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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEVELOPMENT OF EFFECTIVE CATALYSTS FOR OXIDATIVE CONVERSION REACTIONS OF CYCLOPENTANE AND METHYLCYCLOPENTANE

Specialty: 2316.01 – Kinetics and catalysis

Field of science: Chemistry

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The work was performed at the "Zeolite catalysis" laboratory of the "Oxidative heterogenous catalysis" department of the named after acad. M.Naghiyev of Institute of Catalysis and Inorganic Chemistry of Ministry of Science and Education of the Republic of Azerbaijan.

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GENERAL DESCRIPTION OF WORK

Relevance and elaboration degree of the topic. In industry, are considered a quite actual topic of oxidative conversion processes of naphthenic hydrocarbons to alicyclic dienes. This is characterized high reactivity of double bond located cyclic ring of alicyclic dienes. From this point of view, the oxidative conversion reactions of cyclopentane and methylcyclopentane to cyclopentadiene and methylcyclopentadiene are great importance respectively. Cyclopentadiene is mainly used as a base product in the production of cyclopentene and its derivatives. At the same time, it is widely used as a cyclopentadienyl ligand of the cyclopentadiene complex in metallochemistry. It is also used as a main product in the production of aromatic compounds and aldrin, dieldrin insecticides¹.

Cyclopentadiene is mainly obtained by steam cracking of 10-20 g/ton of coal tar and 14 kg/ton of naphthenic oils².

Based on a brief literature summary, it was found that the yield percentage during the thermal and catalytic synthesis of cyclopentadiene is low and the lifetime of the applied catalysts is short. The priority issue in the presented thesis consists of reducing the temperature of the reaction and increasing the yield of cyclopentadiene, the selectivity of the process and the working time of the catalyst.

Methylcyclopentadiene exists in the form of three cyclic isomers, and these isomers are mainly used as primary organic products in the preparation of the methylcyclopentadienyl ligand, which is widely used in organometallic chemistry (ferrocene, etc.). It also has a wide range of applications such as metal derivatives, special adhesives and flame retardants. It is also useful as a biological toxicant and is used as an intermediate in the preparation

¹ Hartwig, J. F. Organotransition Metal Chemistry // From Bonding to Catalysis. New York University Science Books, -2010,10 Feb;1st Edition-p.1160.

² Hönicke, D. Cyclopentadiene and Cyclopentene / R.Födisch, P.Claus // Ullmann's Encyclopedia of Industrial Chemistry. - 2000, 15 June; Vol. 11.15, - p.62-73.

of synthetic rubber composites³. Methylcyclopentadiene is mainly available in 2 phases, liquid and gas phase. Disadvantages of the method of obtaining in the liquid phase are the difficulty of separating the reaction products obtained during this time from the catalyst. For this reason, the scientific research conducted by us refers to the methods of obtaining methylcyclopentadiene in the gas phase. The presence of a methyl substituent group on the cyclic ring makes the methylcyclopentane molecule more reactive than the cyclopentane molecule. In this sense, the methylcyclopentane molecule is more selective towards obtaining alicyclic dienes.

Based on the literature data, we can say that great achievements have been made by prominent Azerbaijani scientists S.C. Mehdiyev, T.N. Shahtakhtinski, A.M. Aliyev, H.M. Alimardanov, etc. in the direction of oxidative dehydrogenation of alicyclic hydrocarbons to tsikoolefins, respectively.

From this point of view, the selection of active and selective catalysts for the oxidative dehydrogenation reaction of cyclopentane and methylcyclopentane molecules to the respective cyclopentadiene and methylcyclopentadiene in the vapor phase, and the detailed investigation of the kinetics and progress of the reactions are of great relevance.

The object and subject of the research:

The research object of the dissertation has been natural clinoptilolite catalysts with modified metal cations, cyclopentane and methylcyclopentane molecules.

The catalytic system formed by clinoptilolite modified with the given percentages of metal cations {Cu²⁺(0.5 wt.%), Zn²⁺(0.2 wt.%), Co²⁺(0.1 wt.%), Cr³⁺(0.1 wt.%)} was more active and selective for oxidative dehydrogenation of cyclopentane and methylcyclopentane to cyclopentadiene and methylcyclopentadiene .

³ Darkwa, J. Bis(η⁵-Methylcyclopentadienyl) Titanium Pentasulfide, Bis (η⁵-Methylcyclopentadienyl) -Divanadium Pentasulfide, and Bis (η⁵-Methylcyclopentadienyl) Divanadium Tetrasulfide / D.M.Giolando, C.J.Murphy, T.B.Rauchfuss // Inorganic Syntheses,- 1990, February. v.27.p.52-55.

Aims and objectives of the research:

The aim of the dissertation work is the synthesis of active zeolite catalysts modified with various transition metal cations of clinoptilolite and the study of step-by-step mechanisms and kinetic regularities of oxidative dehydrogenation reactions of cyclopentane and methylcyclopentane to cyclopentadiene and methylcyclopentadiene on these catalysts, and the construction of a theoretically based kinetic model of the process. To fulfill this goal, the following tasks were solved:

- Synthesis of active zeolite-containing catalysts for the oxidative dehydrogenation of cyclopentane to cyclopentadiene and methylcyclopentane to methylcyclopentadiene in the vapor phase.
- Experimental study of the kinetic laws of this reaction on selected active catalysts.
- Determination of the probable stepwise mechanism of the reaction.
- Development of a theoretically based kinetic model of the process.
- Carrying out the reaction at low temperature.
- Increasing the yield of cyclopentadiene and methylcyclopentadiene, process selectivity and catalyst lifetime in one step.

