B/HZSM-5 and P/HZSM-5 catalysts containing 2.0-5.0 wt.% modifier were prepared by impregnation using solutions of orthoboric acid and  $(\text{NH}_4)_2\text{HPO}_4$  salt. Catalytic experiments were carried out in a flow-type reactor in a nitrogen or hydrogen gas current.

It was found that the alkylation reaction in the presence of zeolite catalyst HZSM-5 proceeds with a number of parallel reactions, and the composition of products along with ethylbenzene,



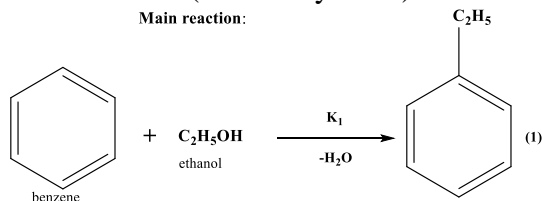
which is the target product, includes a sufficient amount of extraneous products - toluene, xylenes, diethylbenzene (DEB), triethylbenzene (TEB), and other C<sub>9+</sub> aromatic hydrocarbons (Scheme 1).

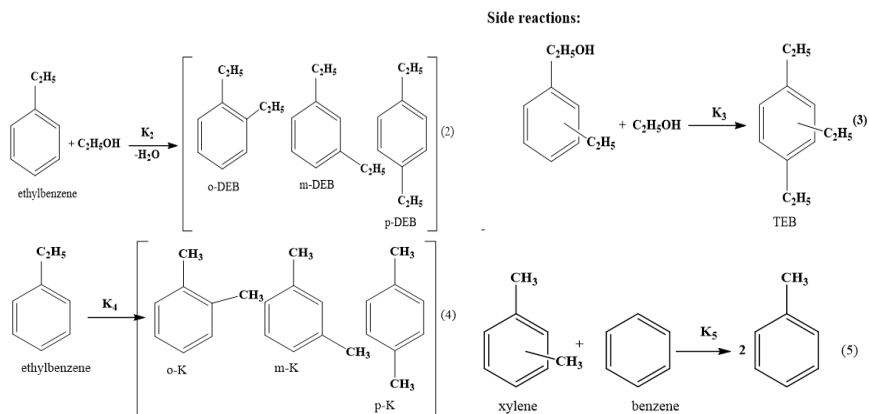
Figure 1 shows that alkylation in the presence of H-ultrasil in the temperature range of 300-400 °C is not selective (50.3-55.2 wt%) and the yield of EB is low, 21.8-28.1 wt%. When the reaction temperature is raised to 450 °C, the ethylbenzene yield increases to 31.7 % by weight, but the selectivity is low (56.5%).



**Figure 1. Effect of temperature on selectivity and EB yield during alkylation of benzene with ethanol in the presence of zeolite H-ultrasil (benzene/ethanol=2:1).**

When the temperature increases up to 500 °C, notwithstanding the rise of selectivity for ethylbenzene up to 65.2 %, the EB yield sharply decreases due to accumulation of coking products on the zeolite surface (12.4 % by mass).

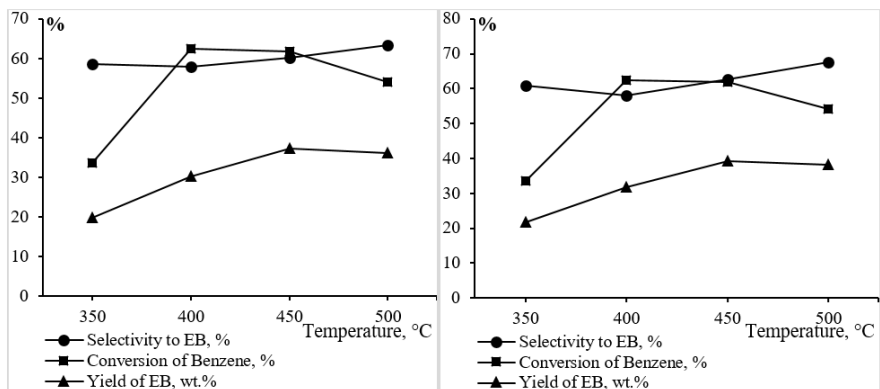




**Scheme 1: A probable scheme of main and side reactions in the process of benzene alkylation with ethanol.**

Figure 2 shows that the addition of 2.0-4.0 wt.% boron to H-ultrasil zeolite leads to a decrease in by-product yield, an increase in selectivity and EB yield. Compared to H-ultrasil when 2.0 wt.% boron is loaded to its composition, the EB yield grows up to 35.8-36.1 wt.% in the temperature range of 450-500 °C, and the EB selectivity is 58.6-63.3%. As the amount of boron in the catalyst is increased to 4.0 wt.%, the amount of by-products dramatically decreases and the EB yield up to 37.6-38.6 wt.% and the selectivity to 61.7-66.5% rises. Increasing the boron content in zeolite up to 5.0 wt. %, the degree of benzene conversion and EB yield slightly decline, but the EB selectivity increases up to 68.1 %. Notably, the addition of 4.0-5.0 wt.% modifier to the H-ultrasil prevents the formation of undesirable m- and o- xylenes.

This pattern is also observed when zeolite HTsVM ( $\text{SiO}_2/\text{Al}_2\text{O}_3=33$ ) is modified with phosphorus. High selectivity and EB yield in the presence of modified catalysts are observed in the 450-500 °C temperature range. In comparison with HTsVM, when 4.0 wt% phosphorus is loaded to the composition, the yield of EB at 450 °C varies from 31.2 wt% to 39.3 wt%, and the selectivity for EB ranges from 54.6% to 61.8%. Modification of HTsVM zeolite with 4.0 wt.% phosphorus resulted in elimination of undesirable m- and o-xylenes in the reaction yields.



