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Vapour phase Guerbet condensation of ethanol to 1-butanol on CsX zeolite

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Nowadays, the conversion of ethanol into valuable chemical products is getting wider application. One of such promising processes is Guerbet condensation of alcohols, which permits the obtaining of 1-butanol from renewable raw materials that are alternatives to petroleum ones. Oxide systems combining acid and basic sites in their composition are promising catalysts for such a transformation. In this study, the efficiency of the magnesium-aluminum oxide and zirconium-oxide catalysts was compared to the activity of the cesium form of X-type zeolite produced by hydrothermal ion exchange in the condensation of ethanol to 1-butanol. The integrity of the zeolite structure was confirmed by using the XRD and XRF analysis, as well as by the IR spectroscopy. The depth of exchange of native sodium for cesium was 82 %. It was also found that cesium cations are localized only in ion-exchange positions of faujasite, in places SIII (supercages) and SI' (sodalite cages). CsX zeolite acid to basic sites ratio was found to be close to optimal for this reaction. Cesium-containing zeolite at 300 °C shows ethanol 35-55 % conversion and 20-25 % selectivity for 1-butanol, which is higher than the same characteristics for zirconium samples, but slightly inferior to magnesium-aluminum oxide catalysts. The obtained results indicate the promising use of zeolites of a similar nature in the process of condensation of ethanol to 1-butanol.

Keywords: ethanol condensation, 1-butanol, acid sites, basic sites, 1-butanol yield, process selectivity

Introduction

1-Butanol is widely used as a solvent, extractant, and raw material for the production of methacrylates and butyl acrylate for coatings, enamels, and varnishes [1, 2]. A relatively new field of application for 1-butanol is its addition to gasoline instead of ethanol [2-5]. The world production of butanol-1 in 2017 was about 5.4 million tons, but according to forecast estimates, in the near future, the demand for butanol will reach about 20 % of world fuel needs [6].

Traditionally, 1-butanol is obtained in the process of hydroformylation of petroleum-derived propylene with subsequent hydrogenation of the obtained 1-butanol under high pressure conditions (~ 30 MPa) using cobalt (Rh or Ru) catalysts in the first stage and nickel catalysts in the second stage [7]. Another commercial approach to obtaining butanol is the fermentation of carbohydrates by anaerobic bacteria of the *Clostridia* class, the ABE (acetone-butanol-ethanol) process. The main problems with the latter are the significant duration of the process, the high cost of the substrate, and the low concentration of the obtained biobutanol [6, 8].

Guerbet condensation of alcohols, consisting of the doubling of the alcohol chain, is a promising method of converting light alcohols into higher ones [9]. Currently, industrial production of higher alcohols by Guerbet condensation is carried out on combined catalysts (liquid alkalis together with a solid catalyst based on transition metals) [10-12]. Its implementation requires high-cost equipment design for separation, purification, recovery, and processing of waste, as well as the use of catalysts with precious

metals. As a result, the production of alcohols by Guerbet condensation is so far only profitable for the particularly valuable higher alcohols C₈₊.

Therefore, there is considerable interest in the development of cheaper solid catalysts that would allow the process to be implemented in flow mode, eliminating the problems of separating them from the reaction mixture and the corrosion of the equipment. On the one hand, carrying out the reaction in the vapor phase would allow the process to be implemented at atmospheric pressure, which, accordingly, would have fewer technological limitations than in liquid-phase systems with high pressure [9].

Systems based on MgO-Al₂O₃ and ZrO₂ are considered promising for the development of effective catalysts for the production of 1-butanol, for which there is a possibility of targeted regulation of structural-dimensional and acid-base characteristics at the synthesis stage by changing the ratio of active components in the composition of catalysts, the conditions of their formation, and also by introducing modifying additives [13-15].

Works [13-15] show that for the effective conversion of ethanol into 1-butanol, the MgO-Al₂O₃ binary oxide catalyst must include Lewis acid-base pairs (Mg-O-Al) formed during the calcination of hydrotalcites. The highest yield of 1-butanol (18 %) was achieved in the presence of a catalyst with a Mg/Al ratio of 2. It was found that the modification of Mg-Al-oxide systems with cerium cations leads to an increase in the concentration of acid and basic sites on the surface of the catalysts, which ensures an increase in the specific rate of 1-butanol formation compared to the unmodified catalyst.

