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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**SYNTHESIS OF PURPOSEFUL CATALYSTS BASED ON
ZEOLITES FOR OXIDATION REACTION OF ALIPHATIC
ALCOHOLS AND STUDY OF ACTIVITIES**

Speciality: 2303.01–Inorganic chemistry
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Field of science: Chemistry

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The dissertation work was accomplished at the Institute of Catalysis and Inorganic Chemistry, named after academician M. Nagiyev of the National Academy of Sciences of Azerbaijan, in the “Zeolite catalysis” laboratory.

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GENERAL CHARACTERISTICS OF WORK

Relevance of the topic and level of study. The world's scientists have called zeolites "minerals of the XXI century." They are effectively used in many industries due to their unique physical and chemical properties and technological qualities. Industrial processes such as purification of normal paraffin hydrocarbons, catalytic reactions of hydrocarbons (cracking, isomerisation, oxidation, dehydrogenation, etc.) as well as the acquisition of carriers for catalysts, as well as separation of radioactive isotopes from atmospheric liquid wastes, carbon dioxide from natural gas processes of decontamination are sufficient to show the vast area of use of zeolites.

The widespread use of zeolites is due to their unique structure. At the same time, along with the essential practical significance of zeolites, the study and explanation of their physicochemical and catalytic properties is also an important issue and is the focus of experts working in this field.

The use of mainly synthetic zeolites in catalytic processes in the industry indicates the tremendous theoretical and practical importance of the synthesis of zeolites.

Production of synthetic zeolites based on natural raw materials has become widespread in recent years. In producing any product, simple technological, low-cost, and environmentally friendly production methods are preferred. From an economic point of view, this process is very convenient due to the low price of the initial components for the synthesis of zeolites, the production of high-purity and durable carcass structural zeolites.

Given the presence of natural aluminosilicate (kaolinite, bentonite clay) deposits in the country, the synthesis of zeolites based on these raw materials and the study of their physicochemical and catalytic properties are significant issues.

The application of zeolites synthesized in the oxidation of small molecular weight (C_1-C_5) alcohols promises excellent prospects. Thus, the high selectivity of oxidation reactions on zeolite catalysts for products of particular importance, the simplicity of the

process of separation of products, the wide range of applications of the products in the chemical, food and pharmaceutical industries are of great interest.

The objectives and tasks of the research.

The study's purpose is to synthesise effective zeolite catalysts for the catalytic oxidation reactions of aliphatic alcohols, study the activities of these catalysts, and study the kinetics and mechanism of oxidation reactions.

To achieve the purpose of the research, we have planned the following tasks:

- Synthesis of mordenite zeolite based on natural raw materials (kaolinite) by hydrothermal method, production of CaA zeolite by ion–exchange method;
- Identification of zeolites synthesized by modern research methods, determination of their composition and physical and chemical properties;
- Modification of synthesized mordenite and CaA zeolites with ions of transition metals, the study of the activity of prepared metal–zeolite catalysts in oxidation reactions of butanol–2 and 1–pentanol;
- Selection of the probable step–by–step scheme of the mechanism of the studied reaction;
- Development of a theoretically substantiated kinetic model of the process.

Research methods. Composition of raw materials for the synthesis of zeolites, as well as synthesized zeolite samples before and after heat treatment, physical and chemical properties by x-ray Diffraction (XRD), X-Ray Fluorescence (XRF), Derivatographic Analysis (DTA), Fourier Transform Infrared Spectroscopy (FTIR) identified, the mineralogical and elemental composition was studied in Atomic Absorption Spectrometry (AAS) and Atomic Emission Spectroscopy (ICP–OES). Raw materials and reaction products taken for the oxidation process were determined by Thermal Conductivity Gas Chromatography (GC–TCD) and Mass Spectrometry Gas Chromatography (GC–MS).

The main provisions of the defence are as follows:

- Synthesis of zeolites based on natural raw materials

(kaolinite, bentonite) found in the territory of our republic, the influence of various factors on synthesis conditions, the study of synthesis conditions;

- Identification of the obtained zeolites, the study of their composition and physical and chemical properties;

- Preparation of purposeful catalysts from modified zeolites and study of the activity of these catalysts in the process of oxidation of butanol–2 and 1–pentanol alcohol;

- Experimental study of the kinetic regularities of oxidation processes, statistical analysis of the stepwise kinetic model of reactions based on experimental evidence and calculation of numerical values of constants of the kinetic model.

The scientific novelty of the research. For the oxidation reaction of aliphatic alcohols on modified zeolite catalysts, a method of synthesizing effective catalysts by a hydrothermal method based on natural aluminosilicates kaolinite, bentonite clay was developed. Based on this system, mordenite, analcym type zeolites were synthesized, and CaA type zeolite was obtained by the ion–exchange method, were determined these zeolites' significant physical and chemical properties. In addition, were studied the catalytic activity of synthesized zeolites (MOR, CaA) and their ion–modified forms of transition elements in the oxidation processes of butanol–2 and 1–pentanol. Found that these zeolites show high catalytic activity and selectivity in the reactions mentioned above. A kinetic model of the oxidation process of butanol–2 and 1–pentanol on MOR and CaA zeolites was developed, and the values of the kinetic model parameters were calculated.

The theoretical and practical significance of the research.

Local mineral resources such as kaolinite and bentonite, widespread in Azerbaijan, were used to prepare zeolites. The selected starting materials have been proven to be entirely suitable for the direct synthesis of zeolites with high stability and adsorption capacity. Synthesized zeolites can be used in various industries as an adsorbent and catalysts. Catalysts based on synthesized mordenite and CaA zeolites can be used in the oxidation process of aliphatic alcohols and the esterification reactions of aliphatic alcohols. A

theoretically substantiated kinetic model of the oxidation of aliphatic alcohols on catalysts based on synthesized zeolites can be adopted for the construction and optimal design of a mathematical model of the process. During the synthesis of zeolites, the established laws can be used in the purposeful synthesis of various aluminosilicates.

Approbation and application:

The main results of the dissertation were reported and discussed at the following national and international conferences:

- Scientific Conference dedicated to the 105th anniversary of Academician MF Nagiyev (Baku, 2013);
- 1st International Scientific Conference of young scientists and specialists, (Baku, 2014);
- II Russian Congress on Catalysis "Roscatalysis" (Novosibirsk, 2014);
- Republic. Scientific conf., Posv. To the 90th anniversary of academician Togrul Shakhtakhtinsky (Baku, 2015);
- International Turkic world conference on Chemical sciences and technologies (Sarajevo, 2015);
- Republican scientific conference dedicated to the 80th anniversary of the Institute of Catalysis and Inorganic Chemistry named after M. Nagiyev (Baku, 2016).

The organisation where the dissertation work is performed.

The dissertation work was carried out in the "Zeolite catalysis" laboratory of the Institute of Catalysis and Inorganic Chemistry, named after academician Murtuza Nagiyev of the Azerbaijan National Academy of Sciences.

Degree of publication of the research. 16 scientific works on the topic of the dissertation were published. 8 of them are articles, 6 abstracts and 2 patents of the Republic of Azerbaijan. Two papers were published mono-author, and four articles were published in international summary and indexing systems.

The author's contribution covers the development of the purpose of the dissertation, the result of a methodological approach to its solution, the implementation of most of the experimental research and their generalisation.

The structure and scope of the dissertation. The dissertation

consists of an introduction (7918 symb.), four chapters (I chapt.–59820 symb., II capt.–51062 symb., III chapt.–38282 symb., IV chapt.–37408 symb.) and general results. The volume of the dissertation consists of 163 pages with computer printing. The work consists of 219542 characters, including 24 figures, 18 tables and a list of references to 164 titles.

MAIN CONTENT OF THE WORK

The introductory part reflects the relevance of the research topic, the purpose of the work, the issues to be solved, scientific innovations, the practical significance of the work, the main provisions of the defence and the summary of individual chapters.

The first chapter provides information on the global distribution of zeolites, zeolite-forming systems, existing synthesis methods of zeolites and synthesis based on natural aluminosilicates, adsorption, ion-exchange and catalytic properties of zeolites. The scientific literature was analysed and the issues facing were identified.

The second chapter describes the methods of synthesising zeolites based on natural aluminosilicates (bentonite, kaolinite) and identifying synthesized zeolites, structural and chemical properties. The application of infrared spectroscopy, X-ray spectral, radiographic, dervitographic, atomic absorption and atomic emission spectrometry was shown to explain the chemical, phase composition of primary raw materials and products and the thermal transformation of primary substances.

