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Original Research Article

The Effect of Boron Concentration on the Properties and Paraselectivity of Zeolite HZSM-5 in the Methylation Reaction of Ethylbenzene

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Abstract

In order to increase the selectivity for p-ethyltoluene, catalytic systems based on HZSM-5 zeolite modified with orthoboric acid were obtained, which were used in the alkylation of ethylbenzene with methanol. The reaction was carried out in a continuous flow reactor with a fixed catalyst bed in the temperature range of 300-400 °C at atmospheric pressure to study the effect of boron concentration in the composition of HZSM-5 on the selectivity of the formation of ethyltoluenes and p-ethyltoluene. Physicochemical and textural characteristics of the catalysts were characterized by X-ray Diffraction (XRD), Infra Red (IR) spectroscopy, NH_3-Temperature Program Desorption (TPD) and low-temperature Nitrogen Adsorption (NA). It was found that the decrease in the density of strong acid sites, reduction in the volume of micropores and increase in the mesoporosity of zeolite as a result of modification are the main reasons for the enhancement of the catalyst selectivity to p-ethyltoluene. Catalyst 5 %B-HZSM-5 in the temperature range of 300 - 350 °C with conversion of ethylbenzene equal to 14.7-18.4 % shows a sufficiently high selectivity for p-ethyltoluene (60.5-70.2 %).

Keywords: HZSM-5 zeolite; boron modification; selectivity for p-ethyltoluone; ethylbenzene; methanol

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1. Introduction

The products of methylation of ethylbenzene p- and m-ethyltoluenes (ET) are widely used in the petrochemical industry for the production of methylstyrenes [1,2]. The most valuable isomer is p-ethyltoluene (p-ET). Polymers based on p-ET have a number of advantages over polystyrene: a higher glass transition temperature and boiling point. Traditional acid catalysts of the Friedel-Crafts type [2] used in industry in the processes of alkylation of aromatic hydrocarbons have significant disadvantages related to environmental pollution, corrosion of equipment, non-regenerability of the catalyst and its high consumption. Recently, ZSM-5 type zeolites have been widely used as catalysts in the petrochemical industry [1,3]. Catalysts based on ZSM-5 zeolite possessing nanosized sinusoidal (0.51×0.53nm) and straight (0.53×0.55 nm) channels showed higher para-selectivity in alkylation and disproportionation reactions of alkylaromatic hydrocarbons [4-6]. The use of methanol as an alkylating agent for the production of p-ET seems to be more competitive due to its huge industrial availability compared to other alkylating agents.

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In order to increase the para-selectivity of ZSM-5 type zeolites in the processes of disproportionation and alkylation of aromatic hydrocarbons with monoatomic alcohols C_1-C_3, various methods of modifying its surface properties were used [7,8]. It was noted that silylation of the zeolite surface with tetraethyl orthosilicate (TEOS) improves its selectivity for p-xylene and p-ethyltoluene [9,10]. Modification of zeolite ZSM-5 by treatment with phosphorus compounds leads to the appearance of new types of acid centers, which improve its para-selectivity in the alkylation of toluene with methanol [11,12], alkylation of ethylbenzene with ethanol [13], and disproportionation of toluene and ethylbenzene [14,15]. Improvement of para-selectivity of zeolites of the ZSM-5 type can also be achieved by modification with compounds of Mg, Ni, Co, Ru, Pt and lanthanides [16-19].

Alkylation of toluene with ethanol in the presence of ZSM-5 zeolites to produce para-ethyltoluene in the temperature range of 250-350 °C provides higher toluene conversion and selectivity for p-ethyltoluene (>50 %) [7,19]. It was shown in [20-24] that in toluene ethylation reactions the improvement of selectivity for p-ethyltoluene can be achieved by modifying the ZSM-5 zeolite with Cd, Ga, Al, Mg, as well as by changing the acid centers. However, the alkylation of ethylbenzene with methanol was mainly carried out on cationic forms (Rb, Cs) of low-silica zeolites of X and Y types [25], which yield vinyl derivatives of aromatic hydrocarbons. There are very few studies on the alkylation of ethylbenzene with methanol to produce p-ethyltoluene. However, the use of methanol as an alkylating agent for the production of p-ethyltoluene seems to be more competitive due to its huge industry availability compared to other alkylating agents.