In paper [16] different metals (Cu, Ni and Co), at various metal loadings were deposited on the alumina support. Consequently, the catalytic reactions were carried out in a continuous laboratory-scale fixed bed reactor operated at 240 °C and 70 bar [16]. On the best catalysts, the selectivities towards 1-butanol close to 70 % were reached, while the ethanol conversions typically varied between 10 and 30 %. The latter strongly depends on the metal applied.

Rubidium-modified zeolites were also studied as catalysts for gas-phase condensation of lower alcohols [17, 18]. The selectivity for butanol-1 was 40, 37, and 20 % on rubidium-modified zeolites Rb-LiX, Rb-NaX, and Rb-KX, respectively. At the same time, samples without rubidium only catalyzed dehydrogenation.

Selective zeolite catalysts for the alkylation of toluene with methanol in the side chain [19, 20] also possess a combination of acidic and basic active sites. Moreover, according to the proposed reaction mechanism, acid sites are responsible for alkylation of toluene in the benzene ring, while basic ones are necessary for alkylation in the side chain. Faujasite-type zeolites modified with cesium act as effective catalysts for this transformation [21].

Therefore, the purpose of this work was to evaluate the efficiency of a cesium-containing zeolite of the faujasite-type in the gas-phase conversion of ethanol to 1-butanol, as well as to compare its activity with magnesium-aluminumoxide and zirconiumoxide systems.

Experimental

Catalyst synthesis

X-type zeolite (SiO₂/Al₂O₃ = 2.3, TU 38.102168-85, static capacity for water vapor: 0.30 cm³/g, for benzene vapor: 0.29 cm³/g, fraction 0.5-1 mm) was subjected to a two-time exchange for cesium cations from a 1 N aqueous solution of nitrate (chemically pure, TU 6-09-437-83) for cesium form synthesis. The ratio of solid to liquid phases in hydrothermal ion exchange was 1:5. Exchanges were carried out sequentially at 140-150 °C for 2 h in a rotating stainless steel autoclave with intermediate

washing with distilled water. The elevated temperature was used to destroy the hydrate shell of the introduced cations and thereby increase the depth of the exchange. After completion of the procedure, the sample was thoroughly washed with distilled water until the absence of NO_3^- ions and dried in air.

Catalyst characterization

^{23}Na , ^{27}Al , ^{133}Cs NMR spectra were recorded on an AVANCE 400 spectrometer (Bruker). Recording was carried out in accumulation mode at frequencies ν 105.842, 104.261, and 52.482 MHz, respectively. Chemical shifts δ were determined relative to the standards: solutions of NaCl , $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and CsNO_3 . The sample was placed in borate glass ampoule (5 mm diameter).

FTIR spectroscopy. IR spectra in the region of framework vibrations ($400\text{--}1200\text{ cm}^{-1}$) were recorded on an IR-Fourier spectrometer IR Affiniti-1s (Shimadzu, Japan) with a Specac Quest GS 10801-B disturbed total internal reflection (ATR) attachment. The sample was applied to the surface of the diamond prism of the ATR attachment, and the spectrum was recorded. The spectral resolution was 2 cm^{-1} .

N_2 adsorption. Low temperature nitrogen adsorption/desorption isotherms for samples were measured on a Quantachrome Autosorb NOVA 1200e® automatic sorbometer (USA) after thermal dehydration at $180\text{ }^\circ\text{C}$ for 20 hours. Utilizing the NOVAV in 11.04 software, the parameters of the porous structure were computed.

X-ray fluorescence (XRF) analysis. The elemental analysis of the samples were carried out by XRF spectroscopy on the Oxford Instruments X-Supreme 8000 analyzer (Great Britain) using the mineral analysis program.

XRD. The XRD patterns of the zeolite sample was recorded on a DRON-4-07 diffractometer in the $\text{CuK}\alpha$ radiation of the anode line with a Ni filter in the reflected beam in the Bragg-Brentano shooting geometry in the angular range of $3.5\text{--}80$ degrees 2θ with a step of 0.05 degrees and exposure at a point of 1 sec.

Catalytic investigations

Catalytic studies were carried out in a flow unit under atmospheric pressure in a quartz reactor (internal diameter 10 mm) with a fixed catalyst layer (0.5 g, 0.25-0.5 mm) at 300, 325 and $350\text{ }^\circ\text{C}$. Ethanol (azeotrope 95.6 %, the rest H_2O) was fed into the evaporator using a syringe infusion pump ($\text{WHSV} = 0.14\text{ g}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$). Argon was used as a carrier gas at a flow rate of 10 ml/min. Reactants and reaction products were analyzed on a NeoCHROM gas chromatograph equipped with a flame ionization detector and a capillary column (HP-FFAP, $50\text{ m}\times 0.32\text{ mm}$).

