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Original Research Article

The Effect of Zinc Modification and Heat Treatment on the Catalytic Properties of Zn/HZSM-5 in the Conversion of Bioethanol to Hydrocarbons

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Abstract

The effect of zinc concentration in HZSM-5 zeolite and high-temperature treatment on its catalytic properties in the conversion of bioethanol to hydrocarbons was investigated. The catalysts were characterised using XRF, Fourier-transform infrared spectroscopy, NH_3-TPD and physical low-temperature N_2 adsorption-desorption. It was found that the zinc concentration and the calcination temperature of the zeolite strongly influence the distribution of products obtained from bioethanol. In the temperature range 300–350 °C, Zn-containing zeolites exhibit high isomerisation activity. The 3% Zn/HZSM-5 catalyst exhibits the highest isomerisation activity, with an iso-C_5–C_{14} yield of 19.8–21.8 %. In the temperature range of 400–450 °C, Zn-containing samples exhibit high aromatisation activity. The highest yield of benzene-toluene-xylene (BTX) is achieved on the 3% Zn/HZSM-5 catalyst at 400 °C and amounts to 21.9 %. High-temperature treatment (650–750 °C) of the 3 % Zn/HZSM-5 catalyst significantly reduces its isomerisation and aromatisation activity, but leads to a significant increase in the yield of C_2–C_4 olefins (71.2 %). It has been established that the reason for the increased isomerization activity of the catalysts at low temperatures (300 °C–350 °C) is a significant reduction in the density of strong acid sites, the formation of new types of Lewis cation sites and $Zn^{\delta+}$-O^- acid pairs, which confer a bifunctional character on the zeolite. The observed high yield of C_2–C_4 olefins and the increased stability of the Zn-containing catalyst heat-treated at 750 °C are evidently associated with the deactivation of strong acid sites, a reduction in the hydrogen transfer rate, and an increase in its mesoporosity.

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Keywords: HZSM-5; bioethanol; heat treatment; hydrocarbons; selectivity; zinc

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1. Introduction

Olefinic and aromatic hydrocarbons, such as ethylene, propylene, benzene, toluene and xylenes (BTX), are important precursors widely used in the petrochemical industry. These hydrocarbons are mainly produced through the pyrolysis, catalytic reforming and cracking of crude oil [1]. With the rapid development of the global economy, the conflict between the growing demand for C_2–C_4 lower olefins aromatic hydrocarbons and the increasing depletion of oil reserves, rising prices for petroleum resources, as well as the tightening of environmental protection requirements worldwide, are driving the use of renewable feedstock resources [2,3]. One type of

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renewable raw material is bioethanol, produced by the fermentation of biomass [4,5].

At present, bioethanol is mainly used as a fuel additive [5]. Heterogeneous catalysts are required to convert bioethanol into fuel and valuable chemical compounds. Catalysts based on molecular sieves (Beta, Y-HZSM-5, SAPO-34, HMCM-22) and oxides with various acidic properties and porous structures are active in the conversion of bioethanol into hydrocarbons [6,7]. However, due to intense coke deposition, catalysts based on these zeolites are rapidly deactivated [6,8].

Zeolite ZSM-5 is the catalyst of choice for the production of C_6–C_8 olefins, isoparaffins and aromatic hydrocarbons due to its suitable acidic properties and unique three-dimensional structure featuring sinusoidal and straight pores [9-13]. Catalytic conversions of bioethanol also involve stages such as dehydration, oligomerization, cyclisation and hydrogen transfer. Intermediate products, such as C_6–C_8 cycloalkenes, can be converted into aromatics and light alkanes via hydrogen transfer [14-16] or dehydrogenation reactions [17,18]. The introduction of transition metals (Co, Ni, Mn, Zr) [11,19-22] and rare earth elements (La, Ce) [23-25] with isomerising and dehydrogenating activity, which interact with the proton acid sites of the zeolite to form cationic and metal-based Lewis acid sites, can deactivate the strong acid sites responsible for the formation of heavy aromatic hydrocarbons C_{9+} and improve the catalyst's selectivity towards C_6–C_8 olefins, isoparaffins and aromatic hydrocarbons. On the other hand, high-temperature pre-treatment of a metal-modified catalyst based on ZSM-5 zeolite can also enhance stability, alter its catalytic properties depending on the reaction temperature, and steer the conversion of bioethanol in the desired direction

In this regard, we investigated the effect of modifying HZSM-5 zeolite with zinc and the temperature of the preliminary heat treatment on the structure, acidity, textural and catalytic properties of the Zn/HZSM-5 catalyst in the conversion of bioethanol into isoparaffinic, aromatic and light olefinic hydrocarbons.

