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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**NaX-BASED ZEOLITE MODIFICATIONS AND CATALYTIC  
CONVERSION OF C<sub>2</sub>-C<sub>3</sub> SATURATED MONOHYDRIC  
ALCOHOLS IN THEIR PRESENCE**

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Applicant: **Asmar Valiyeva Dadash**

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The dissertation work was performed at the Azerbaijan State University of Oil and Industry.

Scientific supervisor: doctor of chemical sciences, professor  
**Jabrayil Mirzai Israfil**

Official opponents: doctor of technical sciences,  
academician  
**Aghadadash Aliyev Mahmud**

doctor of chemical sciences, professor  
**Nazim Shamilov Telman**

doctor of chemical sciences,  
associate professor  
**Muslum Gurbanov Ahmad**

Dissertation Council ED 2.16 of the Supreme Attestation Commission under the President of the Republic of Azerbaijan operating under Baku State University

Chairman of the Dissertation Council:



doctor of chemical sciences, professor  
**Valeh Ismayilov Mehrali**

Scientific secretary of the dissertation council:

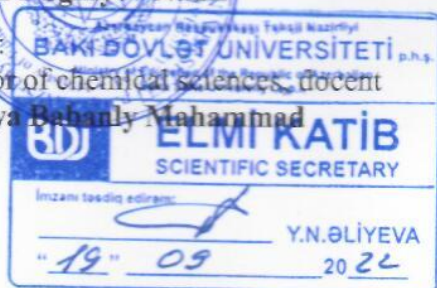


candidate of chemical sciences, docent  
**Farid Naghiyev Nadir**

Chairman of the scientific seminar:

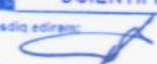


doctor of chemical sciences, docent  
**Dunya Baharly Mahammad**



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Stamp: **ELMI KATİB**  
SCIENTIFIC SECRETARY

İmzayı təsdiq edirəm:  **Y.N.ƏLİYEVA**

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## GENERAL DESCRIPTION OF WORK

**Relevance and development of the subject.** The fact that zeolites from the group of crystalline aluminosilicates have a regular structure, the ability to be modified by various methods, high sorption and catalytic activity have made them an indispensable research object in the field of heterogeneous catalysis. By purposefully modifying synthetic zeolites, which are included in separate structural groups, and which initially contain an alkali metal cation (mostly  $\text{Na}^+$  ion) as an exchange cation, with various methods, the possibilities of preparing effective sorbents and catalysts of practical importance based on them are very wide. The inner surface of zeolites with well-developed porosity consists of a system of pores distributed in three-dimensional space, and in this respect they are superior to most heterogeneous catalysts in which their active centers are distributed on the surface or in defects of the crystal lattice.

The acid-base or oxidizing-reducing centers found in zeolite catalysts are where catalytic processes involving those catalysts can occur. Contrary to acid-base centers, the activities taking place in oxidizing-reducing centers have been researched comparatively infrequently, according to an analysis of a significant number of literature materials.

Zeolites possessed nearly incredibly poor oxidation-reduction characteristics when an alkali metal cation was retained as the main exchange cation. However, it is possible to obtain highly active oxidizing catalysts by introducing transition metals into their crystal lattice in various ways. On the other hand, recently there has been a lot of interest in processes involving nano-sized catalytic systems. On the other hand, the basis of the work carried out in this direction is the development of methods for the synthesis of catalytic systems with nanostructured particles, the determination of their structure and morphology, and the determination of methods that allow changing the main properties of the catalyst.

The mentioned demonstrates that the research of metal-retaining zeolites is of great significance and relevance in terms of both the theory of catalysis and the creation of new multifunctional catalytic

systems and the development of new catalytic processes.

Currently, despite the fact that a lot of information has been gathered in this area, there is still a lot of interest in research involving the use of metal zeolite catalysts in diverse processes.

The conversion of alcohols can be converted on variety of catalysts in real-world applications. Traditional catalysts of this process are considered to be zeolites, and this is reflected in relevant literature materials. This is due to the fact that in the case of the application of zeolites, the researcher has the opportunity to preselect the type of structure of the catalyst and the size of the pores, thereby directing the process in the desired direction.

Depending on the circumstances, the conversion of alcohols on zeolites including low-mass diatomic alcohols like ethanol and propanol is typically a difficult process that involves numerous steps. One of the current critical concerns facing the petrochemical industry complex is the investigation of the characteristics (legalities) of this process.

**The object and subject of the research.** The oxidative conversion of C<sub>2</sub>-C<sub>3</sub>-saturated diatomic alcohols was chosen as the subject of study in the dissertation work using synthetic NaX zeolite modified with La, Pd, Ni, and Co metals.

The subject of the research is to determine the oxidizing-reducing properties of those metal zeolite catalysts and the ways of their optimal modification based on the research conclusions of the conversion processes of ethanol and propanol, which are representatives of C<sub>2</sub>-C<sub>3</sub>-saturated diatomic alcohols, in the presence of NaX zeolite catalysts modified with La, Pd, Ni and Co metals.

**Goals and objectives of research.** The goal of the work is to examine the activity of zeolite modifications, or catalysts made by modifying NaX zeolite with a variety of transition metals, in the conversion processes of ethanol and n-propanol, which are examples of saturated monoatomic C<sub>2</sub>-C<sub>3</sub> alcohols. Additionally, the relationship between the physico-chemical characteristics and activity of the synthesized catalysts will be examined.

The following research projects were carried out with this goal in mind:

– La, Pd, Co, and Ni-containing NaX zeolite catalysts were made by the ion-exchange and impregnation procedures, and their precise surfaces were identified through the nitrogen thermal desorption method.

– In the presence of created catalysts, ethanol and propanol oxidation processes were investigated over a wide temperature range.

– Modern research techniques were used to examine the physico-chemical properties of synthesized catalysts were studied, the relationship between these properties and catalytic activity was investigated, the effect of the nature of transition metals and their amount in the zeolite's elementary lattice on the activity of the catalyst was studied in detail.

**Research methods.** Modern physical and physico-chemical techniques, such as RFA, IR spectroscopy, EPR, DTA, and scanning electron microscopy, were used to analyze the produced catalysts (SEM). Analysis of the reaction products obtained in the processes was carried out by the chromatographic method.

#### **Main clauses defended.**

– Utilizing ion exchange and impregnation techniques, metallic modifications of synthetic NaX zeolite can be obtained. These alterations can then be used to create efficient oxidizing catalysts.

– Based on the research of the synthesized catalysts by RFA, IR-spectroscopy, SEM, EPR methods, their physico-chemical properties, including the determination of the relationship between the magnetic properties of the synthesized catalysts and their catalytic activity in the processes of oxidative conversion of ethanol and n-propanol.

– Studying how the quantity of transition metal (La, Pd, Co, and Ni) in the zeolite's elemental lattice affects the ratio of acid-base and oxidizing-reducing centers in the produced catalysts, as well as the related catalytic activity

– Summarized results of the research of the activity of the synthesized catalysts in the processes of oxidative conversion of ethanol and n-propanol.

