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EFFECTIVE MODIFICATION OF NaX ZEOLITE WITH Ni METAL AND ITS CATALYTIC PERFORMANCE IN OXIDATION OF ETHANOL

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Abstract. The presented data showed that the chemical treatment of NaX with Nichel medium resulted in the formation of highly developed hierarchical structures. The esterification of the hydroxyl groups by metal allowed modifying the hydrophobicity of zeolite surface and obtaining truly micro/mesoporous material. The preservation of microporous characteristics was confirmed by XRD and low temperature nitrogen sorption studies. Detailed information on acidic properties of mesoporous titanosilicalites was delivered by IR studies of ethanol oxidation and implicitly from EPR investigations. Well-developed internal microporosity together with the retaining of atoms in tetrahedral framework positions offered higher catalytic activity for the conversion of ethanol molecules than the native microporous of zeolite.

Keywords: *Oxidation of alcohols, zeolite, catalytic activity, Ni-modified zeolites, ethanol oxidation.*

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1. Introduction

Determinants of the catalytic activity of zeolites and their structural analogues are the nature and accessibility of catalytic sites influenced by the textural properties. The architecture of the zeolite/zeotype framework also influences its catalytic potential by, related to the confinement effect, method of adsorption, activation and transformation of reactant molecules. Changes in grain structure and/or morphology microporous material, occurring at the level of the pore hierarchy are direct translates into the speciation of its active centers and consequently, activity selectivity and viability as a catalyst. In this light, the main stream of work is determined by the study of the influence of parameters structural and textural hierarchical zeolites/zeotypes on center speciation active, which, as it was assumed, will be reflected in catalytic activity investigated structures with a hierarchical intra- or intergranular pore system character. The main modification path is demetallation processes based on desilication, dealumination, steaming and sequential combinations of the above. Demetallation is an easily accessible and economical tool to obtain intragranular microporosity. The idea behind this stage of research is willingness expanding knowledge about the hierarchy of zeolites that differ in window size and

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content aluminum in the structure, for which similar research has not been conducted so far or not brought the expected results. To check its effectiveness transferability of desilication methods to zeotype materials that do not have trivalent atoms in its structure Among features responsible for unique catalytic properties, the NAX zeolite shows versatility towards isomorphous substitution of Al and/or Si atoms by metal ions such as (Cronstedt, 1756; Masters & Maschmeyer, 2011). Thus, the NaX structure is an excellent starting point for the developing of the group of new zeotype catalysts where one of the most important materials is Na. Many efforts have been devoted to introducing intracrystalline microporosity into NaX structure in order to reduce the micropore environment restrictions, e.g. modified crystallization methods (Breck *et al*., 1956a), hard (Breck *et al*., 1956b) and soft (Weisz & Frilette, 1960) templating and demetallation (Argauer & Landolt, 1972; https://www.iza-structure.org/databases/). In group of post-synthetic methods of modification of zeolitic materials one of the most effective and most economical seems to be desilication process. The desilication is identified with the process of selective extraction of silicon from the framework in the alkaline medium. The effectiveness of Si extraction from the framework depends on a number of parameters, including the value of Si/M ratio, framework topology, type and concentration of the desilication agent, temperature and time of process (Smith, 1984). There is common agreement that nickel in the active catalyst is present in the tetrahedral environment, both in microporous and mesoporous catalysts. Thus all modification approaches are focused on retaining of Ni atoms in tetrahedral environment.

The interaction of alcohols with oxide surfaces, in particular with SiO_2 and Al_2O_3, as well as with zeolites has been extensively investigated (Qureshi *et al*., 2022). Regardless of the weak proton-donor character of the SiO_2 surface it has been found that, even at room temperature, a chemisorption of methanol led to the formation of the single bond ethoxy groups (Hölderich & Van Bekkum, 2001). The esterification of the silanol groups was reported to be enhanced as the temperature increased and the triple bond bond were resistant to temperatures of ~400°C in vacuum or 150°C in air (He & Liu, 2014; Zhang *et al*., 2020). This work was attempted to show that the chemical treatment of NaX with ethanol medium resulted in the formation of intracrystalline microporosity. As the formation of ethoxy species strongly modified the hydrophobicity of the surface such procedure was employed for the zeolite material influencing its utility for desilication process. Additionally, the textural and acidic characteristics were faced with catalytic data of ethanol oxidation processes.

