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Original Research Article

Alkylation of Benzene with Ethanol over ZSM-5 Based La–P Catalysts

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Abstract

Benzene ethylation in the presence of HZSM-5 zeolites is a promising method for producing ethylbenzene. This study examined the effects of modifying lanthanum and phosphorus as additives to the HZSM-5 catalyst, tested in the temperature range of 300-500 °C, at a benzene to ethanol molar ratio of 2:1 in a hydrogen stream. The influence of promoters on acidity and pore structure was investigated using X-ray Diffraction (XRD), NH_3 Temperature Programmed Desorption (NH_3-TPD), Scanning Electron Microscope (SEM), Brunauer, Emmett, and Teller (BET), and Barrett-Joyner-Halenda (BJH). Among 4%La samples, 4%P/HZSM-5 demonstrated higher ethylbenzene selectivity and operational stability associated with a decrease in the density of strong acid sites and an increase in zeolite mesoporosity because of modification.

Keywords: Alkylation; benzene; ethanol; lanthanum; phosphorus; ethylbenzene; selectivity

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1. Introduction

Alkylation of aromatic hydrocarbons is one of the main directions of the chemical industry for the production of ethylbenzene and cumene. Ethylbenzene (EB) and cumene are among the most important industrial derivatives of benzene [1]. Ethylbenzene is a key intermediate chemical compound, and over 90% of the ethylbenzene produced worldwide is used in the manufacture of styrene. Other applications of ethylbenzene include the production of diethylbenzene (DEB), cellulose acetate, acetophenone, paint solvents, and pharmaceutical intermediates [2–3].

Currently, about 40% of the global ethylbenzene production capacity still relies on the $AlCl_3$-based Friedel–Crafts alkylation process. This reaction is typically carried out at 250 °C with a benzene to ethylene ratio of 2:3.5 [3,4]. However, the use of Friedel–Crafts catalysts presents serious economic and technological challenges related to corrosion activity, operational safety, and waste disposal.

These disadvantages have driven many producers to adopt zeolite-based catalytic processes. Alkylation of benzene with ethylene over zeolite catalysts has been commercialized under licenses from companies such as Mobil–Badger, Lummus–UOP, and CDTech Dow Chemical. The vapor-phase alkylation process developed by Mobil–Badger in 1980 remains the most widely used method for ethylbenzene production. In this process, benzene is alkylated with ethylene over a ZSM-5-based catalyst in a fixed-bed reactor at 370–420 °C and 0.69–2.79 MPa, with a low benzene to ethylene ratio (5:20) [4]. A number of authors [5–7] have proposed the

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use of ethanol instead of ethylene as an alkylating reagent for the production of ethylbenzene. Considering the increasing availability of bioethanol derived from biomass, benzene alkylation with ethanol could offer both economic and environmental advantages by eliminating the ethylene production step.

Large-pore zeolites, such as X, Y, Beta, MCM-22, $MnAPO_4$-5, and $MnAPO_4$-11, have shown catalytic activity in benzene alkylation with ethanol [4, 8–12]. However, in these cases, di- and tri-substituted aromatic hydrocarbons are formed alongside ethylbenzene in significant amounts, and catalyst deactivation occurs after several hours of operation. The vapor-phase ethylation of benzene with ethanol has also been studied over aluminophosphate molecular sieves such as $AlPO_4$-5, MAPO-5, ZMAPO-5, and MnAPO-5 [12]. It has been found that MnAPO-5 exhibits higher activity compared to other catalysts. When benzene conversion reached 47% over $MnPO_4$, the yield of ethylbenzene was 14%. Meanwhile, the yields of diethylbenzene and polyalkylbenzenes (1,2,4-; 1,3,5-triethylbenzenes and 1,2,4,5-tetraethylbenzene) were 14.04% and 17.0 wt%, respectively. Thus, aluminophosphate molecular sieves exhibit low yield and selectivity to ethylbenzene.

Although the incorporation of divalent metal ions (Mg, Mn, Zn) into aluminophosphate zeolites increases their acidity, the presence of large pores promotes the formation of polyalkylbenzenes. Among the catalysts used in the alkylation of aromatic hydrocarbons with C_1–C_3 monohydric alcohols, the most suitable type is the ZSM-5 zeolite, which possesses intersecting straight and sinusoidal channels (approximately 0.55 nm). In such zeolites, mono- and para-isomeric dialkylbenzenes are formed selectively [13–16]. According to Ref. [17], during benzene alkylation with ethanol (volume ratios of 2:1 and 4:1) over an HZSM-5 (Si/Al = 90) catalyst, ethylbenzene is formed as the primary product, while diethylbenzenes and xylenes are obtained as secondary products. However, higher selectivity (68.84%) and yield (45.03%) of ethylbenzene were achieved only at a high benzene to ethanol ratio (4:1 by volume).

Alkylation of benzene with ethanol in a CO_2 stream was studied using HMCM-22, H-Beta, and HZSM-5 zeolites modified with La_2O_3 [18]. The results showed that catalysts based on ZSM-5 zeolite (Si/Al = 200) modified with 3.0-5.0 wt.% La_2O_3 exhibit high selectivity for ethylbenzene (92.72%) only at very low benzene conversion (~25%). The high selectivity for ethylbenzene was associated with low benzene conversion and the presence of corresponding acidic sites. Unlike irregular block-shaped ZSM-5 catalysts, ZSM-5 nanoaggregates synthesized via the interzeolite transformation method demonstrate enhanced resistance to carbon deposition during benzene alkylation with ethanol [19].

Hierarchical zeolite composites and dual-framework ZSM-5 samples (obtained by recrystallizing ZSM-5 nanocrystals on a mordenite surface) provide a significant improvement (>60%) in ethylbenzene selectivity during benzene alkylation with ethanol. ZSM-5 nanospheres synthesized using homogeneous aluminosilicate (AS) nanopowders exhibit superior catalytic performance in terms of benzene conversion and ethylbenzene selectivity compared to those prepared by conventional methods. The mesoporous structure formed in the presence of AS nanopowders and the uniform distribution of Al species in the framework lead to improved catalytic behavior of the Hie-SZSM-5-AS sample, achieving 60% benzene conversion and 62% ethylbenzene selectivity [20]. However, this catalyst exhibits low selectivity for ethylbenzene (62%).