#### **Scientific novelty of the research.**

Synthesis of modifications containing La, Pd, Co, NI metals in

NaX zeolite using ion exchange and impregnation methods, physical and physicochemical methods study and systematic study of their activity in the process of oxidation of ethanol and n-propanol from representatives of C2-C3-saturated diatomic alcohols was then thoroughly studied.

The method of zeolite modification, the amount and state of the transition metal in the zeolite crystal structure, and the physico-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 Pd metal at the nanoparticle level show higher activity in the process of alcohol oxidation.

It was determined that when zeolite is modified with Pd 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.

**Theoretical and practical significance of research.** Decontamination of harmful oxygen-containing organic substances released into the environment by chemical industry enterprises in the presence of synthesized zeolite-containing catalysts by complete oxidation to carbon dioxide and water is of great practical importance. In addition, the fact that the catalysts used in the work are cheap, have high activity and can be fully recovered in a short period of time after being used in the process allows them to be used as oxidizing-reducing catalysts in various fields of the chemical industry.

The results obtained in the experimental studies aimed at solving a specific issue related to the application of purposefully modified zeolites as an oxidizing catalyst may have a certain share in the development of the theoretical concepts of catalysis as well as having the above-mentioned practical significance.

**The applicant's personal contribution to the conducted research.** The applicant's role in carrying out the research work, specifically in conducting experiments, is direct. The research of the activity of the catalyst samples obtained from the modification of NaX zeolite with a number of transition metals in the process of conversion of C2-

C<sub>3</sub>-saturated diatomic alcohols and the relationship between the physicochemical properties of the synthesized catalyst samples and their activity and analyzed the literature materials in this direction. In the discussion and compilation of scientific works reflecting the outcomes of the performed research, she presented and supported her scientific opinions.

**Approbation and implementation of research.** The results of the dissertation were presented at the following international and national conferences: I international scientific conference of young researchers April 25-26, 2013, Baku, p. 391; “Mendeleev-2014” The 8<sup>th</sup> All-Russian conference with international part of Molydkh students' chemistry, p. 249-250, St. Petersburg, 2014.; International Conference on Green Chemistry and Sustainable Engineering, p. 110, Barcelona, 2014; Republican Scientific Conference dedicated to the 90<sup>th</sup> anniversary of Academician Togrul Shahtakhtinsky, p.53, Baku, 2015; X Republican Scientific Conference “Actual Problems of Chemistry” of doctoral students, masters and young researchers dedicated to the 93<sup>rd</sup> anniversary of National Leader Heydar Aliyev; XX Mendeleev Congress on General and Applied Chemistry, p. 120, Ekaterinburg, 2016; International Scientific Conference dedicated to the 85<sup>th</sup> anniversary of Academician Rafiga Aliyeva. Chemistry of Coordination Compounds: Current Problems in Analytical Chemistry p. 196, Baku, 2017.

**Publications:** On the topic of the dissertation, 20 scientific works, including 9 articles, 11 theses reports, were published.

**The name of the institution where the dissertation work was performed:** The dissertation work was completed in accordance with the theme of the scientific research projects of the Azerbaijan State Oil and Industry University's department of “Chemistry and technology of inorganic substances.”

**The total volume and structure of the dissertation.** An introduction, four chapters, conclusions, and a bibliography compiled from 200 sources make up the dissertation. There are 45 photos, 19 tables, and 170 page that makes up the total volume of the dissertation.

## MAIN CONTENT OF THE DISSERTATION

**Introduction** The opening section reflects the relevance of the research topic, the objectives and tasks of the work, the issues to be solved, scientific innovations, the practical significance of the work, and the concise substance of each chapter.

**The first chapter** is dedicated to the analysis and review of the periodical literature related to the partial and complete oxidation of oxygenated organic compounds and mainly diatomic saturated alcohols over catalysts of various compositions.

**In the second chapter**, the methods of preparation of catalysts used in research by ion-exchange and impregnation methods are described, the scheme of the device used for studying their activity is given, the methods of analysis of reaction products and the physico-chemical research methods of catalysts, their capabilities are explained in detail.

**In the third chapter**, the research results of ethanol and propanol conversion processes on NaX-based La, Pd-containing catalysts obtained by ion-exchange method, as well as the nature of changes occurring in the catalysts during those processes (rotary or non-rotary) are given. The NaX zeolite itself and its ion-exchanged variants were first studied physico-chemically.

The X-ray phase analysis approach was used to compare studies on primary NaX zeolite, its Pd, and its La-forms. Corresponding values of the interplanar distance in the radiograph of the catalyst containing NaPdX (1%Pd) indicate that Pd is in the form of a free metal in the zeolite structure. X-ray analysis of the catalyst containing NaLaX (5% La) shows that the sample contains a phase with the formula  $\text{La}_{7.52}\text{Al}_{21.60}\text{Si}_{26.4}\text{O}_{96} \cdot 8 (\text{H}_2\text{O})$ . In this structure, La is in the Si position in the zeolite lattice.

The IR-spectra of NaX zeolite used 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°C 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.

### **Research of the activity of zeolite catalysts obtained by the ion-exchange method in the process of ethanol conversion**

**NaX catalyst.** The obtained results display that the intramolecular dehydration of ethanol prevails on this zeolite at relatively low temperatures. With the increase in temperature, the yield of ethylene, a product of that process, increases, and at the temperature of 573 K it takes the maximum value (15.4%). However, with the subsequent growth in temperature, a decrease in the yield of ethylene and an increase in the yield of diethyl ether are observed, which indicates that intermolecular dehydration of alcohol takes place with the purchase of diethyl ether as a reaction product at relatively high temperatures. The maximum yield of this product, which is 9.2%, corresponds to the temperature of 623 K. Research shows that starting from a temperature of 630K, the yields of ethylene and diethyl ether decrease sharply, while the yields of carbon 4-oxide and acetaldehyde, on the contrary, increase sharply. This is due to the fact that at high temperatures, oxidation of alcohol and its dehydration products occurs.

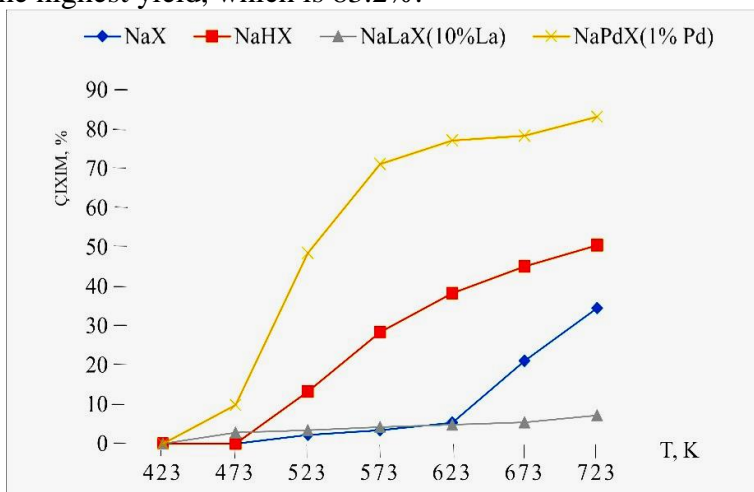
**NaHX catalyst.** The intramolecular dehydration of the alcohol over the decationized hydrogen form is further accelerated compared to the original NaX catalyst. As a result, with the presence of this catalyst, the yield of ethylene at the temperature of 573 K is 33.4%, while the yield of ether is only 0.9%. At relatively high temperatures, the increase in the release of carbon 4-oxide is mainly due to the complete oxidation reaction of ethylene, which is an intramolecular dehydration product of ethanol.