In addition, this part of the paper presents the results of experiments conducted to study the conditions for the synthesis of zeolites and touches on the preparation of catalysts from synthesized zeolites. The processes of obtaining catalysts from zeolites in the presence of metal cations by the ion-exchange method are widely covered.

Synthesis of mordenite zeolite.

Bentonite clay was used as a raw material for the synthesis of mordenite zeolite. Even though the conditions of synthesis and the proportions of raw materials taken vary widely, the crystallisation process was observed mainly in the direction of obtaining analysm zeolite. Therefore, kaolinite was taken as a natural source of aluminosilicate, heat-treated at 650⁰C, converted into a highly active metakaolin form, and used in synthesis.

The process of hydrothermal synthesis was carried out in autoclaves of “MORI” type at a temperature difference of $\pm 2^{\circ}\text{C}$ at

100–220⁰C, at intervals of pH=9~13 and τ =48~216 hours. At the end of the process, the solid phase was collected on a filter, washed with distilled water, then dried at 110⁰C for 24 hours and thermally treated at 550⁰C for 8 hours. This method increased the ratio of SiO_2/Al_2O_3 in the product and reduced the proportion of Na_2O/SiO_2 in the initial raw material mixture.

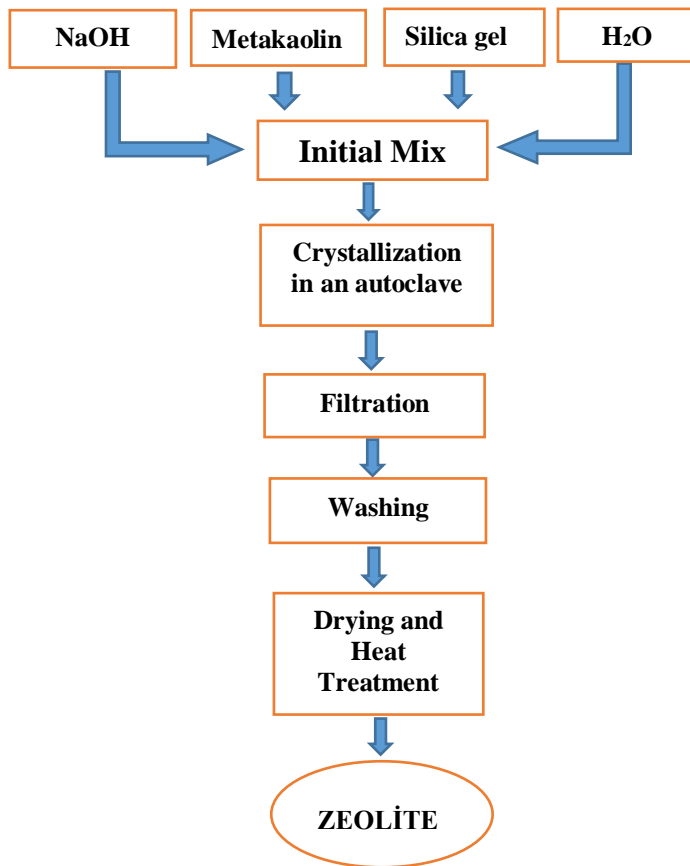


Figure 1. Scheme of synthesis of mordenite zeolite by hydrothermal method.

A stainless steel autoclave with a nylon lid capacity of 35 ml and a furnace equipped with a thermometer was used to carry out the synthesis process. The formula of the reaction mixture can be expressed as $4\text{Na}_2\text{O}\times\text{Al}_2\text{O}_3\times 26\text{SiO}_2\times 226\text{H}_2\text{O}$. It was found that keeping the starting material mixture at room temperature for 8 hours before inclusion in the crystallisation process (incubation period) positively affected the crystallisation process. The experimental products were filtered through filter paper, washed with 250 ml of distilled water at a temperature of 70–80°C, and dried at 110°C for 3 hours, and were studied their physical and chemical properties.

Better crystallisation at $T=170^\circ\text{C}$, $\tau=24$ hours, $\text{pH}=10$ and the ratio of $2\text{Na}_2\text{O}\times\text{Al}_2\text{O}_3\times 18\text{SiO}_2$ of the components was observed. Under these conditions, pure mordenite crystallises. In this case, the yield of the crystallisation process is 100% for Al_2O_3 .

It leads to the formation of mordenite/analsym mixture (70/30%) when the synthesis time is extended to $\tau=72$ hours, and other conditions are the same. Quartz is obtained together with the analsym when $\text{pH}=13$, $T=180^\circ\text{C}$ when the mole ratio of the initial components and the duration of the synthesis is $\tau=120$. As a result, it was possible to obtain mordenite–mordenite/analsym–analsym–analsym/quartz phase transitions. This method's crystalline shape of mordenite varies from an irregular spherical shape to a rhombic form. An X-ray diffractometer determined the size ($\sim 5 \mu\text{m}$) and composition of the crystal. The prominent characteristic peaks for mordenite were $d = 3.49, 3.91, 9.16, 3.36$ and 3.31 \AA .

The transitions shown in Figure 2 occur as follows. As is well known, all zeolites are considered to be metastable phases, and when stored in an alkaline environment for a long time, they tend to disintegrate and transition to a more stable phase. The highly crystallised mordenite zeolite obtained by us is not resistant to the alkaline environment due to its open structure and low carcass density (1.70 cm^3), which leads to the gradual disintegration of the mordenite structure by dissolving SiO_4 tetrahedrons (desilicization).

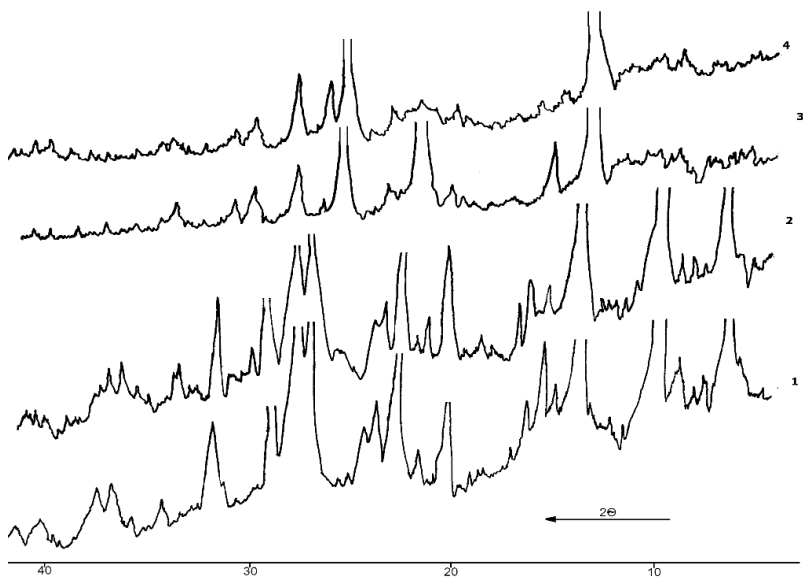


Figure 2. Diffractogram of synthesis products: 1–pure mordenite, 2–mordenite+analsym, 3–analsym, 4–analsym+quartz.

This process results in the formation of a low–silicate, analsym zeolite structure with a carcass density of 1.85 cm³, which is more thermodynamically stable.

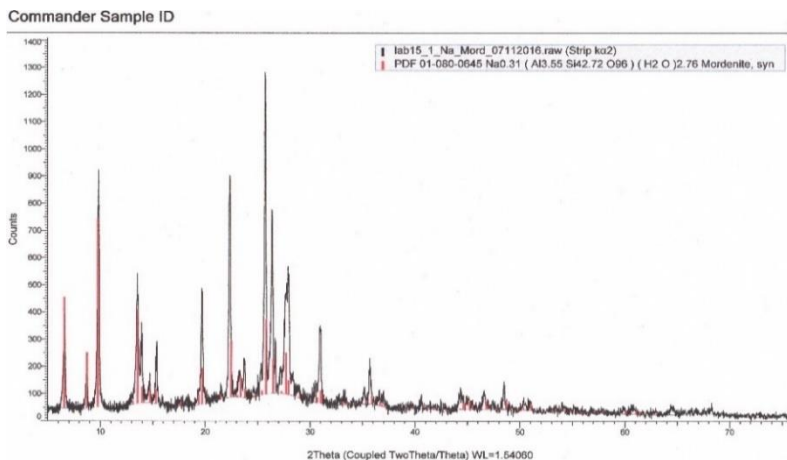


Figure 3. Diffractometric results of synthesized mordenite.