2. Methods

The results obtained from the study of the activity of the synthesized catalyst samples in the process of ethanol oxidative conversion using different method were given.

In the study, catalyst samples were prepared on the basis of NaX zeolite using different modification methods. The reaction products were analyzed using a Clarus 580 gas chromatograph (PerkinElmer, USA) equipped with a TCD detector and an Elite Plot Q capillary column 30 mm long and 0.53 mm in diameter. TOF (Turnover Frequency) values were calculated.

The RF was used to obtain NaX zeolite catalysts containing Ni-transition metals. For this, the nitrate salt solution of the appropriate metal was impregnated on the initial zeolite and then the mass was dried at a temperature of 100C. Then the obtained mass was heated at a temperature of 300C until the salt was completely decomposed. In the

end, the obtained mass was baked at 550C for twelve hours and catalyst samples were obtained. Thus, using the impregnation method, catalyst samples containing 1%, 2.5% transition metal (Ni) were synthesized. To prepare the synthesized samples for the process, they were first pelletized and then crushed into 1-2 mm particles.

2.1. Research of the synthesized catalyst samples by RF-analysis, IR-spectroscopy, SEM-analysis methods and the specific surface of the catalyst samples was determined.

Using the nitrogen thermal desorption method, the specific surface of some catalyst samples used in the process was studied. Using the differential-thermal analysis method, the catalysts were the study was conducted both before and after the oxidation process of ethanol. Also, thermal analysis was conducted in "STA 6000 Perkin Elmer" thermal analyzer. The mass of the samples was taken between 7-10 mg. The heating range was 25-1000°C and the rate of heating was 40°C per minute. Catalyst samples were studied by IR-spectroscopy method. IR Fourier absorption spectra were recorded in the range of 4000-400 cm^{-1} at room temperature on a Varian 640FT-IR spectrometer. For this, the powdered samples were made into tablets with a thickness of 50-100 μm. NaX zeolite catalysts and all new modified catalizies were studied using the X-ray analysis method. During these studies, the phase composition of the catalysts, the amount and size of the metal in the metal oxide phase were determined. iC 3000 from Thermos Scientific X-ray diffractometer D2, Bruker, X-ray fluorescence microscope XGT-7000, Horiba, Japan and EMX Micro, Bruker, Germany were used to determine the phase composition of the catalysts, the distribution of active components in the catalyst and magnetic properties during redox treatments, exposure to the reaction medium, before and after the catalytic cycle, respectively.

2.2. Chromatographic analysis of the products obtained from the process was carried out. Using the EPR- analysis method, the relationship between the catalytic activities of the studied catalyst samples and the magnetic properties was determined.

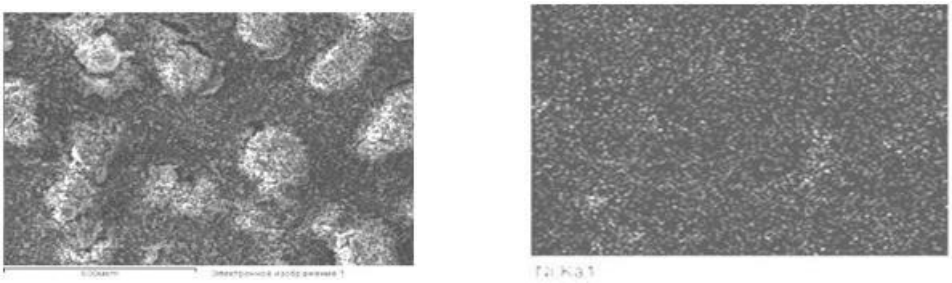
In the process, the chromatographic method was used for the analysis of initial substances and reaction products. Carbon monoxide analysis was carried out. At this time, C-22 brand zeolite with vaseline oil was taken as an adsorbent and placed in a three-meter-long column. A Clarus 580 gas chromatograph (PerkinElmer, USA) equipped with a flame-ionized detector was used to analyze the organic compounds obtained from the process. In this case, polysorb-1 polymer sorbent was taken as adsorbent. The length of the colon was three meters. It is clear that there is a direct relationship between the rate of formation of reaction products (W) and the activity of the catalyst. The rate of formation of reaction products means the number of moles of reaction products formed per unit time on 1 m^2 surface of the catalyst.