**NaLaX-containing catalysts.** The amount of lanthanum cation in the samples of the NaLaX catalyst used in the research is 1.0; 5.0 and 10.0%. Experiments demonstrate that the conversion of ethanol on catalysts containing NaLaX commences at a lower temperature than NaX catalyst and its H-form. Based on experiments, it was determined that at relatively low temperatures, intramolecular and intermolecular dehydration of alcohol occurs, so the reaction product consists mainly of ethylene and diethyl ether. The release of acetaldehyde and carbon 4-oxide in the reaction product rises as a result of the acceleration of the oxidation process of alcohol with a rise in temperature.

Therefore, it is reasonable to draw the conclusion from the results that ethanol dehydration happens most frequently on catalysts containing NaLaX. On the other hand, the large yield of diethyl ether demonstrates that these catalysts primarily cause intermolecular dehydration of ethanol.

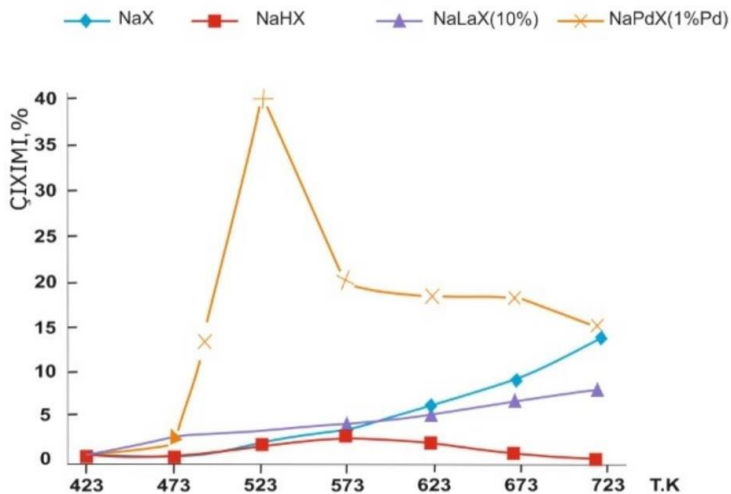
**NaPdX containing catalysts.** These catalysts contain 0.1, 0.5, and 1.0% Pd respectively. The conversion of alcohol increases with the amount of Pd metal in the zeolite. On a NaPdX (1.0% Pd) catalyst, alcohol conversion is 98% at 723 K. Alcohol dehydrates either intramolecularly or intermolecularly up to a temperature of 473 K. Comparison of the individual results shows that the nature of ethanol conversion over catalysts comprising La and Pd at low temperatures is identical. However, starting at 523 K, in contrast to NaLaX catalysts, the yield of carbon dioxide and acetaldehyde increases significantly in the presence of NaPdX catalysts.

Figure 1 depicts the relationship between the initial NaX and its various forms and the temperature at which carbon dioxide, the entire oxidation product of ethanol, is released. As can be observed, the emission of carbon dioxide increases with temperature in all scenarios and reaches its maximum amount at 723 K. The NaPdX (1.0% Pd) sample has the highest yield, which is 83.2%.



**Figure 1. Dependence of the carbon dioxide yield obtained in the conversion of ethanol on catalysts of various compositions on temperature**

Figure 2 demonstrates the temperature dependency of the yield of carbonyl compound-acetaldehyde from partial oxidation products in the process for the purpose of comparing the oxidizing-reducing capabilities of the examined catalysts.



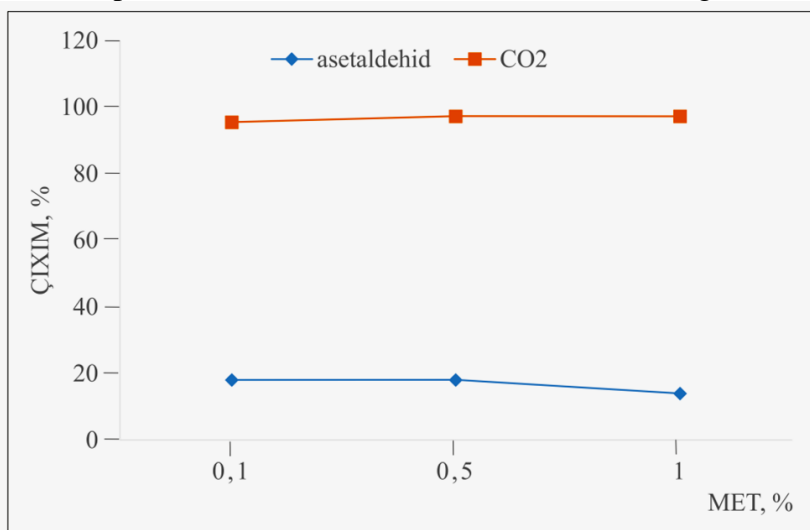
**Figure 2. Dependence of the yield of acetaldehyde obtained in the conversion of ethanol on catalysts of various compositions on temperature**

Acetaldehyde production on all catalysts is mainly observed after the temperature of 473 K, as can be seen from the figure. Additionally, the NaPdX (1.0%Pd) catalyst is more selective for this end product. The maximum yield of acetaldehyde on this catalyst is observed at a temperature of 523 K and is 37.1%. In the further increase of the temperature, its yield starts to decrease and is 14.0% at the temperature of 723 K.

Let us also mention that multiple iterations of the experiment, which involved the conversion of ethylene over the NaPdX (1.0%Pd) catalyst, validated the temperature dependency curve of acetaldehyde production (this experimental approximation was also used to confirm other extreme dependences observed in our research).

Based on the results obtained for the primary NaX and its H-form, it can be said that ethanol dehydration primarily takes place

intramolecularly on these catalysts. As a result, the yield of ethylene increases in the presence of both catalysts up to a temperature of 573 K. In the subsequent increase in temperature, an increase in the output of carbon dioxide is observed mainly due to the oxidation of ethylene. Pd-containing catalysts show high activity in the process of ethanol oxidation. Naturally, this activity depends on the catalytic properties of the metal, its amount in the elementary lattice of the zeolite and the method of modification of the zeolite. The influence of the amount of transition metal in the elementary lattice of zeolite on its oxidizing-reducing properties is reflected in the graph of the dependence of acetaldehyde and carbon dioxide, which are products of the oxidative conversion process of ethanol, on the amount of metal (figure 3).



**Figure 3. Acetaldehyde and carbon dioxide emissions from the conversion of ethanol over Pd-containing NaX catalysts are dependent on the amount of metal used ( T=723 K )**

As can be seen from the graph, as the content of Pd metal in the catalyst increases, the release of carbon dioxide increases. Its maximum yield is 83.2% and corresponds to that of NaPdX (1.0% Pd). Acetaldehyde release increases slightly when metal content increases from 0.1% to 0.5%, but decreases to 14% when metal content is 1%.