The chemical and mineralogical composition of pure mordenite, determined by X-ray Fluorescent (“EDXRF–7000”) and X-ray Diffractometric (“D2 Phaser”) methods (Figure 3.), showed that the synthesized mordenite corresponds to the formula $\text{Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times 18\text{SiO}_2$, and the rate of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is equal to 18. This indicates that the silicate modulus of the obtained mordenite zeolite is higher than the natural and comparable synthetic analogues.

Comparison of the synthesized mordenite with its natural and synthetic analogues ($\text{SiO}_2/\text{Al}_2\text{O}_3=16$) obtained from the Gorky Experimental Base due to their crystal-chemical properties is given in Table 1.

Table 1. Basic crystal-chemical parameters of Mordenite zeolite

Zeolite	Parametrār					$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	Cage type
	a	b	c	α	β		
MOR ¹	18.1	20.49	7.52	1.47	1.48	10	Romb.
MOR ²	18.1	20.51	7.53	1.21	1.34	16	Romb.
MOR ³	18.2	21.2	7.38	1.56	1.61	18	Romb.

¹–natural; ² – synthetic; ³–synthesized sample.

As can be seen from the table, the crystal-chemical results of the synthesized zeolite fully reflect that it is a mordenite zeolite.

Synthesis of analysm zeolite.

Applying analysm zeolite in modern times as a raw material with high adsorption capacity in solving several environmental and artificial problems and in the field of treatment in the form of nano-sized particles in high–tech processes is essential. Natural analysm zeolite contains a mixture of caesium (Cs) and rubidium (Rb), limiting its application. In this regard, the synthesis of analytical zeolite from environmentally friendly raw materials is of great interest for application in these areas. Due to the high sorption capacity, the diversity of applications, and the importance of its use in practice, the synthesis of analysm has been studied in detail. Moreover, we have determined the optimal conditions for synthesis.

Synthesis of analysym type zeolites by the hydrothermal method was carried out using the technique of crystallisation in a bentonite clay–liquid glass system. An increase in the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the crystallisation products was achieved by reducing the proportion of $\text{Na}_2\text{O}/\text{SiO}_2$ in the mixture of primary products and increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$.

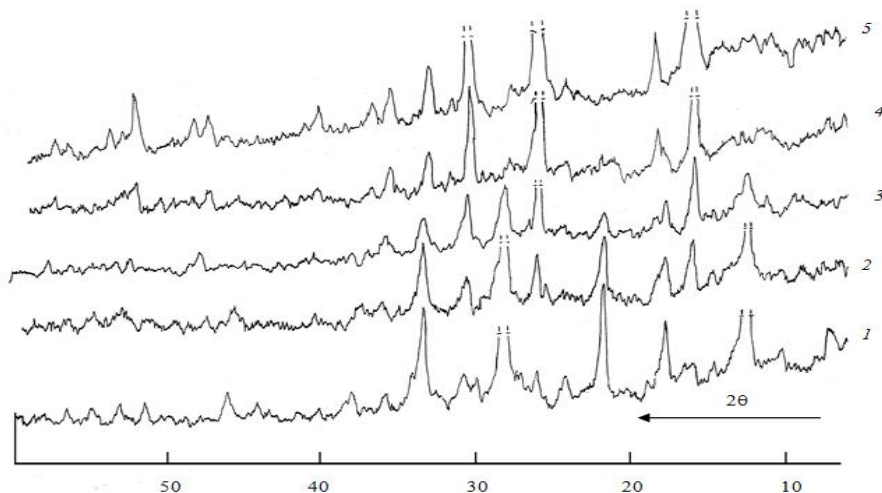


Figure 4. Diffractogram of crystallization products:
1–montmorillonite, 2–montmorillonite+traces of analysym,
3–traces of analysym+montmorillonite, 4–analysym,
5–pure analysym.

Bentonite, NaOH solution, silica gel, and distilled water were used as raw materials during the synthesis.

The chemical composition of pure analysym zeolite synthesized by the XRF method was determined to correspond to the formula $\text{Na}_{15}\text{Al}_{15}\text{Si}_{33}\times 15\text{H}_2\text{O}$.

Obtained analysis from XRD results based on the diffractogram shown in Figure 6 and Table 2.

Based on the diffractogram, were determined the parameters of the elementary cage. It is shown that the sample is a pure analysym that crystallises in cubic syngony at the parameter $\alpha = 13.77\text{\AA}$.

Table 2. Diffractometric results of analysm zeolites synthesized from bentonite.

№	hkl	Synthesis product		After heat treatment at 550°C	
		d, Å	I	d, Å	I
1	208	5.6232	93	5.6041	89
2	221	4.851	19	4.8436	20
3	323	3.671	14	3.6512	20
4	401	3.444	96	3.4301	101
5	334	2.933	61	2.9281	58
6	421	2.808	12	2.7933	14
7	433	2.692	17	2.6916	18
8	519	2.511	17	2.5054	29
9	441	2.429	8	–	–
10	612	2.231	10	2.2288	9
11	543	2.125	4	2.1149	13
12	632	2.028	6	–	–
13	541	1.934	4	1.91856	11
14	638	1.905	15	1.906	19
15	631	1.874	11	–	–
16	644	1.839	5	–	–
17	731	1.746	23	1.749	21

Obtaining the CaA zeolite.

NaA ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2,0$), CaCl_2 solution was used as a raw material to synthesise zeolites by the **ion-exchange method**. For comparison, CaA zeolites synthesized at the Gorky Experimental Base in Russia were taken.

For synthesis, 25 g of NaA zeolite was taken and placed in a three-necked flask equipped with a thermometer, separator funnel and mixer. For the exchange, a solution of CaCl_2 containing Ca^{2+} ions equivalent to Na_2O was prepared in the original zeolite. The amount of Ca^{2+} ions included in zeolite was studied by Atomic Emission (ICP–AES) and Atomic Absorption (AAS) devices. Prolongation of the exchange time (3 hours) or increase in the concentration of CaCl_2 solution (5.33%) did not affect the maximum amount of Ca^{2+} ions exchanged (65.5%).

Based on X-ray phase tests of the synthesized CaA zeolite, it was determined that zeolite has a crystalline structure in the composition of CaO –62.2, Na_2O –6.5, SiO_2 –25.9, Al_2O_3 –4.80 (w/w,

%) (α =SiO₂:Al₂O₃=5.4) (Fig. 5).

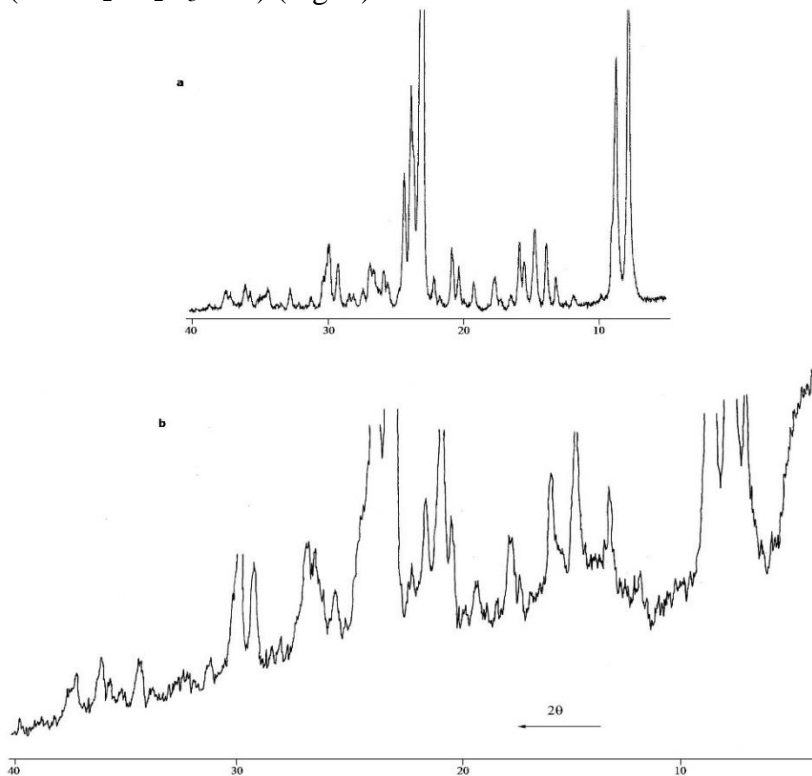


Figure 5. Diffractometric results: a) synthetic CaA and b) synthesized CaA.