Research methods:

The results of the dissertation work were determined based on experimental research methods applied with high accuracy and sensitivity mentioned below;

- Chromatographic method in "Agilent-7820" gas chromatograph,
- Ultraviolet (UV) and Infrared (IR) spectroscopy methods;
- Electron Paramagnetic resonance (EPR) method;
- Physical-chemical and chemical analysis methods;
- Kinetic method;

Based on the kinetic method, the step-by-step mechanism of the reactions was given, and appropriate kinetic equations were drawn up, and their correctness was checked based on experimental evidence.

The main provisions of the defense are as follows:

- Testing of the catalytic activity of the primary forms of natural and synthetic zeolites in the oxidative dehydrogenation of cyclopentane and methylcyclopentane.
- Preparation of samples of catalysts modified clinoptilolite with transition metal cations.
- Testing the catalytic activities of these prepared catalysts in the oxidative dehydrogenation of cyclopentane and methylcyclopentane.
- Building the kinetic model based on a stepwise mechanism according to theoretical data for both processes.
- Checking the possibility that the presented parameters of kinetic model fully reflected the mechanism of the reaction in the given interval.

Scientific innovation of research:

- For the selective oxidative dehydrogenation of cyclopentane to cyclopentadiene and methylcyclopentane to methylcyclopentadiene in the presence of dissociatively adsorbed oxygen, the mass of clinoptilolite {Cu²⁺(0.5 wt.%), Zn²⁺(0.2 wt.%), Co²⁺(0.1 wt.%), Cr³⁺(0.1 wt.%)} active and selective catalytic system modified with cations was chosen.
- The scheme of the possible stepwise mechanism of the oxidative dehydrogenation reaction of cyclopentane and methylcyclopentane molecules was proposed on the modified CuZnCoCr-KL zeolite catalysis and were studied the kinetic regularities of these reactions.
- Based on these mechanism was constituted a theoretically based kinetic model of the processes.

Theoretical and practical significance of research:

- ✓ The proposed CuZnCoCr-clinoptilolite metal zeolite catalyst for the selective oxidative dehydrogenation of cyclopentane to cyclopentadiene and methylcyclopentane to methylcyclopentadiene can be used as well as being an active catalyst to obtain alicyclic dienes for both representatives of the same class in the industrial implementation of the mentioned process.
- ✓ The theoretically determined kinetic model of the process can be

applied in the development of the mathematical model and in the optimal design of this process.

- ✓ Also, the fact that the process is carried out at atmospheric pressure and at the expense of air oxygen is a clear proof that the work is a practical importance.

Approbation and application:

The main results of the dissertation were presented at the following national and international conference:

- Международная научно-техническая конференция «Нефтехимический синтез и катализ в сложных конденсированных системах», посвященная 100-летию юбилею академика Б.К.Зейналова – 2017, 29-30 июня, Баку;
- Международная научно-техническая конференция «Нефтехимический синтез и катализ в сложных конденсированных системах», посвященная 100-летию юбилею академика Б.К.Зейналова – 2017, 29-30 июня, Баку;
- Akademik M.Nağıyevin 110 illiyinə həsr olunmuş “Nağıyev Qıraətləri” elmi konfransının materialları – 2018, Bakı;
- Second International Scientific-Practical Conference: Modern Information, Measurement and Control Systems: Problems and Perspectives– 2020, 07-08 december, Bakı;
- The XVIII International Science Conference “ Perspective directions for the development of science and practice” –2021, 14-16 June, Athens, Greece;
- Modern problems of theoretical & experimental chemistry. Devoted to the 90th anniversary of academician Rafiga Aliyeva. Baku state university. 29 - 30 September 2022, Baku, Azerbaijan.
- Техногенные Системы Экологический Риск VI Международная (XIX региональная) Научная Конференция, тезисы докладов, 20-21 апреля 2023. Обнинск.

The name of the organization where the dissertation work was performed:

The dissertation work was carried out in accordance with the plan of relevant research works at the “Zeolite catalysis” laboratory of the Institute named after M. Nagiyev of Catalysis and Inorganic Chemistry of the Ministry of Science and Education of the Republic

of Azerbaijan.

Published scientific works: According to the results of the dissertation work, a total of 19 scientific works, including 10 articles and 7 theses, were published and two inventions have been patented.

The total volume of the dissertation indicating the volume of the structural sections of the dissertation separately:

Introduction consists of 9284, chapter I - 70878, chapter II - 23361, chapter III - 40564, chapter IV - 29678, results - 2646 characters. The used references consist of 15 pages; the dissertation consists of 202751 characters in total.

Structure and scope of the dissertation: The dissertation consists of an introduction and 4 chapters - a literature review, an experimental part, and a discussion of the results (chapters 3 and 4 are four). The dissertation consists of general conclusions, a list of 129 cited literature, as well as a list of abbreviations and conventional signs. The volume of the dissertation consists of 141 pages with computer printing. Here are 27 images and 19 tables.

MAIN CONTENT OF WORK

The introduction the relevance of the topic is substantiated and information is provided about research methods, the scientific novelty and practical importance of the work is indicated, the purpose, structure and content of the work are reported the main provisions of defence and approbation of the work are indicated.

The first chapter available literature data and their analysis are noted in accordance with the dissertation topic. The modern state of research in the field of oxidative dehydrogenation of naphthenic hydrocarbons was reviewed and were given the main available methods of obtaining alicyclic dienes [17]. At the same time, the study of the kinetics and was shown mechanism of the oxidative dehydrogenation reaction of naphthenes.

The second chapter the experimental part of the dissertation is described. A flow-type laboratory experiment facility is shown for the study of heterogeneous catalytic processes, the analysis of

reagents and reaction products, the preparation of catalysts and are mentioned the method of conducting experiments. The products and intermediates obtained were analyzed using gas chromatography, IR and UV-spectroscopy after the reaction [4].

Based on the available methodical data, a number of modified zeolite catalysts from natural and synthetic zeolites were prepared and tested in the experiment. To monitor the reaction progress, the reactor is directly connected to an Agilent 7820A gas chromatograph, and the reaction products were analyzed by gas chromatography. Figures 1 and 2 show the chromatographic analysis of the products of the oxidative dehydrogenation reactions of cyclopentane and methylcyclopentane [4, 6, 7].