2. Materials and Methods

2.1. Catalyst Preparation

For catalyst preparation, a commercial ZSM-5 zeolite (SiO_2/Al_2O_3 = 40, Na_2O < 0.05 wt.%) produced by Nizhny Novgorod Sorbents (Russia) was calcined at 550 °C for 6 h. The resulting H-form of ZSM-5 was modified by aqueous impregnation using a zinc acetate solution, $Zn(CH_3COO)_2$ (0.03–0.30 g per 10 mL of water), depending on the target zinc loading. The solid-to-liquid mass ratio (zeolite to solution) was 1:10. The suspension was continuously stirred at 80 °C for 2 h and then evaporated to dryness. The resulting solid was ground into a powder, kept at room temperature for 24 h, dried at 110 °C for 6 h, and calcined at 350 and 550 °C for 4 h. No filtration or washing steps were performed because the entire suspension was evaporated to dryness. The nominal zinc content in the catalysts ranged from 1.0 to 3.0 wt.%. The actual zinc contents determined by atomic absorption spectroscopy (AAS) were 0.95, 1.92, and 3.05 wt.% for the catalysts with nominal zinc loadings of 1, 2, and 3 wt.%, respectively. To investigate the effect of thermal treatment on the catalyst properties, the obtained samples were additionally calcined at 650 °C and 750 °C for 4 h. Samples of 3%Zn/HZSM-5 following high-temperature treatment are designated as 3%Zn/HZSM-5 (650 °C) and 3%Zn/HZSM-5 (750 °C), where 650 °C and 750 °C denote the heat treatment temperatures.

2.2. Catalyst Characteristics

Fourier-transform infrared (FTIR) spectra of the framework, unmodified and modified zeolites were obtained using a Brucer ALPHA II FTIR spectrometer. Measurements were recorded in the range from 500 cm^{-1} to 1500 cm^{-1}. X-ray diffraction (XRD) of the catalyst samples was performed on a Rigaku Miniflex II X-ray diffractometer equipped with CuKα radiation (λ = 0.150 nm, 30 kV, 15 mA) The scanning range was set from 5° to 60° with a scanning speed providing an equivalent counting time of 14.7 s/step. Temperature-programmed desorption (TPD) analyses of NH3 for the samples were carried out on a USGA-101 chemisorption analyser (Unisit, Russia). The amounts of weak and strong acid sites were evaluated from the integrated NH3-TPD signal over the temperature intervals of 100–300 °C and 300–600 °C, respectively. The corresponding concentrations are reported in Table 1 [26]. Nitrogen adsorption/desorption isotherms for the samples were measured on a Micrometrics analyser at a temperature of −196 °C. Prior to measurement, samples weighing approximately 0.3 g were degassed at 400 °C under high vacuum for 5 h. The total surface area and micropore volume of the samples were calculated using the BET method and the *t*-plot method.

2.3. Catalytic Experiments

The conversion of ethanol to hydrocarbons was carried out in a continuous-flow reactor equipped with a quartz fixed-bed reactor with an internal diameter of 10 mm. The catalysts, which had been pressed into a plate, were ground and sieved to a particle size of 0.6–0.8 mm. The reactor was loaded with 2.0 g of catalyst and pre-treated in a stream of air (50 ml/min) for 2 hours at a

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temperature of 550 °C. Thermal pre-treatment of the 3%Zn/HZSM-5 catalyst was carried out directly in the reactor at 650 °C and 750 °C, respectively, for 4 hours in an air stream.

Following pretreatment, ethanol was fed into the reactor at a flow rate of 2.0 h^{-1}. The experiments were conducted in the temperature range 300–450 °C in a nitrogen stream (40 mL/min at atmospheric pressure). Liquid and gaseous products were separated using a cold trap. The gaseous products of ethanol conversion were analysed on an Agilent GC-782A gas chromatograph, equipped with a thermal conductivity detector, using two columns 3 m long and 2 mm in diameter, packed with Poropac Q sorbents and a '5 Å' molecular sieve, in online mode [13]. The liquid organic phase was analysed on a Perkin Elmer Autosystem XL chromatograph, equipped with an FID and a quartz glass capillary column (100 m × 0.25 mm × 0.25 μm) packed with ZB-1 liquid phase [13].

The conversion of ethanol to hydrocarbons was carried out in a continuous-flow reactor equipped with a quartz fixed-bed reactor with an internal diameter of 10 mm. The catalysts, which had been pressed into a plate, were ground and sieved to a particle size of 0.6–0.8 mm. The reactor was loaded with 2.0 g of catalyst and pretreated in a stream of air (50 mL/min) for 2 h at 550 °C. Air was used to provide an oxidizing environment for removing residual organic compounds and other combustible surface contaminants; this pretreatment was not intended to remove inorganic impurities. Thermal pretreatment of the 3%Zn/HZSM-5 catalyst was carried out directly in the reactor at 650 and 750 °C, respectively, for 4 h in an air stream.