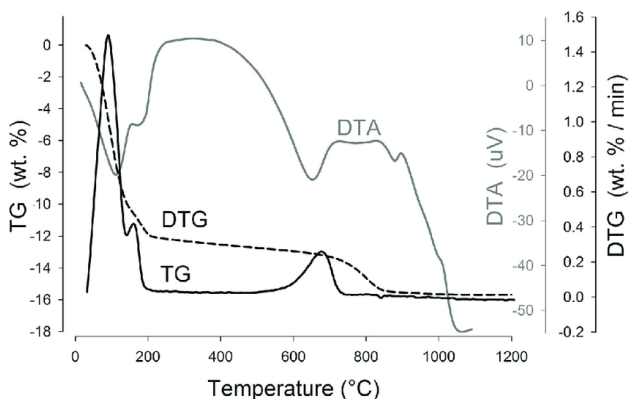


Figure 6. Derivatogram of synthesized CaA zeolite.

Synthesized CaA zeolite was studied by the DTA method. The dervitogram revealed an endo effect corresponding to zeolite dehydration at a temperature of 50–350⁰C (maximum 170⁰C) on the DTA curve. The total weight loss is 4.11% (Fig. 2).

The radiograph of the synthesized CaA zeolite shown in Figure 3 was studied using a Brucker D2 Phaser X-ray diffractometer.

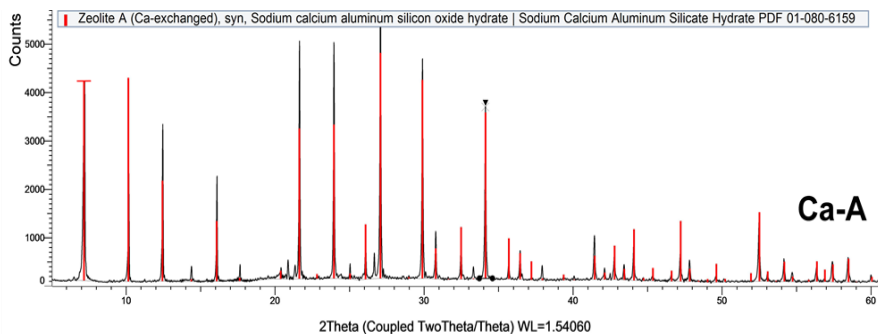


Figure 7. XRD result of synthesized CaA zeolite.

The obtained radiographic results proved that the zeolite synthesized by us belongs to CaA type zeolites.

Modification of zeolites. To obtain H⁺ forms of zeolites used in the study, zeolites dried at 120–150⁰C were first treated in a three-necked flask with a solution of 1.0–3.0 N NH₄Cl (NH₄NO₃) three times, for 2 hours every time at 80–90⁰C by ion-exchange method NH₄⁺ forms were received. These samples were then washed in Cl⁻ (NO₃⁻) ions, dried in an oven at 80–120⁰C for five hours, and obtained at H⁺ forms at 350–400⁰C and 500–550⁰C for 3–5 hours. At the end of the exchange, the catalyst was washed with Cl⁻ ions in distilled water, dried in a drying oven at 125⁰C for 3–5 hours and thermally treated in a temperature range of 450–500⁰C. The H⁺ forms of the synthesized mordenite and CaA zeolites were obtained by first working in a solution of 0.5 N HCl and then 1 N NH₄Cl for one hour and then washed, dried and thermally treated as described above.

Modification of zeolites with cations of transition elements (Cu²⁺, Pd²⁺, Zn²⁺, etc.) was carried out by the ion-exchange method. For this

purpose, a sample of 10 grams of dried Na⁺ and H⁺ forms of zeolites used was placed in a one-litre round flask. Then a solution of the chloride salt of transition elements (Cu²⁺, Zn²⁺) up to 0.02–5.0% of its dry mass was added drop by drop on the zeolite sample and heated to 95–98°C. Modification with Pd²⁺ ions was carried out in [Pd (NH₃)₄] Cl₂ complex salt solution.

Atomic Absorption Spectrometry (AAS) and Atomic Emission Spectroscopy (ICP–AES) analysis methods were used to determine the number of metal cations included in the zeolite.

It was determined that the amount of cations exchanged in zeolite was Cu²⁺–1.0–4.0% by mass, Pd²⁺–0.1–0.2% by mass, Zn²⁺–1.0–0.0 by mass%.

The third chapter gives an experimental laboratory equipments scheme and working principle for studying the catalytic activities of synthesized zeolite samples. The experiments were performed in a flow-type reactor made of pyrex glass at 200–380°C, a volume velocity of 400–4000 s⁻¹, and different molar ratios of reagents (alcohol / O₂ / N₂). The procedure for conducting experiments, analysis of reagents and products, preliminary processing of experimental results, the study of the catalytic activity of synthesized (MOR, CaA), synthetic (NaA, NaY, MOR, CaA,) and natural mordenite zeolites in the oxidation of butanol–2 and 1–pentanol experimental results are reflected.

The catalytic properties of the oxidative reaction of 1–pentanol to valeric acid on mordenite zeolite were studied based on catalyst samples prepared by incorporating different amounts of metal cations Cu²⁺, Zn²⁺ and Pd²⁺ by the ion–exchange method into natural and synthetic mordenite zeolites. The experimental results of the catalytic activities of some of these samples and the unmodified forms of catalysts in the oxidative reaction of 1–pentanol to valeric acid are given in Table 3.

The results, shown in Table 3, present that the unmodified forms of natural and synthetic mordenite zeolites show low catalytic activity in the oxidative dehydrogenation reaction of 1–pentanol to valeric acid, thus providing a dehydration reaction of 1–pentanol to amylenes (e.g. №1, 9). The yield of amylenes on mordenite is higher

than that of natural mordenite zeolite, which is explained by the fact that synthetic mordenite zeolite has a higher crystallinity (98%) than natural mordenite.

Table 3. Experimental results of catalytic activities of natural and synthetic mordenite zeolites and their modified forms with Cu^{2+} , Zn^{2+} and Pd^{2+} cations in the reaction of oxidising 1-pentanol alcohol to valeric acid at a temperature of 280°C , volume velocity 2000 h^{-1} and alcohol ratio of reagents: O_2 : $\text{N}_2=1: 1:3.8$.

№	Zeolite	Amount of cations, w/w, %			Con-version X, %	Yield, %			
		Cu^{2+}	Pd^{2+}	Zn^{2+}		Valeric acid, A_1	Valeric aldehyde, A_2	Amy-lens, A_3	CO_2 , A_4
1	H-Mor (nat.)	–	–	–	11.9	6.7	0.6	4.3	0.3
2	–	10	–	–	23.3	18.9	1.7	1.9	0.8
3	–	3.0	–	–	32.5	26.2	2.4	2.6	1.3
4	–	4.0	–	–	32.6	25.6	2.2	3.2	1.6
5	–	3.0	0.1	–	48.2	37.5	3.6	4.9	2.5
6	–	3.0	0.2	–	47.5	36.1	3.4	5.1	2.9
7	–	3.0	0.1	2.0	53.1	42.6	4.4	3.7	2.1
8	–	3.0	0.1	3.0	51.1	39.2	4.1	5.3	2.5
9	H-Mor (synthesized.)	–	–	–	16.4	10.2	0.8	4.7	0.7
10	–	1.0	–	–	30.5	24.6	2.2	2.6	1.1
11	–	3.0	–	–	36.6	29.1	2.8	3.1	1.6
12	–	4.0	–	–	36.9	28.4	2.6	3.8	2.1
13	–	3.0	0.1	–	57.8	43.8	4.7	5.6	3.7
14	–	3.0	0.2	–	56.7	42.4	4.4	5.8	4.1
15	–	3.0	0.1	2.0	64.9	51.4	5.5	4.9	3.1
16	–	3.0	0.1	3.0	61.7	47.3	4.9	6.1	3.4

Based on the analysis of the results given in Table 6, it can be concluded that the mordenite metal-zeolite catalyst synthesized from hydrothermal kaolinite and containing 3.0% Cu^{2+} , 2.0% Zn^{2+} and 0.1% Pd^{2+} has a high oxidative conversion activity of the 1-pentanol to valeric acid (exp. №15). The kinetic regularity of the reaction has been studied in the absence of diffusion inhibition on this catalyst.

Table 4 presents the results of an experimental study of the kinetic regularity of the oxidative conversion of 1-pentanol to valeric acid on a CuZnPdMor (synth.) catalyst (3% Cu^{2+} , 2% Zn^{2+} , 0.1% Pd^{2+}).

Table 4. Experimental results of the study of the kinetic regularity of the oxidative conversion of 1–pentanol to valeric acid on the catalyst mordenite (synthesized), modified by 3.0% Cu²⁺, 2.0% Zn²⁺ and 0.1% Pd²⁺.