The activity of the obtained catalyst samples was investigated in the process of conversion of ethanol and n-propanol in air oxygen environment. The process was carried out in a flow unit equipped with a tubular reactor in the temperature range of 423-773K. The volume of the catalyst taken for the study was 5 ml and the rate of feeding the initial reaction mixture to the reactor was 2400 h-1. At this time, alcohol:air = 1:10 ratio was fed to the reactor. Chromatographic method was used for the analysis of initial substances and reaction products in the process. The specific surface area of synthesized Ni - containing catalysts was determined using the nitrogen thermal desorption method.

Table 1. Results obtained from the determination of the specific surface area of NaX+Ni catalyst samples

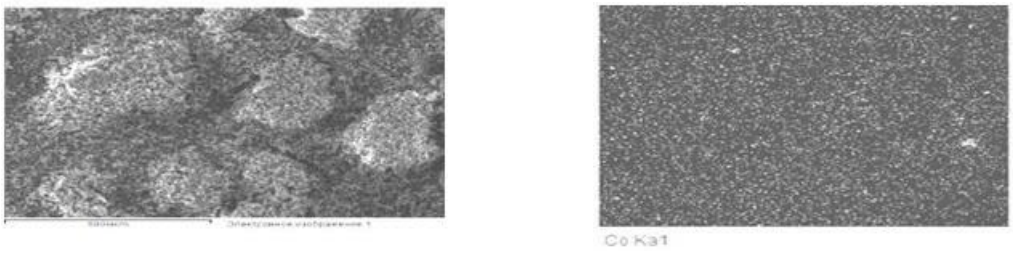
Catalizator	weight (m,q)	Surface (S_C, m^2/q)
NaX+1,0%Ni	1,0	7,8
NaX+2,5%Ni	1,0	8,4

Using the scanning electron microscope method Microphotographs of the surface of catalizator were taken in the first case and the distribution of elements at the same time. Its distribution has been decided. Visually, the distribution of elements can be seen through electron microscopic element analysis. Shows the structure of the surface of the NaX(+1.0%Ni) catalyst, the formation of zeolite. The spectrum of the elements in bin and the distribution of the Ni element are given. As can be seen from the distribution of nickel, this metal is homogeneously distributed in zeolite. That is, Nickel atoms appear to be well-dispersed within the zeolite structure rather than forming random aggregates. The amount of NI element corresponds to the amount NaX(1%Ni) taken when preparing the catalyst. Initial NaX using scanning electron microscope a microphotograph of the surface of the sample was taken (Figure 2) and the element at the same time.



a) b)

Figure 1. SEM image of Ni-modified NaX zeolite showing uniform Ni dispersion.



a) b)

Figure 2. SEM photomicrograph of the surface of the initial NaX(+2.5% Ni) sample (a), Ni element distribution map (b) The obtained Ni-containing

3. Results and Discussion

Studies show that Catalysts containing NaX(+Ni) the maximum yields of ether and aldehyde in catalysts with this composition correspond to NaX(+1.0% Ni) catalyst. The maximum yield of ethylene corresponds to the content of NaX(+2.5% Ni) and at temperatures higher than 573K, its yield decreases. This fact can be explained by the complete oxidation of olefin to carbon dioxide at high temperatures. The maximum yield of CO_2 also corresponds to NaX(+2.5% Ni) catalyst and is 82.3% at 723K temperature.