The NaPdX (1.0% Pd) catalyst, which shows high efficiency in the ethanol conversion process, was studied by thermogravimetric method in the initial state and after working in the process. is 6%. This weight loss is matched by a blunt, high-temperature asymmetric endo peak in the DTA (differential thermal analysis) curve with a maximum corresponding to 164 temperatures. In contrast to NaX zeolite, a weak endo peak at 723 is observed in the DTA curve of NaX(1.0%Pd) catalyst. This peak is due to the fact that after a certain dehydration stage of zeolite, the hydroxyl groups formed as a result of the solid-phase hydrolysis process, which is realized under the influence of the electric field of the multivalent cation, leave the zeolite cage. Naturally, these hydroxyl groups are formed during the tabulation of NaX(1.0%Pd) zeolite before the catalytic experiment.

After 6 hours of operation at 723 C in the catalytic process, there is no significant change in the TG and DTA curves of the NaPdX catalyst, which once again indicates that irreversible structural changes do not occur in this catalyst after operating at 723K in the ethanol conversion process. However, it is necessary to state the following ailments in the thermographic analysis indicators of the NaX(1.0%Pd) catalyst after working in the process compared to the initial sample, which are undoubtedly due to the influence of the catalytic process:

- in the developed process, the total weight loss is somewhat greater;

- the area of the low-temperature endopeak observed in the DTA curve in the exhausted catalyst is smaller;:

In the DTA curve of the exhausted catalyst, a very weak, non-sharp endoeffect is observed at the temperature of 563, which is due to the displacement of a small amount of condensation products combined as a residue on the catalyst surface after the process (3.8% weight loss).

### **Study of the activity of zeolite catalysts included by the ion-exchange method in the process of propanol conversion.**

**NaX catalyst.** A comparison of the relevant studies shows that the conversion of n-propanol on NaX is significantly reduced compared to ethanol under the same conditions. Thus, while the

conversion of ethanol at the temperature of 723 K is 53.4%, this indicator is 36.0% for propanol. Besides, unlike ethanol, intermolecular dehydration of propanol-1, on NaX is almost not observed.

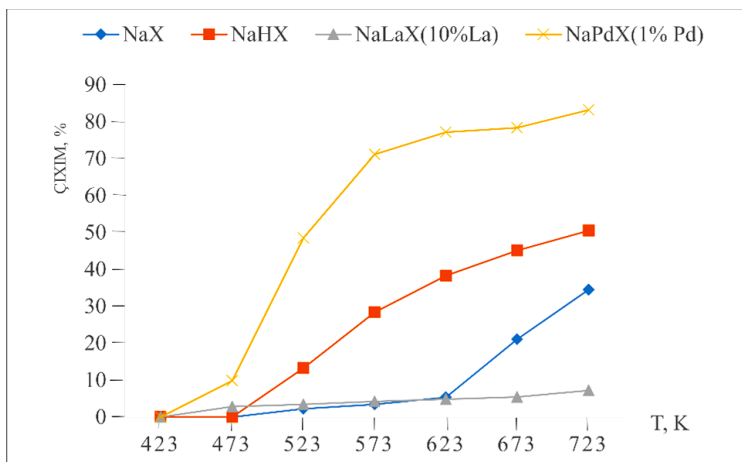
Acquisition of carbonyl compounds is observed in the temperature range of 473-573 K, and their maximum yield is 3.4% at 473 K temperature. The practical absence of carbonyl compounds after the temperature of 623 K is explained by the fact that they are completely oxidized at high temperatures and turn 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.

**NaHX catalyst.** Compared to the NaX catalyst, the conversion of propanol under similar conditions on NaHX is significantly increased and is 74.2% at 723 K. The maximum yield of propylene is observed at this temperature - 35.6%. As expected, the yield of carbon dioxide, the product of complete oxidation, increases with increasing temperature and is already 36.8% at 723 K.

**NaLaX-containing catalysts.** The common feature for all three compositions (La – 1.0; 5.0 and 10.0%) is that NaLaX zeolite has a relatively weak oxidizing property, so the oxidation of intermediate products (propylene and carbonyl compounds) to carbon dioxide is slow. In contrast to ethanol conversion reaction, in the process of propanol conversion, the most yield of reaction products belongs to propylene, which is an intramolecular dehydration product (44.5%). The output of carbon dioxide, which is a complete oxidation product, is only 8.8%.

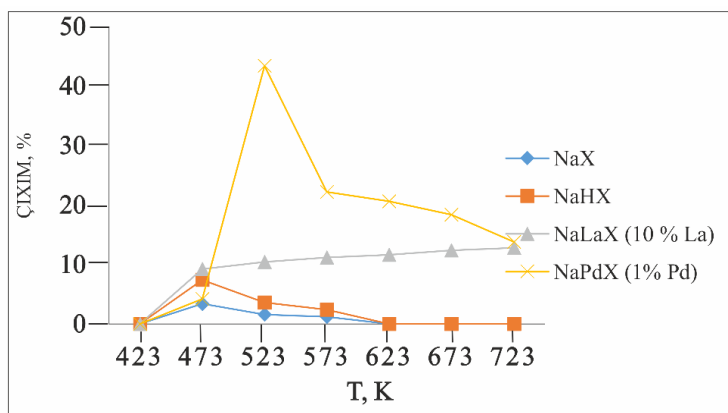
**NaPdX-containing catalysts.** Unlike other studied catalysts, the conversion of alcohol on Pd-containing catalysts starts at lower temperatures. Thus, at a temperature of 423 K, 8.4% propylene is obtained on NaPdX (1.0% Pd). The maximum yield of this alkene corresponds to the temperature of 473 K and it is equal to 41.5%. In the subsequent increment in temperature, the yield of propylene decreases sharply, which can be explained by its complete oxidation.

Figure 4 shows the graphs of temperature dependence of carbon dioxide output during the conversion of propanol on catalysts with different compositions. As it is observed in the graph, the release of carbon dioxide increases with increasing temperature over all catalysts.



**Figure 4. Temperature dependence of carbon dioxide yield obtained in the conversion of propanol over catalysts of different compositions**

The temperature dependences of the yield of carbonyl compounds obtained from the conversion of propanol on catalysts with different compositions (Figure 5) show that the maximum yield of carbonyl compounds on NaX and NaHX catalysts is observed at a temperature of 473 K.