№	Vol. Velocity, V, h ⁻¹	T, °C	P _{sp}	P _{O₂}	Conv. X, %	Yield, %			
						Valeric acid, A ₁	Valeric aldehyde, A ₂	Amy–lens, A ₃	CO ₂ , A ₄
1	1500	260	0.15	0.18	64.2	47.9	8.6	4.6	3.1
2	1800	260	0.15	0.18	60.5	45.5	8.1	4.2	2.7
3	2000	260	0.15	0.18	56.7	42.8	7.6	3.9	2.4
4	2200	260	0.15	0.18	52.9	40.1	7.2	3.5	2.1
5	2500	260	0.15	0.18	49.8	38.2	6.8	3.1	1.7
6	1500	280	0.17	0.17	72.3	56.3	6.5	5.6	3.9
7	1800	280	0.15	0.31	70.8	53.1	6.2	6.3	5.2
8	2000	280	0.17	0.17	64.9	51.4	5.5	4.9	3.1
9	2200	280	0.14	0.29	74.1	55.2	6.8	6.6	5.5
10	2500	280	0.15	0.18	70.2	58.1	4.7	4.3	3.1
11	1500	300	0.15	0.18	81.6	66.4	4.2	6.1	4.9
12	1800	300	0.15	0.31	74.3	54.8	6.7	6.9	5.8
13	2000	300	0.13	0.25	76.8	56.6	6.9	7.2	6.1
14	2200	300	0.14	0.29	79.2	58.2	7.1	7.5	6.4
15	2500	300	0.15	0.31	68.1	50.6	5.9	6.2	5.4
16	1500	320	0.15	0.31	78.1	57.2	7.2	7.4	6.3
17	1800	320	0.13	0.25	78.7	57.6	7.2	7.5	6.4
18	2000	320	0.14	0.29	82.4	60.2	7.5	7.8	6.9
19	2200	320	0.15	0.31	74.5	54.6	6.9	7.1	5.9
20	2500	320	0.14	0.29	79.7	58.9	7.1	7.3	6.4

The results in Table 4 show that the oxidative conversion of 1–pentanol alcohol to valeric acid on these catalysts is accompanied by the oxidative dehydrogenation of amyl alcohol to valerian aldehyde, the dehydration and deep oxidation of amyl alcohol to amylenes and carbon dioxide, respectively.

Analysis of the results obtained for the studied samples shows that the effective catalyst for the oxidative conversion of 1–pentanol to valeric acid was synthesized by us and got based on mordenite zeolite modified with metal cations in the amount of 3% Cu²⁺, 2% Zn²⁺, 0.1% Pd²⁺.

Catalytic properties of CaA zeolite for the oxidative dehydrogenation reaction of 1–pentanol to valerian aldehyde.

Studies have shown that the catalytic oxidation reactions of amyl alcohol on zeolite catalysts are almost non-existent. Therefore,

the oxidative dehydrogenation of 1-pentanol on synthetic CaA and CaA zeolites synthesized by us is of great interest. For this purpose, modified forms of zeolites with different amounts of metal ions were taken by primary and ion-exchange methods, comparative study of catalytic activity was carried out.

Experimental results of the catalytic activity of the initial and modified forms of these catalyst samples in the oxidative dehydrogenation reaction of amyl alcohol to valerian aldehyde are given in Table 5.

Table 5. Experimental results of catalytic activities of synthesized CaA, synthetic CaA zeolite and their modified forms with Cu^{2+} , Zn^{2+} and Pd^{2+} cations in the reaction of oxidative dehydrogenation of 1-pentanol alcohol to valerian aldehyde at a temperature of 320°C , volume velocity 1600 h^{-1} and alcohol reagents: $\text{O}_2:\text{N}_2=1:0.75:2.9$.

№	Zeolite	Amount of cations, w/w, %			Conversion X, %	Yield, A, %		
		Cu^{2+}	Pd^{2+}	Zn^{2+}		Valeric aldehyde, A_1	Amilens, A_2	CO_2 , A_3
1	CaA (synthetic)	–	–	–	45.9	39.6	5.1	1.2
2	–	1.0	–	–	57.8	53.3	2.7	1.8
3	–	3.0	–	–	64.8	58.9	3.5	2.4
4	–	4.0	–	–	64.2	57.1	4.2	2.9
5	–	3.0	0.1	–	80.3	70.1	5.9	4.3
6	–	3.0	0.2	–	79.4	68.4	6.2	4.8
7	–	3.0	0.1	2.0	85.7	76.8	5.3	3.6
8	–	3.0	0.1	3.0	83.5	72.3	6.9	4.3
9	CaA (synthesized)	–	–	–	50.4	43.2	5.6	1.6
10	–	1.0	–	–	62.1	56.6	3.4	2.1
11	–	3.0	–	–	67.7	61.1	3.9	2.7
12	–	4.0	–	–	68.2	60.4	4.6	3.2
13	–	3.0	0.1	–	85.1	73.8	6.4	4.9
14	–	3.0	0.2	–	84.4	72.4	6.7	5.3
15	–	3.0	0.1	2.0	92.7	82.7	5.8	4.2
16	–	3.0	0.1	3.0	90.4	78.4	7.2	4.8

The results in Table 5 show that synthetic and unmodified forms of CaA zeolite synthesized by us show low catalytic activity in the oxidative dehydrogenation reaction of 1-pentanol to valerian aldehyde, thus ensuring the dehydration reaction of 1-pentanol to

amylene (exp., 1, 9). Also, the yield of amylene on synthesized CaA is higher than that of synthetic CaA zeolite. For this reason, the synthesized CaA zeolite modified with metal cations has a relatively higher catalytic activity compared to synthetic CaA (№2–8 and №10–16).

It can be seen from Table 5 that the distribution of acid centres on the surface of zeolite, the concentration of cation and nature have a significant effect on the yield of individual products. When copper ions are added to CaA zeolite (synthesized), the density of dissociatively adsorbed oxygen molecules increases, which leads to an increase in the catalytic activity of zeolite for the reaction under consideration (Fig. №2, 10). When the cations' concentration increases from 1% to 3%, the valerian aldehyde yield for synthetic CaA ranges from 53.3% to 58.9% (№2, 3), and for synthesized CaA from 56.6% to 61.1%, a subsequent increase in the concentration of copper cations (up to 4.0%) has little effect on the release of valerian aldehyde (№4.12). This can be explained by the change in the distribution of copper ions at relatively high concentrations to decrease the amount of medium–strength Brensted acid centres on the catalyst's surface.

Table 6. Selectivity and yield of reaction products of oxidative dehydrogenation of 1–pentanol alcohol to valerian aldehyde with different molar ratios of reagents (alcohol: O₂:N₂=1:(0.6–0.95):(2.0–3.5)), temperature and volume velocities on the CaA (synthesized) catalyst containing cations 3% Cu²⁺, 2% Zn²⁺, 0.1% Pd²⁺.

№	Vol. velocities h ⁻¹	T, °C	1–pent.:O ₂ :N ₂ mol.ratio	Conv.,%	Selektivitiy, %	Yield,%		
						Valeric aldehyde	Amilens	CO ₂
1	1600	280	1:0.85:3.2	76.1	90.8	69.1	4.1	2.9
2	2000		1:0.85:3.2	70.1	92.9	65.1	3.2	1.8
3	1600	300	1:0.85:3.2	88.3	89.8	79.3	5.2	3.8
4	2000		1:0.85:3.2	81.6	91.8	74.9	3.8	2.9
5			1:0.75:2.9	75.4	91.1	68.7	4.1	2.6
6	1600	320	1:0.85:3.2	98.7	88.9	87.8	6.1	4.8
7			1:0.65:2.5	81.8	90.2	73.8	4.6	3.4
8			1:0.75:2.9	92.7	89.2	82.7	5.8	4.2
9			2000	1:0.85:3.2	91.1	90.9	82.9	4.5
10	1:0.75:2.9	87.1		91.6	79.8	4.2	3.1	
11	1600	340	1:0.85:3.2	98.9	86.4	85.5	7.1	6.3
			1:0.75:2.9	93.1	86.5	80.6	6.7	5.8

The inclusion of small amounts of palladium (0.1%) and zinc (1–2%) cations creates favourable conditions for the distribution of acid centres on the surface of the catalyst for the reaction under consideration (e.g. №5–8 and №13–16). In addition, these cations increase the concentration of dissociatively adsorbed oxygen molecules.

As shown in Table 6, the highest yield of valerian aldehyde is observed at 87.8% and selectivity at 88.9%. In this case, the volume corresponds to the value of speed 1600 h^{-1} , temperature 320°C (Table 6).