**Figure 2. Effect of boron modification (a) 2% B-N-ultrasil, b) 4% B-N-ultrasil) and temperature on EB selectivity and EB yield in the benzene alkylation reaction with ethanol (benzene/ethanol = 2:1).**

Thus, in the alkylation of benzene, boron and phosphorus have a promoting effect on the catalytic properties of HZSM-5 type zeolites.

The effect of boron and phosphorus on the catalytic properties of HZSM-5 zeolite can be explained by the change in its acidic properties and the porous structure of the zeolite as a result of modification. When the amount of boron in HZSM-5 grows, its sorption capacity for water vapor, benzene and n-heptane drops. For instance, by increasing the boron content of HZSM-5 zeolite to 1.0 wt.%, the sorption capacity for n-heptane and benzene reduced from 0.164 to 0.148 cm<sup>3</sup>/g and from 0.080 to 0.066 cm<sup>3</sup>/g, respectively.

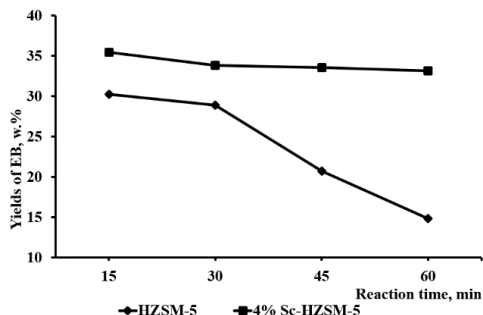
Increasing the amount of boron in the zeolite composition up to 5 wt.%, the sorption capacity for n-heptane and benzene decreases significantly to 0.086 and 0.059 cm<sup>3</sup>/g. Similarly, the sorption capacity for water vapor, benzene and n-heptane reduces with an increase in the amount of phosphorus in HZSM-5 zeolite. The narrowing of the pores creates steric hindrance in the diffusion of large molecules of o-, m-xylenes, DEB and TEB. Small-sized EB molecules easily diffuse through the zeolite channels. This would explain the enhancement of EB adsorption selectivity in the

modified zeolites.

The modification changes the concentration and strength of acidic sites of HZSM-5 zeolite. The concentration of strong Brønsted acid sites drops from 528 to 151  $\mu\text{mol/g}$  when the boron content of HZSM-5 zeolite increases to 2.0 wt.%. Upon increasing the amount of boron in the catalyst up to 4.0-5.0 wt.%, the concentration of strong Brønsted acid sites decreases sharply and amounts to 87-110  $\mu\text{mol/g}$ . When the boron content in zeolite is increased up to 5.0 wt.%, the ratio of the concentration of weakly acidic sites ( $C_1$ ) to strongly acidic sites ( $C_2$ ) decreases significantly and becomes equal to 1.9. The amount of phosphorus significantly affects the strength and concentration of acidic sites of HZSM-5(33) zeolite. The maximum of the ammonia desorption peak, which characterizes the strong Brønsted acid sites, shifts to the lower temperature region with increasing phosphorus content in HZSM-5, indicating a decrease in the strength and concentration of these strong Brønsted acid sites. By adding 4.0 wt% phosphorus to H-pentasil, the concentration of strong Brønsted acid sites drops from 542  $\mu\text{mol/g}$  to 104  $\mu\text{mol/g}$ . Due to the modification, the ratio of weak acid sites ( $C_1$ ) to strong acid sites ( $C_2$ ) increases from 1.15 to 1.7. The high concentration of medium strength acid sites precludes the formation of by-products and enhances the selectivity for ethylbenzene.

### **Regularities of benzene alkylation with ethanol in the presence of ZSM-5 zeolite catalysts modified with scandium**

The yield and selectivity of EB depend on the amount of Sc and temperature. When the content of Sc in HZSM-5 zeolite is increased to 4.0 wt.%, the yield of EB in the temperature range of 400-450 °C (from 25.7-27.1 wt.% to 31.8-34.1 wt.%) and an enhancement in selectivity (from 45.6-48.2% to 52.2-54.8%) is observed. The yield of EB decreases slightly (33.8% by mass), when the reaction temperature is increased to 500 °C. Increasing the amount of modifier up to 5.0 wt.%, the benzene conversion rate and EB yield slightly decline, but the selectivity partially increases due to the reduction of by-product yield.



**Fig. 3. Dependence of ethylbenzene yield on reaction time (conditions: T=500 °C; C<sub>6</sub>H<sub>6</sub>:C<sub>2</sub>H<sub>5</sub>OH=2:1).**

For the first 30 min of the reaction, the yield of ethylbenzene at 500 °C in the presence of HZSM-5 zeolite is 28.9 wt.%. However, as the duration of the reaction increases, the amount of coke on the surface of the catalyst rises. The amount of coke increases approximately twice and is 8.8% when the reaction time reaches 1.0 hour. The yield of ethylbenzene declines to 14.8 wt.%. In contrast to HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=33), after running the 4.0 % Sc-HZSM-5 catalyst for 1.0 h the EB yield decreases by 2.3 wt.% (Figure 3).

As a result of coking, the concentration of strong Brønsted acid sites, which are responsible for the alkylation reaction, decreases sharply, and most of the pores of zeolite are blocked by coke. Modification of HZSM-5 zeolite with 4.0 wt% scandium reduces the concentration of strong acid sites from 542 μmol/g to 243 μmol/g (Table 1). This catalyst works stably for 60 minutes.

**Table 1.**

**Acid properties of HZSM-5 and 4% Sc-HZSM-5 catalysts before and after the reaction**

Sample	Reaction time, minute	NH <sub>3</sub> desorption peaks, T°C		Concentration of acid sites, μmol/g	
		I Form	II Form	c <sub>1</sub>	c <sub>2</sub>
HZSM-5	-	198	418	628	542
	30	171	294	287	189
	60	164	270	234	32
4% Sc-HZSM-5	-	193	319	369	243
	60	191	317	373	239

This is due to the fact that the concentration of weak and strong acid sites of the catalyst does not change during that time.