Following pretreatment, ethanol was introduced into the reactor through an evaporator, where it was vaporized before entering the reaction zone. The ethanol vapour was transported into the reactor by a nitrogen stream (40 mL/min at atmospheric pressure), which served as the carrier gas. The ethanol feed rate corresponded to a weight hourly space velocity (WHSV) of 2.0 h^{-1}. The experiments were conducted in the temperature range of 300–450 °C. Liquid and gaseous products were separated using a cold trap. The gaseous products of ethanol conversion were analysed on an Agilent GC-782A gas chromatograph equipped with a thermal conductivity detector, using two columns 3 m long and 2 mm in diameter, packed with Poropac Q sorbents and a 5 Å molecular sieve, in online mode [13]. The liquid organic phase was analysed on a Perkin Elmer Autosystem XL chromatograph equipped with an FID and a quartz glass capillary column (100 m × 0.25 mm × 0.25 μm) packed with ZB-1 liquid phase [13].

The ethanol conversion (X_{EtOH}), carbon-based selectivity (S_i), carbon-based product yield (Y_i), and space-time yield (STY_i) can be calculated using the following equations:

Ethanol conversion:

$$X_{\mathrm{EtOH}}\,(\%) = \frac{F_{EtOH,in} - F_{EtOH,out}}{F_{EtOH,in}} \times 100 \quad (1)$$

where $F_{\mathrm{EtOH,in}}$ and $F_{\mathrm{EtOH,out}}$ are the molar flow rates of ethanol at the reactor inlet and outlet, respectively.

Carbon-based selectivity:

$$\mathrm{S}_i(\%) = \frac{n_{C,i} \cdot F_i}{2(F_{EtOH,in} - F_{EtOH,out})} \times 100 \quad (2)$$

where $n_{\mathrm{C,i}}$ is the number of carbon atoms in product i and F_i is its molar flow rate.

Carbon-based product yield:

$$Y_i = \frac{X_{EtOH} \cdot S_i}{100} \quad (3)$$

Space-time yield:

$$STY_i = \frac{m_i}{m_{cat}} \quad (4)$$

where m_i is the mass production rate of product i and m_{cat} is the catalyst mass.

3. Results and Discussion

The Figure 1 shows the X-ray diffraction patterns of HZSM-5, 2%Zn/HZSM-5 and 2%Zn/HZSM-5 (750 °C). It can be seen that all samples exhibit characteristic MFI-type zeolite peaks at 8.2°, 9.1°, 23.4°, 23.9° and 24.7°. The characteristic diffraction peaks for ZnO at 31.7°, 34.4° and 36.6° are not observed. This indicates that no crystalline ZnO phase detectable by XRD is present in the analysed samples and that the MFI-type zeolite structure is retained after modification and heat treatment at 750 °C. The absence of detectable ZnO reflections may be associated with a low concentration, small crystallite size, high dispersion, or an amorphous state of the zinc-containing species. However, XRD data alone do not establish the spatial distribution or dispersion of zinc species. The preservation of the zeolite structure after modification and heat treatment is also confirmed by Fourier-transform infrared (FTIR) spectroscopy data (Figure 2).

The absorption bands observed at 1223, 1083, 794 and 539 cm^{-1} are characteristic of the HZSM-5 framework [26]. The band at 1223 cm^{-1} is assigned to external asymmetric stretching vibrations of the TO_4 tetrahedral units, while the band at 1083 cm^{-1} is attributed to internal asymmetric stretching vibrations of Si–O–T bonds (T = Si or Al). The band at 794 cm^{-1} is associated

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with symmetric stretching vibrations of framework T–O–T bonds, and the band at 539 cm^{-1} is characteristic of the double five-membered ring units of the MFI framework. After zinc modification and thermal treatment, the band initially observed at 1083 cm^{-1} shifts to approximately 1068–1072 cm^{-1}. This shift may be related to changes in the local chemical environment of framework oxygen atoms and their interaction with zinc-containing species. The slight changes in the 539–794 cm^{-1} region may also reflect modifications in the local environment of the framework units. Nevertheless, the characteristic MFI bands remain present, indicating that the principal zeolite framework is retained. Thus, no significant changes occurred in the IR spectra following the addition of Zn and its heat treatment.

Figure 3 illustrates the effect of zinc concentration and temperature on the isomerization activity of HZSM-5 zeolite. It can be seen that HZSM-5 exhibits low activity in the conversion of bioethanol to C_5–C_{14} isoparaffinic hydrocarbons. The yield of isoparaffins C_5–C_{14} does not exceed 12.9 %. The introduction of zinc into the HZSM-5 composition significantly increases the catalyst's isomerization activity. The highest isomerization activity is observed in the temperature range 300–350 °C. The maximum yield of iso-C_5–C_{14} (21.8 %) is achieved on the 2%Zn/HZSM-5 sample at a temperature of 300 °C. A further increase in the zinc concentration to 3.0 wt.% reduces the yield of iso-C_5–C_{14} to 16.3 %. Raising the reaction temperature above 350 °C leads to a decrease in the isomerization activity of the modified catalysts. At a reaction temperature of 450 °C, all modified samples exhibit low isomerization activity. At this temperature, on samples containing 2.0 and 3.0 wt.% zinc, the yield of iso-