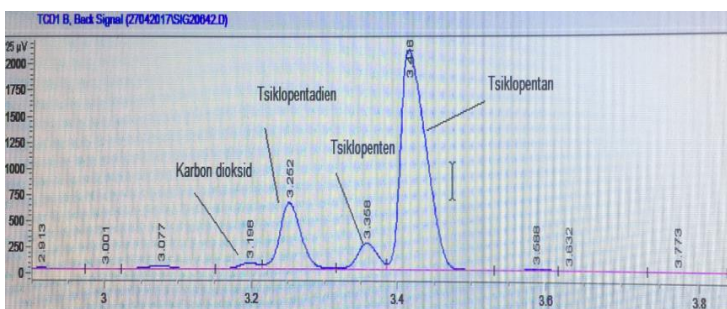


Figure 1. Chromatographic analysis products of cyclopentane dehydrogenation reaction

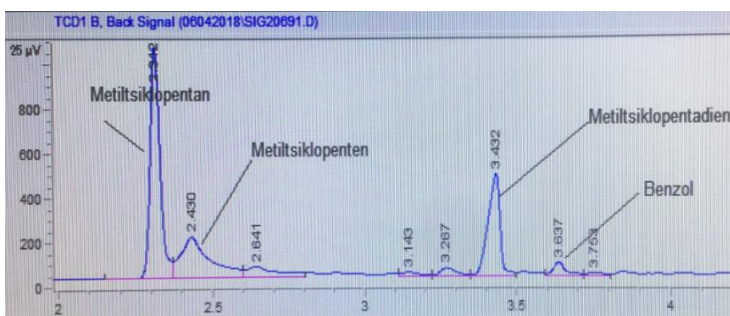


Figure 2. Chromatographic analysis products of methylcyclopentane dehydrogenation reaction

In pictures 3 and 4 below, Cu^{2+} of cyclopentane and methylcyclopentane is 0.5%; Zn^{2+} —0.2%; Co^{2+} —0.1%; The results

of the analysis of the products of the oxidative dehydrogenation reaction on the catalyst of Cr^{3+} -0.1% clinoptilolite under the influence of IR rays are given. The substances obtained from the reaction were studied by the Fourier-IR spectroscopy method in the Varian 640 FT-IR spectrometer in the frequency range of $4000\text{-}400\text{cm}^{-1}$.

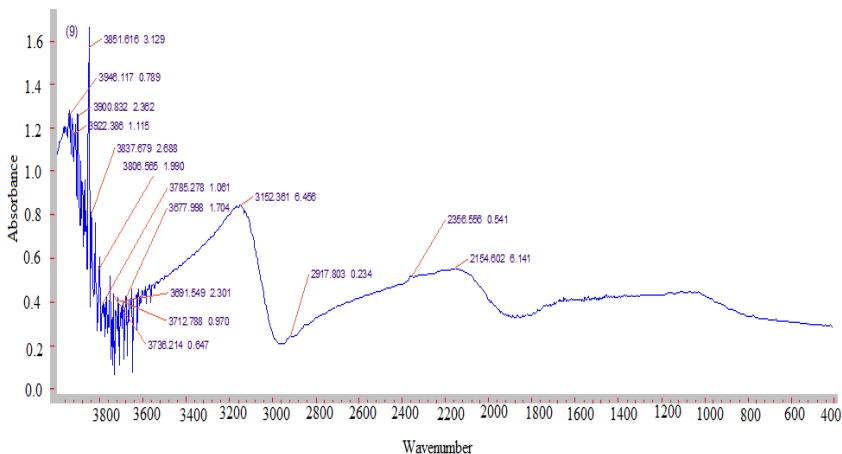


Figure 3. IR spectrum of cyclopentane dehydrogenation reaction products

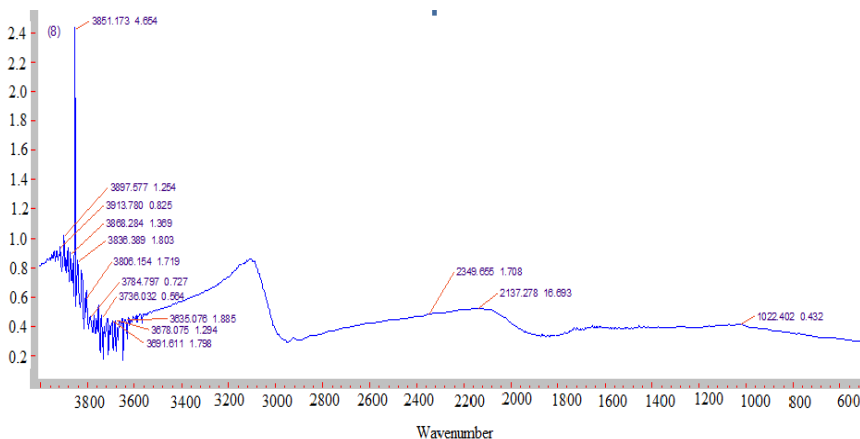


Figure 4. IR spectrum of methylcyclopentane dehydrogenation reaction products

The groups observed in the spectra can be shown accordingly as follows:

- region of valence oscillations for N-H and O-H groups ($3650-2500\text{ cm}^{-1}$); - C-H ($3300-2800\text{ cm}^{-1}$): -C-H- 3300 cm^{-1} , C(arom)-H – 3100 cm^{-1} , C(alif)-H – 2800 cm^{-1} region of valence vibrations; - “transparency” area ($2700-1850\text{ SM}^{-1}$) –C-N, -C-C, C=C=C, etc. area of valence dances; - double ($1950-1350\text{ cm}^{-1}$) – C=O (strong absorption at $1850-1650\text{ cm}^{-1}$), C=C (weak absorption at about 1650 cm^{-1}), etc. it was determined that the bonds correspond to valence vibrations. Two more intense absorption bands belong to C-H valence vibrations ($3100-2990\text{ cm}^{-1}$) and deformation vibrations of these bonds (1450 cm^{-1}). The intensity of absorption bands corresponding to valence ($1200-800\text{ cm}^{-1}$) and deformation vibrations (less than 500 cm^{-1}) of C-C bonds is relatively small. As expected, in the spectrum, for example, O-H or N-H, as well as C=O, C=C, etc. there are no absorption bands corresponding to the valence vibrations of the bonds. The region of the IR spectrum from 1350 to 750 cm^{-1} is called "fingerprints". Absorption in this region can be complicated because it is difficult to assign individual bands to specific dances.