As the reaction time increases, the specific surface area and total pore volume of HZSM-5 zeolite decrease (table 2). It is clear from the obtained results that during the coking process, the active sites of HZSM-5 zeolite are deactivated, and the pores are blocked by coke. As a result of these factors, HZSM-5 zeolite does not work stably (Figure 3).

The results obtained on the textural properties of HZSM-5 and 4% Sc-HZSM-5 catalysts before and after reaction are given in Table 2. Conversely, after 60 minute running time, the modified sample exhibited an enhancement in the concentration of its acidic sites (from 243  $\mu\text{mol/g}$  to 239  $\mu\text{mol/g}$ ) (Table 1) and the specific surface area (from 242.1 to 239.6  $\text{m}^2/\text{g}$ ) kept its catalytic activity due to a slight change in the total pore volume (from 0.21 to 0.20  $\text{cm}^3/\text{g}$ ) (Table 2).

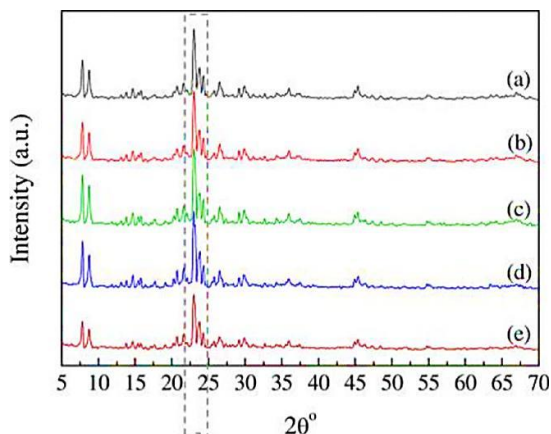
**Table 2.**  
**Texture properties of HZSM-5 and 4% Sc-HZSM-5 catalysts before and after the reaction**

Sample	Reaction time, minute	S ( $\text{m}^2/\text{g}$ )	V <sub>por.</sub> ( $\text{cm}^3/\text{g}$ )	Amount of coke, wt.%
HZSM-5	-	288,5	0,24	-
	30	192,6	0,13	4,6
	60	82,7	0,09	8,8
4% Sc-HZSM-5	-	242,1	0,21	-
	60	239,6	0,20	0,6

Thus, modification of zeolite HZSM-5 with scandium accelerates the alkylation of benzene with ethanol (route 1) and the alkylation of ethylbenzene with ethanol (route 2), reduces the rates of other routes (4,5) (Scheme 1) and therefore it enhances the selectivity for EB. Catalysts modified with 4.0 - 5.0 wt.% Sc show higher yield and selectivity. In their presence, the yield of ethylbenzene at 450-500°C is 33.8 - 35.9 wt.%, and the selectivity is 54.8 - 58.3%.

## Effect of the nature of the metal modifier (Sc, Y, La, Gd, Yb, Ho) on the properties of high-silica zeolites in the alkylation of benzene with ethanol

The effect of modification with metals on the structure and catalytic properties of HZSM-5 zeolite (H $\alpha$ BM) was studied. X-ray patterns of initial H-H $\alpha$ BM and samples modified with Sc, La, Gd, Yb show that the structure of zeolite practically does not change after modification (Fig. 4). The diffraction peaks of 4% Me-H-H $\alpha$ BM catalysts correspond to the diffraction peaks of H-H $\alpha$ BM zeolite ( $2\theta=7.8^\circ; 8.7^\circ; 23.0^\circ; 24.2^\circ$ ). On the other hand, new peaks at  $2\theta=23.2^\circ$  and  $23.6^\circ$  appear in the 4% Me-H-H $\alpha$ BM catalysts compared to the initial H-H $\alpha$ BM, but the peak at  $24.2^\circ$  partially decreases.



**Figure 4. X-ray patterns of catalysts: (a) 4.0 wt.% La/H-H $\alpha$ BM, (b) 4.0 wt.% Yb/H-H $\alpha$ BM, (c) 4.0 cu.% Gd/H-H $\alpha$ BM, (d) 4.0 cu.% Sc/H-H $\alpha$ BM, (e) H-H $\alpha$ BM.**

The temperature dependence of the yield of ethylbenzene in the modified H-H $\alpha$ BM zeolite is given in figure 5a. In the temperature range of 350-500 °C, the degree of conversion of ethanol and benzene in the presence of H-H $\alpha$ BM is 85.4-91.2 and 66.2-68, respectively. H-H $\alpha$ BM shows low activity and selectivity in the alkylation of benzene with ethanol. At 450 °C, the maximum yield of ethylbenzene is 27.8 wt.%, at 500 °C, its yield sharply decreases

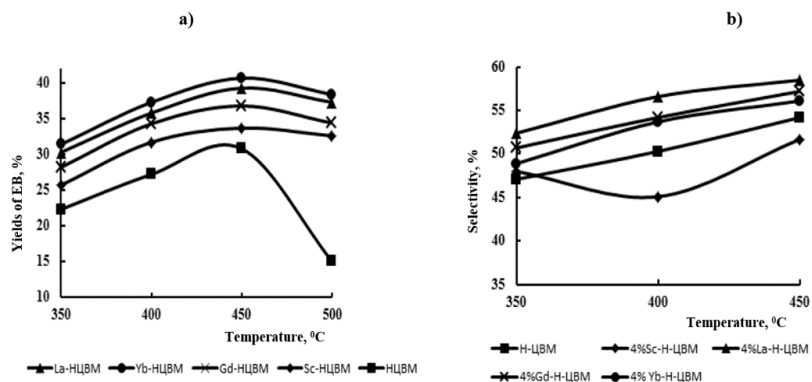
to 14.5wt.% (Figure 5a). Modification of zeolite with metals significantly affects its activity and selectivity. Modification of H- $\text{H}\beta\text{M}$  zeolite with 4.0 wt.% metal significantly reduces the yield of by-products and increases the selectivity to ethylbenzene. Increasing the reaction temperature from 350 °C to 450 °C leads to an increase in the yield and selectivity of ethylbenzene. The maximum yield of ethylbenzene (40.7 wt.%) is observed over Yb-modified catalyst (Figure 5a). Catalysts for the yield of ethylbenzene are as follows:

Yb- $\text{H}\beta\text{M}$  > La- $\text{H}\beta\text{M}$  > Gd- $\text{H}\beta\text{M}$  > Sc- $\text{H}\beta\text{M}$  >  $\text{H}\beta\text{M}$

The selectivity of the alkylation process with respect to ethylbenzene also depends on the nature of the modifier. A higher selectivity for ethylbenzene is observed in the La-modified  $\text{H}\beta\text{M}$  catalyst and is 59.5% (Fig. 5b). Depending on the nature of the modifying metal, catalysts are located in the following order according to the selectivity of ethylbenzene:

La- $\text{H}\beta\text{M}$  > Gd- $\text{H}\beta\text{M}$  > Yb- $\text{H}\beta\text{M}$  > Sc- $\text{H}\beta\text{M}$

The selectivity observed on the La-modified catalyst is significantly higher than that on the catalyst containing ytterbium, where the maximum yield of ethylbenzene is achieved.

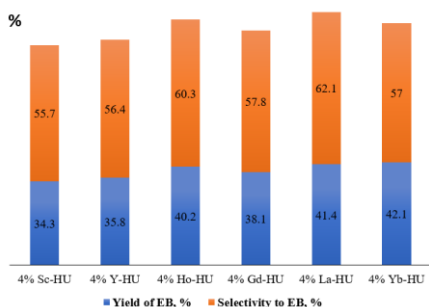


**Figure 5. Temperature dependence of yield (a) and selectivity (b) of EB in the presence of modified pentasils**

The maximum selectivity for ethylbenzene is 59.5% in the case of the La- $\text{H}\beta\text{M}$  catalyst, and 56.1% in the presence of the Yb- $\text{H}\beta\text{M}$  catalyst.

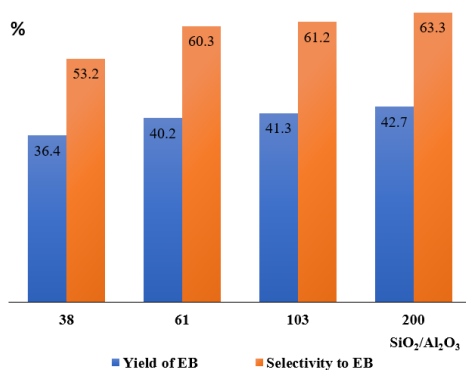


The absence of xylenes in the products obtained in the presence of catalysts modified with La and Gd significantly increases the selectivity of the catalysts for ethylbenzene.



**Figure 6. Effect of nature of Sc, Y and lanthanides in 4% Me-ultrasilic catalysts on yield and selectivity of EB (conditions: 450°C, C<sub>6</sub>H<sub>6</sub>:C<sub>2</sub>H<sub>5</sub>OH=2:1)**

The same regularity is also observed when H-ultrasilic zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=61) is modified with Sc, Y and lanthanides (La, Yb, Gd, Ho) (figure 6). It can be seen that the selectivity and yield according to EB depend to a significant extent on the nature of the metal. The lowest selectivity is the sample modified with Sc (55.7%), and the highest selectivity is the sample modified with La (62.1%).



**Figure 7. Effect of zeolite silicate module on EB yield and selectivity in 4% Ho-H-ultrasil catalysts (conditions: 450°C, C<sub>6</sub>H<sub>6</sub>:C<sub>2</sub>H<sub>5</sub>OH=2:1)**

The effect of silicate modulus on the yield and selectivity of EB was studied in the presence of modified ultrasilic zeolite and it was determined that when the silicate modulus of zeolite in the catalyst increases from 38 to 200, the selectivity and yield due to EB gradually increase. A higher selectivity (63.3 %) is achieved in the presence of 4% Ho-H-ultrasil zeolite catalyst with a silicate modulus of 200.

Because of modification, the redistribution of acid sites in zeolite and the change of textural properties of catalysts are observed, which reflected in the effect of the nature of modification and modifiers on the activity and selectivity of zeolite catalyst (table 3). HLI $\bar{B}$ M zeolite has a larger number of strong acid centers. The modification of HLI $\bar{B}$ M with lanthanum reduces the concentration of strong-acid sites by a greater amount. The concentration of strong acidic sites drops from 542  $\mu\text{mol/g}$  to 145  $\mu\text{mol/g}$  when 4.0 wt% lanthanum is modified into HLI $\bar{B}$ M zeolite. When comparing the acid and catalytic properties of zeolite catalysts, it is acknowledged that a decrease in the total number of acid sites leads to an enhancement of selectivity for ethylbenzene, whereby the ratio of medium and strong acid sites play a crucial factor.

**Table 3.**

**Acid characteristics of modified catalysts**

Catalysts	NH <sub>3</sub> desorption peaks, T°C		Concentration of acid sites, $\mu\text{mol/g}$		* $c_1/c_2$
	I form	II form	$c_1$	$c_2$	
HLI $\bar{B}$ M	198	418	628	542	1.16
4% Sc-HLI $\bar{B}$ M	193	319	369	243	1.51
4% Cd-HLI $\bar{B}$ M	189	302	253	158	1.60
4% La-HLI $\bar{B}$ M	188	296	249	145	1.71
4% Yb-HLI $\bar{B}$ M	191	316	364	236	1.54

\* $c_1$  and  $c_{II}$ — concentration of acid sites of form I and II, respectively

Better results are provided by medium-strength acid sites. For example, 4% La-HLI $\bar{B}$ M zeolite with a ratio of  $c_1/c_2=1.71$  of medium and strong acid sites shows a higher selectivity for ethylbenzene.