Table 2. Results obtained from conversion of ethanol on NaX+Ni catalysts with different compositions

Catalizator	Temperature, K	Convension of products, %				Convension of Alchols %
		CO_2	C_2H_4	olefin	Asetal dehid	
NaX+1,0% Ni	423	0,0	0,0	0,0	0,0	0,0
	473	0,0	0,0	0,0	0,0	0,0
	523	1,5	0,8	0,0	5,0	7,3
	573	7,3	7,8	8,8	8,8	35,1
	623	18,8	11,3	4,5	5,8	40,4
	673	23,4	10,7	2,8	4,8	41,7
	723	26,9	8,8	0,5	4,0	42,3
NaX+2,5% Ni	423	0,0	0,0	0,0	0,0	0,0
	473	0,0	0,0	0,0	0,0	0,0
	523	0,8	0,6	0,0	2,8	4,2
	573	43,0	14,4	5,5	4,8	65,4
	623	70,4	10,2	3,2	2,6	83,8
	673	81,6	3,1	2,0	2,0	88,7
	723	82,3	2,2	0,0	1,0	89,5

Figure 3 illustrate temperature dependence of the carbon dioxide output during the conversion of ethanol over NaX catalysts containing Ni. As can be seen from the figure, the maximum yield of carbon dioxide obtained from the conversion of ethanol on Ni-containing catalysts is 86.3%, respectively. Study of the activity of NaX zeolite catalysts including Ni obtained by impregnation in the process of ethanol conversion. For these compositions, NaX(+Ni)-containing catalysts. The conversion of alcohol starts at a temperature of 473K and the degree of conversion of alcohol decreases as the amount of metal in the catalyst increases. In the processes involving NaX(+Ni)-containing.

A comparison of the relevant studies shows that the oxidation of ethanol over NaX zeolite conversion of ethanol at the temperature of 723 K is 53.4%.

Acquisition of carbonyl compounds is observed in the temperature range of 473-573 K and their maximum yield is 3.4% at 473 K temperature. The practical absence of carbonyl compounds after the temperature of 623 K is explained by the fact that they are completely oxidized at high temperatures and turn into carbon dioxide. With the increase in temperature, the output of carbon dioxide and propylene increases and is 19.2 and 16.8%, respectively, at the temperature of 723 K.

Catalysts, mainly intra-molecular dehydration of alcohol takes place with the purchase of olefin. A decrease in the yield of olefin is observed in the subsequent increase in temperature, which can be explained by the acceleration of the process of its complete oxidation to carbon dioxide at high temperatures. From what has been said, it can be concluded that the acid-base centers of the catalyst play a key role in the conversion of ethanol at relatively low temperatures. The production of carbonyl compounds starts at a temperature of 473K. The carbon dioxide release of all the investigated NaX(+Ni) catalysts increases with increasing temperature. Catalysts containing NaX(+Ni). In the presence of these catalysts, the maximum conversion of alcohol and the maximum yield of carbonyl compounds is observed at 723K.

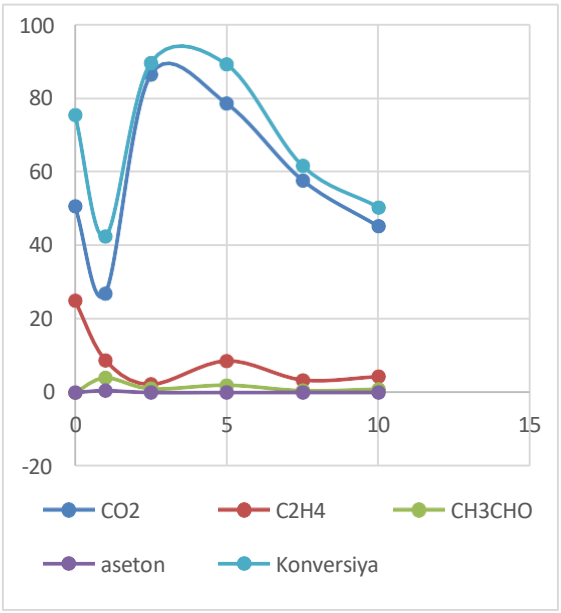


Figure 3. Temperature dependence of the yield of carbon dioxide obtained from the conversion of ethanol on catalyst samples with distinct compositions