One of the possible approaches to modifying the catalytic and molecular sieve properties of zeolites is the regulation of pore size and acidity characteristics. For this purpose, partial removal of strong Brønsted acid sites and optimization of the ratio between medium-strength Brønsted and Lewis acid sites are important. In this regard, chemical modification of zeolites with metal and non-metal modifiers is considered promising, as it can enhance the stability and selectivity of zeolite catalysts in the alkylation of aromatic hydrocarbons with C_1–C_3 monohydric alcohols [7,13,14,18,21–23]. To regulate acidity and improve selectivity toward ethylbenzene, chemical modification methods are commonly applied. As reported in Ref. [24], modification of HZSM-5 zeolite with praseodymium (Pr) and neodymium (Nd) enhances the selectivity of benzene alkylation with ethanol, particularly toward ethylbenzene. However, high yields of ethylbenzene were not achieved with these catalysts.

The addition of zinc nitrate during the synthesis of ZSM-5-type zeolite significantly affects the crystal size of the catalyst, as well as the ratio of Lewis and Brønsted acid sites, leading to an increase in ethylbenzene selectivity in the benzene ethylation reaction [25]. On the Zn/HZSM-5 sample with a SiO_2/Al_2O_3 molar ratio of 96.1, containing 0.026 wt.% Zn at 380 °C, a benzene to ethanol molar ratio of 4:1 and a feed space velocity of 4 h^{-1}, high selectivity for EB was observed only at low benzene conversion (21.02 %). Improvement of the selectivity for EB formation can be achieved by modifying the HZSM-5 zeolite with rare earth metals. The modified catalysts are ranked according to their selectivity for ethylbenzene formation as follows: La–HTsVM > Yb–HTsVM > Gd–HTsVM > Sc–TsVM. The highest selectivity for ethylbenzene

(59.5%) is achieved on the zeolite modified with La [25]. Modification of HZSM-5 zeolite by impregnation with boron and phosphorus compounds has been shown to improve the catalytic properties of ZSM-5 in benzene ethylation reactions [27]. The authors reported that phosphorus and boron modification of HZSM-5 increases the formation efficiency of ethylbenzene (EB), which is attributed to the reduction of strong Brønsted acid sites in the zeolite structure as a result of modification.

The performance of HZSM-5 zeolite in benzene ethylation can be further improved through bimetallic modification methods [23–28]. According to the literature [28,29], compared to monometallic catalysts, dual-component (boron and magnesium) modified catalysts show higher benzene conversion. For the 5%Mg 4%B/HZSM-5 catalyst, higher selectivity (72.8%) and yield (38.1%) toward ethylbenzene were obtained. However, all the studies discussed lack data on catalyst stability, which is a key performance characteristic. Therefore, to develop a promising benzene ethylation catalyst, further research is needed to determine the effect of modification on the acid site distribution and catalyst stability based on HZSM-5 zeolite

Thus, the aim of this study is to investigate the effect of two-component modifications of zeolite HZSM-5 with lanthanum and phosphorus on its acidity, textural characteristics, catalytic activity, selectivity for the formation of ethylbenzene and the stability of the catalyst in the process of benzene ethylation.

2. Materials and Method

2.1. Materials

In the experiments, a commercial ZSM-5 zeolite (SiO_2/Al_2O_3 molar ratio = 40, Na_2O content ≤ 0.05 wt.%) was used. The zeolite powder was supplied by *Nizhniy Novgorod Sorbents* (Russia). The following reagents from Sigma-Aldrich were used as raw materials: benzene, C_6H_6 (CAS No.: 71-43-2, purity ≥ 99.8 %), ethanol, C_2H_5OH (CAS No.: 64-17-5, purity ≥ 99.5%). The following chemicals were used in the preparation of the catalyst: lanthanum (III) nitrate hexahydrate, $La(NO_3)_3.6H_2O$ (CAS No.: 10277-43-7, purity 99.9 %), ammonium hydrogen phosphate, $(NH_4)_2HPO_4$ (CAS No.: 7722-76-1, purity ≥ 98 %).

2.2. Catalyst Preparation

The initial ZSM-5 zeolite was calcined at 550 °C for 2 hours to obtain its HZSM-5 form. The HZSM-5 zeolite was impregnated with lanthanum nitrate and ammonium hydrogen phosphate solutions at a mass ratio of 4.0 wt.%. The modification process was carried out at 80 °C for 4 hours. The resulting powder was dried at 110 °C for 4 hours and then calcined in a muffle furnace at 550 °C for 5 hours to activate it. The obtained zeolite powders were granulated under a pressure of 2.5×10^7 Pa and then crushed to particles of 0.4–0.6 mm in size. Catalyst particles of this fraction were loaded into the reactor for activity testing.

2.3. Analytical Methods

X-ray diffraction (XRD) analyses of the powdered samples were performed on a RIGAKU MINIFLEX diffractometer using CuK_α radiation (λ = 0.1504 nm, 45 kV, 35 mA). The diffraction patterns were recorded over a 2θ range of 10°–80° with a scanning speed of 0.01 °/s and a step size of 0.02°. The vibration spectra of the zeolite catalyst framework were recorded using Fourier Transform Infrared (FTIR) spectroscopy on a (Bruker ALPHA II) spectrometer in the range of 500–1500 cm^{-1}.

The morphology of the zeolite samples was examined using scanning electron microscopy (SEM) on a (JEOL JSM-6610-2LV) instrument equipped with an EDS-230 X-ray analyzer. The textural properties of the unmodified and modified catalysts were determined by nitrogen adsorption measurements at –196 °C using a Micromeritics-2000 analyzer. Prior to physical adsorption, the samples were degassed under vacuum (8–5 torr) at 200 °C for 4 hours. The specific surface area was calculated using the BET method based on adsorption data in the P/P_0 = 0.4–0.9 range. The micropore surface area and pore volume were determined by t-plot analysis.