**Figure 5. Temperature dependence of the yield of carbonyl compounds obtained from the conversion of propanol on catalysts of distinct compositions**

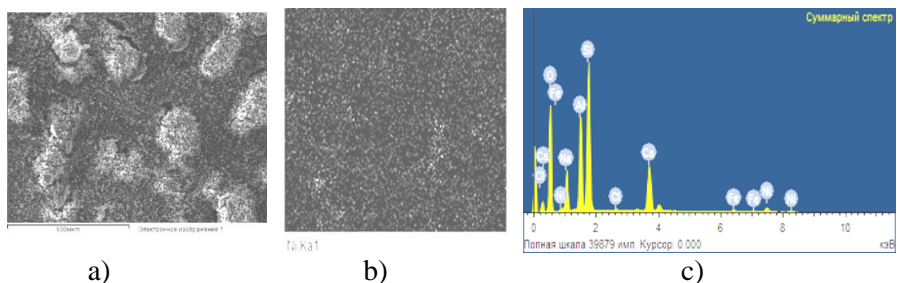
Formation of carbonyl compounds with increasing temperature over NaLaX (10.0% La) catalyst increases. On the surface of NaPdX (1.0% Pd) catalyst, the release of carbonyl compound passes through extremum.

**In the fourth chapter**, the research results of ethanol and propanol conversion processes on NaX-based Co and Ni-containing catalysts obtained by impregnation, as well as the nature of the changes occurring in the catalysts during those processes (rotating or non-rotating) are given.

Based on the radiograph of the NaX (+2.5% Ni) catalyst, it was determined that certain values of the interplanar distances prove the presence of the NiO phase in the sample. X-ray analysis of the NaX (+5.0%Co) catalyst shows that the Co metal in the catalyst is in the form of a Co<sub>3</sub>O<sub>4</sub> spinel type phase.

Using the scanning electron microscopy method, a photomicrograph of the surface of the NaX(+1.0%Ni) catalyst in the initial state was taken and similarly, the distribution of elements was determined. Visually, the distribution of elements can be observed from the electron microscopic element map.

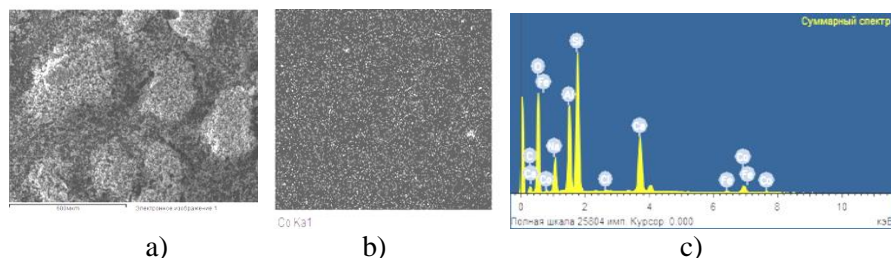
It is shown in the Figure 6, the surface structure of the NaX(+1.0%Ni) catalyst, the spectrum of the elements contained in the zeolite, and the Ni element are given in the distribution map. As can be seen from the distribution map of nickel, this metal is homogeneously distributed in zeolite. Additionally, nickel atoms are most likely not chaotically distributed in the pores of zeolite.



**Figure 6. Scanning electronic microscope photomicrograph of the surface of the initial NaX(+1.0% Ni) sample (a), Ni element distribution map (b) and element distribution spectrum (c).**



Using the scanning electron microscopy method, a photomicrograph of the surface of the initial NaX(+2.5%Co) sample was taken (Figure 7) and at the same time the distribution of elements was determined.



**Figure 7. Scanning electron microscope photomicrograph of the surface of the initial NaX(+2.5% Co) sample (a), Co element distribution map (b) and element distribution spectrum (c).**

### **Study of activity over zeolite NaX catalysts that contains Co and Ni obtained by impregnation method in ethanol conversion process**

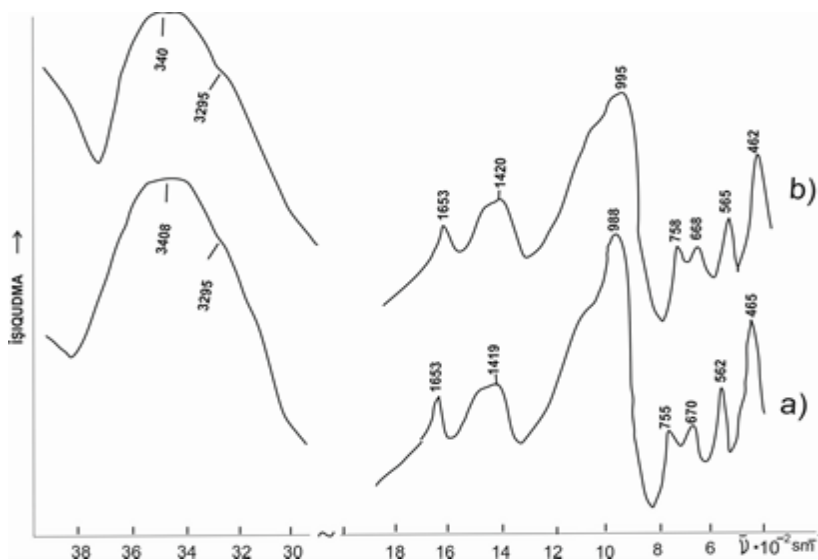
**NaX(+Co)-containing catalysts.** Obtained by impregnation method and contains 1.0; 2.5; Ethanol conversion in the presence of NaX catalysts with 5.0 and 10.0% Co was studied. The maximum value of alcohol conversion rate corresponds to NaX (+10.0% Co) catalyst and it is 95.1% at 723 K. The obtained results suggest that intermolecular dehydration of ethanol occurs at low temperatures in the presence of these catalysts, and as a result, the reaction product consists of only diethyl ether up to a temperature of 473 K.

The production of acetaldehyde on all Co-containing catalysts begins at a temperature of 523K. The maximum yield of this substance corresponds to the NaX (+5.0% Co) catalyst and is 14.2% at a temperature of 523K. In catalysts with a low amount of cobalt (1.0% and 2.5%), the rise in temperature in the range of 523-573K is observed with an increase in the yield of acetaldehyde, while in catalysts with a high amount of metal (5.0 and 10.0%), the opposite is observed. This suggests that as the amount of transition metal in the catalyst increases,

its oxidizing capacity increases and the complete oxidation process of aldehyde to carbon dioxide accelerates.

The production of ethylene, which is an intramolecular dehydration product, on all catalyst samples begins at a temperature of 523K, and at this temperature its maximum yield is observed in the NaX (+1.0% Co) catalyst (33.1%). In the subsequent increase in temperature, the yield of ethylene on this catalyst decreases. A similar picture is observed in the case of NaX (+2.5% Co) catalyst.

The release of CO<sub>2</sub> gas, which is a complete oxidation product in the process, starts at 523K. Figure 8 shows the IR spectra of the NaX(+5.0% Co) catalyst in the initial state and after working in the ethanol conversion process.



**Figure 8.** IR-spectra of the NaX(+5.0% Co) catalyst in the initial case (a) and after working at 723 K in the ethanol conversion process (b)

It should be stated that, compared to the spectrum of NaX zeolite, there are certain shifts in the maxima of the bands observed in the 300-1200 cm<sup>-1</sup> range.

It should be noted that a complex absorption band with a non-sharp maximum at 1419 cm<sup>-1</sup> is observed in the IR-spectrum of

NaX(+5.0% Co) zeolite before working in the ethanol conversion process. This absorption band is also detected in the spectrum of the zeolite catalyst used in the process. Note that this catalyst (as well as other investigated multivalent cation-retaining zeolite catalysts) is annealed at 500 for several hours before processing. In this case, it is possible to form thermally stable surface structures (including in the presence of CO<sub>2</sub> in the air), and the complex absorption band mentioned above is related to those groups.