Catalytic activity of the catalysts was characterized by ethanol conversion (X_{EtOH}):

$$X_{\text{EtOH}} = \frac{n_{\text{EtOH}}^0 - n_{\text{EtOH}}}{n_{\text{EtOH}}^0} \cdot 100, \text{ mol } \%,$$

where n_{EtOH}^0 is the initial amount of moles of ethanol in the feed, mol/h; n_{EtOH} is unreacted ethanol at the exit of reactor, mol/h.

Selectivity to products (S_i) and butanol yield (Y_{BuOH}) have been calculated in accordance with:

$$S_i = \frac{n_i}{(n_{\text{EtOH}}^0 - n_{\text{EtOH}})} \cdot 100, \text{ mol } \%,$$

$$Y_{\text{BuOH}} = \frac{X_{\text{EtOH}} \cdot S_{\text{BuOH}}}{100}, \text{ mol } \%,$$

where n_i is amount of moles of identified product.

The productivity of the catalyst has been calculated using the formula:

$$P_{\text{BuOH}} = \frac{Y_{\text{BuOH}} \cdot W \cdot 0.8}{100}, \text{ mmol}/\text{g}_{\text{cat}}\cdot\text{h}$$

where Y_{BuOH} - yield of butanol, mol %; W - ethanol weight hourly space velocity $\text{mmol}_{\text{EtOH}}/(\text{g}_{\text{cat}} \cdot \text{h})$, 0.8 - is the maximum possible amount of butanol (g) that can be produced from 1 g of ethanol.

Results and Discussion

Catalyst characterization

Based on the X-ray fluorescence analysis data, the SiO_2 to Al_2O_3 ratio in the zeolite framework and the degree of cesium exchange were calculated to be 2.5 and 82 %, respectively. Therefore, during the ion exchange procedure, the chemical composition of the aluminosilicate framework of the zeolite undergoes only minor changes.

The porous characteristics of the original sodium form and the exchanged cesium form were investigated by the low-temperature nitrogen adsorption/desorption. The calculated characteristics are summarized in the Table. 1. As can be seen, as a result of the exchange of native sodium for cesium, the BET surface (S^{BET}) and the surface of micropores (S_{micro}) are significantly reduced. Correspondingly, the volumes of total pores (V_{Σ}) and micropores ($V_{\text{micro}}^{\text{t}}$) also decrease. These effects can be related, firstly, to the destruction of the sample and, secondly, to the almost twice larger size of the effective diameter of the cesium cation (3.38 Å) compared to the sodium cation (1.9 Å). The second one is more realistic.

Table 1. Characteristics of porous structure of zeolite samples according to low temperature nitrogen adsorption/desorption

Sample	S^{BET} , m^2/g	S_{micro} , m^2/g	$V_{\text{micro}}^{\text{t}}$, cm^3/g	V_{Σ} , cm^3/g	$V_{\text{micro}}/V_{\Sigma}$	R, nm
NaX	689	669	0.279	0.323	0.86	0.9
CsX	345	329	0.140	0.180	0.79	1.0

The degree of exchange for cesium cations and the integrity of the crystal structure of the CsX catalyst were confirmed by NMR.