Figure 3 temperature dependence of carbon dioxide yield obtained from conversion of ethanol on catalyst samples with different compositions Ni-containing catalysts used in the oxidation of ethanol were studied by X-ray phase analysis and EPR methods before and after processing. In Figure 3 X-ray images of NaX catalysts with 1% and 2.5% Ni in their initial state and before and after ethanol conversion are given. The peaks at observed in the roentgenograms correspond to the standard pattern of primary NaX zeolite. The sharpness and intensity of these peaks suggest that the NiO - nanoparticles have a high degree of crystallinity. Based on this, it can be concluded that nickel (II) nitrate impregnated on the surface of zeolite is completely decomposed into NiO nanoparticles when heated at 500 °C. The average size of NiO crystals was determined. As a result of the calculation, it was determined that the average size of NiO particles included in the structure of NaX zeolite is 28,314 nm.

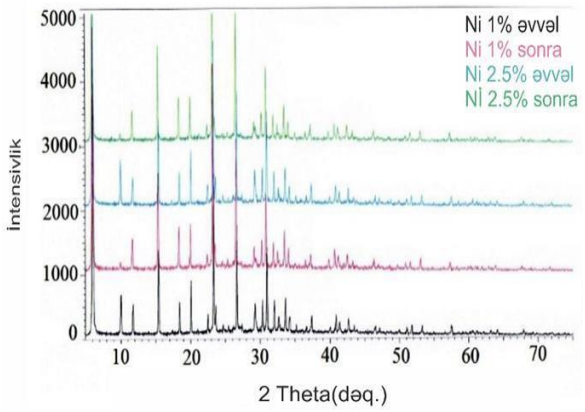
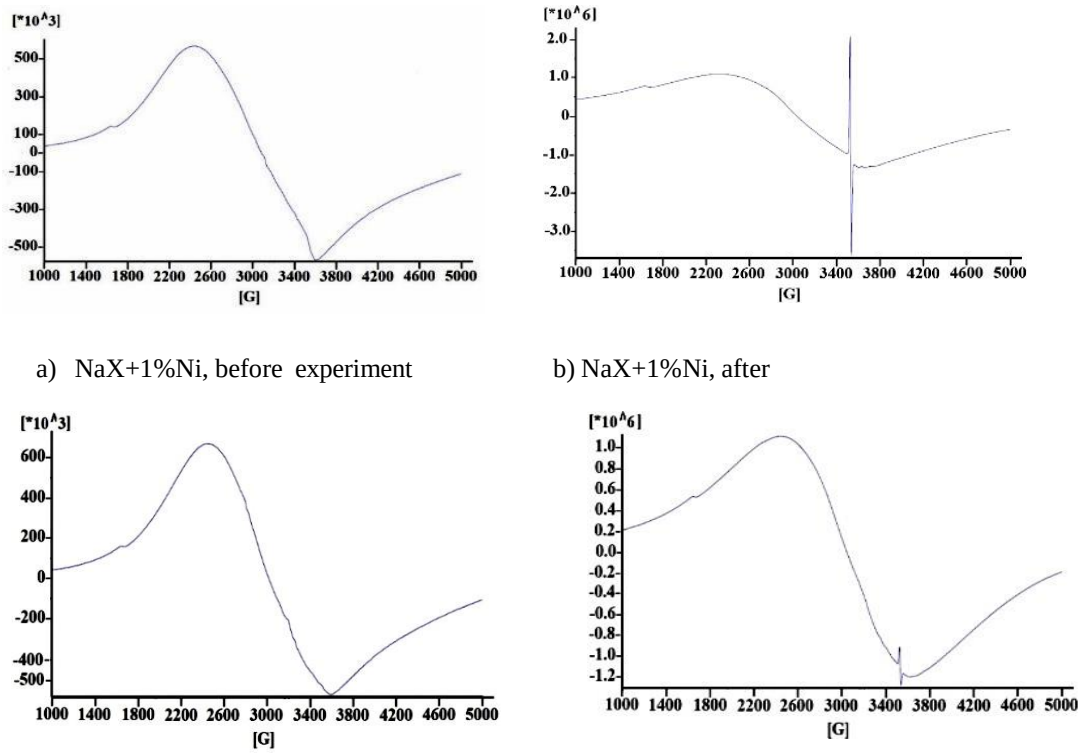