Thus, using a metal–zeolite catalyst based on CaA zeolite synthesized and modified with metal cations made it possible to obtain valerian aldehyde with higher yield and selectivity by lowering the reaction temperature compared to synthetic CaA zeolite. Thus, the increased output of valerian aldehyde is observed at 87.8%, the selectivity of the process is at 88.9%. The activity of the catalyst did not decrease during the 300 hours of operation.

Catalytic properties of the oxidative dehydrogenation reaction of butanol–2 alcohol on methyl ethyl ketone over CaA zeolite.

Based on synthesized CaA zeolite was prepared the number of samples modified by metal cations Cu^{2+} , Zn^{2+} and Pd^{2+} with the ion-exchange method. Table 7 shows the study results of the catalytic activity of these samples and the catalytic activity of CaA zeolites not modified by metal cations in the oxidative dehydrogenation reaction of butanol-2 alcohol to methyl ethyl ketone. And dehydrogenation of butanol-2 to carbon dioxide and butylene. The yield of other products is affected by the distribution of acid centres on the surface of the catalysts (the location of acid centres on the surface changes with the inclusion of metal cations), the concentration, and the cation's nature.

The study results of the catalytic activity of CaA zeolite modified by metal cations were analysed in the oxidative dehydrogenation reaction of butanol–2 alcohol to methyl ethyl ketone (Table 7.).

The obtained results show that the synthesized CaA zeolite

containing 3,0% Cu²⁺, 2,0% Zn²⁺ and 0,1% Pd²⁺ is highly active for the oxidative dehydrogenation reaction of butanol–2 alcohol to methyl ethyl ketone.

Table 7. Results of the study of catalytic activity in the catalyst prepared by modification of synthesized CaA zeolite with metal cations Cu²⁺, Zn²⁺ and Pd²⁺ in the reaction of oxidation of butanol–2 to methyl ethyl ketone at a temperature of 300°C, at volumetric velocity V=2500 h⁻¹ and mole ratio of reagents alc.:O₂:N₂=1:0.69:2.5 mol.

№	Zeolite	Amount of kations, w/w, %			Conv. X, %	Yield, A %		
		Cu ²⁺	Pd ²⁺	Zn ²⁺		MEK, A ₁	Butilens, A ₂	CO ₂ , A ₃
1.	CaA	–	–	–	18,4	12,1	6,0	0,3
2.		0,5	–	–	48,1	45,0	2,5	0,6
3.		1,0	–	–	58,5	54,6	3,0	0,9
4.		3,0	–	–	63,8	58,0	4,3	1,5
5.		4,0	–	–	64,1	57,6	4,6	1,9
6.		0,5	0,1	–	80,4	74,7	3,7	2,0
7.		3,0	0,1	–	84,9	78,8	4,0	2,1
8.		3,0	0,1	1,0	88,0	82,4	3,4	2,2
9.		3,0	0,1	2,0	91,1	86,9	2,0	2,2
10		3,0	0,1	4,0	87,2	80,0	4,4	2,8
11		3,0	1,0	4,0	95,3	81,8	9,1	4,4

The effect of the partial pressures of alcohol and oxygen on the oxidation of butanol–2 is shown in Figures 8 and 9.

Figure 8 shows the yield and conversion curves of butanol–2 depending on the partial pressure.

As can be seen from the figure, at a temperature of 320°C, the volume velocity of 2500 h⁻¹, the partial pressure of oxygen equal to 0.16 atm. And the partial pressure of butanol–2 is P_{B-2}=0.12–0.36 atm. The output curve of the MEK is extreme when it varies in the interval. The maximum output of the MEK (86.9%) is happening at a P_{B-2}=0.24 atm. The subsequent increase in partial pressure of alcohol from 0.24 to 0.36 atm leads to a decreasing yield of MEK from 86.9 to 80.0%, which can be explained by the blocking of the coordination of oxygen in the active centres of the catalyst by butanol–2

molecules.

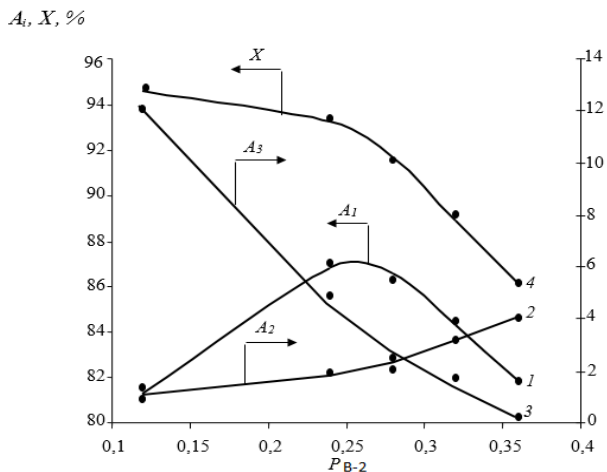


Figure 8. Influence on the course of the partial reaction pressure of butanol-2 at a temperature of 320⁰C, at a volumetric velocity, $V=2500 \text{ h}^{-1}$ and at a partial pressure of oxygen of 0.16 atm. 1–methyl ethyl ketone, 2–butylenes, 3–carbon dioxide, 4–conversion.

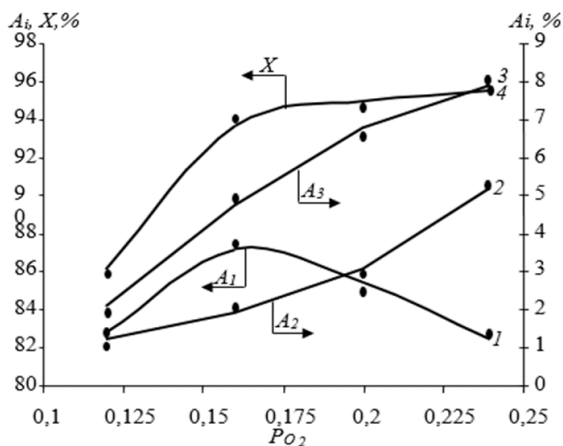


Figure 9. Influence on the course of the partial reaction pressure of oxygen at a temperature of 320⁰C, at a volumetric velocity, $V=2500 \text{ h}^{-1}$, and at a partial pressure of butanol-2 of 0.24 atm. 1–methyl ethyl ketone, 2–butylenes, 3–carbon dioxide, 4–conversion.

The effect of partial pressure of oxygen on the yield of reaction products of butanol-2 at the value of $P_{B-2}=0,24$ atm ($T = 320^{\circ}\text{C}$ and $V = 2500 \text{ s}^{-1}$) are given in Figure 9. As can be seen from the figure, the increase in pressure P_{O_2} from 0.12 to 0.16 atm increases the MEK output from 82.4% to 86.9%. But rise in the pressure to $P_{O_2}= 0.24$ atm decreases MEK yield. The decrease in the production at pressures above 0.16 atm can be explained by the increase in the rate of deep oxidation and the dehydration of butanol-2 to carbon dioxide and butylene, respectively.

The fourth chapter studied the kinetic regularity of conversion of butanol-2 alcohol to methyl ethyl ketone, 1-pentanol to valerian aldehyde and valeric acid and the possible mechanism of the reaction on synthesized mordenite and CaA zeolite catalysts, and a kinetic model of the process was developed.

Based on the obtained experimental results, it is possible to suggest the following step-by-step mechanism of formation of valeric acid and valerian aldehyde:

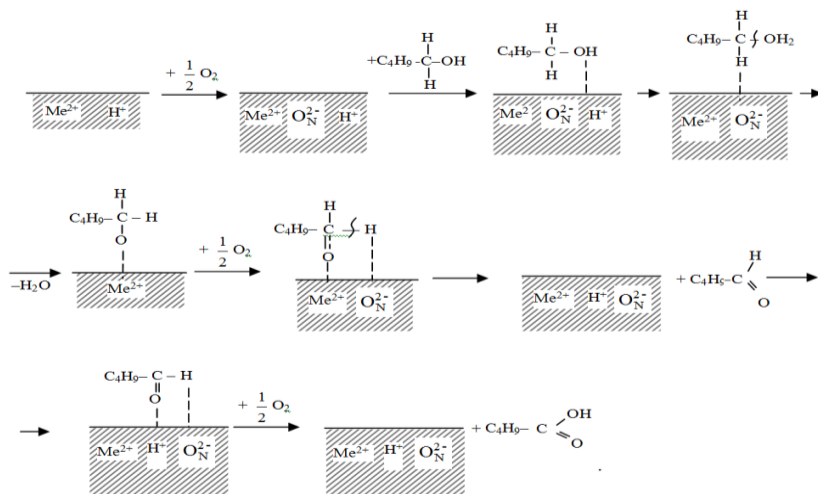
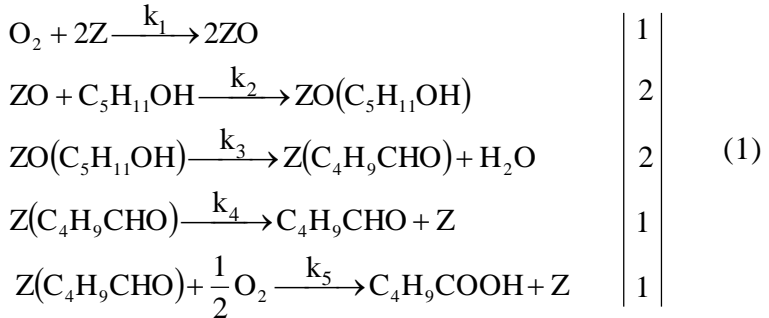


Figure 10. Stepwise mechanism of oxidation reaction of 1-pentanol to valeric acid on the catalyst CuZnPdMOR (synthesized).