Ammonia Temperature-Programmed Desorption (NH_3-TPD). The acidity properties of the catalysts were determined by the NH_3-TPD method in the temperature range of 50–600 °C using a USGA-101 (UNISIT, Russia) sorption analyzer. The zeolite samples were placed in a U-shaped quartz cell and first activated at 300 °C for 1 hour in a dry nitrogen flow at a rate of 25 mL/min. After activation, the samples were cooled to room temperature and exposed to adsorption in a helium–ammonia mixture for 30 minutes at a flow rate of 35 mL/min. The excess ammonia was removed by flushing with helium (purity >99.01%) for 5 minutes. Temperature-Programmed Desorption was carried out in the range of 100–600 °C at a heating rate of 10 °C/min under a helium flow rate of 20 mL/min.

2.4. Experimental Setup

Catalytic experiments were conducted in a continuous-flow, fixed-bed catalyst system. The catalyst was placed in the center of a vertical quartz tubular reactor (0.9 cm in diameter, 10 cm in length) between inert quartz beads. The reactor was mounted inside a microprocessor-controlled furnace equipped with a heating system and a condenser (Figure 1). In a typical experiment, 0.8

g of catalyst was loaded into the reactor. Reactions were conducted at atmospheric pressure using both unmodified and modified catalyst samples. Before each experiment, the catalyst samples were activated in an air stream at 500 °C for 2 hours.

The benzene ethylation reaction was carried out in the temperature range of 300–500 °C, at a feed rate of 1.0 h^{-1}, in the presence of nitrogen as a carrier gas. The feed mixture consisted of benzene and ethanol in a 2:1 molar ratio. Nitrogen was fed into the reactor at a flow rate of 0.4 l/min. The reaction products, together with unreacted benzene and ethanol, were condensed in a cooler. The collected liquid samples were analyzed using a gas chromatograph (Agilent HP-88) equipped with a capillary column (100 × 0.25 × 0.25 µm) and a flame ionization detector (FID) according to the procedure described in [26]. The conversion of benzene, selectivity for ethylbenzene, and yield were calculated according to the following equations:

$$\%\ \text{benzene conversion} = \frac{\text{wt.\% benzene in feed} - \text{wt.\% benzene in product}}{\text{wt.\%benzene in feed}} \times 100 \quad (1)$$

$$\%\ \text{ethylbenzene selectivity } S_{EB} = \frac{\text{wt.\% ethylbenzene (EB)in product}}{\text{wt.\% of all products}} \times 100 \quad (2)$$

$$\%\ \text{ethylbenzene yield } Y_{EB} = \frac{\text{wt.\% of ethylbenzene obtained}}{\text{wt.\% of benzene converted}} \times 100 \quad (3)$$

3. Results and Discussion

The X-ray diffraction patterns (XRD) of the unmodified HZSM-5, 4%La/HZSM-5, and 4%La4%P/HZSM-5 catalyst samples are shown in Figure 2. All samples exhibit two diffraction peaks at 2θ = 7.7° and 10°, as well as three peaks at 2θ = 22.5°, 23.5°, and 25°, which correspond to the molecular sieve structure of HZSM-5 (MFI-type). It is evident that modification of the zeolite with lanthanum nitrate and ammonium hydrogen phosphate does not alter its crystalline structure. Furthermore, no distinct diffraction peaks corresponding to lanthanum or phosphorus oxides were detected. These results indicate that the modifiers are highly dispersed and distributed over the external surface and within the pores of the zeolite.

The FTIR spectra of the aluminosilicate framework in the 500–1500 cm^{-1} range (Figure 3)

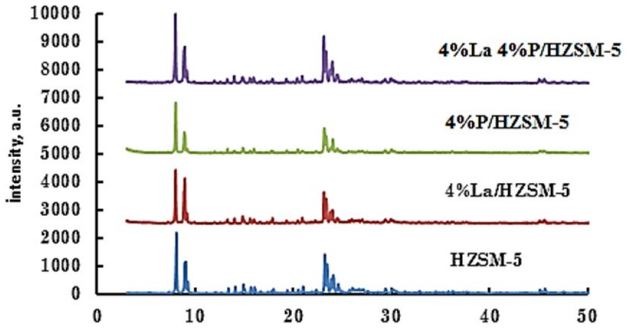

Figure 1. Schematic representation of the flow experimental setup.

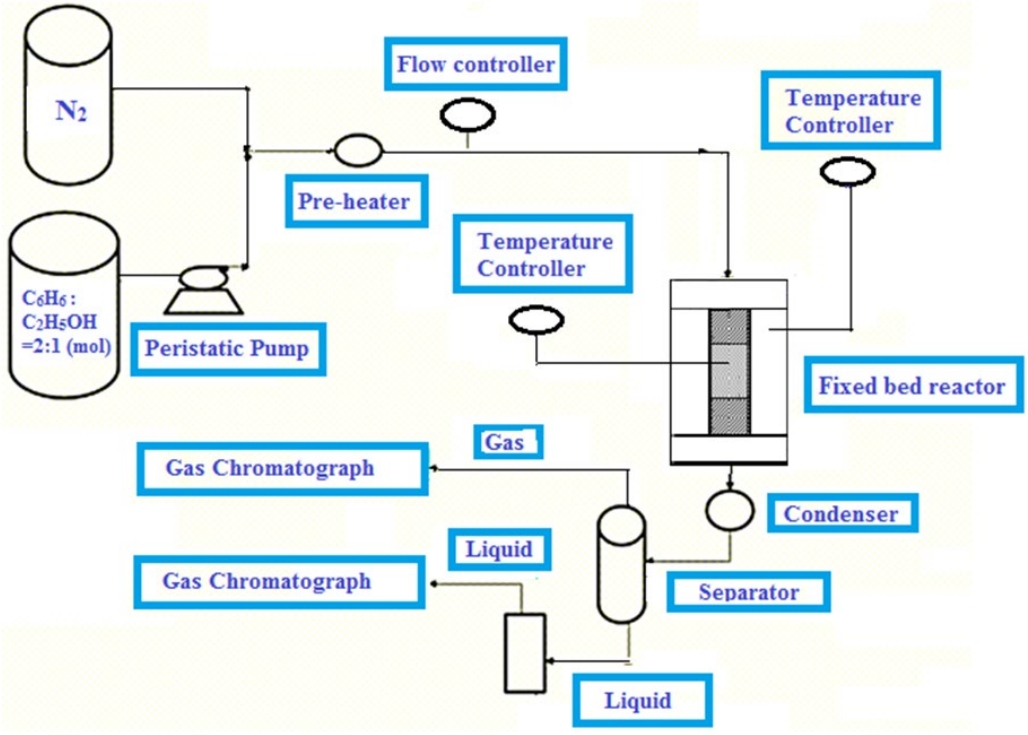

Figure 1. Schematic representation of the flow experimental setup.