Therefore, the aim of the present work is to study the effect of boron concentration on acidic, structural characteristics of HZSM-5 zeolite and selectivity of p-ethyltoluene formation in the process of ethylbenzene methylation.

2. Materials and Method

2.1 Catalyst Preparation

Commercial zeolite ZSM-5 (SiO_2/Al_2O_3=40; Na_2O<0.05 %) produced by "Nizhnegorod Sorbents" Russia was used for the study. To obtain the H-form, the initial zeolite was calcined at 550 °C for 4 hours. Catalysts modified with 3.0-5.0 wt.% boron were prepared by impregnation (0.10-0.30 g (10 mL)) using an aqueous solution of orthoboric acid at 80 °C for 6 hours.

The resulting powder was dried at 110 °C for 4 hours, then calcined in a muffle furnace at 350 °C and 500 °C for 4 hours, respectively. Unmodified and modified zeolites were granulated by pressing at a pressure of 2.5×10^7 Pa and sieved to obtain particles with a diameter of 0.5-0.8 mm.

2.2 Catalysts Characterizations

X-ray structural diffraction patterns of the initial and modified catalysts were obtained by X-ray phase analysis using a RIGAKU MINIFLEX X-ray diffractometer with Cu-K_α radiation (λ=0.15046 nm). The scanning range was 2θ from 3° to 80° at a rate of 2° per minute. The IR spectrum of adsorbed pyridine for zeolite catalysts was obtained on a FTIR-7600 Fourier spectrometer, according to the method described in [26,27].

The specific surface area and textural characteristics of the catalysts were studied by the method of low-temperature nitrogen adsorption at 77 K on an ASAP-2010 installation from Micromeritics according to the method described in [28]. The acid characteristics of the catalysts were obtained by the method of temperature-programmed desorption of ammonia (NH_3-TPD) on a USGA-101 sorption analyzer (UNISIT, Russia) according to the method described in [29].

2.3. Catalytic Reaction

Catalytic experiments were carried out in a continuous flow setup with a quartz reactor (15 cm in length, 1.0 cm internal diameter) with a catalyst loading of 2.0 g. Before the experiments, the catalysts were activated in an air flow at 500 °C for 2 h. The methylation reaction of ethylbenzene was carried out at atmospheric pressure in the temperature range of 350-400 °C with a feed volumetric feed rate of 1.0 h^{-1} and an ethylbenzene to methanol molar ratio of 2:1. The reaction products were analyzed on an Agilent GC 7820A gas chromatograph using the procedure described in [29].

The conversion (C_{EB}), product selectivity (S) and para-selectivity ($S_{p\text{-}ET}$) were determined using the following relations:

$$\%\, C_{EB} = \frac{\text{EB in feed} - \text{EB in product}}{\text{EB in feed}} \times 100 \quad (1)$$

$$\%\, S = \frac{\text{wt.\%, product}_i}{\text{wt.\% } \sum \text{product}_i} \times 100 \quad (2)$$

$$\%\, S_{p\text{-}ET} = \frac{\text{wt.\% of p-ET in product}}{\text{wt.\% of ET in product}} \times 100 \quad (3)$$

3. Results and Discussion

X-ray diffraction patterns of freshly prepared HZSM-5 and boron-modified zeolite catalyst are shown in Figure 1. The modification of HZSM-5 zeolite with boron does not affect the zeolite structure, it remains unchanged after it is modified. The observed peaks at 2θ = 7.96°, 8.88°, 23.2°, and 24° are characteristic of zeolite with MFI framework [30,31]. The diffraction peak 2**θ** =

28°, related to the B_2O_3 diffraction peak, was not detected in the X-ray diffraction patterns, indicating good dispersion of the modifier particles on the zeolite surface [32]. However, the modification changes the acidic, textural and catalytic properties of HZSM-5 zeolite.

Table 1 presents the catalytic data obtained in the methylation of ethylbenzene on unmodified and modified catalysts based on zeolite HZSM-5 as a function of temperature. The results obtained cover the conversion of ethylbenzene and methanol, selectivity for ethyltoluenes and by-products. Along with ethyltoluenes, benzene, toluene, xylenes, trimethylbenzenes, diethylbenzene and gaseous products C_1-C_4 are formed in sufficient quantities.