According to the scheme, during the absorption of 1-pentanol, the catalyst is protonated in the presence of Brensted acid centres, which subsequently separates the water and results in the formation of surface alcohol. The conversion of surface alcohol to valerian aldehyde is made possible by constructing a surface aldehyde-like compound formed by its combination with surface nucleophilic oxygen. The aldehyde-like surface compound then decomposes into valerian aldehyde. The interaction of an aldehyde-like a surface compound with surface nucleophilic oxygen produces valeric acid.

The scheme of the stepwise mechanism of the above reaction for the favourable construction of kinetic equations can be described as follows:



Here Z is the active centre of zeolite.

All these stages are practically irreversible. Taking into account their simplicity, the following expressions can be written for the speed of the steps:

$$r_1 = k_1 P_{\text{O}_2} \theta_1^2, r_2 = k_2 P_{\text{sm}} \theta_2, r_3 = k_3 \theta_3, r_4 = k_4 \theta_4, r_5 = k_5 \theta_4 P_{\text{O}_2}^{\frac{1}{2}} \quad (2)$$

Where $\theta_1, \theta_2, \theta_3, \theta_4$ are the proportions of accessible areas of modified zeolite which is capable of absorbing the oxygen, covered with sorbent atomic oxygen, atomic oxygen and 1-pentanol molecules, and aldehyde-like Z ($\text{C}_4\text{H}_9\text{COH}$) intermediate compound with oxygen respectively; $P_{\text{O}_2}, P_{\text{sp}}$ – are the partial pressure of indexed components; k_1, k_2, k_3, k_4, k_5 – velocity constants of the corresponding indexed steps; r_1, r_2, r_3, r_4, r_5 – are the velocities of the phases with the corresponding index.

Given the general rate of the process in the stationary state, it is

possible to obtain the following equations for the rate of formation of valerian aldehyde, taking into account equations (2):

$$r_{v.t.} = k_5 \cdot P_{O_2}^2 \left[\frac{-\sqrt{\frac{k_4}{k_1 P_{O_2}}} + \sqrt{\frac{k_4}{k_2 P_{sp}} + 4 \left(\frac{k_4}{k_2 P_{sp}} + \frac{k_4}{k_3} + 1 \right)}}{2 \left(\frac{k_4}{k_2 P_{sp}} + \frac{k_4}{k_3} + 1 \right)} \right]^2 \quad (3)$$

Assuming that carbon dioxide is formed by the interaction of weakly adsorbed 1-pentanol molecules with adsorbed oxygen molecules according to the Langmuir-Hinshelwood mechanism, then the kinetic equation corresponding to this mechanism will be as follows:

$$r_{CO_2} = \frac{k_6 K_1 K_2 P_{O_2} P_{sp}}{\left(1 + K_1 P_{O_2} + K_2 P_{sp} \right)^2} \quad (4)$$

Where k_6 is the rate of formation of carbon dioxide, K_1 , K_2 are the adsorption equilibrium constants of oxygen and 1-pentanol molecules in the active centres. Differential equations (4) and (5) are kinetic models of the oxidative transformation of 1-pentanol over MOR zeolite.

The pre-exponential values of velocity constants, $\ln k_i^0$, $\ln K_i^0$, activation energies, E_i , and adsorption temperatures, Q_i were calculated using the "variable boundaries" and Powell methods using the Search system program, where the target function was obtained as follows:

$$F = \min \sum_{j=1}^m \sum_{i=1}^n \left(\frac{A_{ji}^{exp.} - A_{ji}^{calc.}}{A_{ji}^{exp.}} \right)^2 \quad (5)$$

The values of the parameters of the kinetic model are given in Table 8.

The kinetic model developed for the oxidative reaction of 1-pentanol to valeric acid reflects the experimental results quite well. Thus, the average relative error of the practical and calculated results is not more than 5%.

Table 8. Estimates of the kinetic model constants of the oxidative reaction of 1-pentanol to valeric acid on the catalyst CuZnPdMOR (synthesized).

№	$\ln k^0, \ln K^0$		$E, Q, \text{kcal/mol}$	
	1	$\ln k_1^0$	6.86	E_1
2	$\ln k_2^0$	2.23	E_2	2.00
3	$\ln k_3^0$	3.18	E_3	2.86
4	$\ln k_4^0$	-1.43	E_4	1.99
5	$\ln K_1^0$	-17.06	Q_1	5.99
6	$\ln K_2^0$	-3.29	Q_2	4.89

Experimental study of the effect of acid centres on the possible mechanism of the reaction. CuZnPdMOR. (3%, 2%, 0.1%) The catalyst was treated with different amounts of pyridine to determine the role of acid centres on the surface of the metal-zeolite catalyst in the process. The study results of the effect of pyridine on the activity of the metal-zeolite catalyst CuZnPdMOR (3%, 2%, 0.1%) are given in Figure 11. As seen from the figure, increasing the amount of pyridine leads to a decrease in the conversion of 1-pentanol.

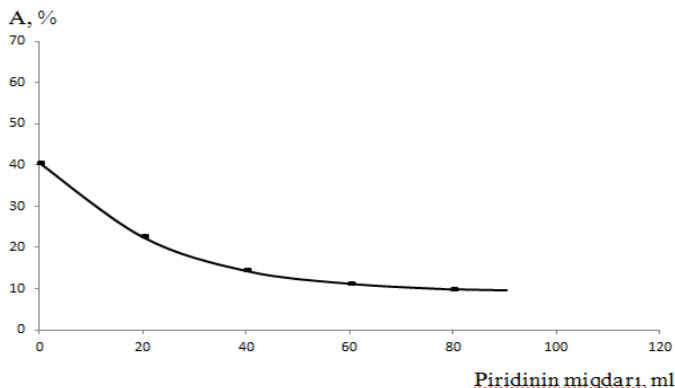


Figure 11. Effect of pyridine content on the activity of CuZnPdMOR (3%, 2%, 0.1%) zeolite catalyst; A is the release of valeric acid.

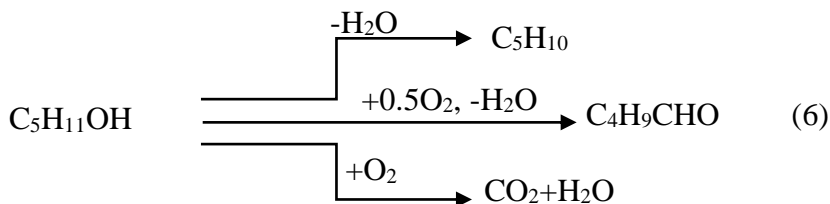
In the absence of ion-exchange metal cations on the surface of the zeolite catalyst, the concentration of Brønsted acid centres on the surface is relatively high. When Cu^{2+} , Zn^{2+} and Pd^{2+} ions are added to the zeolite, the strength distribution of the acid centres on the surface changes. Thus, the concentration of solid acid centres decreases.

Study the kinetics and mechanism of the oxidation reaction of 1-pentanol to valerian aldehyde on the catalyst CuZnPdCaA (synthesized).

Based on experiments, it can be assumed that two mechanisms form valerian aldehyde. According to the first mechanism, the aldehyde is formed from a dehydrogenation reaction; the use of oxygen is associated with the oxidation of the released hydrogen. According to another mechanism, valerian aldehyde is created by oxidative dehydrogenation.

Experiments without oxygen were performed to clarify the role of the dehydrogenation reaction. During these experiments, the conversion of alcohol did not exceed 4%. The products of the reaction were only small amounts of amylenes. This indicates that valerian aldehyde is obtained only from the oxidative dehydrogenation reaction.