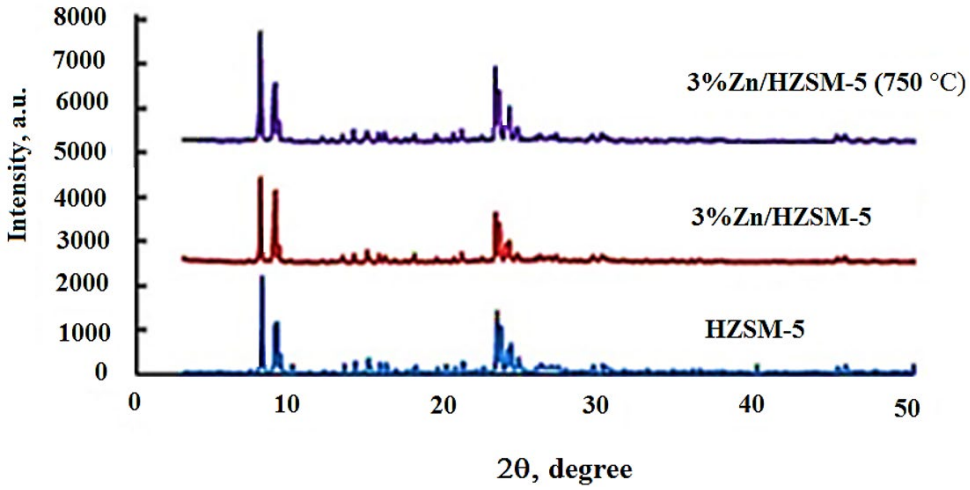


Figure 1. X-ray diffraction patterns of catalysts HZSM-5, 3%Zn/HZSM-5 and 3%Zn/HZSM-5(750 °C)

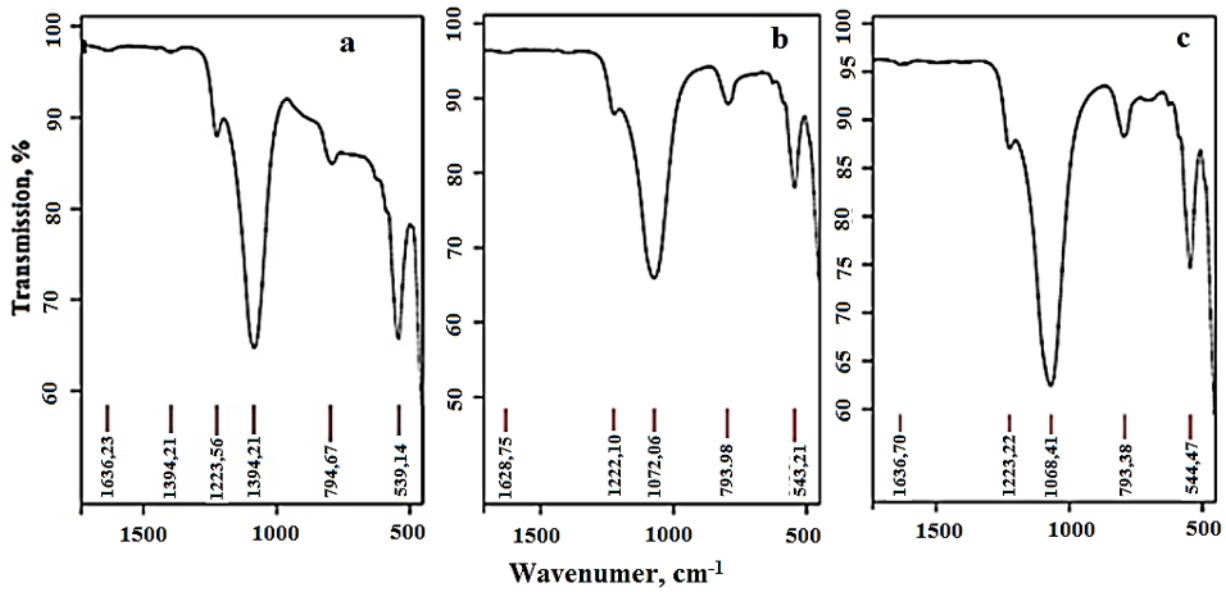


Figure 2. FTIR spectra patterns of catalysts HZSM-5, 3%Zn/HZSM-5 and 3%Zn/HZSM-5 (750 °C).

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C_5–C_{14} decreases to 11.0–8.1 wt.%, respectively. Thus, Zn-containing samples exhibit isomerization activity in the conversion of bioethanol to iso-C_5–C_{14} hydrocarbons within the temperature range of 300–350 °C. The most active catalyst is 2%Zn/HZSM-5, on which the resulting liquid product is enriched with high-octane, isoparaffinic C_5–C_{14} hydrocarbons, which can be used as an additive to improve the octane properties of petrol fractions. Zinc-modified catalysts are most active in the bioethanol aromatization reaction in the high-temperature range (400–450 °C). In this temperature range, the yield of the benzene-toluene-xylene (BTX) fraction in the presence of the modified samples is significantly higher compared to the unmodified zeolite. The maximum yield of the BTX fraction (21.8 wt.%) is achieved on the 3%Zn/HZSM-5 sample at 400 °C. On HZSM-5, which possesses a high density of strong acid sites, the yield of heavier C_{9+} aromatic hydrocarbons is significantly higher than on the modified samples. Consequently, the 3%Zn/HZSM-5 catalyst can be used to produce the valuable BTX fraction from bioethanol (Figure 4).