Increasing the reaction temperature from 300 °C to 450 °C increases the selectivity of by-products and decreases the selectivity for ethyltoluenes (Figure 2). When the reaction temperature is increased from 300 °C to 400 °C, the conversion of ethylbenzene increases from 33.8 % to 49.9 %, the selectivity for the formation of BTX (benzene-toluene-xylenes) and the sum of TMB+DEB increases from 15.4 % to 20.1 % and from 7.8 % to 12.8 %, respectively. As a result of the increased rate of the side reactions of disproportionation, transalkylation and isomerization of the initial ethylbenzene and the reaction products, the selectivity of the formation of ethyltoluenes decreases from 72.9 % to 55.2 % on HZSM-5.

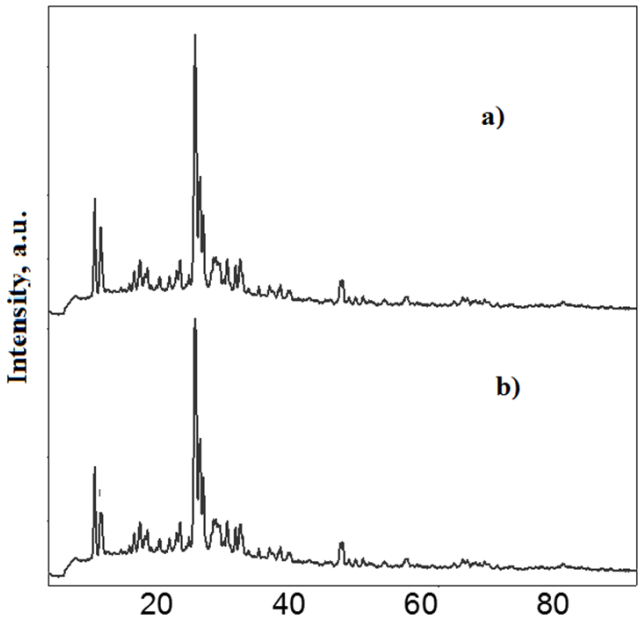

Figure 1. X-ray diffraction patterns of unmodified zeolite HZSM-5 (1) and modified catalyst 5% B/HZSM-5.

The presence of areas of strong acid sites in unmodified HZSM-5 zeolite (Table 2) and the high rate of hydrogen transfer reaction leads to a relatively large number of by-products, which significantly reduce the activity, selectivity for the target product and stability of the catalyst (Figure 2). Incorporation of modifier into the zeolite structure is one of the methods to improve the catalytic properties and para-selectivity of the catalyst [15,18,20].

Boron modification can reduce the hydrogen transfer efficiency of the catalyst, which is a key parameter controlling product distribution. Light olefins formed in the alkylation process by alcohol cracking can be converted into aromatic compounds by cyclisation and dehydrogenation via hydrogen transfer reaction. Moreover, aromatic compounds cause coke formation, which leads to catalyst deactivation [33,34]. The addition of boron to HZSM-5 zeolite inhibits the reactions involving hydrogen transfer, prevents the coke formation and increases the stability of the catalyst. Modification of zeolite HZSM-5 with boron in an amount of 1.0-5.0 wt.% significantly changes the distribution of products: the yield of by-products decreases and the selectivity for ethyltoluenes increases. With increasing boron concentration in HZSM-5, there is a significant

Table 1. Effect of boron modification of zeolite HZSM-5 on product selectivity in ethylbenzene methylation reaction (TMB- trimethylbenzenes, DEB – diethylbenzenes)

Catalyst	T, °C	Conversion, %		Selectivity to products, %								
		EB	alcohol	Gas C_1-C_4	Benzene	Toluene	Xylenes	*p*-ET	*m*-ET	*o*-ET	TMB	DEB
HZSM-5	300	33.8	88.2	9.8	6.5	4.4	4.5	25.2	42.3	5.4	1.3	6.5
	350	44.6	90.8	10.0	7.8	5.8	5.1	19.4	35.7	5.7	2.0	8.5
	400	49.9	97.6	11.5	8.4	6.2	5.5	14.9	33.6	7.2	2.6	10.2
1%B-	300	29.4	85.5	8.8	6.0	3.9	3.3	30.4	36.7	4.4	0.7	5.8
HZSM-5	350	33.4	91.8	10.1	6.2	4.2	3.7	26.9	37.4	4.6	0.9	6.0
	400	40.6	97.4	10.8	7.8	4.7	4.4	20.7	36.0	5.0	2.0	8.6
3%B-	300	19.8	84.8	8.7	5.9	3.6	3.4	43.9	25.8	4.0	0.5	5.5
HZSM-5	350	24.6	91.3	8.9	5.7	3.2	3.2	41.0	27.2	4.1	0.8	5.3
5%B-	300	14.7	83.5	6.0	5.3	3.4	2.8	54.2	21.9	1,1	0.5	4.8
HZSM-5	350	18.4	90.7	8.2	5.4	3.6	3.2	44.8	25.6	3.6	0.6	5.0