The experiments allow us to propose the following kinetic scheme for the oxidative dehydrogenation reaction of 1-pentanol on valerian aldehyde on the catalyst CuZnPdCaA:



According to the scheme, during the absorption of 1-pentanol in the presence of Brønsted acid centres of the catalyst, its protonation occurs, which results in the subsequent separation of water and the formation of surface alcohol. The conversion of surface alcohol to valerian aldehyde is made possible by forming the

surface aldehyde-like compound formed by its combination with surface nucleophilic oxygen. The aldehyde-like surface compound then decomposes into valerian aldehyde.

Taking into account the continuity of the total value of the surface areas $\theta_1+\theta_2+\theta_3+\theta_4=1$, we can find the density of the intermediate compound θ_i ; the rate of formation of valerian aldehyde $r_{v.a}$:

$$\theta_1 = \sqrt{\frac{k_4\theta_4}{k_1P_{O_2}}}; \quad \theta_2 = \frac{k_4\theta_4}{k_2P_v}; \quad \theta_3 = \frac{k_4\theta_4}{k_3} \quad (7)$$

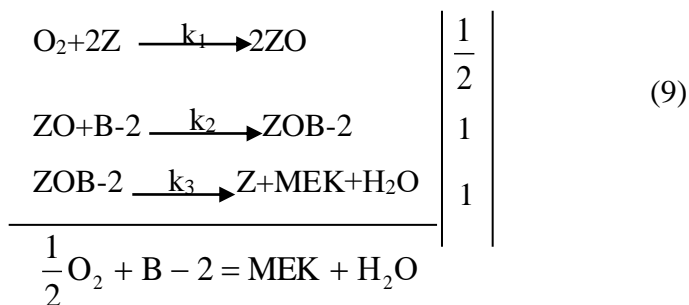
for the rate of formation of valerian aldehyde we obtain the following equation:

$$r_{v.a} = k_4 \left[\frac{-\sqrt{\frac{k_4}{k_1P_{O_2}} + \sqrt{\frac{k_4}{k_2P_{v.a}} + 4\left(\frac{k_4}{k_2P_{v.a}} + \frac{k_4}{k_3} + 1\right)}}}{2\left(\frac{k_4}{k_2P_v} + \frac{k_4}{k_3} + 1\right)} \right]^2 \quad (8)$$

If we accept that carbon dioxide is formed by the interaction of weakly adsorbed amyl alcohol molecules with adsorbed oxygen molecules according to the Langmuir-Hinshelwood mechanism, then the kinetic equation corresponding to this mechanism can be obtained.

Study of the kinetic regularity of the oxidation reaction of butanol-2 alcohol on methylethyl ketone on the catalyst CuZnPdCaA (synthesized).

Based on the experiments, the following step-by-step mechanism can be proposed for the partial oxidation reaction of butanol-2 alcohol on the CuZnPdCaA catalyst:



According to the yields of reaction products, butanol-2 n_{sp}^0 and

initial amount $n_{O_2}^0$ of oxygen, the molar amount of reagent in the flow is determined by the following equations.

$$\left. \begin{aligned} n_{B-2} &= n_{B-2}^0 - (A_1 n_{B-2}^0 + A_2 n_{B-2}^0 + A_3 n_{B-2}^0) / 100 = \\ &= n_{B-2}^0 - n_{B-2}^0 (A_1 + A_2 + A_3) / 100 \\ n_{MEK} &= A_1 n_{B-2}^0 / 100 \\ n_{C_4H_8} &= A_2 n_{B-2}^0 / 100 \\ n_{CO_2} &= 4A_3 n_{B-2}^0 / 100 \\ n_{N_2} &= n_{N_2}^0 \end{aligned} \right\} \quad (10)$$

According to the proposed kinetic scheme, the equation for the rate of formation of methyl ethyl ketone can be written as follows:

$$r_{MEK} = \kappa_1 P_{O_2} \left\{ \frac{\sqrt{1 + 4 \left(\frac{\kappa_1 P_{O_2}}{2\kappa_2 P_{B-2}} + \frac{\kappa_1 P_{O_2}}{2\kappa_3} \right)} - 1}{2 \left(\frac{\kappa_1 P_{O_2}}{2\kappa_2 P_{B-2}} + \frac{\kappa_1 P_{O_2}}{2\kappa_3} \right)} \right\}^2 \quad (11)$$

Given that the reaction rate is inhibited by adsorbed alcohol and water molecules, the observed rate of the response is as follows:

$$r_{C_4H_8} = k_5 \frac{P_{B-2} - \frac{1}{K_P} P_{C_4H_8} \cdot P_{H_2O}}{K_3 P_{B-2} + K_4 P_{H_2O}} \quad (12)$$

where the K_P is the equilibrium constant of the dehydration reaction of butanol-2 alcohol.

The values of the parameters of the kinetic model are given in Table 9.

The kinetic model developed for the oxidation reaction of butanol-2 alcohol to MEK on the synthesized CaA zeolite fully reflects the experimental results. The average relative error of the experiments is not more than 7%.

Table 9. Estimates of the kinetic model constants of the reaction of oxidation of butanol-2 to methyl ethyl ketone.

Pre-exponential factor		Activation energies, kcal/mol	
$\ln k_1^0$	7,19	E_1	5,15
$\ln k_2^0$	4,03	E_2	6,47
$\ln k_3^0$	7,67	E_3	5,28
$\ln k_4^0$	20,91	E_4	21,27
$\ln k_5^0$	9,98	E_5	16,40
$\ln K_1^0$	-3,21	Q_1	1,98
$\ln K_2^0$	4,08	Q_2	4,00
$\ln K_3^0$	-4,67	Q_3	1,50
$\ln K_4^0$	4,54	Q_4	4,19

RESULTS

1. Hydrothermal synthesis of mordenite, analcym, zeolites based on natural raw materials (kaolinite, bentonite) found in the territory of the Republic of Azerbaijan, as well as methods of obtaining CaA zeolite by ion-exchange method and optimal conditions of synthesis, and the influence of various factors on synthesis conditions was studied.
2. Research methods such as XRD, XRF, DTA, AAS, ICP-AES, FTIR, chromatographic, etc., were used to identify, composition, physical and chemical properties of obtained zeolites.
3. Synthesized mordenite zeolite has been shown to have higher activity and selectivity in the oxidation reactions of 1-pentanol alcohol to valeric acid and CaA zeolite oxidation of butanol-2 to methyl ethyl ketone and 1-pentanol to valerian aldehyde.
4. The synthesized mordenite and CaA zeolites were modified with different amounts of metal cations (Zn^{2+} , Cu^{2+} , Pd^{2+} , etc.), and their catalytic properties were studied in the oxidation reactions of butanol-2 and 1-pentanol alcohols. It was determined that the yield of valeric acid on the modified mordenite in the oxidation processes of the above aliphatic alcohols is 66.4%. The yield of MEK on CaA zeolite is 86.9%, and the yield of valerian aldehyde is 87.8%.
5. The effect of cations of transition elements on the distribution of existing acid centres on the surface of synthesized zeolites Zn^{2+} , Cu^{2+} , Pd^{2+} and the course of oxidation reactions of these centres was studied.
6. The catalytic properties of the synthesized zeolites were studied in the oxidation reactions of butanol-2 and 1-pentanol. The kinetic regularity of catalytic oxidation processes has been studied experimentally over a wide temperature range (200–380°C), at volumetric velocities $V=400-4000\text{ h}^{-1}$, and different molar ratios of reagents (alcohol: $O_2:N_2$).
7. Based on the obtained experimental results and kinetic regularities, a possible mechanism of the catalytic oxidation

reaction of butanol-2 and 1-pentanol alcohol was proposed, and a theoretically based kinetic model of the process on zeolites synthesized according to this mechanism was developed.

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

1. Алиев А.М., Агаев Ф.А., Сарыджанов А.А., Мамедова У.А. Применение синтетических и природных цеолитов для создания катализаторов этерификации уксусной кислоты этиловым спиртом / *Akademik M.F.Nağiyevin 105 illiyinə həsr olunmuş elmi konfransın materialları*, Bakı, 2013, s.9–14.
2. Алиев А.М., Агаев Ф.А., Сарыджанов А.А., Мамедова У.А. Исследование кинетики парциального окисления втор-бутилового спирта на цеолите NaY, модифицированном катионами меди, цинка и палладия / *“Kimya Problemləri” jurnalı*, Bakı, 2013, №3, s.283–287
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