also confirm that the crystalline structure of HZSM-5 is preserved after single-component (La) or dual-component (La–P) modification. Impregnation of the zeolite with lanthanum nitrate and ammonium hydrogen phosphate solutions, followed by thermal treatment at 500 °C, does not affect the characteristic distances corresponding to the Si–O–Si and Si–O–Al fragments [30]. In the spectra, a characteristic band observed in the 791.07–794.67 cm^{-1} range corresponds to external vibrations, while asymmetric and symmetric stretching bands at 539.14 and 542.59 cm^{-1} are typical for the ZSM-5 zeolite framework [30]. The characteristic asymmetric tetrahedral stretching vibrations of Si–O and Al–O bonds appear in the 1075.67–1083.07 cm^{-1} and 1223.56 cm^{-1} ranges [31].

To explain the effect of La and P modification of HZSM-5 zeolite on catalytic performance in the benzene–ethanol alkylation process, the acidic and structural properties of the catalysts were studied. Figure 4 shows the effect of one- and two-component modification on the concentration of strong acid sites. It can be seen that HZSM-5 presents two acid site peaks: weak acid sites responsible for NH_3 desorption at low temperature and strong acid sites responsible for desorption at high temperature. In La- and P-modified HZSM-5, the amount of strong acid sites decreases significantly. The high-temperature desorption peak (~405 °C) disappears, while the low-temperature peak slightly shifts to ~198 °C.

The nature of the modifier significantly affects the concentration of strong acid sites. Compared to lanthanum, phosphorus modification causes a greater decrease in strong acid site concentration (from 394 to 104 µmol/g). In the case of the dual component modification, this value reaches its lowest value (89 µmol/g). Modification also affects the textural properties of the catalysts. The unmodified HZSM-5 zeolite exhibits the largest specific surface area and pore volume (Table 1). However, the specific surface area, total pore volume, and micro- and mesopore volumes depend on the nature of the modifier added to the zeolite. During La and P modification of HZSM-5, the specific surface area, total pore volume, and micropore volume decrease significantly. Meanwhile, the mesopore volume increases, leading to a higher V_{meso}/V_{pore} ratio. The largest increase in this ratio (from 25.2 % to 46.8

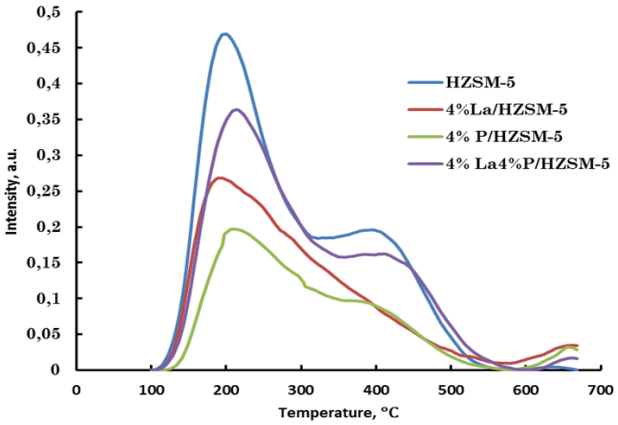

Figure 4. Effect of lanthanum and phosphorus concentration on the strength of acid sites determined by NH_3-TPD.

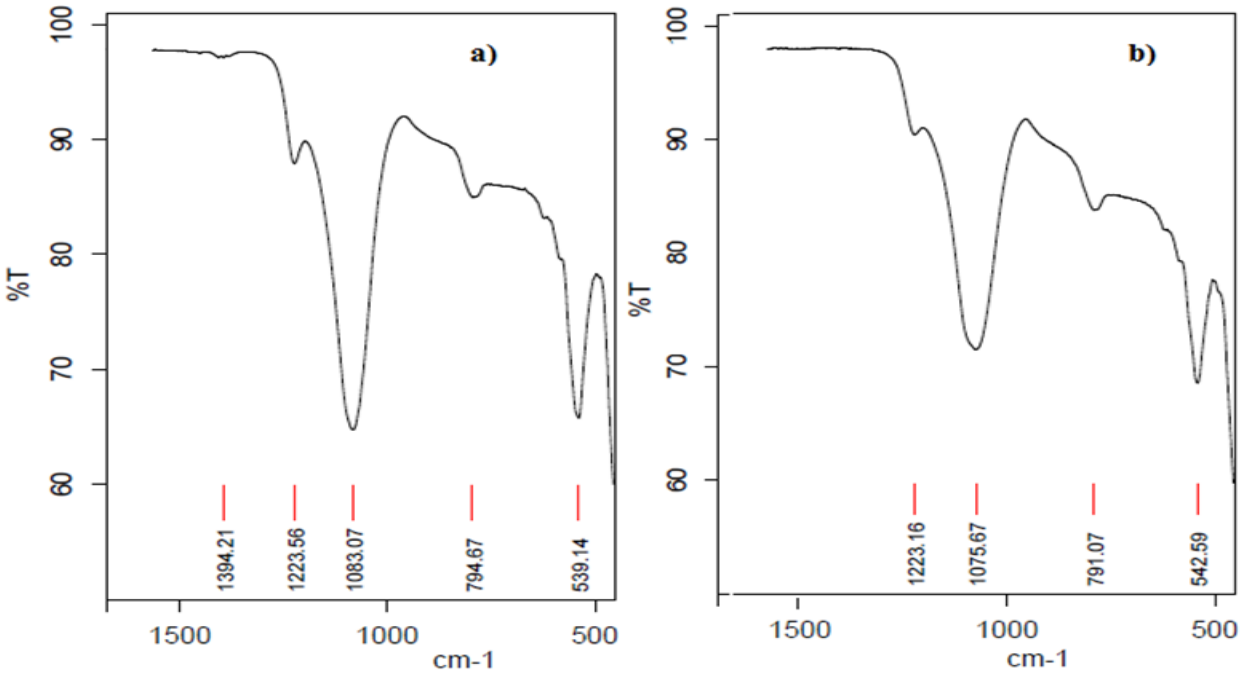

Figure 3. IR- spectra modification of zeolite HZSM-5 with lanthanum (a) and lanthanum-phosphorus (b).