decrease in ethylbenzene conversion and selectivity for by-products and an increase in selectivity for ethyltoluenes. On the sample containing 5.0 wt.% of boron at 350 ^{0}C the selectivity for ethyltoluenes increases up to 74.0 % (Table 1*)*. The greatest decrease in ethylbenzene conversion is observed on the sample modified with 5.0 wt.% boron. At 350 °C, the ethylbenzene conversion on this sample decreases from 44.6% to 18.4%. The selectivity for the formation of BTX and the sum of TMB+DEB decreases to 12.2 % and 5.6 %, respectively (Table 1). The selectivity of the formation of ethyltoluenes and p-ethyltoluene depends significantly on the reaction temperature and the concentration of boron in the catalyst as depicted in Figure 2.

For example, at 350 °C, increasing the boron content in the zeolite to 5.0 wt.% leads to an increase in the selectivity of ET formation from 57.1% to 74.0%. Figure 2 shows the results of the effect of boron concentration on p-ET selectivity at reaction temperatures of 300 °C and 350 °C. Under these conditions on HZSM-5 containing 3 wt.% boron, the n-ET selectivity increases 56.7-59.0 %, further increase of boron in the catalyst up to 5.0 wt.% leads to an increase of p-ET selectivity up to 60.5 %-70.2 %. The maximum p-ET selectivity (70.2 %) is achieved on the sample containing 5.0 wt.% boron at toluene conversion of 14.8 %.

Alkylation of aromatic hydrocarbons with methanol and ethanol on zeolite catalysts depends on the microporous structure, concentration and strength of acid sites. The presence of strong acid sites on the outer surface of HZSM-5 has a favorable effect on the conversion of aromatic hydrocarbons, but is undesirable for the selective formation of dialkylbenzene isomers, especially para-substituted dialkylbenzenes. Prevention of side reactions and improvement of selectivity for para-substituted dialkylbenzenes can be achieved by reducing the density of strong acid sites on the zeolite surface and changing its porous structure [5,11,35].

In the TPD spectrum of HZSM-5 zeolite (Figure 3), two peaks are observed: a low-temperature peak in the region of 100-300 °C with a peak maximum temperature of T_{max}=220 °C, which is related to the desorption of ammonia mainly from weak Lewis acid sites, and a high-temperature peak in the region of 300-600 °C with T_{max}=408 °C, which is related to the desorption of ammonia mainly from strong acid sites, which are hydrogen ions of bridging hydroxyl groups.

The number of strongly acidic sites decreases significantly with increasing boron concentration in the catalyst. On samples containing 3.0 wt.% and 5.0 wt.% boron, the high-temperature peak (408 °C) of ammonia desorption disappears, while

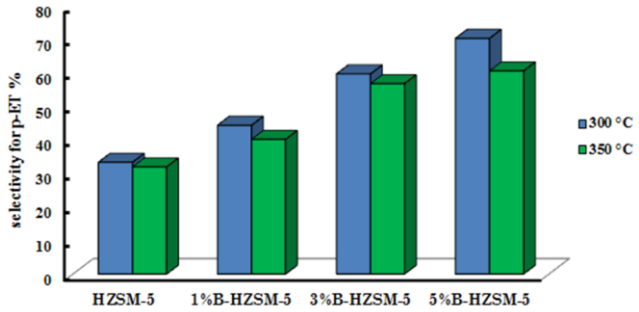

Figure 2. Effect of boron concentration on p-ET selectivity. Reaction temperatures are 300 °C (1) and 350 °C (2).