At the same time, the reaction products were analyzed by the UV spectroscopy method in the Cary 50 Scan spectrometer, in the range of $200-800\text{ nm}$, and the UV spectrum of the oxidative dehydrogenation reaction of cyclopentane and methylcyclopentane is depicted in pictures 5 and 6.

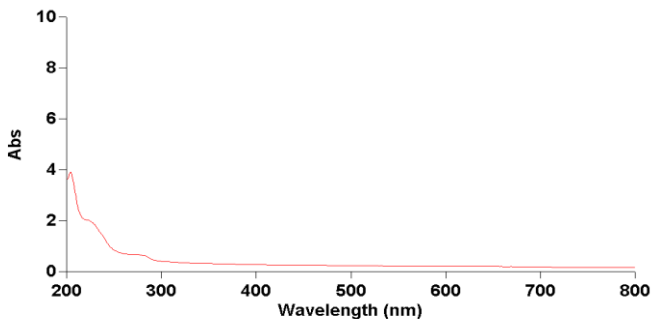


Figure 5. Ultraviolet spectrum of cyclopentane oxidative dehydrogenation reaction products

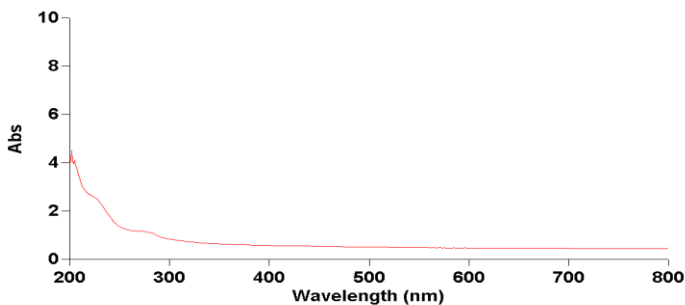


Figure 6. Ultraviolet spectrum of products of oxidative dehydrogenation of methylcyclopentane

EPR radiation of modified clinoptilolite samples: $g_{||}=2.38$ during anisotropy in polycrystalline samples in the spectrum of hydrated CuKL, KL(He)HCu form; Asymmetric lines characteristic of g-factor with parameters $g_{\perp}=2.08$ were observed in Fig. 7. Four components of the superthin structure are observed in the low-ground region, which indicates the presence of Cu²⁺ nuclear spins with $I=3/2$.

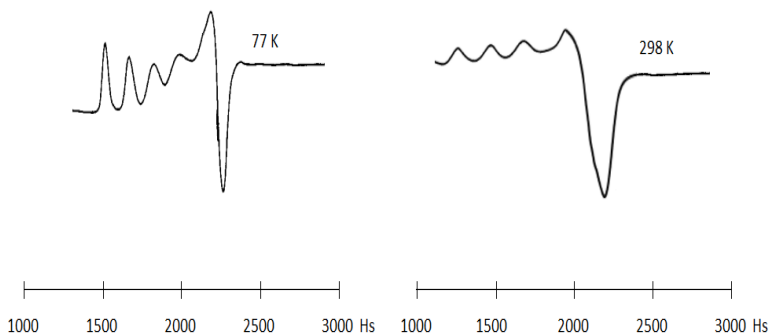


Figure 7. EPR spectra of hydrated KL(He)HCu samples taken at 77 and 298 K

Symmetrical components are located in the clinoptilolite structure in the form of octahedral hexaaqua complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, which is proved to be characteristic of copper ions. In such aqua complexes, as a general rule, rotation is observed, which corresponds to the average g-factor anisotropy and at the same time

leads to the expansion of the superthin structure. It can be assumed that these aquacomplexes are structured in large channels of clinoptilolite.

In the third chapter, are shown the results of experiments related to the selection of active and selective catalysts for the oxidative dehydrogenation reaction of cyclopentane and methylcyclopentane. During the selection of the catalyst, were summarized the literature data on the catalysts used in oxidative dehydrogenation and dehydroisomerization, oxidative dehydrogenation of aliphatic, alicyclic and alkylaromatic hydrocarbons, and was set preparation of active catalysts as a priority.

Oxidative dehydrogenation of cyclopentane: Thus, by adding transition metal cations into the clinoptilolite mineral, was studied catalytic activity in detail in the cyclopentane molecule, and the obtained data are given in figure 8. In the modified Zn^{2+} , Co^{2+} , Cr^{3+} cations, takes place deep oxidative dehydrogenation with the formation of cyclopentene and the formation of carbon dioxide.