The study of the textural properties of the catalysts showed

that when the H<sub>2</sub>QBM zeolite is modified, its specific surface area, pore volume and radius decrease. This is explained by the fact that, as a result of chemical modification, part of H<sup>+</sup> ions are replaced by metal cations, and metal oxides in nanoparticle form are localized on the surface and channels of zeolite, causing changes in its acid properties and the geometry of the zeolite framework. The activity and selectivity of zeolite systems are closely related to these changes.

Thus, modification of HZSM-5 zeolite with solutions of Sc, La, Gd and Yb nitrates by impregnation method provides considerable changes in textural and acidic properties of the catalysts. The modifying effect of Sc, La, Gd and Yb is associated with a decline in the concentration of strongly acid sites, the formation of medium acid sites on the zeolite surface and changes in its porous structure. The nature of the metal plays an important role in the catalytic activity and selectivity of the zeolite catalyst.

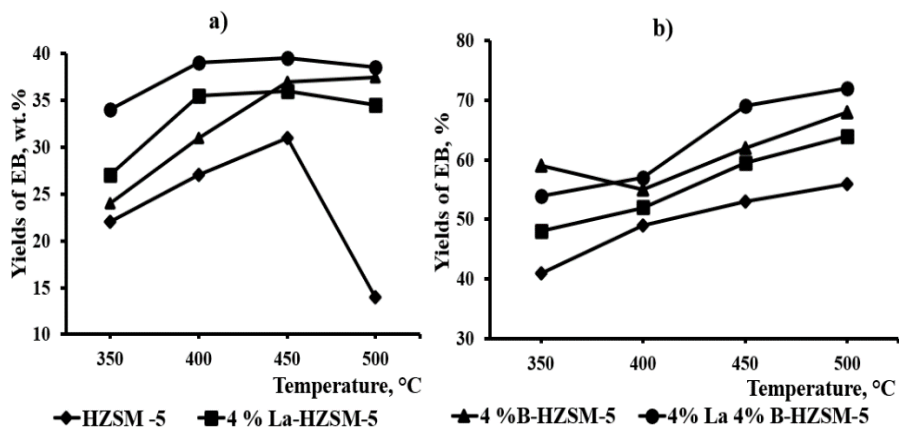
#### **Summary of chapter 4**

##### **Effect of co-modification with lanthanum and boron on physicochemical and catalytic properties of ZSM-5 zeolite in alkylation of benzene with ethanol**

In the presence of HZSM-5 zeolite modified with lanthanum and boron, the maximum yield of ethylbenzene is achieved at 450°C and is 36.2 and 37.3 wt.%, respectively, and the selectivity for ethylbenzene is 59.6 and 62.1 wt.%.

Raising the reaction temperature to 500°C has insufficient effect on the ethylbenzene yield, but the selectivity for ethylbenzene increases to 64.1-68.2%. In contrast to HZSM-5 zeolite, alkylate does not contain xylenes in the presence of modified catalysts in the temperature range of 400-500°C.

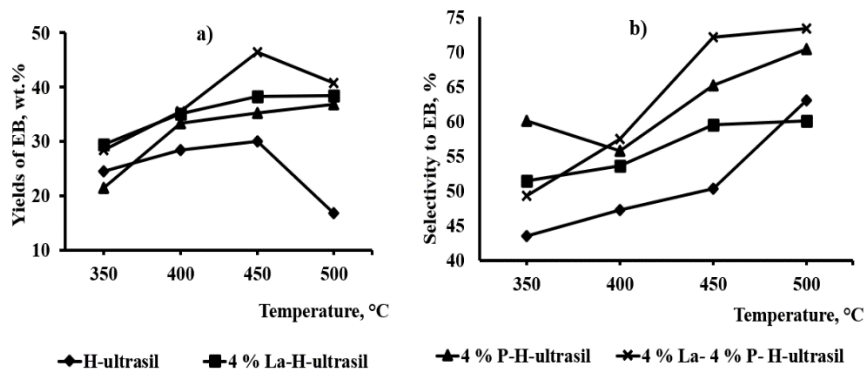
The loading of two modifiers (B, La) in its composition has a higher promoting effect on the activity and selectivity of HZSM-5 zeolite. When the reaction temperature is increased to 450°C, the yield of ethylbenzene increases (Figure 8a).



**Figure 8. Temperature dependence of EB yield (a) and EB selectivity (b) in the presence of modified catalysts (condition:  $C_6H_6:C_2H_5OH=2:1$ )**

### **Catalytic properties of ultrasil zeolite co-modified with lanthanum and phosphorus in the alkylation of benzene with ethanol**

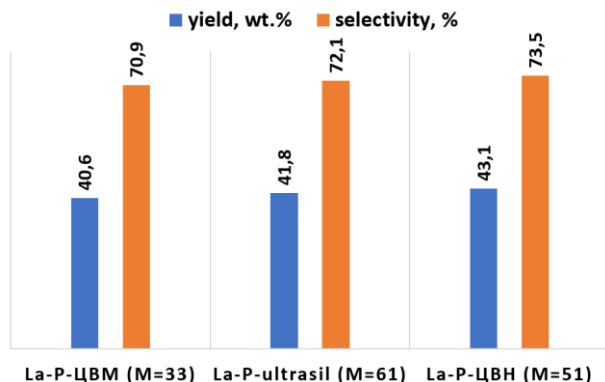
Figure 9 shows the temperature dependence of the yield of ethylbenzene obtained from the alkylation of benzene with ethanol in the presence of H-ultrasil, 4% P-H-ultrasil, 4% La-H-ultrasil and 4% La- 4% P-H-ultrasil zeolite catalysts. It can be seen that the yield of ethylbenzene in the temperature range of 350-500°C in the presence of unmodified H-ultrasil is 16.8-30.1% by mass. The maximum yield is 30.1% by mass at 450 °C. When H-ultrasil zeolite is modified with 4% phosphorus, the yield of ethylbenzene at 350 °C decreases from 24.6% to 22.5%, but when the temperature is increased, the yield of ethylbenzene increases and reaches 35.3% by mass at 450 °C.