%) is observed for the dual component modification.

SEM images show that the morphology of HZSM-5 changes after La and P modification. Comparison of modified and unmodified HZSM-5 reveals voids and cells on the zeolite surface, which facilitate the alkylation reaction and enhance the selectivity and stability of the catalyst after modification. EDAX spectra confirm the presence of lanthanum and phosphorus on the surface of zeolite crystals (Figure 5).

Table 2 shows the effect of temperature on the composition of products in the ethylation of benzene with ethanol over unmodified HZSM-5 zeolite. It was found that ethylbenzene (EB) is the primary product. However, the alkylation process on HZSM-5, which has a high density of strong acid sites (Table 2), is accompanied by secondary

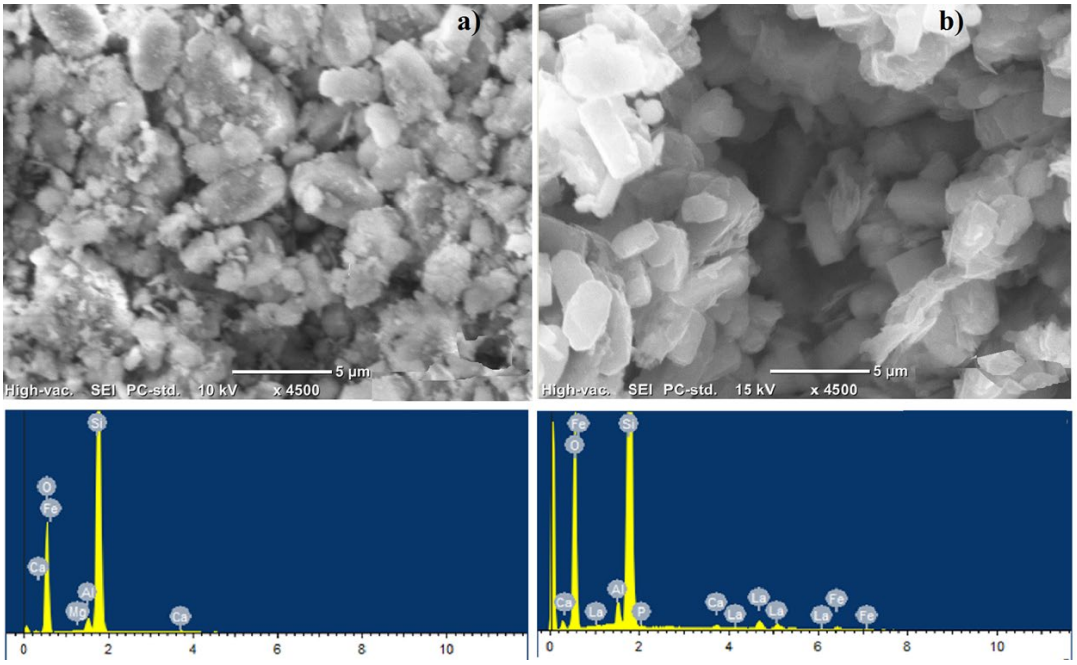

Figure 5. SEM images and EDAX spectra unmodified HZSM-5 (a) and 4%La4%P/HZSM-5 (b).

Table 1. Acidic and structural properties of unmodified and modified catalysts.

Type of catalyst	Weak acid sites, mkmol/g, (100-300 °C)	Strong acid sites, mkmol/g, (300-600 °C)	S_{BET}, m^2/g	V_{pore}, cm^3/g	V_{micro}, cm^3/g	V_{mezo}, cm^3/g	V_{mezo}/V_{pore}, %
Unloaded HZSM-5	394	235	288	0.24	0.178	0.062	25.2
4% P/HZSM-5	225	104	224	0.17	0.098	0.068	42.3
4% La/HZSM-5	262	126	246	0.18	0.112	0.071	37.7
4%La4%P/HZSM-5	179	89	227	0.16	0.085	0.075	46.8

Table 2. Effect of temperature on the ethylation of benzene (catalyst – HZSM-5) (MK – meta-xylene, OK – ortho-xylene, DEB – diethylbenzene, TEB – triethylbenzene. EB-ethylbenzene, PK- para-xylene).

Products	HZSM-5				
	300 °C	350 °C	400 °C	450 °C	500 °C
Ethanol	18.2	15.1	10.9	9.8	13.9
Benzene	42.3	32.9	30.2	32.2	41.1
Toluene	0.8	0.6	0.7	0.8	0.5
EB	22.9	24.1	28.7	32.8	30.6
PK	1.4	2.9	1.6	1.0	0.3
MK	0.7	1.3	1.1	0.9	0.4
OK	0.8	1.4	1.2	0.7	0.3
DEB	3.4	7.4	9.5	8.0	10.7
TEB	6.3	10.4	14.3	12.9	0.8
Others	2.6	3.9	1.8	0.9	1.9

reactions (disproportionation, transalkylation, and cracking), resulting in a product containing xylenes, toluene, diethylbenzene (DEB), and triethylbenzene (TEB). DEB can not be considered a waste product, since after separation from the valuable p-DEB isomer, the remaining DEB can be converted to EB via transalkylation with benzene [25].

As shown in Figure 6, increasing the temperature from 300 °C to 400 °C leads to a rise in the benzene conversion rate, while at higher temperatures, the conversion decreases. The maximum benzene conversion (74.1 %) is observed at 400 °C. At the same time, as the temperature increases from 300 °C to 350 °C, the selectivity toward ethylbenzene decreases (from 55.5% to 46.7%); however, further temperature elevation results in a renewed increase in selectivity. The highest yield of ethylbenzene is achieved at 450 °C, reaching 31.5 wt% (Figure 6).

According to the literatures [5,6,10], the alkylation of aromatic hydrocarbons proceeds via a carbocation mechanism in the presence of acidic catalysts, where the active sites include both Brønsted and Lewis acid centers (Figure 7). On unmodified HZSM-5, which has a large number of strong acidic centers (235 μmol/g), along with the target reaction, side reactions occur intensively, which is the reason for the decrease in the yield and selectivity for EB. In addition to the main reaction, the participation of unmodified zeolite leads to the formation of secondary products such as toluene, xylenes, diethylbenzenes, and triethylbenzenes. Based on literatures data [28,32–34] and the results of our studies, the formation of benzene ethylation products over unmodified HZSM-5 zeolite occurs as a result of parallel primary and secondary reactions.