Figure 4. X-ray images of catalysts containing NaX(+1.0%Ni), NaX(+2.5%Ni) before and after ethonol conversion

EPR spectra taken before and after working for 6 hours during the conversion of NaX(+1.0%Ni) and NaX(+2.5.%Ni) samples. As a result of our research, it was determined that even Ni was included in the original NaX zeolite. The introduction of a small amount of metal (~1%) causes a noticeable change in its EPR spectrum. Against the background of the broad signal created by the large magnetic field, a convex-shaped signal with a g - factor of 2.1 is observed, which corresponds to nanosized NiO particles. It was determined that when the mass amount of Ni included in the composition of the primary zeolite increases to 10.0%, their EPR spectrum becomes complex and consists of a large number of signals.



a) NaX+1%Ni, before experiment

b) NaX+1%Ni, after

c) NaX+2.5%Ni, before experiment

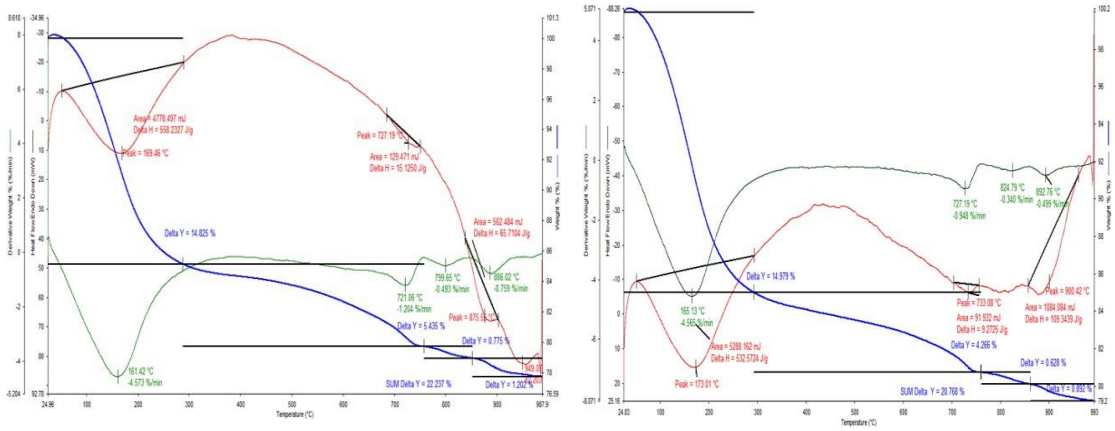
d)NaX+2.5%Ni,after experiment

Figure 5. EPR spectra of NaX samples containing 1.0% (a,b) and 2.5.% (c,d) before and after the 6 hours of operation in the ethanoll conversion process

Based on the EPR spectra of the catalyst samples processed in the process, it is possible to make an opinion about the formation of a certain amount of coke on the surface of the catalyst. Thus, against the background of the broad signal, a narrow signal characterized by the parameters g=2.0026 and ΔH= 0.9 мТ is observed, which corresponds to coke residues with paramagnetic properties. It is believed that the formation of coke on the surface of the catalyst creates con-ditions for the reduction of nickel oxide to metallic nickel. Note that the EPR spectrum of the coked sample taken after annealing in the presence of air at a temperature of 773 K is almost indistinguishable from the EPR spectrum of the original catalyst sample. It is quite possible that the nanosized particles of nickel oxide NiO are the cat-alytically active centers of this reaction and the main participants of the reduction-oxidation stages in the process are Ni and NiO particles.

We can be seen from the thermogram of the NaX(+1.0%Ni) sample taken before processing in the process (Figure 5), four endothermic effects corresponding to the temperatures of 169oC, 727C (very weak), 875C and 949C are observed in the DTA curve. The first peak at 161°C characterizes the release of weakly bound water - the dehydration process. Weight loss in this area is 14.8%. High-temperature Endo effects are due to very small amounts of hydroxyl groups and condensation products -coke - leaving the cage. Pu Endo effects are characterized by three weak steps in the temperature range of 300-950C in the TG curve: 300-750C (weight loss 5.4%); 750-850C (weight loss 0.8%) and 850-950C (weight loss 1.2%).