**Figure 9. Temperature dependence of a) yield b) selectivity of ethylbenzene (conditions:  $C_6H_6:C_2H_5OH=2:1$ )**

When H-ultrasil zeolite is modified with 4.0 wt.% lanthanum, the yield of ethylbenzene increases slightly and is 38.3 wt.% at 450°C. However, a higher yield of ethylbenzene is achieved in the presence of ultrasilic zeolite catalyst modified with 4.0 wt.% La and 4 wt.% P. In the presence of a metal and non-metal co-modified catalyst in the temperature range of 400-500 °C, the yield of ethylbenzene increases to 35.6-40.8wt.%.

Figure 9b shows the temperature dependence of the selectivity of ethylbenzene obtained from the alkylation of benzene with ethanol in the presence of ultrasil zeolites co-modified with unmodified phosphorus, lanthanum and lanthanum and phosphorus (La-P). It can be seen from Figure 8b that H-ultrasil zeolite shows low selectivity for ethylbenzene at 350-450 °C (43.5-50.3 %). The selectivity of H-ultrasil for ethylbenzene is higher at 500 °C (63%); however, the yield of ethylbenzene is very small and is 16.8 wt. %. When H-ultrasil zeolite is modified with 4.0% by mass of lanthanum, the selectivity for ethylbenzene increases up to 51.4-60.1%. The sample modified with 4.0 wt.% phosphorus shows a higher selectivity (60.1-70.4 %) for ethylbenzene than the sample modified with 4.0 wt.% lanthanum.



**Figure 10. Yield and selectivity of ethylbenzene at 450 °C in the presence of metal and non-metal co-modified catalysts based on ΰBM, ultrasil, ΰBH zeolites (4% La 4% P-zeolite) ( $C_6H_6:C_2H_5OH=2:1$ )**

Among these samples, the highest selectivity for ethylbenzene (72.1-73%) is achieved in the presence of 4% La 4%P-H-ultrasilic zeolite at 450-500 °C.

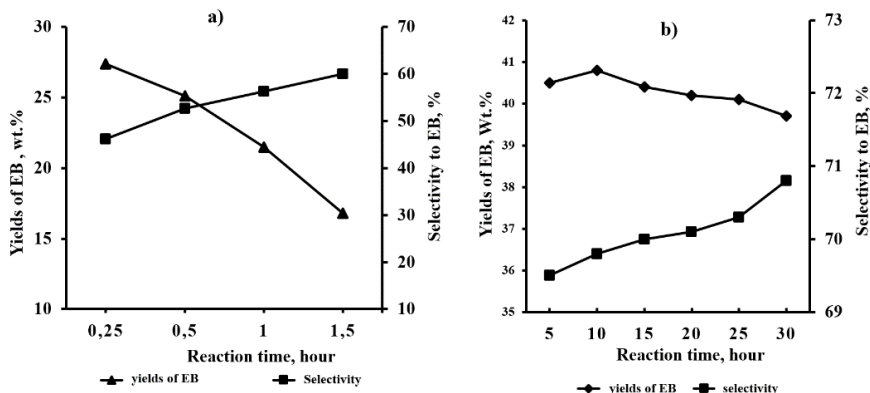
Thus, in contrast to separately modified samples with lanthanum and phosphorus, metal and non-metal co-modified La-P-ultrasil catalyst provides a higher yield (40.5-40.8 wt.%) and selectivity of ethylbenzene in the alkylation of benzene with ethanol (72.1-73.3%). Co-modified catalysts (4% La 4% P-zeolite) based on different high-silica (ΰBM, ultrasil, ΰBH) zeolites of the ZSM-5 type show similar activity and selectivity (Fig. 10).

However, among them, a slightly higher selectivity for ethylbenzene (73.5%) shows a modified catalyst based on ΰBH zeolite.

### **Effect of reaction time on activity and selectivity of modified ZSM-5 based catalysts**

The most important of the performance indicators of the catalyst is its stable operation for a long time. For this reason, the effect of modification on the stable running time of ZSM-5 ( $SiO_2/Al_2O_3=61$ ) zeolite was studied.

Figure 11a shows that the activity of HZSM-5 zeolite changes slightly in only 30 minute. The yield decreases from 27.4 wt.% to 25.1 wt.% for EB.

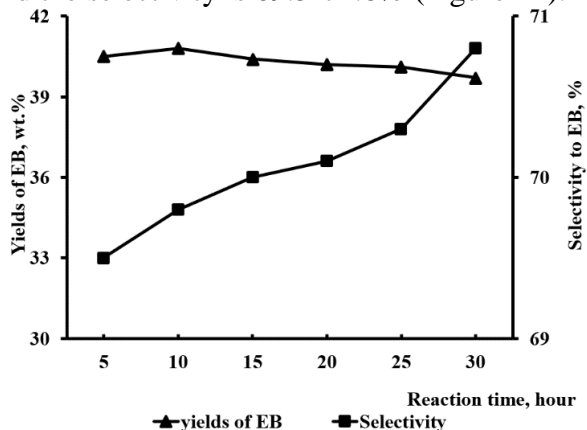


**Figure 11. a) Dependence of reaction time on the yield and selectivity of EB in the presence of HZSM-5 catalyst; b) dependence of the reaction time on the yield and selectivity of EB in the presence of 4% La-HZSM-5 catalyst (condition: T=450 °C).**

The yield of ethylbenzene significantly drops to 20.5wt.%, when the reaction time reaches 1.0 hour. The activity of the catalyst declines dramatically when the reaction running time gets to 1.5 h and the yield of EB drops to 16.1 wt.%. During this period, the amount of coke on the surface of HZSM-5 zeolite increases to 6.7wt.%. The EB selectivity increases from 46.2 % to 60.0 % due to a reduction in the rate of side reactions due to coking. However, modification with lanthanum has a significant effect on the stable running time of HZSM-5 zeolite (Figure 11b).