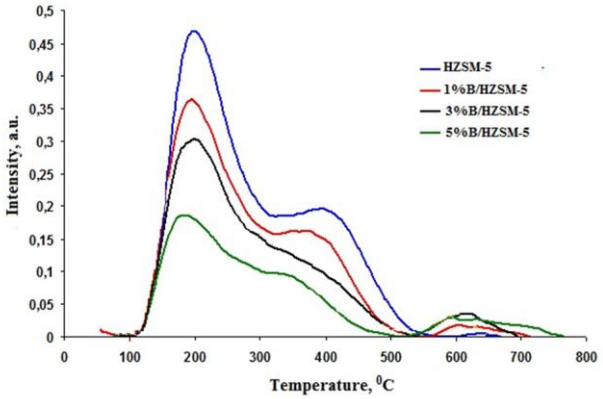

Figure 3. Demonstrates the effect of boron concentration on the strength of acid.

Table2. Effect of modification on the acid characteristics of 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
HZSM-5	392	232	624
1%B-HZSM-	365	186	551
3%B-HZSM-5	325	162	487
5%B-HZSM-5	178	79	257

the low-temperature peaks shift slightly to the low-temperature region (196-200 °C), but are well preserved. Boron concentration significantly affects the density of strong acidic sites. On the sample containing 5.0 wt.% boron, the density of strong acidic sites decreases to 79 µmol/g.

The analysis of IR-Py-spectra of non-modified and boron-modified HZSM-5 zeolite indicates a significant decrease in the peak at 1540 cm^{-1}, representing the Brønsted acid centers [27] as a result of modification of the HZSM-5 zeolite, while the Lewis acid centers (1477 cm^{-1}) [27] decreased insignificantly (Figure 4). From IR-Py-spectra (Figure 4) before and after modification of zeolite HZSM-5 with boron we can conclude that the decline in the density of strong acid sites is due to the replacement of proton sites of zeolite by borate groups – $B(OH)_2$. Substituting Brønsted hydroxyl groups localised on the outer surface, pore mouths and in the zeolite channels by – $B(OH)_2$ groups reduces the density of strongly acidic sites. This is explained by the fact that the formed terminal hydroxyl groups in the $–H_2BO_2$ grouping have lower acidity, as in the case of zeolite modification with phosphoric acid, than the bridging hydroxyl groups of zeolite [36]. The effect of modification on the structural characteristics of zeolite HZSM-5 is given in Table 3.

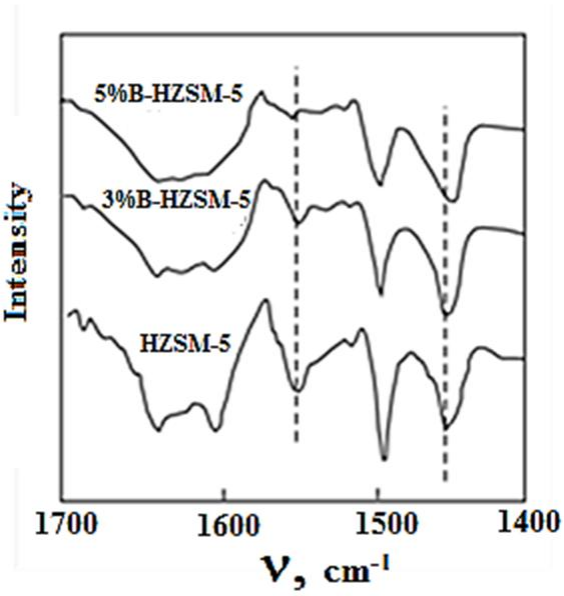

Figure 4. IR-Py-spectra before and after modification of the HZSM-5 zeolite with boron.

It can be seen that the specific surface area, micropore area and total pore volume decrease with increasing boron content in the samples. It is known that selectivity to para-isomers of aromatic hydrocarbons is determined by the size of pores through which molecules of certain sizes and shapes pass [9,10,14]. The occurring narrowing of zeolite channels as a result of boron modification creates additional steric hindrances for the diffusion of bulkier molecules of o- and m-ET (0.62-0.66 nm) from the zeolite channels, which leads to an increase in the para-selectivity of the catalyst.

However, as can be seen from Table 3, increasing the boron content in zeolite also leads to an increase in the ratio of mesopore specific surface area to BET surface area (S_{mezo}^b/S_{BET}^a) and the ratio of mesopore volume to total pore volume (V_{mezo}^b/V_{total}^b). The highest ratio (S_{mezo}^b/S_{BET}^a) and (V_{mezo}^b/V_{total}^b) achieved in the sample containing 5.0 wt.% boron. The changes occurring are obviously related to the localisation of modifier nanoparticles in the pore entrance or channels, as well as on the surface of zeolite crystals [19,32,37]. This is also confirmed by studying the nitrogen adsorption/desorption isotherms for unmodified and modified samples. The isotherms of the samples differ not only in shape but also in the volume of nitrogen adsorbed (Figure 5).