After the indicated catalyst works in the ethanol conversion process, its TG and DTA curves do not change in character (Figure 5a). The change refers to the quantitative indicators of the respective effects. In this case, the high-temperature endopices correspond to temperatures of 733 and 900, 420C. It should be noted that in the DTA curve of the catalyst used in the process, among the above-mentioned Endo effects, there are processes with heat release, albeit with weak enthalpy and a total weight loss of 0.63% corresponds to them. This effect is related to the displacement of different mass condensation products from the lattice. As mentioned earlier, high-temperature Endo effects are related to the processes of dihydroxylation and displacement of condensation products. The total weight loss in this zeolite is 19.02%. The thermogram of the NaX(+2.5% Ni)-containing catalyst before its processing in the ethanol conversion process is given. Three Endo effects are observed in the DTA curve of this catalyst: 150°C, 563°C and 734°C. 150°C Apparently, the removal of physically sorbed water from this zeolite occurs at a relatively low temperature - 1500C and the weight loss in this process is 7.52%.



a) b)

Figure 6. a) Thermogram of the initial NaX(+1.0% Ni) catalyst; b) Thermogram of the catalyst containing NaX(+1.0% Ni) after treatment in the ethanol conversion process

Thermogravimetric analysis of NaX(+2.5% Ni)-containing catalyst was carried out after working in ethanol conversion process (Figure 6). In this case, unlike the initial case, the weight loss in the area where the low-temperature Endo effect (165.9°C) is observed is 15.4% and the total weight loss is 18.2%. A shovel-shaped endoeffect is observed around 700 C. The obtained results show that both the amount and the ionic radius (Ni^{2+} 0.069nm), 500 ^{0}C of the cation introduced into the zeolite lattice through modification play a certain role in the thermal properties of the synthesized zeolite

modification. This is especially evident in the value of the maxima of low-temperature Endo effects.

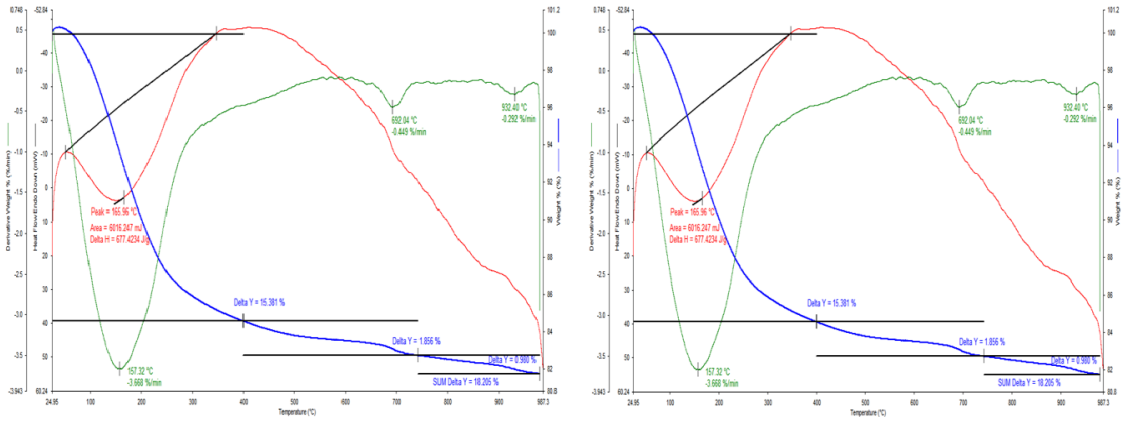


Figure 7. a) Thermogram of the initial NaX(+2.5% Ni) catalyst b) Thermogram of the catalyst containing NaX(+2.5% Ni) after treatment in the ethanol conversion process