Heat treatment of the Zn-containing catalyst 3%Zn/HZSM-5 at 650 °C and 750 °C, respectively, for 4 hours significantly alters its catalytic properties. Figure 5 illustrates the effect of thermal treatment of the 3%Zn/HZSM-5 catalyst on the yield of the BTX fraction and C_{9+} aromatic hydrocarbons. It can be seen that after thermal treatment of the catalyst, there is a decrease in the catalyst's aromatization activity. The greatest

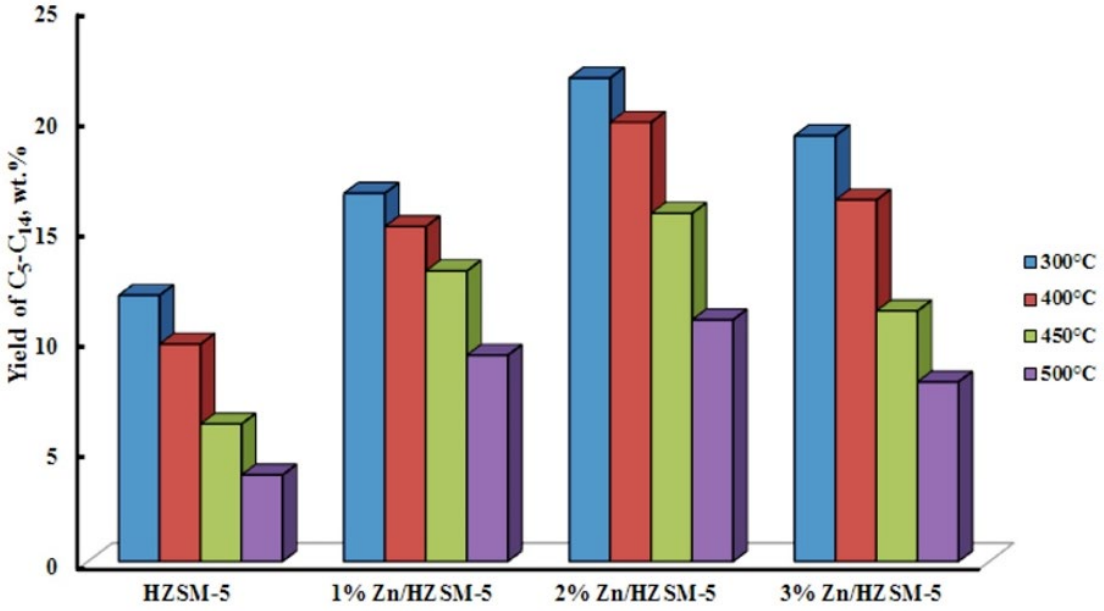


Figure 3. The dependence of the influence of zinc concentration in the composition of zeolite HZSM-5 on the yield of isoparaffin hydrocarbons C_5–C_{14}.

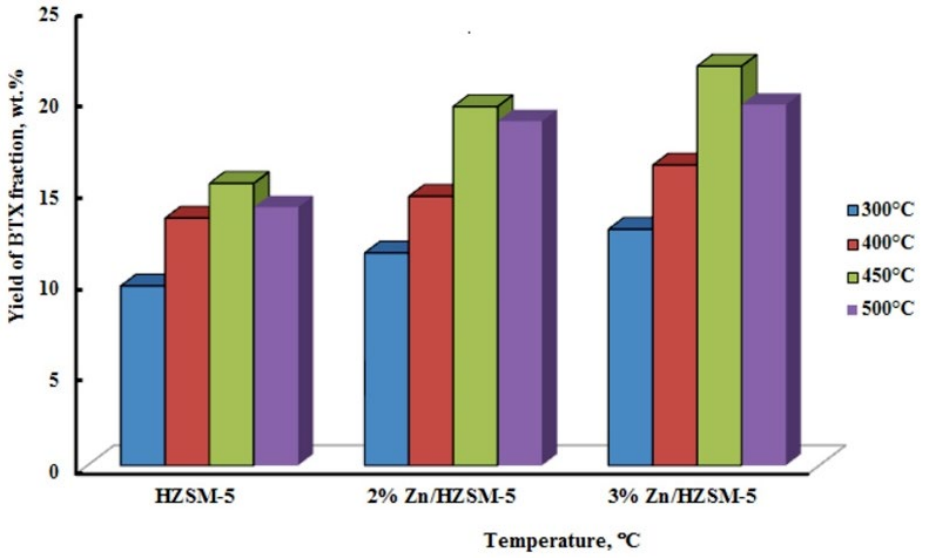


Figure 4. Dependence of the BTX yield on temperature on samples of HZSM-5, 2%Zn/HZSM-5 and 3%Zn/HZSM-5.