The IR spectrum of the NaX(+5.0% Co) catalyst treated in the process coincides with the spectrum of the untreated catalyst in the region of 3000-3800 cm<sup>-1</sup>, which indicates that after treatment, this catalyst improves its adsorption capacity (water adsorption in this case) ability to do) and its direct catalytic activity.

This mentioned result can be obtained on the basis of the superiority of the IR-spectroscopy method compared to RFA. The point is that, as it is known from the literature, during processing of zeolites at high temperatures, irreversible structural changes occur while maintaining their initial crystalline motifs, and as a result, zeolite can significantly lose its ability to adsorb. On the basis of RFA studies, it is not possible to make an unambiguous conclusion about this. However, based on the IR-spectrum of the used catalyst (or sorbent), including the NaX(+5.0%Co) catalyst, such a result is obtained directly.

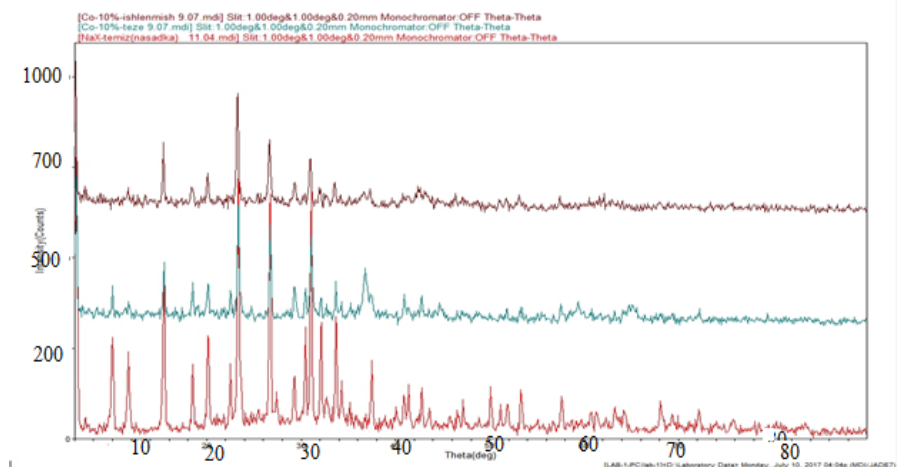
In Fig.9, X-ray images of the initial NaX catalyst and the NaX (+5.0%Co) catalyst before treatment and after treatment for 6 (723K) hours are given.

From the comparison of radiographs, it can be concluded that although the crystal lattice of the original NaX zeolite corresponding to faujasite is practically preserved in the Co modified zeolite, a certain decrease in crystallinity is observed. After working in the process for 6 hours, a little amorphization of the catalyst was observed.

The EPR spectra of NaX zeolite, NaX(+5%Co) and NaX(+10%Co) catalysts taken before the experiment and after 6 hours of operation in ethanol conversion process at 723K were studied.

Based on the obtained EPR spectra, in general, it can be stated that a certain change in the composition of the Co-containing catalyst

samples processed in the ethanol conversion process is observed. Thus, a signal with a g-factor of 2.0026 and a width of  $\Delta H=0.9$  mT is observed, which corresponds to the paramagnetic coke residue. It was determined that the EPR spectrum taken after burning the catalyst sample in the process at a temperature of 773 K in air flow is almost exactly equal with its spectrum in the first state.



**Figure 9. X-ray images of NaX (+10.0%Co) catalyst before ethanol conversion and after 6 h (723K) treatment and NaX catalyst**

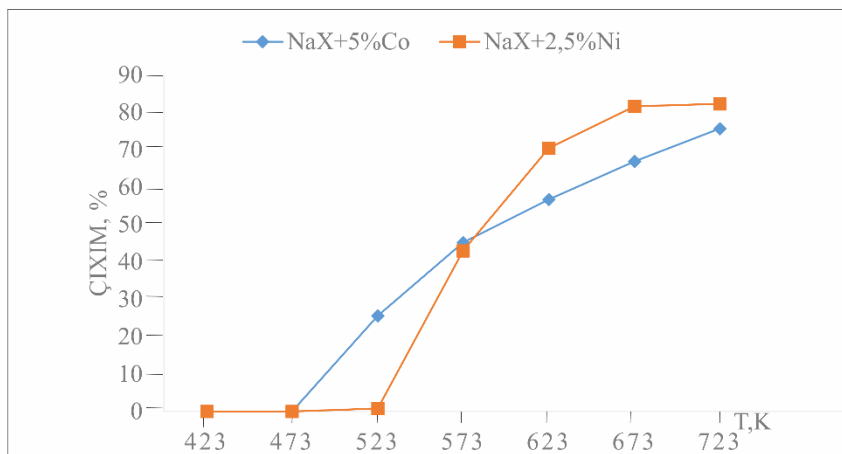
The previously mentioned catalytic studies show that in the process of converting ethanol in the presence of Co-containing samples in the temperature range of 423-723K, the activity of the catalyst increases with the increase in temperature up to 523K, and at this temperature, the yield of carbonyl compounds was maximum for the sample with the optimal content of 5% cobalt 26, It is 8%. However, when the cobalt content of the catalyst exceeds 5%, the yield of carbonyl compounds decreases with increasing temperature. For the NaX(+10% Co) sample at the indicated temperature, this indicator is 14.2%, and at 723K it decreases to almost

zero. In this case, such a sharp decline in activity can be related to both the change in the state of cobalt structures, the formation of large crystallites due to the accumulation of cobalt atoms, and the increase in their amount due to the formation of coke layers and the increase in temperature. During the oxidative dehydrogenation of ethanol, the study of the phase composition, active component distribution, and magnetic and catalytic properties of cobalt-containing catalysts based on NaX zeolite lets to optimize the relevant characteristics of the obtained catalyst samples depending on the modification conditions and to reduce the temperature limit of the reaction.

It was determined that the active phase in all synthesized Co-containing systems is superparamagnetic/ferromagnetic particles of cobalt component with spinel structure ( $\text{CoCo}_2\text{O}_4$ ). Higher catalytic activity in these systems is observed in samples of cobalt structures with superparamagnetic properties characterized by a relatively high content of particles. Such approaches to the synthesis of nanostructured catalysts with the necessary properties and the development of size-dependent catalytic properties control methods are of considerable theoretical and practical interest.

**Catalysts containing NaX(+Ni).** Studies show that 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  $\text{CO}_2$  also corresponds to NaX (+2.5% Ni) catalyst and is 82.3% at 723K temperature.

Figure 10 compares the temperature dependence of the carbon dioxide output during the conversion of ethanol over NaX catalysts containing Co and Ni. As can be seen from the figure, the maximum yield of carbon dioxide obtained from the conversion of ethanol on Co and Ni-containing catalysts is 75.5% and 86.3%, respectively.