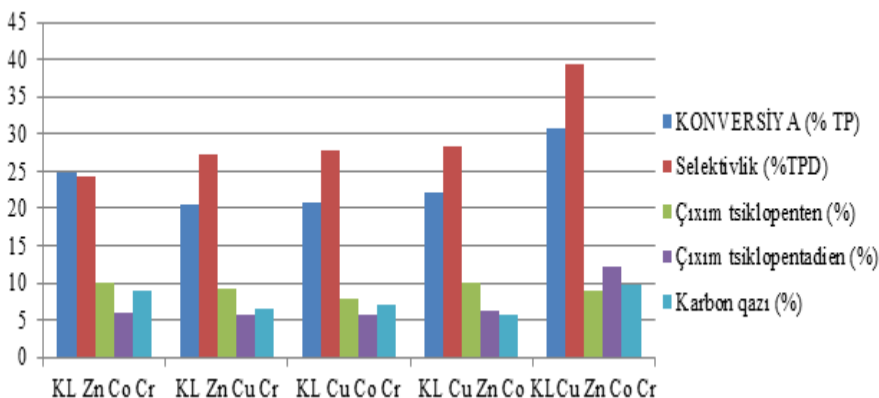


Figure 8. Oxidative dehydrogenation of cyclopentane over clinoptilolite catalysts modified with Cu, Zn, Co, Cr cations (T=380-390°C, V₀=2000h⁻¹, C₅H₁₀:O₂:N₂=2:1:3,7)

Zn metal has a promoting character. As a result of the conducted experiments, it became clear that the highest yield

according to cyclopentadiene contains Cu^{2+} —0,5%; Zn^{2+} —0,2%; Co^{2+} —0,1%; Cr^{3+} —0,1% is observed in clinoptilolite. The influence of temperature and concentration of reactants, partial pressure of oxygen on the yield of reaction products and the selectivity of the process on the determined active catalyst were studied in detail. The yield of cyclopentadiene is 12.1% and the selectivity is 39.4% [5, 19].

Oxidative dehydrogenation of methylcyclopentane: Table 1 lists the catalytic activity of modified triple and quaternary metal composition clinoptilolite catalysts.

Table 1.
Oxidative dehydrogenation of methylcyclopentane over triple and quaternary metal compositions of modified natural clinoptilolites ($T=360^\circ\text{C}$, $V_0=1500\text{h}^{-1}$, $\text{C}_5\text{H}_9\text{CH}_3:\text{O}_2:\text{N}_2=1,74:1:3,72$)

Conversion of MCP, selectivity and reaction products according to MCPD (%)	clinoptilolite			
	2%Cu 1%Pd 2%Zn	0,2%Zn 0,5%Co 0,25Cr	2%Cu 2%Zn 1%Co 0,5%Cr	0,5%Cu 0,2%Zn 0,1%Co 0,1%Cr
Conversion, %	44,1	45,7	50	75,8
Selectivity, MCPD %	33,3	49,7	51,8	55,8
Cyclopenten	2,9	3,4	2,8	1,5
Cyclopentadiene	1,6	2,1	6,3	4,8
Methylcyclopentene	10,8	4,5	5,8	17
MCPD	14,7	22,7	25,9	42,3
Cyclohexene	3,2	2,7	3,4	4,3
Benzene	4,5	2,2	1,1	2
Carbon dioxide	6,4	8,1	4,7	3,9

As a result of the conducted experiments, it became clear that the highest yield according to methylcyclopentadiene contains Cu^{2+} —0.5%; Zn^{2+} —0.2%; Co^{2+} —0.1%; CuZnCoCr - with Cr^{3+} —0.1% is observed in clinoptilolite. The yield of

methylcyclopentadiene is 42.3% and the selectivity is 56.7% [11]. The influence of temperature and concentration of reactants, partial pressure of oxygen on the yield of reaction products and the selectivity of the process on the determined active catalyst were studied in detail. When increasing the concentration of cations in the catalyst, the yield of cyclopentadiene decreases and the yield of partial oxidation products increases. This is mainly related to the increase in the strength of acid centers.

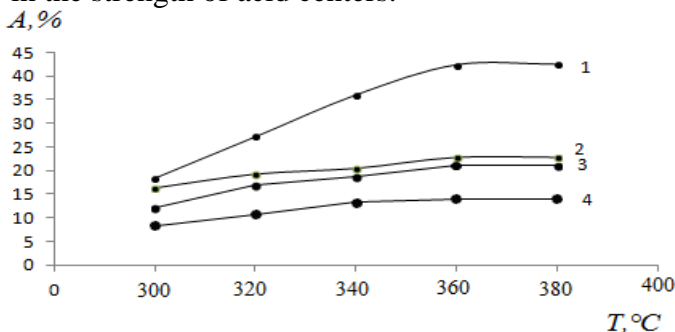


Figure 9. Temperature dependence of the activity of clinoptilolite in the oxidative dehydrogenation reaction of methylcyclopentane

Figure 9 shows the results of the experiments conducted on metal zeolite catalysts in the temperature range of 300-380⁰ C and the molar ratio of C₅H₉CH₃:O₂:N₂=1.74:1:3.72. Here, are given respectively (1–CuZnCoCr-CL; 2–ZnCoCr-CL; 3–CoCr-CL; 4–Co-CL). During the oxidative dehydrogenation reactions of cyclopentane to cyclopentadiene and methylcyclopentane to methylcyclopentadiene, there are two types of active centers. 1) Medium-strength Brønsted acid centers 2) Metal cations.

Role of acid centers: It was found that, catalyst samples with weak acid centers are not active in the oxidative dehydrogenation reaction of cyclopentane. An increase in the strength of acid centers allows for an increase in the rate of acid-base type reactions. In strong acid centers, the electrons of intermediate unsaturated compounds move to the inner orbitals of metal cations, which are considered adsorption centers. At this time, a certain positive charge

is formed in the molecule of the unsaturated compound, which causes its interaction with the oxygen anion and the formation of oxygen-containing compounds.