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reduction in the yield of the BTX fraction and C_{9+} aromatic hydrocarbons is observed in the sample that underwent heat treatment at 750 °C. In this sample, in the temperature range of 400–450 °C, the yield of the BTX fraction and C_{9+} aromatic hydrocarbons decreases to 8.8–10.2 wt.% and 0.6–0.9 wt.%, respectively. However, heat-treated catalysts demonstrate good catalytic properties in the conversion of bioethanol to C_2–C_4 olefins.

The 3%Zn/HZSM-5 catalyst, which has undergone heat treatment at 750 °C, demonstrates excellent catalytic performance in terms of C_2–C_4 olefin yield. On this sample, at 500 °C, the C_2–C_4 olefin yield reaches 71.2 % (Figure 6). To explain the effect of modification on the catalytic properties of HZSM-5, the acid and textural characteristics of the catalysts were investigated. Table 1 shows the effect of zinc concentration and the temperature of preliminary heat treatment on the acid characteristics of HZSM-5-based catalysts. The NH_3-TPD profiles were divided into a low-temperature region (100–300 °C), assigned to weak acid sites, and a high-temperature region (300–600 °C), assigned to strong acid sites. The concentrations of weak and strong acid sites were calculated from the corresponding integrated desorption signals and are reported in Table 1.

The incorporation of 1.0–3.0 wt.% zinc into HZSM-5 zeolite significantly alters the distribution and strength of the acid sites. As the zinc content in the zeolite composition increases, a decrease in the density of strong Brønsted acid sites is observed, from 392 to 237 μmol/g. The greatest decrease in the density of strong acid sites is observed in the 3%Zn/HZSM-5 sample, which underwent heat treatment at 750 °C for 4 hours

The gradual reduction in the number of strong acid sites as the zinc content in HZSM-5

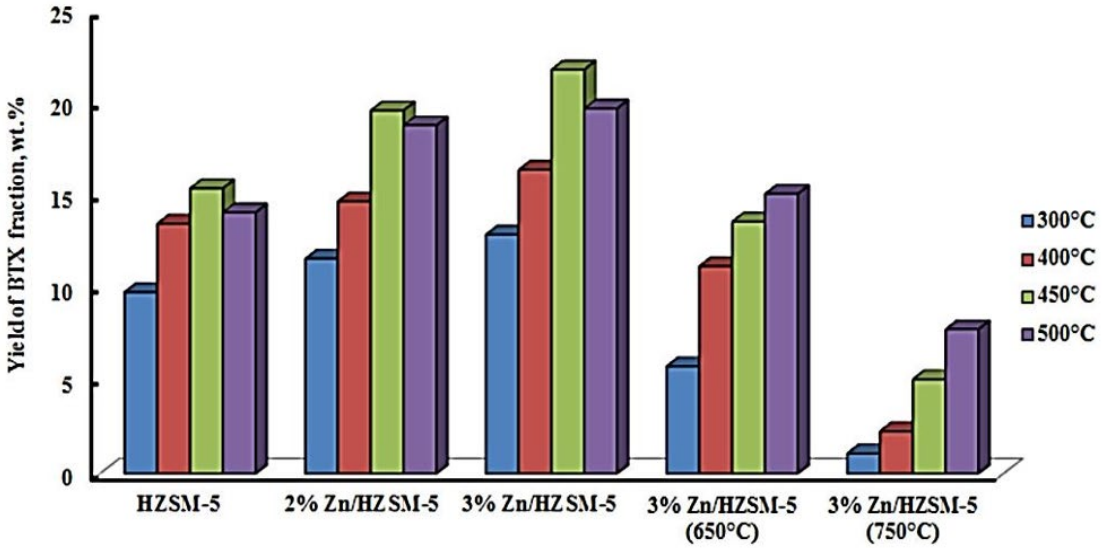


Figure 5. Dependence of the influence of thermal treatment of the 3%Zn/HZSM-5 catalyst on the yield of the BTX fraction and C_{9+} aromatic hydrocarbons.