In the studied samples, the horizontal deviations from a straight line indicate that both samples have micropores [38,39]. In the range of P/P_0 = 0.4-0.9, the investigated samples show obvious hysteresis loops, indicating the presence of mesopores [40]. However, the adsorption/desorption isotherm of the modified 5.0 wt.% boron shows a steeper rise of the isotherm and widening of the hysteresis loop, which proves the increase in the proportion of mesopores in the total pore volume as a result of modification. Decrease in the density of strong acid sites, reduction in pore volume and enhancement in mesoporosity as a result of modification are decisive in increasing the para-selectivity and stable operation of the zeolite catalyst. Zeolite catalysts with moderate acid sites and high mesoporosity provide much longer catalyst lifetime. Figure 6 shows the higher stability (50 h) of the catalyst modified with 5 wt.% boron.

Table 3. Effect of modification on the structural characteristics of catalysts. ([a] –BET Method, [b] – BJH-method, [c]- *t*-plot method)

Catalyst	S_{BET}^a ($m^2 \cdot g^{-1}$)	V_{total}^b ($cm^3 \cdot g^{-1}$)	V_{micro}^b ($cm^3 \cdot g^{-1}$)	V_{mezo}^b ($cm^3 \cdot g^{-1}$)	S_{micro}^c, ($m^2 \cdot g^{-1}$)	S_{mezo}^b/S_{BET}^a, %	V_{mezo}^b/V_{total}^b, %
HZSM-5	288	0.24	0.178	0.062	140	52	25.8
1%B-HZSM-5	270	0.23	0.167	0.063	135	53	27.4
3%B-HZSM-5	236	0.21	0.142	0.068	124	55	32.4
5%B-HZSM-5	220	0.18	0.106	0.074	112	59	41.1

4. Conclusion

The selectivity for ethyltoluene and p-ethyltoluene in the methylation of ethylbenzene in the presence of zeolite HZSM-5 is determined by the concentration of boron, acidity and porous structure of the catalyst. As a result of modification and heat treatment, due to the localization of the modifier on the outer surface and in the micropores of the zeolite, the interaction of modifier particles with strong Brønsted acid centers occurs, which leads to the formation of new types of low-strength acid centers, narrows pores and increases its mesoporosity, which create steric obstacles for the diffusion of bulk m- and o-isomers of ethylbenzene and ensure the selective production of p-ethyltoluene. High selectivity for p-ethyltoluene (60.5-70.2 %) with ethylbenzene conversion (14.7-18.4 %) in the reaction temperature range of 300-350 °C is demonstrated by the 5%-B/HZSM-5 catalyst.

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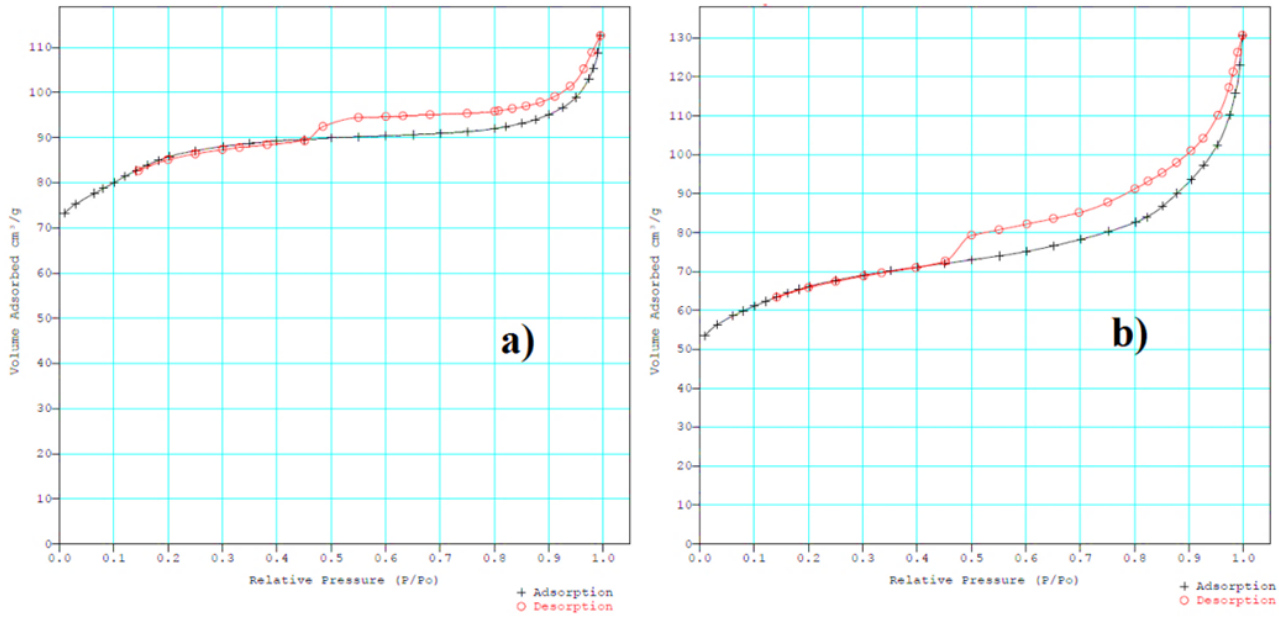