Metal cations: Formation of atomic oxygen through activation of molecular oxygen is important in heterogeneous oxidation processes. During the adsorption of oxygen molecules on metal surfaces, electrons are transferred from metal atoms to oxygen molecules. Such transfer of electrons leads to the dissociation of the oxygen molecule and the formation of Me-O bond between the metal surface and the oxygen atoms. Electron flow from metals to oxygen molecules depends on the structure of Me-O and Me-zeolite bonds. In zeolites, the metal is in the form of Me^+ . Depending on the value of the bond energy formed by exchange cations with dissociatively adsorbed oxygen, it shows different catalytic activity in the reaction of oxidative dehydrogenation of adsorbed cyclopentane and methylcyclopentane. The bonding energy of the cations is calculated in relation to the dissociation energy of the oxygen molecule. We know from the literature that dissociation energy of an oxygen molecule is equal to 500 kc/mol. The bonding energy formed by the components of the catalyst with oxygen will take appropriate values; $q_0(Cr)=612$ kc/g-atom, $q_0(Zn)=370$ kc/g-atom, $q_0(Cu)=489$ kc/g-atom, $q_0(Co)=459$ kc/g-atom. Hence, it is important that the bond energy of the cations is $q_0(Me-O) \geq ED(O_2)$. Depending on the grouping of the active centers of the catalyst components, is observed the formation of methylcyclopentene and methylcyclopentadiene. If we look at the schematic representation of the oxidative dehydrogenation reaction in the active center of the modified clinoptilolite catalyst in Fig 10, we can easily see the grouping of the active centers.

During the oxidative dehydrogenation reaction of methylcyclopentane to methylcyclopentadiene, it was observed that there are three types of active centers formed by metal cations on the catalyst; a) $\{M_1(1), M_2(2)\}$; b) $\{M_1(1), M_2(4)\}$; c) $\{M_1(2), M_2(4)\}$. Due to the strength of bonds formed by cations with oxygen atoms; Cr^{3+} , Co^{2+} and Cu^{2+} have a very strong attraction to the hydrogen atoms of methylcyclopentane [3].

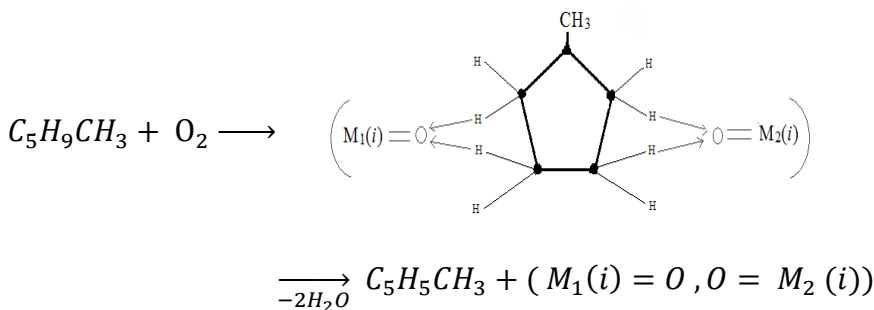


Figure 10. Schematic representation of the formation of methylcyclopentadiene in the active center of the modified (KLCuCrCoZn) clinoptilolite catalyst {M₁(1), M₂(4)}. i-exchange cations (i=1-4; 1-Cr³⁺, 2-Cu²⁺, 3-Zn²⁺, 4-Co²⁺)

Three types of active centers can also be proposed for the oxidative dehydrogenation reaction of methylcyclopentane to methylcyclopentene through the analysis of experimental data and the bond energies of the catalyst components with oxygen atoms; a) {M₁(1), M₂(3)}; b) {M₁(2), M₂(3)}; c) {M₁(4), M₂(3)}. By adding Zn, simultaneous stabilization is observed, so playing promoting character.

The fourth chapter presents the results of the experimental studies conducted on the study of the kinetic regularities of the oxidative dehydrogenation reaction of cyclopentane and methylcyclopentane. The probable step-by-step scheme of the mechanism of the reaction and are shown the results related to the development of theoretically based kinetic model of the reaction. The change of the catalytic activity of the catalyst as a function of time is shown in figure 11 [14]. It was found that cyclopentane:(C₅H₁₀:O₂:N₂=2:1:3.7 mol ratio) on the modified catalyst formed by clinoptilolite (0.5% Cu²⁺, 0.2% Zn²⁺, 0.1% Co²⁺ and 0.1% Cr³⁺) cations, 380-390⁰ C at a temperature and a volume rate of 2000 h⁻¹) methylcyclopentane: (C₅H₉CH₃:O₂:N₂=1.74:1:3.72 mol ratio, at a temperature of 360⁰ C and a volume rate of 1500 h⁻¹) during 400 hours of oxidative dehydrogenation does not undergo any changes of practical catalytic activity of catalysts.

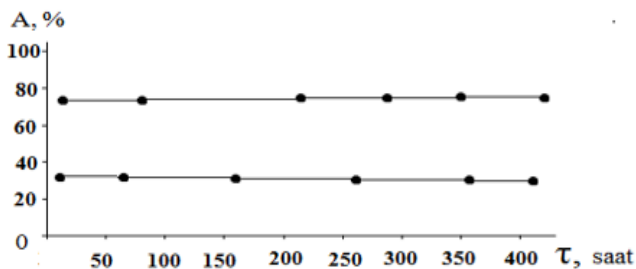


Figure 11. Dependence of the catalytic activity of the CuZnCoCr-clinoptilolite catalyst on the duration of the experiment (τ) ($T=380^{\circ}\text{C}$, $V=2000\text{ h}^{-1}$, $\text{C}_5\text{H}_{10}:\text{O}_2:\text{N}_2=2:1:3,7$)

The determination of the effect of catalyst size on the catalytic system is given in table 2 [14]. The absence of a diffusion factor was determined by keeping the volume velocity of the reactants constant or changing (external) or by changing the sizes of the catalyst particles (internal). It was found that the reaction takes place in the kinetic oblast.