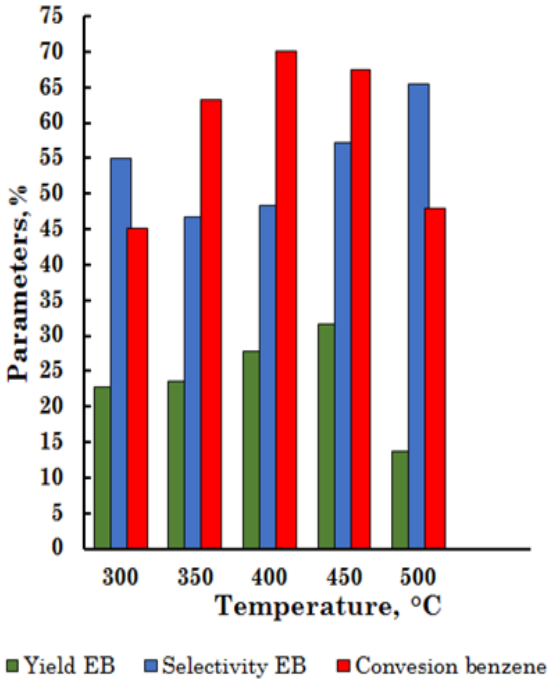

Figure 6. Dependence of conversion, selectivity and EB yield in the concept of unmodified zeolite HZSM-5.

The results of the benzene alkylation reaction with ethanol carried out in the temperature range of 350–500 °C over HZSM-5 and modified catalysts are presented in Table 3. It is evident that the reaction products are identical to those obtained with the unmodified HZSM-5 catalyst. For the 4%La/HZSM-5 catalyst, the highest benzene conversion (71.2 %) is observed at 400 °C (Figure 8(a)). Increasing the temperature up to 500 °C leads to a decrease in benzene conversion (down to 57.8 %). The main product over the 4 %La/HZSM-5 catalyst is ethylbenzene (EB), which is likely due to the unhindered diffusion of EB molecules through the ZSM-5 zeolite pores (~0.5 nm). It is clear that the EB molecules formed and diffused within the zeolite pores are primary alkylation products, whereas diethylbenzene (DEB) and triethylbenzene (TEB) are secondary alkylation products formed on the external surface of zeolite crystals through further alkylation of ethylbenzene with ethanol. In the La-modified sample, as benzene conversion

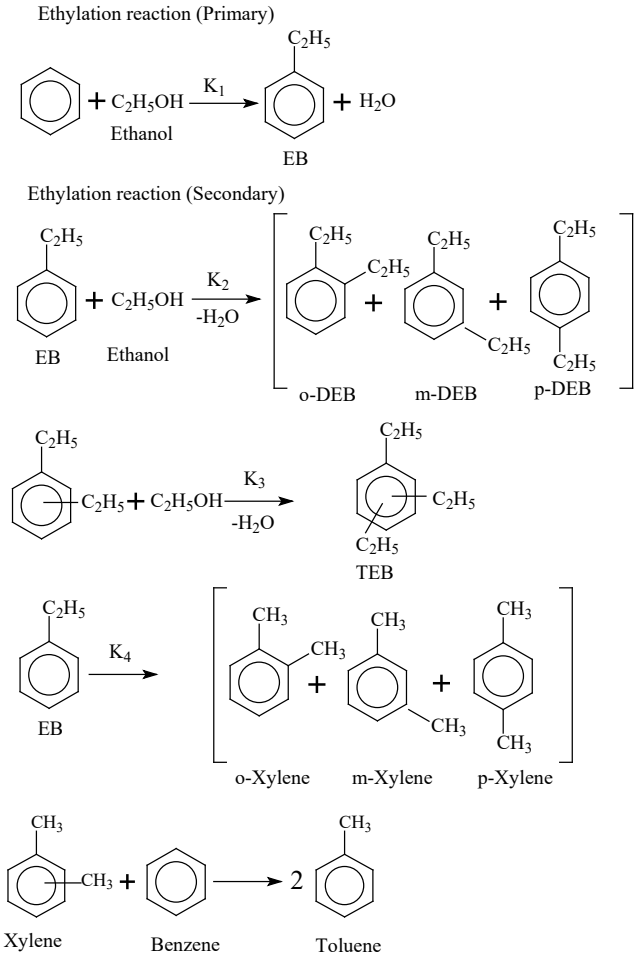

Figure 7. Scheme of the ethylation reaction of benzene with ethanol in the presence of HZSM-5.

decreases, EB selectivity increases. Increasing the temperature leads to an increase in EB yield, with the maximum EB yield (34.5 %) observed at 500 °C. Table 3 and Figure 8(b) present the effect of temperature on the alkylation of benzene with ethanol over the 4 %P/HZSM-5 phosphorus-containing zeolite catalyst. Compared to the unmodified HZSM-5 and La-modified samples, the 4 %P/HZSM-5 catalyst exhibits higher selectivity and yield toward EB. Moreover, the formation of undesired by-products such as m-xylene and o-xylene is not observed, and the amount of secondary alkylation products is significantly reduced. The highest EB conversion (62 %) is observed at 400 °C. As benzene conversion decreases, EB selectivity increases. The maximum selectivity (71.6 %) is achieved at 500 °C, while the maximum yield (37.5 %) is obtained at 450 °C (Figure 8(c)). Table 3 and Figure 8(c) also show the temperature-dependent catalytic performance of the 4%La4%P/HZSM-5 catalyst obtained by dual-component (La–P) modification of HZSM-5 zeolite. In this case, within the 300–500 °C temperature range, benzene conversion increases from 58.0 % to 74.2 % as the temperature rises to 400 °C, and then decreases (to 62.5 %) at higher temperatures. This is likely due to ethanol decomposition at elevated temperatures. The decrease in benzene conversion above 400 °C is also associated with the acceleration of transalkylation and ethylbenzene disproportionation reactions. EB selectivity and yield increase with temperature. For the 4%La4%P/HZSM-5 catalyst, the maximum selectivity (74.2 %) and yield (38.4 %) of EB are achieved at 450 °C, where ethylbenzene is the main product.