The catalyst remains active for 15 hours of operation. During this period, the yield of EB decreases by only 3.2 wt.%. During 20 hours of running, the yield of ethylbenzene drops to 33.2%. The catalyst co-modified with lanthanum and boron (4%La-4%B-HZSM-5) works more stably than the monometallic (4%La-HZSM-5) catalyst and practically does not change its activity during the studied period of 30 hours. For this period, the EB yield is 39.7-

40.5wt.% and the selectivity is 69.5-71.8% (Figure 12).



**Figure 12. Dependence of reaction time on the yield and selectivity of EB in the presence of 4%La-4%B-HZSM-5 catalyst (conditions: T=450 °C)**

The results of the performed experiments provide a basis to propose metallic and nonmetallic co-modified catalysts La-B-HZSM-5 and La-P-HZSM-5 suitable for the process of benzene alkylation with ethanol, as a new method of ethylbenzene production.

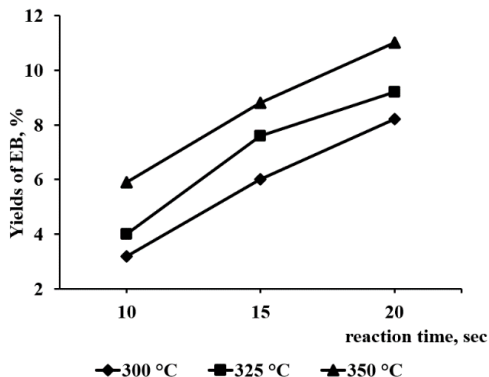
### **Study of patterns of benzene alkylation with ethanol in the presence of modified zeolite ZSM-5.**

Kinetic studies were carried out in the presence of 4%La-4%B-HZSM-5 catalyst in hydrogen gas flow in a fixed bed at atmospheric pressure in the 300-350 °C temperature range. The molar ratio of benzene to ethanol taken as 1:1, 2:1, 3:1. The molar ratio of H<sub>2</sub>/benzene was maintained at 1:2.

In order to evaluate the effects of external diffusion, experiments were performed using catalyst samples weighing 1.0 g and 2.0 g, keeping the effective contact time constant ( $W/F_B$  g·h/mol) and it was found that the effective contact time for both series of catalysts was 25-40 g·h/mol, the benzene conversion was almost unchanged. Experiments were conducted on various sizes of catalyst samples (0.6, 1.0 and 1.3 mm) to test the effect of internal



diffusion on the reaction rate and it was found that the benzene conversion at constant contact time was independent of the catalyst size. The benzene conversion was found to enhance with increasing reaction temperature and time at molar ratios of benzene and ethanol of 1:1, 2:1 and 3:1.



**Figure 13. Reaction time dependence of EB yield, benzene:ethanol=1:1**

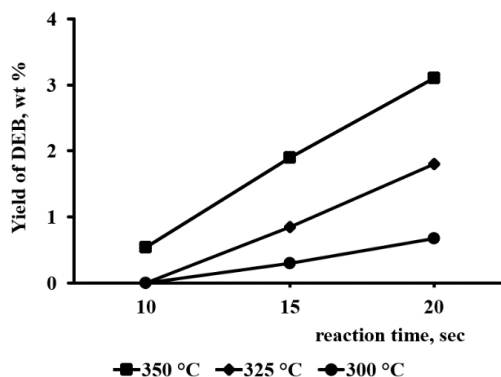
Higher growth occurs at molar ratios of benzene and ethanol of 1:1 and 2:1. When the reaction time was extended from 10 to 20 seconds and the molar ratios of benzene to ethanol of 1:1 and 2:1, the benzene conversion enhanced from 6.4% to 14.5% and from 5.1% to 14.1%, respectively. The yield of ethylbenzene goes up with increasing reaction time at each temperature investigated. For example, increasing the reaction time from 10 to 20 seconds at 350 °C with a 1:1 molar ratio of benzene to ethanol raises the yield of ethylbenzene from 3.2 wt.% to 10.9 wt.% (Figure 13).

There is no DEB acquisition response in the first 10 seconds. If the conversion of benzene is very low (3.0-3.3%), only ethylbenzene is obtained. The formation of diethylbenzenes is observed in the 15th second of the reaction, and as the temperature increases, their amount rises. On the 15th second of the reaction at 300 °C in molar ratios of benzene and ethanol of 1:1 and 2:1, mainly p-DEB is formed, while the amount of m-DEB is insignificant and amounts to 0.04- 0.08% by mass. In this state o-DEB is not

obtained. At a reaction time of 20 seconds, the yield of p-DEB increases twice, the yield of m-DEB rises to 0.12-0.19 wt.%, and the yield of o-DEB grows to 0.02 wt.%. By increasing the reaction time and temperature up to 350 °C, the yield of m- and o-DEB along with p-DEB marginally enhances. Hence, the formation of o-DEB depends on reaction time and temperature.

With increasing molar ratio of benzene to ethanol, the conversion of benzene at 350 °C for 20 s declines and the selectivity for ethylbenzene increases. For example, when the mole ratio of benzene to ethanol is increased by 3 times, the conversion of benzene decreases from 14.5 wt.% to 8.9 wt.%, and the selectivity to ethylbenzene enhances from 74.8% to 82.6%. Variation of the molar ratio of benzene to ethanol also influence the selectivity of diethylbenzenes. As the molar ratio of benzene to ethanol increases, the selectivity for diethylbenzenes decreases. Increasing the mole ratio of benzene to ethanol from 1 to 3 reduces the selectivity to diethylbenzenes from 25.2% to 17.4%.