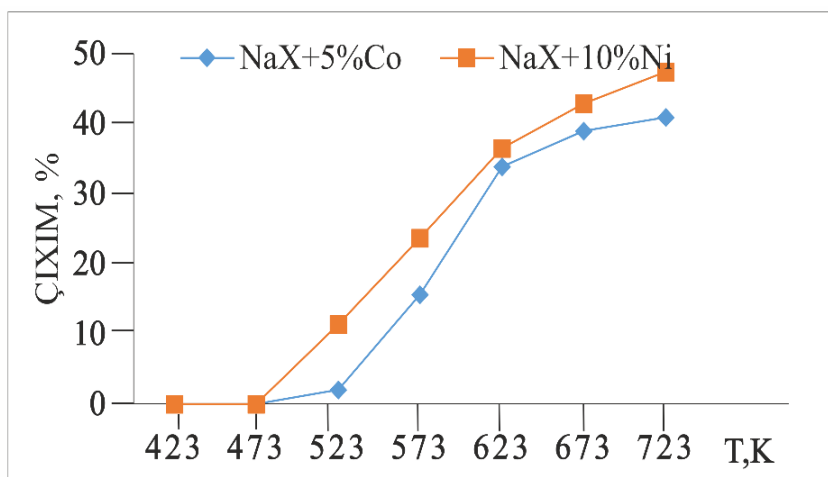
**Figure 10. Temperature dependence of the yield of carbon dioxide obtained from the conversion of ethanol on catalyst samples with distinct compositions**

**Study of the activity of NaX zeolite catalysts including Co and Ni obtained by impregnation in the process of propanol conversion**

**NaX(+Co)-containing catalysts.** For these compositions, 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(+Co)-containing catalysts, mainly intramolecular 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 propanol at relatively low temperatures. The production of carbonyl compounds starts at a temperature of 473K. The carbon dioxide release of all the investigated NaX(+Co) 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, and it corresponds to the composition of NaX(+5.0% Ni). The maximum yield of carbon dioxide, which is a complete oxidation product of alcohol, corresponds to the NaX(+10.0%Ni) catalyst and is 47.4% at 723K.

Figure 11 shows the temperature dependence of the yield of carbon dioxide formed as a result of the conversion of propanol over NaX catalysts containing Co and Ni: the maximum yield of this product corresponds to the temperature of 723K and it is 40.4% and 47.4%, respectively.

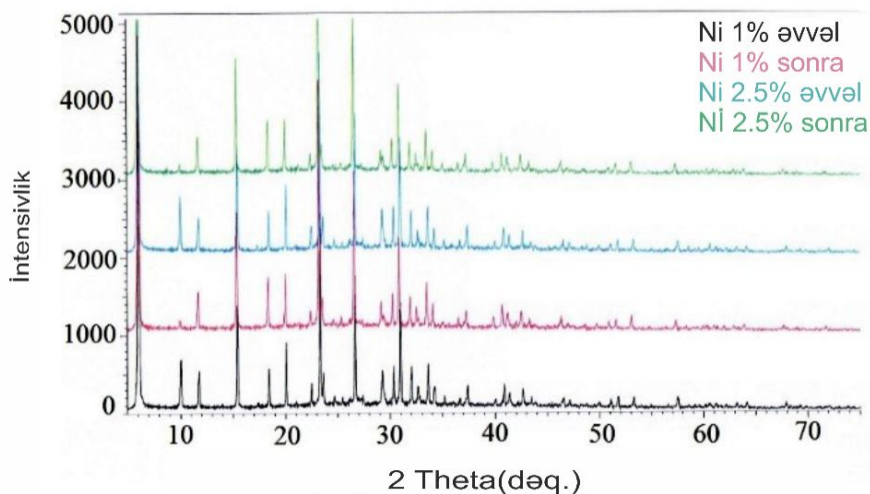


**Figure 11. Temperature dependence of carbon dioxide yield obtained from conversion of propanol on catalyst samples with different compositions**

Ni-containing catalysts used in the oxidation of propanol were studied by X-ray phase analysis and EPR methods before and after processing. In figures 12 and 13, 1.0; 2.5; 5.0; X-ray images of NaX catalysts with 10.0% Ni in their initial state and before and after propanol conversion are given.

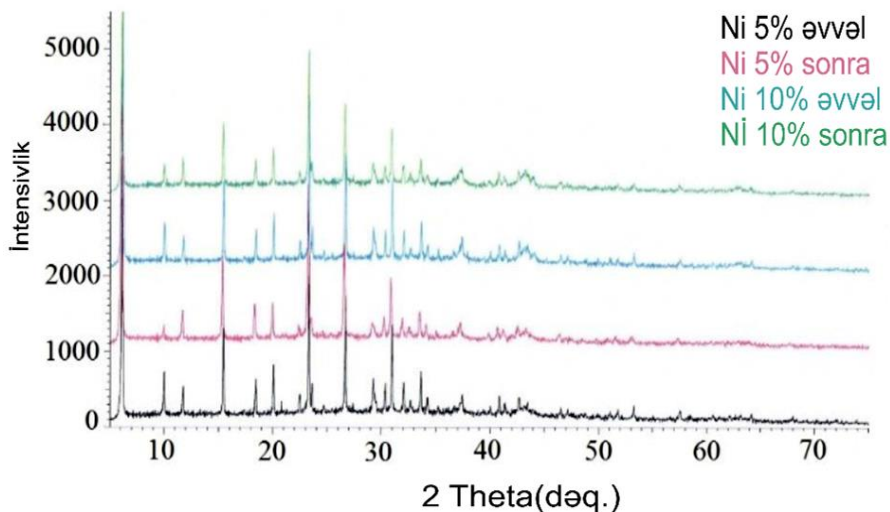
The peaks at  $32.037^\circ$  observed in the roentgenograms-  $2\theta = 6.116; 10,002; 23,347; 26,669$  correspond to the standard pattern of primary NaX zeolite.  $2\theta = 37,386$  (111); The peaks of  $43.478$  (200) and  $63.222^\circ$  (220) indicate the presence of NiO particles in NaX(+Ni) samples. 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  $500^\circ\text{C}$ .

The average size of NiO crystals was determined using the formula  $D = k\lambda / \beta\cos\theta$ . Here,  $\lambda$  is the wavelength of X-rays and it is  $1.54056\text{ nm}$ .  $\beta = \text{FWHM}$  and  $\theta$  -diffraction angle is calculated based on the peak.  $k$  is an empirical coefficient and is  $0.9$ . As a result of the calculation, it was determined that the average size of NiO particles included in the structure of NaX zeolite is  $28,314\text{ nm}$ .