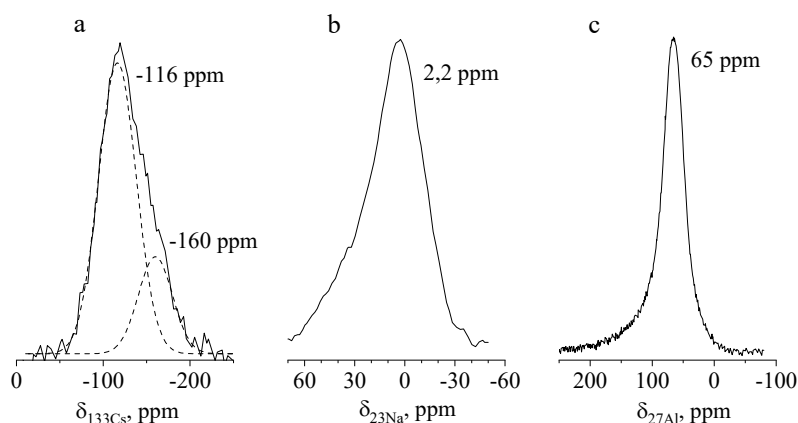


Fig. 1. ^{133}Cs (a), ^{23}Na (b), and ^{27}Al (c) NMR spectra for CsX sample

The ^{133}Cs spectrum of the CsX sample is a superposition of two signals with chemical shifts of -116 ppm and -160 ppm (Fig. 1 a), which indicates the presence of cesium in the sample in ion exchange positions. The first intense signal corresponds to cesium cations in the SIII positions of the supercages of the faujasite structure, and the second to cations in the SI' positions in the sodalite cages [22]. The ^{23}Na spectrum (Fig. 1 b) is dominated by the signal ($\delta = 2.5$ ppm) corresponding to residual sodium cations in

hexagonal prisms (SI sites) [23]. Significant in intensity signals, which would indicate the presence of sodium cations in sodalite cages and/or in supercages, are not observed in the ^{23}Na NMR spectrum of the CsX sample. All this confirms the high degree of exchange of the original sodium cations for cesium cations.

The only signal of tetrahedrally coordinated aluminum present in the ^{27}Al spectrum (Fig. 1 c) ($\delta = 65$ ppm [24, 25]) proves the integrity of the crystal structure of the sample.

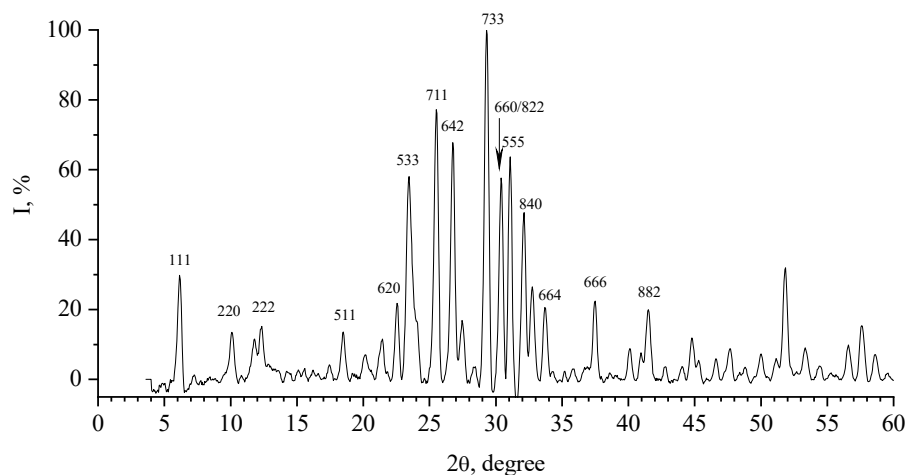


Fig. 2. XRD pattern of CsX sample. Main characteristic lines in accordance with [26, 27]

The main lines of the XRD pattern (Fig. 2) correspond to the faujasite zeolite phase, however due to the change in the sample cationic composition and the addition of cesium cations, there is a redistribution of the strength of several reflexes in comparison to the native sodium form [26]. There were no cesium-containing compounds in the crystalline form in the sample.

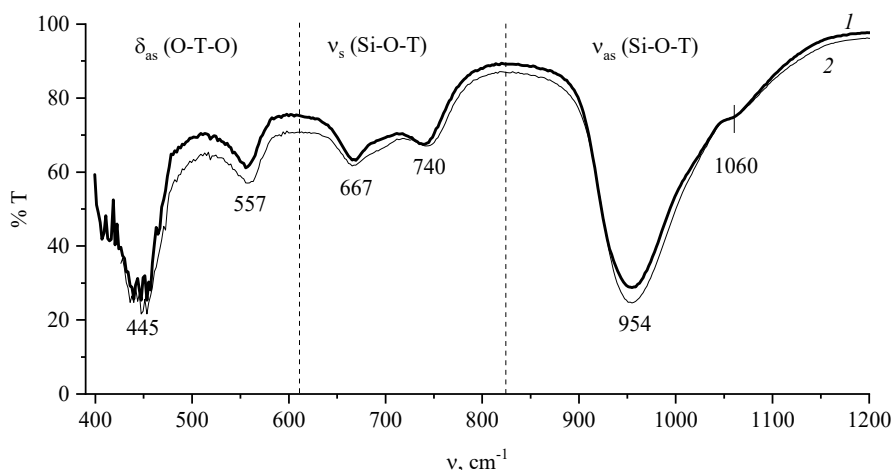


Fig. 3. IR spectrum of CsX (1) sample in comparison with spectra of origin NaX (2) zeolite in the region of lattice vibrations