Figure 5. Nitrogen adsorption/desorption isotherms for unmodified HZSM-5 (a) and modified samples 5%-B/HZSM-5 (b).

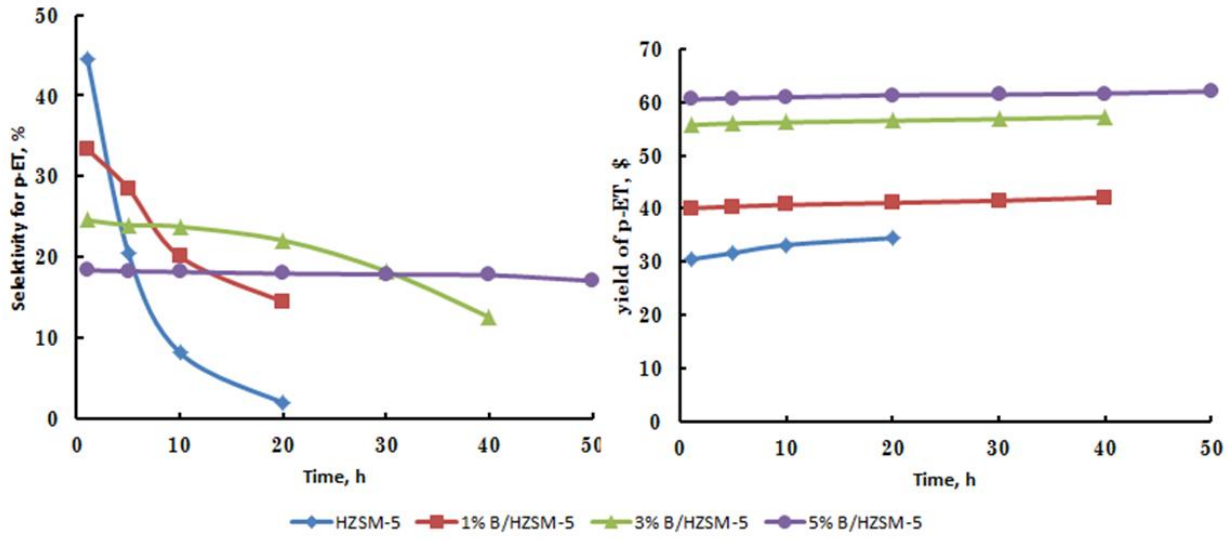

Figure 6. Dependence of toluene conversion and selectivity to p-ethyltoluene on catalyst reaction time.

CRediT Author Statement

T.O. Gahramanov: Investigation, Data Curation, Project Administration. A.Z. Mammadova: Investigation, Formal Analysis, Supervision. N.F. Akhmedova: Investigation, Writting Draft Preparation, Data Curation, Software. S.E. Mammadov: Conceptualization, Methodology, Resources, Review and Editing, F.Sh. Kerimli: Methodology, Investigation, Resources, Validation. E.İ. Ahmadov: Review and Editing, Validation. All authors have read and agreed to the published version of the manuscript.

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