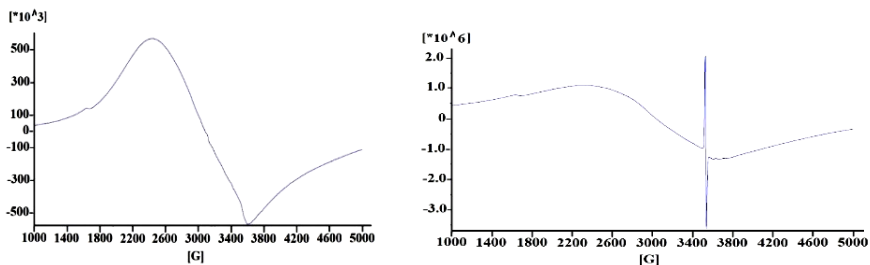
**Figure 12. X-ray images of catalysts containing NaX(+1.0%Ni), NaX(+2.5%Ni) before and after propanol conversion**





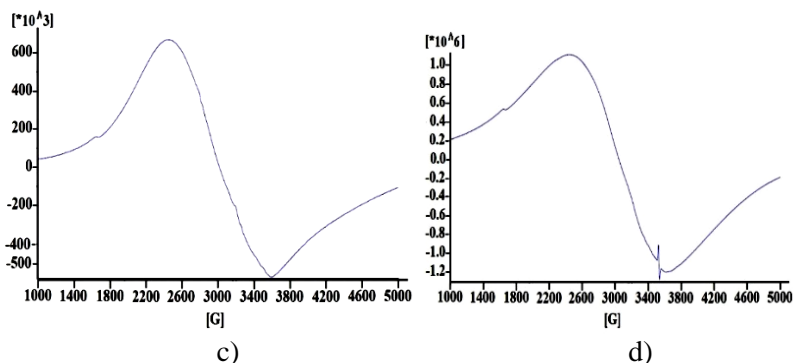
**Figure 13. X-ray images of NaX(+5.0%Ni), NaX(+10.0% Ni) catalysts taken before and after propanol conversion**

Figure 14 shows the EPR spectra taken before and after working for 6 hours during the conversion of NaX(+1.0%Ni) and NaX(+5.0%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 and a width of  $\Delta H=19-20$  mT 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. Studies have shown that the EPR spectrum of catalyst samples involved in the conversion of propanol for six hours undergoes a noticeable change.



a) NaX+1.0% Ni before the Propanol conversion process

b) NaX+1.0% Ni, after the conversion process of Propanol



c)

d)

c) NaX+5.0% Ni, before conversion of Propanol

d) NaX+5.0% Ni, after conversion of Propanol

**Figure 14. EPR spectra of NaX samples containing 1.0% (a,b) and 5.0% (c,d) before and after the 6 hours of operation in the propanol conversion process of NiO**

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  $\Delta H=0.9$  mT 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 conditions 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 catalytically active centers of this reaction, and the main participants of the reduction-oxidation stages in the process are Ni and NiO particles.

Table 1 shows the size (as a result of RF analysis) and values of magnetic resonance parameters (as a result of EPR analysis) of the NiO crystallite formed in the still state and on the surface of NaX zeolite. As can be seen from the results in the table, the size of NiO nanoparticles formed on the surface of NaX zeolite is smaller than the size of still NiO crystallite.

**Table 1**

**Size and value of magnetic resonance parameters of NiO crystallite formed in still state and on the surface of NaX zeolite**

Parameters	Still NiO crystallite	NiO/NaX
Nanoparticle Size (nm)	32,65	28,31
the value of the factor g	1,92	2,1
The width of EPR spectrum, $\Delta H_{pp}$ (mT)	72,5	66,9

Summarizing the conducted studies, it can be noted that in the process of ethanol and propanol oxidation, the selectivity of the studied catalyst forms with respect to carbon dioxide growth in the following order:



Thus, according to the conducted studies, it can be stated that the NaPdX (1.0%Pd) sample containing Pd at the nanoparticle level shows the highest activity in the process of complete oxidation of saturated monoatomic alcohols with a small molecular mass.

## RESULTS

1. The H-form of NaX zeolite modified with La and Pd metals was obtained by ion-exchange method and their catalytic activity was studied in the process of ethanol and propanol oxidation. It was determined that in La-containing catalysts, the process mainly occurs in acid-base active centers, while in Pd-containing samples, it mainly occurs in oxidizing centers. In the H-form, the strength of both centers is almost the same.
2. It was determined that the conversion of C2-C3-saturated monohydric alcohols in the presence of Pd-containing zeolite catalysts occurs at a lower temperature than in H- and La-containing samples. Thus, while the conversion of ethanol on samples containing H and La is controlled at a temperature of nearly 473K, this temperature is 423K for samples including Pd.
3. The maximum ethanol conversion rate is 75.5, 89.8, and 98.0% (773K) for H, La, and Pd samples, respectively. At the same time, it was determined that the selectivity for carbon dioxide, which is the complete oxidation product of alcohol, increases among La, H, and Pd samples and is 7.2%, 50.5%, and 83.2%, respectively.
4. Binary catalyst samples containing  $\text{CoOC}_2\text{O}_3/\text{NaX}$  and  $\text{NiO}/\text{NaX}$  were synthesized by the impregnation method and their catalytic activity was widely studied in the process of ethanol conversion. It was determined that Co-containing samples show higher activity than Ni-containing samples. Thus, the maximum conversion rate of ethanol was 95.1% and 89.5%, respectively. It was determined that Ni-containing catalysts show higher activity than Co-containing samples due to their oxidizing-reducing properties. So, while the maximum release of carbon dioxide on the Co-containing samples corresponds to the NaX+5% Co sample, it is 75.5% (723K), while on the Ni-containing samples, this indicator corresponds to the NaX+2.5%Ni sample and is given as 86.3 % (723K).
5. The process of oxidation of propanol on prepared catalyst samples has been widely studied and it has been declared that although its conversion on all samples is essentially the same as the conversion

- of ethanol, the degree of conversion of propanol and the output of carbon dioxide from the process are significantly reduced.
6. 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.
  7. It was determined that when the amount of transition metal in Co-containing catalyst samples exceeds 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 cobalt structures changes.
  8. It was determined that the NaPdX (1%Pd) sample containing Pd at the nanoparticle level shows the highest activity in the process of complete oxidation of saturated monoatomic alcohols of small molecular mass. The highest activity was shown by the NaPdX (1 % Pd) sample. Thus, during the transformation of ethanol and propanol on this sample, the maximum yield of carbon dioxide was 83.2 and 74.8%, respectively.

**The main results of the dissertation work were published in the following articles and theses:**

1. A.D.Valiyeva. Characteristics of oxidation of ethanol over NaX and its cationic forms / Scientific conference of doctoral students and young researchers entitled "Azerbaijan 2020 prospects of the oil and gas industry" dedicated to the 90th anniversary of the National Leader of the Azerbaijani people Heydar Aliyev.
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  13. P.A.Nadirov, A.D.Valieva Study of ethanol oxidation process on cobalt-containing nanostructured NaX zeolite catalyst / The International Scientific "Actual problems of Modern Chemistry" Dedicated to the 90 th anniversary of the Academician Y.H.Mammedaliyev institute of Petrochemical Processes, October 2-4, -2019. - p. 339.
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the reaction of oxidative conversion of propanol-1 / Chemical problems no. 3 (18) 2020. p. 410-417

18. A.D.Valiyeva Metal supported on natural zeolite as catalysts for conversion of propanol /Baki Universitetinin Xəbərləri -2021. №4, -s. 22-27.



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