The analysis of IR spectra (Fig. 3) showed the preservation of the type X zeolite characteristic absorption bands [28] and the invariance of the zeolite structure after ion exchange. In particular, in the spectrum of the CsX sample compared to the spectrum of the original NaX zeolite, there is no high-frequency shift of the absorption band related to asymmetric valence vibrations of T-O bonds of tetrahedra (954 cm^{-1}), and therefore, structural dealumination of the CsX sample does not occur. Also, the absorption

band in the region of 900 cm^{-1} , which is often associated with various types of structural defects, is not observed in the CsX spectrum.

Catalytic properties

Before the reaction, the catalyst was activated by dehydration in an argon flow up to $500\text{ }^{\circ}\text{C}$ with exposure for 1 h. After cooling to $300\text{--}350\text{ }^{\circ}\text{C}$, the reaction mixture was fed. Ethanol conversion and selectivity for the main products were calculated based on their quantities recorded in the time period from 0.5 to 6 h from the start of the experiment.

The dependences of ethanol conversion and product selectivity on time on stream (TOS) for 6 h are shown in Fig. 4. As is known, in addition to the target reaction of the formation of 1-butanol (BuOH), a number of other side transformations occur [13–15]. The target product 1-butanol reacts both with itself (self-condensation) and with the original ethanol (cross-condensation) with the formation of higher alcohols: 2-ethyl-1-butanol, 1-hexanol (HeOH), 2-ethyl-1-hexanol, and 1-octanol. Dehydration of 1-butanol and the formation of a mixture of butenes (But) also occur. In addition, ethylene (Et), light C_{2-4} transformation byproducts, acetaldehyde, diethyl ether, acetone, ethyl acetate, heavier C_{6+} condensation products (higher aldehydes, ketones, and aromatics) were recorded among the byproducts.

The initial conversion of ethanol (TOS = 0.5 h) at 300 , 325 , and $350\text{ }^{\circ}\text{C}$ in the presence of the CsX catalyst has close values of 31–35 %. At $350\text{ }^{\circ}\text{C}$, X_{EtOH} significantly increases at TOS = 1 h to 58 %, while at 300 and $325\text{ }^{\circ}\text{C}$, the ethanol conversion values during the experiment do not exceed the initial ones. For all investigated temperatures, a decrease in X_{EtOH} over time is observed, presumably due to catalyst deactivation.

The highest selectivity for 1-butanol of 31 % is achieved at $300\text{ }^{\circ}\text{C}$, but it decreases over time. Also, the yield of the target product is very small due to low ethanol conversion. At $350\text{ }^{\circ}\text{C}$, the selectivity for 1-butanol is stable over time at a level of 20 %, and the yield is 10 % (TOS = 2 h). In general, it was established that in the presence of CsX zeolite, there is a predominant formation of C_{6+} products of deep condensation—further transformations of 1-butanol with ethanol and other compounds with the formation of higher oxygenates (aldehydes/ketones) and possibly aromatics.

The results of catalytic tests on the synthesized sample are summarized in Table 2 in comparison with magnesium-aluminum and zirconiumoxide catalysts [13–15].

Table 2. Catalytic properties of zeolite CsX and comparison samples (Mg-Al [13], Zr [14, 15])

Sample	TOS, h	X_{EtOH} , mol %	S_{BuOH} , mol %	Y_{BuOH} , mol %
CsX ¹	2	50	20	10
CsX ¹	4	43	23	10
CsX ²	2	15	26	4
CsX ²	4	13	22	3
Mg-Al-2 ²	2	27	65	18
Mg-Al-Ce-2 ²	2	20	70	14
Mg-Al-Ce-1 ²	2	12	68	8
ZrO ₂ ¹	2	10	20	2
ZrO ₂ -Ce-10 ¹	2	13	32	4.2

1 – $350\text{ }^{\circ}\text{C}$; 2 – $300\text{ }^{\circ}\text{C}$

As can be seen, cesium-containing zeolite X occupies an intermediate position between magnesium-aluminumoxide samples and zirconium samples in terms of its efficiency, demonstrating at $350\text{ }^{\circ}\text{C}$ 1-butanol yields at the level of 10 % with selectivity for 1-butanol about 20 % at medium level of ethanol conversion (43–50 %).