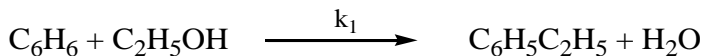
Considering that the conversion of benzene is very low when the molar ratio of benzene to ethanol is 3:1, the optimal molar ratio is 2:1.



**Figure 14. Time dependence of DEB yield at different temperatures (benzene:ethanol = 1:1)**

It was determined that the p-DEB/o-DEB ratio decreases with time. The unavailability of o-DEB at low benzene conversion and the existence of only p-DEB in the products at the initial time of

reaction suggest that it is the primary product of transalkylation. Thus, a p-DEB molecule (~0.55 nm) is formed in the catalyst channels, the kinetic diameter of which corresponds to the size of the ZSM-5 zeolite channels. Since m- and o-DEB molecules with large kinetic diameter (0.59-0.62 nm) are larger than the cross-section of zeolite channels, their desorption into the gas phase is difficult, and their formation occurs by isomerization of p- DEB diffuses from the pores to the surface. In the benzene alkylation reaction with ethanol, taking into account the absence of the reverse reaction at low benzene conversion, the lack of water adsorption and DEB formation, the progress of the reaction can be presented as follows.



Based on the two-center Langmuir-Hinshelwood mechanism, the conversion rate of benzene to ethylbenzene was determined and the numerical values of its constants were calculated. It was determined that the proposed kinetic model adequately describes the experimental results in the investigated range of temperature, volume velocity and mole ratio of reagents.

$$r_B = \frac{dX_B}{dT} = k_1 \cdot P_B \cdot P_{\text{EtOH}} / Z^2$$

$$\text{Here, } k_1 = k_B \cdot k_{\text{EtOH}}$$

$$Z = 1 + k_B P_B + k_{\text{EtOH}} P_{\text{EtOH}} + k_{\text{EB}} P_{\text{EB}}$$

$k_B$ ,  $k_{\text{EtOH}}$ ,  $k_{\text{EB}}$ - are adsorption constants

$$r_B = \frac{k_1 P_B P_{\text{EtOH}}}{(1 + k_B P_B + k_{\text{EtOH}} P_{\text{EtOH}} + k_{\text{EB}} P_{\text{EB}})^2}$$

P- total pressure, the molar ratio of benzene to ethanol and molar ratio of hydrogen to benzene, was the 1:1 and 1:2, respectively.

The equation is expressed with four unknown parameters-  $k$ ,  $k_{\text{EtOH}}$ ,  $k_B$  and  $k_{\text{EB}}$ . The unknown kinetic parameters and adsorption constants were estimated from the experimental results for each temperature using a non-regression program. The integration of the equations was carried out using a four-order

Runge-Kutta optimization program.

$$\Phi = \sum_{i=1}^n (y_i - \hat{y}_i)^2$$

Here, n is the number of points,  $y_i$  and  $\hat{y}_i$  are the experimental and calculated values of the conversion.

The activation energy (E) was determined based on the temperature dependence of the kinetic constant. The activation energy of alkylation of benzene with ethanol is 62.5 kC/mol. The theoretical and experimental values of benzene conversion are in good agreement.

## KEY FINDINGS

1. For the first time catalysts modified with metals (elements Mg, Sc, Y, Ln) and nonmetals (P, B) were prepared based on ZSM-5 pentasil type zeolites to provide a selective catalyst for the reaction process of benzene alkylation with ethanol and their physico-chemical and catalytic behavior and patterns of the process of benzene alkylation with ethanol were studied.

2. A significant correlation between the yield and selectivity of ethylbenzene and the nature and concentration of the modifier, as well as the favorable amount of the modifier in the catalyst (4.0 wt %) was found. Yb modified pentasil zeolite exhibits high ethylbenzene yield and La modified pentasil zeolite reveals high selectivity. In the presence of 4% La-HZSM-5 catalyst, the maximum selectivity for ethylbenzene (59.5%) is reached at 450 °C.

3. Based on the results of XRD, low-temperature nitrogen adsorption, TPD of ammonia, acetone, butylamine, phenol, n-heptane, benzene adsorption methods and catalytic properties of modified catalysts it was established, that the part of the modifier included in the composition of the modifier chemically contacting with the crystal lattice of zeolite - lanthanum ions replace the proton in its "bridging" hydroxyl groups, and the other part of the

modifier is located in the channels and on the surface of zeolite in the form of nanoparticles of lanthanum oxide, causing redistribution of acid sites, increase of mesopores and reduce the volume of pores. The increase in the selectivity of the catalyst for ethylbenzene was explained by the influence of these factors.

4. The study of the patterns of the process of benzene alkylation with ethanol on unmodified and modified catalysts based on zeolite ZSM-5 showed that in the presence of unmodified catalyst HZSM-5 a small part of the target product - ethylbenzene is isomerizes and forms by-products - o- and m-xylenes. Co-modification of HZSM-5 with metal and nonmetal (catalysts La-B-HZSM-5, La-P-HZSM-5) prevents isomerization of ethylbenzene into o- and m-xylenes, enhances the selectivity of the catalyst for ethylbenzene and provides stable running.

5. The reaction mechanism of benzene alkylation with ethanol in zeolite pores is proposed. It is revealed that moderate Brønsted and Lewis acid sites formed because of co-modification of HZSM-5 zeolite with metal and non-metal activate ethanol and benzene molecules. The alkylating particle-ethoxonium ion interacts with benzene and provides alkylation of benzene.

6. For the first time, a combination of metal and nonmetal with optimal Brønsted and Lewis acid sites, porosity and adsorption capacity was obtained, providing high yield (40-45 %), selectivity (75-80 %) and stability of ethylbenzene. Modified catalytic systems 4% La-4 % B-HZSM-5, 4% La-4% P-HZSM-5 were developed for the process of benzene alkylation with ethanol.

**The main results of the thesis are published in the following publications.**

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