The IR-spectra of used zeolite in the synthesis of catalysts, as well as its modifications obtained by ion- exchange and impregnation, in the initial state and after heating at 500^0C for use in catalytic studies, describe the spectral landscapes observed in the oscillation fields of crystal lattice elements and adsorbed water and it practically coincides in terms of quantity. This experimental fact demonstrates that the structure of zeolite does not change when it is heated at the specified temperature. The result related to the preservation of the structure is also obtained in the thermographic study of all zeolite and its metallic modifications. The comparison of the corresponding spectra shows that no significant changes of the spectral landscape occur in the oscillation regions of either the crystal lattice or water after the mentioned catalytic process. Naturally, small shifts are observed in the maxima of some absorption bands. In addition, after the process, there is an increase in the integral intensity of absorption bands observed at 1400-1500 cm^{-1} in the region of carboxylate structures.

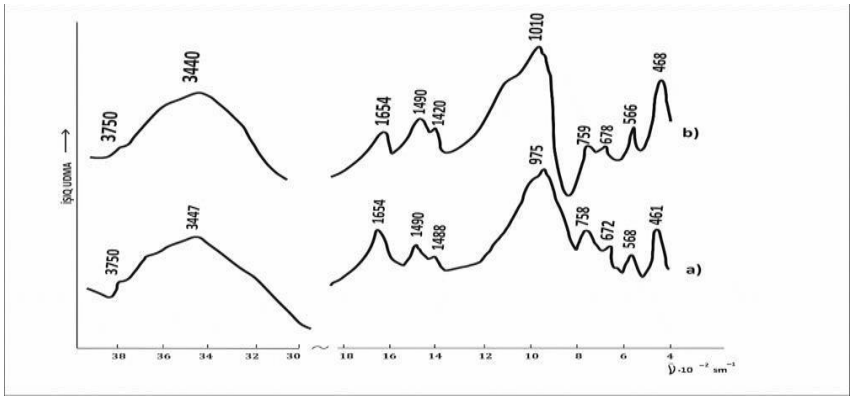


Figure 8. IR-spectra of the NaX(+2.5.% Ni) catalyst in the initial case (a) and after working at 723 K in the ethanol conversion process (b)

The conducted studies show that the physicochemical properties and catalytic activities of Ni-containing NaX zeolite catalysts obtained by the impregnation method

depend on the amount and size of the metal included in their composition.

Binary catalyst samples containing NiO/NaX were synthesized by the impregnation method and their catalytic activity was widely studied in the process of ethanol conversion. It was determined that Ni-containing samples. Show the maximum conversion rate of ethanol was 95.1% and 89.5%, respectively. It was determined that Ni-containing catalysts show higher activity due to their oxidizing- reducing properties. So, while the maximum release of carbon dioxide on the on the Ni-containing samples, this indicator corresponds to the NaX+2.5% Ni sample and is given as 86.3% (723K). Based on the results of RF and EPR analysis, it was determined that the NiO particles in the NiO/NaX catalyst sample are at the nanoparticle level. Thus, based on the results of RF analysis, it was determined that the size of the particles in the pure NiO crystallite is 32.65 nm, while the average size of the NiO particles in the NiO/NaX sample is 28.14 nm. According to the results of the EPR analysis, the value of the g-factor in the pure NiO crystallite is 1.92, while this indicator is 2.1 in the NiO/NaX sample.

It was determined that when the amount of transition metal in Ni containing catalyst samples exceeds 2.5%, the oxidizing property of the catalyst decreases sharply with increasing temperature. This is explained by the fact that cobalt atoms collect on the surface of zeolite and form large crystallites and at the same time, the state of nickel structures changes.

3. Conclusions

Transition metal in the zeolite crystal structure and the physio-chemical characteristics of the catalysts were all determined to influence the catalytic activity of the synthesized zeolite modifications, including their oxidation properties. It was discovered that catalysts containing Ni metal at the nanoparticle level show higher activity in the process of alcohol oxidation. It was determined that when zeolite is modified with Ni metal, the oxidizing properties of the obtained catalyst and as a result, the release of carbon dioxide, which is the complete oxidation product of alcohol, significantly increase. Well-developed internal microporosity together with the retaining of atoms in tetrahedral framework positions offered higher catalytic activity for the conversion of ethanol molecules than the native microporous of zeolite.

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