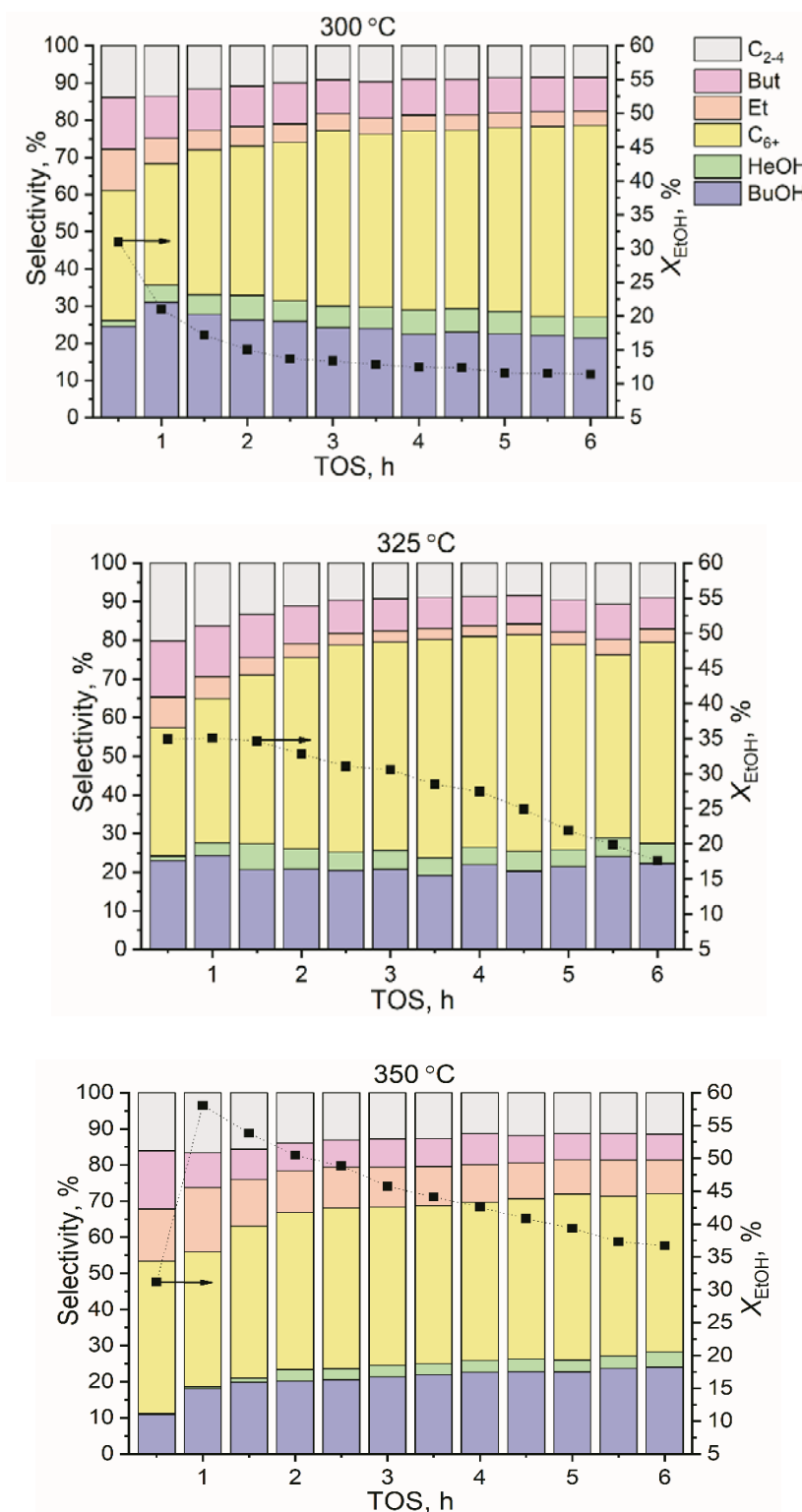


Fig.4. Catalytic performance of CsX sample in ethanol conversion in a flow mode during 6 h time on stream

Since the presence of both acidic and basic sites in the catalysts is necessary for the targeted transformation, it was interesting to compare the samples according to this indicator. Table 3 shows the acid to basic sites ratio determined by using desorption of ammonia and carbon dioxide for the comparison samples, as well as the zeolite sample. For the latter, this ratio is given based on the yield of the products of alkylation of toluene with methanol in the side chain (basic sites) and into the benzene ring (acid sites) [21], which was stable in the temperature range from 400 to 500 °C.