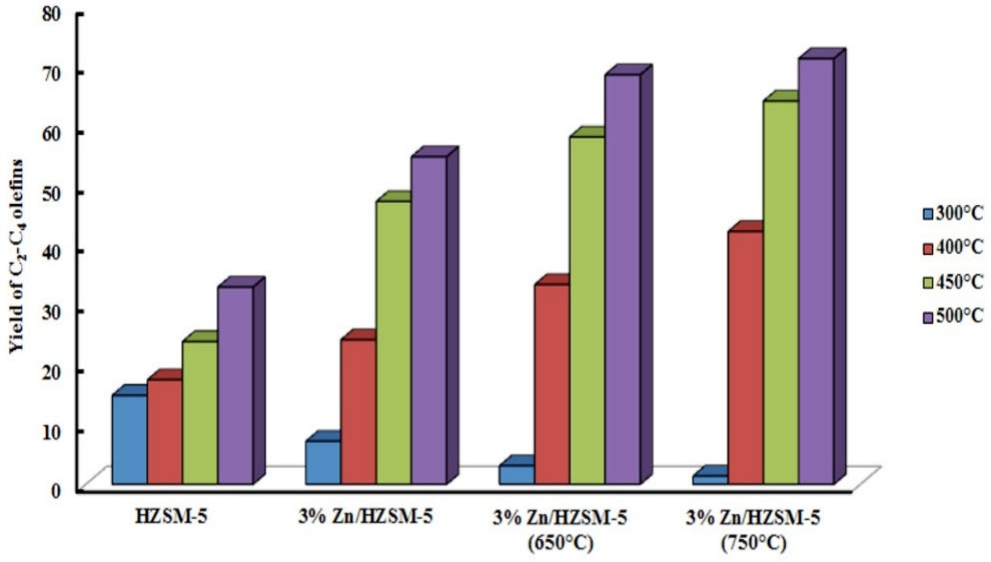


Figure 6. Effect of thermal treatment of 3%Zn/HZSM-5 catalyst on the yield of C_2-C_4 olefins.

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increases may be associated with interactions between zinc-containing species and the protonic sites of the zeolite. During modification with an aqueous zinc acetate solution, partial ion exchange or neutralization of Brønsted acid sites by Zn^{2+} and $ZnOH^{+}$ species may occur. During subsequent thermal treatment, zinc-containing species may undergo further transformations and interact with the acidic sites of HZSM-5. However, the relative contributions of ion exchange and the formation of zinc oxide species, as well as their exact locations within the zeolite channels or on the external surface, cannot be established conclusively from the XRD data alone [13].

As a result, the density of strong acid sites decreases, and the structural characteristics of the catalysts are altered. The zinc-modified HZSM-5 catalysts may contain different types of zinc species, including isolated Zn^{2+} and $ZnOH^{+}$ ions, as well as highly dispersed zinc oxide species [13,27,28]. The presence and relative abundance of these species may influence the acid–base properties of the catalyst and its ability to activate bioethanol molecules and reaction intermediates. The specific distribution of zinc species, however, requires complementary characterization and cannot be determined from XRD alone.

It is known that aromatic hydrocarbons can be formed via two pathways: the first involves a transfer reaction between lower olefins and cycloalkenes, and the second involves the dehydrogenation of cycloalkene molecules [27,28]. The data in the table show that preliminary heat treatment affects the acidic, textural and active sites of the catalyst. This is due to a sharp decrease in the rate of hydrogen transfer between cycloalkenes and light olefins, which significantly reduces the selectivity towards aromatic hydrocarbons.

In zeolite, the active sites for dehydrogenation are ZnO and $ZnOH^{+}$ species [27,29]. During thermal treatment, the interaction between ZnO species and the zeolite's acidic Brønsted sites is significantly enhanced, leading to an increase in the $ZnOH^{+}$ content (Figure 7). This process results in a reduction in the density of strong sites and significantly accelerates the dehydrogenation of intermediates. Due to the significant reduction in the number of strong acid sites, the rate of oligomerization of unsaturated hydrocarbons is greatly reduced, leading to an increase in selectivity towards C_2–C_4 olefins and a decrease in selectivity towards aromatic hydrocarbons.

The corrected textural data in Table 2 show that the total pore volume decreases from 0.24

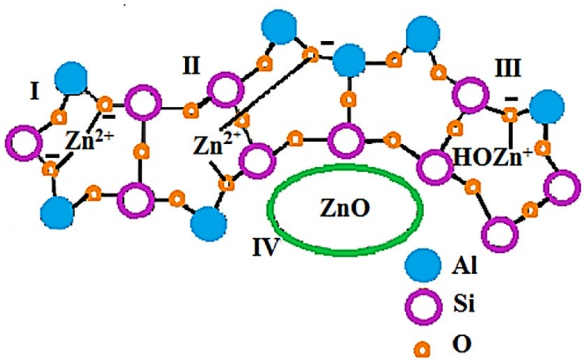


Figure 7. Schematic representation of catalytically active species of Zn centers in zeolite HZSM-5.

Table 1. Effect of zinc concentration and heat treatment on the acid properties of HZSM-5-based catalysts.

Type of catalyst	Weak acid sites, µmol/g, (100-300 °C)	Strong acid sites, µmol/g, (300-600 °C)	Total concentration of acid sites, µmol/g
ZSM-5	392	237	629
1% Zn/HZSM-5	354	208	556
2% Zn/HZSM-5	318	176	494
3%Zn/HZSM-5	272	142	454
3%Zn/HZSM-5(650 °C)	226	108	334
3%Zn/HZSM-5 (750 °C)	203	82	285

Table 2. Effect of zinc concentration and pre-heat treatment temperature on the structural characteristics of catalysts.