Table 2. CuZnCoCr-CL effect of particle size on the catalytic system

№	Catalyst particle size, mm	Linear velocity of reactants, m/hours	Yield of the reaction product %		Selectivity %	
			CPD	MCPD	CPD	MCPD
1	0,23-0,40	71,56	12,0	42,3	39,4	56,8
		31,43	12,1			
		21,77	11,8			
2	0,40-0,63	71,56	11,9	42,1	39,1	56,6
		31,43	11,7			
		15,50	12,0			
3	0,63-1,25	71,56	12,1	42,2	39,3	56,5
		31,43	11,9			
		15,50	11,7			
4	1,25-1,75	71,56	11,8	42,0	39,2	56,7
		21,77	12,0			
		15,50	12,1			
5	1,75-2,00	71,56	11,0	42,1	39,3	56,6
		21,77	11,8			
		15,50	12,0			

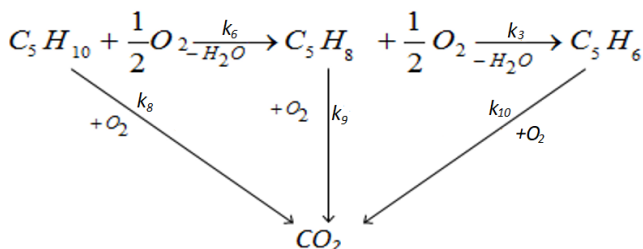
Experimental study of kinetic regularities in the reaction of oxidative dehydrogenation of cyclopentane to cyclopentadiene: Table 3 shows the effect of partial pressure for conversion of cyclopentane and temperature, volume rate, yield of reaction products over CuZnCoCr-clinoptilolite (0.5 mass % Cu²⁺, 0.2 mass % Zn²⁺, 0.1 mass % Co²⁺ and 0.1 mass % Cr³⁺) catalyst.

Table 3.
Effects of partial pressures and mole ratios of reagents and reaction condition on the production of cyclopentadiene

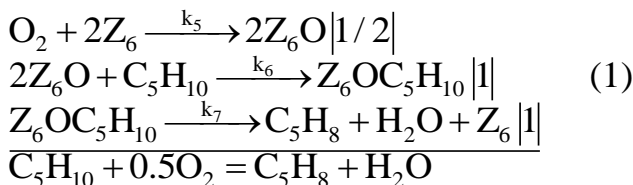
The partial pressure of the reactants, atm		The molar amount of reagents, (mol/hours).			Volume speed hours ⁻¹	Temperature, T, °C	Conversion, X, %	Percentage of reaction products, %		
$P_{C_5H_{10}}$	P_{O_2}	$n_{C_5H_{10}}^0$	$n_{O_2}^0$	$n_{N_2}^0$				C ₅ H ₈	C ₃ H ₆	CO ₂
0.2738	0.1540	0.0654	0.0368	0.1367	2000	320	6.6	1.8	3.9	0.9
0.2738	0.1540	0.0654	0.0368	0.1367	2000	340	8.2	0.7	5.1	2.4
0.2738	0.1540	0.0654	0.0368	0.1367	2000	360	11.9	3.2	5.5	3.2
0.2738	0.1540	0.0654	0.0368	0.1367	2000	370	13.6	3.7	6.3	3.6
0.2738	0.1540	0.0654	0.0368	0.1367	2000	390	30.7	8.9	12.1	9.7
0.2980	0.1489	0.0368	0.0184	0.0683	1000	320	19.8	14.7	3.2	1.9
0.2980	0.1489	0.0368	0.0184	0.0683	1000	340	11.7	2.1	7.0	2.6
0.2980	0.1489	0.0368	0.0184	0.0683	1000	350	11.0	1.1	3.3	6.6
0.2980	0.1489	0.0368	0.0184	0.0683	1000	370	12.3	2.8	5.1	4.4
0.2980	0.1489	0.0368	0.0184	0.0683	1000	380	9.4	2.5	5.7	1.2
0.2980	0.1489	0.0368	0.0184	0.0683	1000	390	13.4	3.8	6.6	3.0
0.3225	0.0768	0.0189	0.0045	0.0352	500	390	14.8	0.8	5.6	8.4
0.5641	0.1491	0.0841	0.0421	0.1561	2500	370	13.1	6.6	4.9	1.6
0.5641	0.1491	0.0841	0.0421	0.1561	2500	390	15.4	15.4	7.3	3.1

From the table shows that increasing the partial pressure of oxygen from 0.0768 to 0.1540 atm leads to an increase in the yield of cyclopentadiene from 5.6 to 12.1%. On the other hand, in the subsequently increase in the partial pressure of oxygen, is observed decrease the yield of the target products. This can be attributed to the formation of partial oxidation products at higher values of oxygen density [12].

The kinetic scheme of the oxidative dehydrogenation reaction of the cyclopentane molecule on the catalyst formed by modified clinoptilolite (0.5% Cu²⁺, 0.2% Zn²⁺, 0.1% Co²⁺ and 0.1% Cr³⁺) cations can be given as follows based on experimental evidence [14, 18].



The following stepwise mechanism can be proposed for the cyclopentene formation reaction.



The rate of acquisition of stages can be written in the following expressions:

$$r_5 = k_5 \theta_5^2 P_{O_2} \quad , \quad r_6 = k_6 \theta_6 P_{C_5H_{10}} \quad , \quad r_7 = k_7 \theta_7 \quad (2)$$

Accordingly, the cyclopentene formation rate equation is formulated on the basis of the proposed step-by-step mechanism,

taking into account the stationary state of the process, and can be written as the following equations (3).

$$r = r_{C_5H_8}^1 = k_6 P_{C_5H_{10}} \left\{ \frac{-\sqrt{\frac{k_6 P_{C_5H_{10}}}{k_5 P_{O_2}}} + \sqrt{\left(\sqrt{\frac{k_6 P_{C_5H_{10}}}{k_5 P_{O_2}}}\right)^2 + 4\left(\frac{k_6 P_{C_5H_{10}}}{k_7} + 1\right)}}{2\left(\frac{k_6 P_{C_5H_{10}}}{k_7} + 1\right)} + \frac{\sqrt{\left(\sqrt{\frac{k_6 P_{C_5H_{10}}}{k_5 P_{O_2}}}\right)^2 + 4\left(\frac{k_6 P_{C_5H_{10}}}{k_7} + 1\right)}}{2\frac{k_6 P_{C_5H_{10}}}{k_7}} \right\}^2 \quad (3)$$