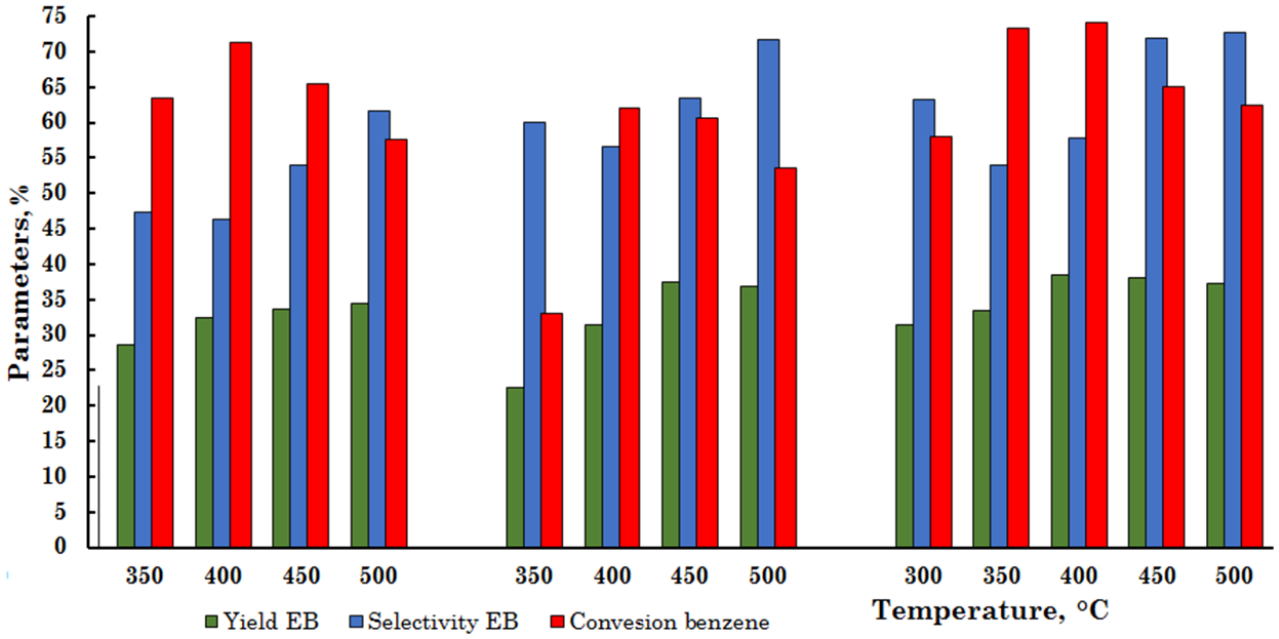

Figure 8. Effect of lanthanum and phosphorus modification of HZSM-5 zeolite on benzene conversion, selectivity, and ethylbenzene yield.

Table 3. Effect of temperature on the catalytic performance of modified catalysts in the ethylation of benzene.

Products	4%La-HZSM-5				4%P-HZSM-5				4%La-4%P/HZSM-5			
	350 °C	400 °C	450 °C	500 °C	350 °C	400 °C	450 °C	500 °C	350 °C	400 °C	450 °C	500 °C
Ethanol	2.5	2.0	1.9	3.8	15.9	9.8	-	-	1.9	2.0	4.5	2.8
Benzene	35.6	27.4	31.9	40.1	55.1	33.2	38.7	46.1	34.1	32.2	41.3	45.9
Toluene	1.5	0.9	0.7	0.7	-	-	-	-	0.7	0.6	0.5	0.8
EB	39.4	31.8	33.7	33.9	23.1	33.1	38.4	38.0	34.9	38.0	37.4	37.1
PK	2.3	1.9	1.3	0.6	5.9	2.0	1.7	0.7	5.0	2.8	0.8	0.5
MK	1.9	1.6	1.1	0.5	-	-	-	-	2.1	1.6	-	-
OK	1.2	1.1	0.8	0.4	-	-	-	-	1.3	0.9	-	-
DEB	12.1	15.2	10.7	5.9	-	6.9	5.3	3.0	8.5	9.3	3.5	2.8
TEB	11.4	15.9	15.2	10.7	-	15.1	15.9	10.1	10.3	11.8	7.5	5.2
Others	2.1	2.2	2.0	3.4	-	-	-	2.1	1.2	0.8	4.7	4.9

To compare the performance of unmodified and modified catalysts, Figure 9 shows the selectivity and yield of EB as a function of reaction temperature. As Figure 9 shows, at temperatures below 400 °C, the highest selectivity for ethylbenzene (EB) is observed for the phosphorus-modified catalyst. At temperatures above 400°C, the highest EB selectivity is achieved with the HZSM-5 catalyst modified with both metallic and non-metallic modifiers. It has been established that the selectivity toward EB over 4%La/HZSM-5, 4%P/HZSM-5, and 4%La4%P/HZSM-5 catalysts is higher compared to unmodified HZSM-5. Figure 9 also shows that at temperatures below 450 °C, the highest EB yield (38.4 %) is achieved with the 4%La4%P/HZSM-5 catalyst, while at temperatures above 450 °C, the highest yield (37.5 %) is observed with the 4%P/HZSM-5 catalyst. In comparison, the unmodified HZSM-5 catalyst exhibits the lowest EB yield (31.7 %). Additionally, when the reaction temperature is increased to 500 °C, a sharp decrease in EB yield (down to 13.8 %) is observed due to catalyst deactivation.