Type of catalyst	S_{BET}, m^2/g	V_{pore}, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g	V_{meso}/V_{pore},
HZSM-5	267	0.24	0.18	0.06	25.0
2% Zn/HZSM-5	259	0.22	0.14	0.08	36.4
3%Zn/HZSM-5	247	0.21	0.12	0.09	42.8
3%Zn/HZSM-5 (650 °C)	278	0.18	0.10	0.08	44.5
3%Zn/HZSM-5 (750 °C)	290	0.16	0.07	0.09	56.2

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cm^3/g for the parent HZSM-5 to 0.16 cm^3/g for the 3%Zn/HZSM-5 sample treated at 750 °C. In contrast, the absolute mesopore volume increases from 0.06 cm^3/g for the parent zeolite to 0.09 cm^3/g for 3%Zn/HZSM-5. For the samples treated at 650 and 750 °C, the mesopore volumes are 0.08 and 0.09 cm^3/g, respectively. The relative contribution of mesopores (V_{meso}/V_{pore}) increases from 25.0% for the parent zeolite to 56.2% for the sample treated at 750 °C. Thus, the absolute mesopore volume and its relative contribution should be distinguished when interpreting the textural changes.

The increased relative contribution of mesopores may improve the accessibility of reactant and product molecules to catalytically active sites and may facilitate the transport of C_2–C_4 olefins. Nevertheless, the effect of the pore structure on diffusion should be interpreted cautiously and supported by the nitrogen adsorption–desorption isotherms and BJH pore-size distribution curves. These data should be included in the revised manuscript when the corresponding original measurements are available (Figure 8). The effect of modification and heat treatment on the operational stability of HZSM-5 zeolite-based catalysts is shown in Figure 8. It can be seen that as the operating time increases, there is a significant decrease in the activity of unmodified HZSM-5. After 10 hours of operation, the yield of C_2–C_4 olefins decreases from 32.9 % to 12.3 %. Modification of HZSM-5 with zinc increases its operational stability to 20 hours. Heat treatment of the Zn/HZSM-5 catalyst improves its stability. The 3%Zn/HZSM-5 catalyst, which has undergone heat treatment at 750 °C, demonstrates excellent catalytic performance, maintaining a high olefin yield (69.8–71.2 %) over 50 hours of operation. Thus, by modifying and heat-treating catalysts based on HZSM-5 zeolite, it is possible to steer the conversion of bioethanol in the desired direction and also improve their operational stability.

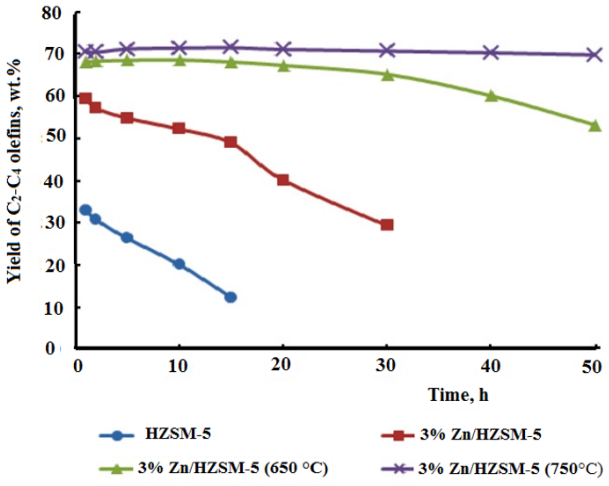


Figure 8. Dependence of the influence of modification and heat treatment on the stability of catalysts based on zeolite HZSM-5.

4. Conclusion

In this study, the main focus was on the conversion of bioethanol into isoparaffinic, aromatic and olefinic hydrocarbons, catalysed by catalysts based on HZSM-5 zeolite modified with zinc, as well as those heat-treated at 650 °C and 750 °C. Modification and preliminary heat treatment affect the product composition, acid and textural properties of the Zn/HZSM-5 catalyst, as well as its operational stability. Modification of HZSM-5 zeolite with zinc in the temperature range 300–350 °C increases the isomerization activity, and in the temperature range 400–450 °C – the aromatization activity of the catalyst. High-temperature treatment of the 3%Zn/HZSM-5 catalyst deactivates strong Brønsted sites and thereby suppresses the hydrogen transfer reaction, which prevents the formation of aromatic hydrocarbons, improves stability (50 h) and selectivity for C_2–C_4 olefins (71.2 %).

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CRediT Author Statement

Authors Contributions: S.E. Mammadov: Conceptualization, Writing-Review & Editing, Project administration; N.F. Akhmedova: Software, Visualization, Writing; A.Z. Mamedova: Methodology, Formal analysis; Kh.M. Mammadova: Resources, Investigation; T.A. Babayeva: Software, Investigation; E.M. Babayev: Writing-Review & Editing, A.A. Iskenderova: Data Curation; E.S. Mammadov: Formal analysis, Validation. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Declaration of Generative AI Use

During the preparation of this manuscript, the author(s) used AI to assist with improving academic English, language editing, and enhancing the clarity and readability of the text.

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