Table 3. Acid-to-basic sites ratio (C_a/C_b) in the samples

Sample	C_a/C_b	Sample	C_a/C_b
CsX	3.2 *	Mg-Al-2	2.9
ZrO ₂	1.9	Mg-Al-Ce-2	3.0
ZrO ₂ -Ce-10	1	Mg-Al-Ce-1	2.6

* calculated using data for alkylation of methanol in side chain and in the benzene ring

The highest yields of 1-butanol are characterized by samples in which acid sites three times predominate over basic ones (Mg-Al-2 and Mg-Al-Ce-2). Significantly smaller ratios for zirconium samples significantly worsen their activity. On the other hand, the synthesized zeolite sample has a slightly higher than optimal proportion of acid sites, which is obviously related to its intermediate activity. The productivities of the catalysts were 0.3-0.4, 0.24, and 0.04-0.06 mmol/g_{cat}/h for Mg-Al-oxides, CsX, and ZrO₂-based catalysts, respectively.

Thus, taking into account the good performance of cesium-modified zeolite X, the latter can be used as a basis for further research. The additional introduction of cesium by impregnation, as well as the addition of cerium, which performed well on magnesium-aluminum and zirconium oxide samples, also look promising.

Conclusions

According to the results of X-ray diffraction and X-ray fluorescence analysis, NMR, and IR spectral studies, the CsX zeolite synthesized by ion exchange with a high degree of sodium to cesium exchange retained its crystalline structure. In particular, in the ¹³³Cs NMR spectrum of zeolite, there are two signals of chemical shifts, -116 and -160 ppm, reflecting cesium cations in supercages and sodalite cages (sites SIII and SI', respectively). The chemical shift at 2.5 ppm reflects residual sodium cations in hexagonal prisms. Signal of tetrahedrally coordinated aluminum confirms the high crystallinity of the sample. The latter is confirmed by diffraction data and IR spectra of vibrations in the region of the zeolite framework. CsX zeolite demonstrates results comparable to magnesium-aluminumoxide systems in the conversion of ethanol to 1-butanol in flowing vapor phase conditions, which indicates the perspective of further research on similar nature zeolite samples.

The obtained results confirm that the number of acid sites in the catalyst should be three times greater than the number of basic sites for an effective course of ethanol conversion into the target direction of the formation of 1-butanol and the minimization of side reactions.

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Парофазна конденсація етанолу до 1-бутанолу за Гербе на цеоліті CsX

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Перетворення етанолу у цінні хімічні продукти набуває все ширшого застосування. Одним із таких перспективних процесів є конденсація спиртів за Гербе, що дозволяє отримувати 1-бутанол із альтернативної нафтової відновлювальної сировини. Багатообіцяючими каталізаторами такого перетворення є оксидні системи, що поєднують у своєму складі кислотні та основні центри. У даній роботі оцінено активність у конденсації етанолу до 1-бутанолу цезієвої форми цеоліту типу X, одержаної гідротермальним іонним обміном, а також проведено порівняння її ефективності з магній-алюміній-оксидними та цирконій-оксидними каталізаторами. Цілісність цеолітної структури підтверджено методами рентгенофазового та рентгенофлуорисцентного аналізу, а також ІЧ-спектроскопії. Ступінь обміну натрію на цезій склав 82 %. Знайдено також, що катіони цезію локалізовані лише у іонообмінних позиціях фожазиту – в місцях SIII (великі порожнини) та SI (содалітові комірки). Встановлено, що цеоліт CsX має близькі до оптимального для даного перетворення співвідношення між кількістю кислотних та основних центрів. Цезійвмісний цеоліт за 350 °C демонструє 35-55 % конверсію етанолу та 20-25 % селективність за 1-бутанолом, що є вищим за показники для цирконієвих зразків, але дещо поступається магній-алюмінієвим каталізаторам. Одержані результати свідчать про перспективність використання цеолітів близької природи у процесі конденсації етанолу до 1-бутанолу.

Ключові слова: конденсація етанолу, 1-бутанол, кислотні центри, основні центри, вихід 1-бутанолу, селективність процесу