The long-term stability and activity of the catalyst are among its most important characteristics. The catalytic activity of unmodified and modified catalysts as a function of reaction time under flow conditions is shown in Figure 10. Indeed, as can be seen from Figure 10, the unmodified HZSM-5 catalyst demonstrates the least stability, and after 20 hours of operation, the yield of ethylbenzene (EB) decreases to 9.0%. Single-component modification of HZSM-5 with lanthanum or phosphorus significantly improves the catalyst's stable performance. Both 4%La/HZSM-5 and 4%P/HZSM-5 catalysts maintain stable EB yield and selectivity for up to 30 hours of operation. However, after this period, the EB yield in these samples decreases

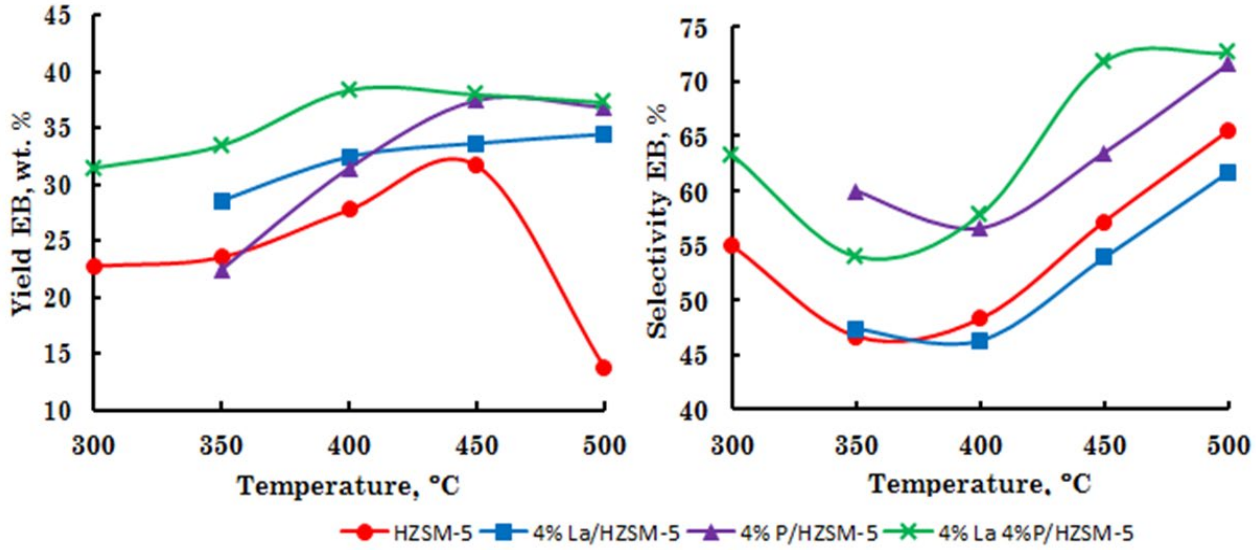

Figure 9. Dependence of benzene conversion and selectivity of ethylbenzene formation on reaction temperature.

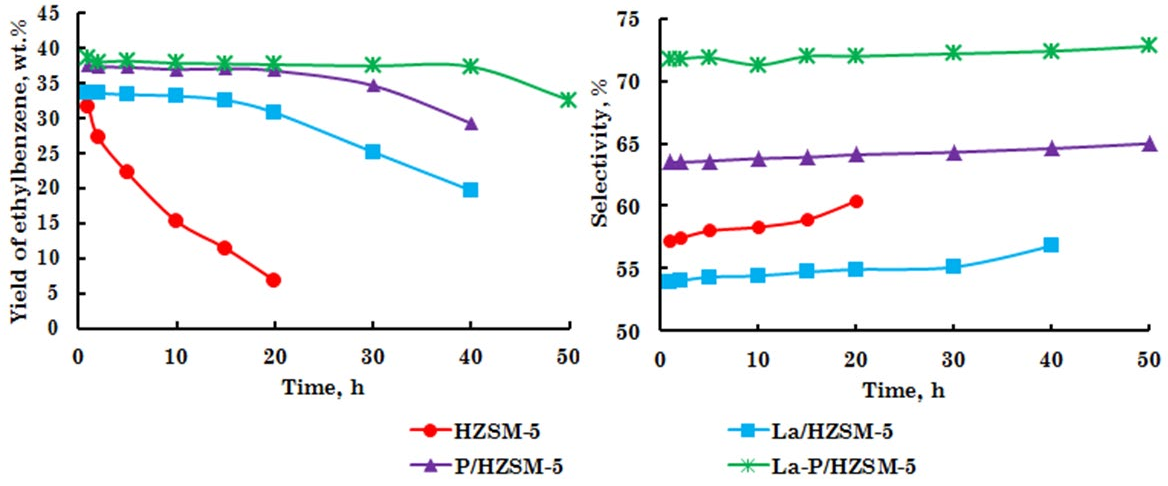

Figure 10. Dependence of benzene conversion and p-ethylbenzene selectivity on the catalyst lifetime.

significantly. The 4%La4%P/HZSM-5 catalyst obtained by two-component modification demonstrates long-term stability, maintaining its initial activity and selectivity for EB for up to 50 hours of operation.

Thus, single- and two-component modification of HZSM-5 zeolite with lanthanum and phosphorus results in a significant increase in the yield and selectivity to EB. These results can be explained by changes in the acidic and structural properties of the zeolite as a result of modification. A comparison of the acidic and structural data for the unmodified and modified catalysts with their activity and selectivity in the alkylation of benzene with ethanol shows that the yield and selectivity for EB are directly related to the density of strong acid sites and the porous structure of the zeolite. Among the studied catalysts, the catalyst obtained by two-component modification (4%La4%P/HZSM-5) exhibits high activity and selectivity for EB. It has the lowest concentration of strong acid sites (89 μmol/g), narrower pores, and a high V_{mezo}/V_{pore} ratio (46.8%).

4. Conclusion

This study demonstrates that modification with lanthanum and phosphorus preserves the crystalline structure of HZSM-5 zeolite but significantly alters its acidic, textural, and catalytic properties during the alkylation of benzene with ethanol. Two-component modification with lanthanum and phosphorus proved to be the most promising strategy, providing higher selectivity for ethylbenzene (74.2%) with stable activity for 50 hours due to a reduction in the density of strong acid sites and an increase in mesopore volume within the total pore volume.

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CRedit Author Statement

Author Contributions: S.E. Mammadov: Methodology, Supervision, Conceptualization, Editing, and Review. A.A. Iskenderova: Investigation, Project administration, Data curation. E.S. Mammadov: Formal analysis, Investigation, Resources. N.F. Akhmedova: Data curation, Investigation, Software, Draft preparation. F.Sh. Kerimli: Methodology, Investigation, Validation, Resources. S.B. İsmayilova: Review and Editing, Validation. All authors have read and agreed to the published version of the manuscript.

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