We can write the kinetic equation for the formation of cyclopentene from cyclopentane in the presence of a dissociative adsorbed oxygen molecule according to the Hinshelwood–Langmuir mechanism:

$$r_1 = \frac{k_6 K_1 P_1 \sqrt{K_2 P_2}}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2} \quad (4)$$

At the same time, CO₂ is formed from cyclopentane and cyclopentene. This mechanism can be described in the kinetic equation as follows:

$$r_2(\text{CO}_2) = \frac{k_8 K_1 P_1 K_5 P_2}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2} \quad (5)$$

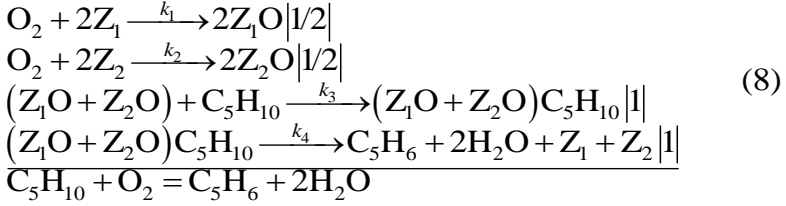
$$r_3(\text{CO}_2) = \frac{k_9 K_3 P_3 K_5 P_2}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2} \quad (6)$$

In the next step, the general rate equation for the formation of cyclopentene is formulated as follows.

$$r_{C_5H_8} = r_1 - r_3(\text{CO}_2) \quad (7)$$

The following stepwise mechanism can be proposed for the

cyclopentadiene production reaction:



The rate of formation of stages is indicated by the following expressions:

$$r_1 = k_1 \theta_1^2 P_{\text{O}_2}, \quad r_2 = k_2 \theta_2^2 P_{\text{O}_2}, \quad r_3 = k_3 \theta_3 P_{\text{C}_5\text{H}_{10}}, \quad r_4 = k_4 \theta_4 \tag{9}$$

Based on this mechanism, the cyclopentadiene formation rate equation was formulated in the form of equations (10) taking into account that the process proceeds in a stationary mode.

$$r = r_{\text{C}_5\text{H}_6}^1 = k_3 P_{\text{C}_5\text{H}_{10}} \cdot \left(\frac{\left(\sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_1 P_{\text{O}_2}} + \frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_2 P_{\text{O}_2}}} \right) + \sqrt{\left(\sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_1 P_{\text{O}_2}} + \frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_2 P_{\text{O}_2}}} \right)^2 + 4 \frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_4}}}{2 \frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_4}} \right)^2 \tag{10}$$

We can write the kinetic equation of the formation of cyclopentadiene according to the Hinshelwood–Langimur mechanism as follows:

$$r_4 = \frac{k_3 K_3 P_3 \sqrt{K_2 P_2}}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 \right)^2} \tag{11}$$

Carbon dioxide is formed from cyclopentadiene. This mechanism can be described in the kinetic equation as follows:

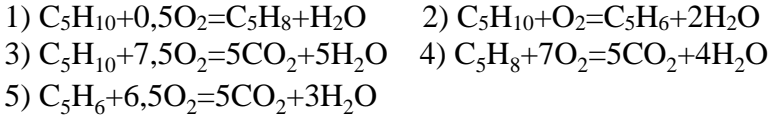
$$r_5(\text{CO}_2) = \frac{k_{10} K_4 P_4 K_5 P_5}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 \right)^2} \tag{12}$$

In the next step, the overall rate equation for the formation of cyclopentadiene and carbon dioxide is formulated as follows.

$$r_{C_5H_6} = r_4 - r_5(CO_2) \quad (13)$$

$$r(CO_2) = r_2(CO_2) + r_3(CO_2) + r_5(CO_2) \quad (14)$$

For Brutto reactions, the stoichiometric equations are shown for obtaining the reaction products.



Based on these equations, we can write the material balance equations of the ingredients as follows:

$$\left. \begin{aligned} n_{C_5H_{10}} &= n_{C_5H_{10}}^0 - (A_1 n_{C_5H_{10}}^0 + A_2 n_{C_5H_{10}}^0 + A_3 n_{C_5H_{10}}^0) / 100 \\ n_{C_5H_8} &= A_1 n_{C_5H_{10}}^0 / 100 \\ n_{C_5H_6} &= A_2 n_{C_5H_{10}}^0 / 100 \\ n_{CO_2} &= 5A_3 n_{C_5H_{10}}^0 / 100 \\ n_{O_2} &= n_{O_2}^0 - (0,5A_1 n_{C_5H_{10}}^0 + 0,5A_2 n_{C_5H_{10}}^0 + 7,5A_3 n_{C_5H_{10}}^0) / 100 \\ n_{H_2O} &= (A_1 n_{C_5H_{10}}^0 + A_2 n_{C_5H_{10}}^0 + 5A_3 n_{C_5H_{10}}^0) / 100 \\ n_{N_2} &= n_{N_2}^0 \end{aligned} \right\} \quad (15)$$

The partial pressure of the ingredients is found by the following formula:

$$P_i = \frac{n_i}{\sum n_i} P \quad (16)$$

(7), (13), (14), (15) equations are given as part of the kinetic model of the process. Pre-exponential multiplication of the constants involved in the reaction $\ln k_i^0 (\ln K_i^0)$, activation energy (E_i^0) and

heat of adsorption (Q_i^0) calculation was carried out in the «Poisk» search system based on "variable boundaries within the accuracy limit" and Powell's method, the objective function is shown as follows. According to the equations, K_i is the adsorption equilibrium coefficient (k_i is the reaction rate constant).

$$F = \min \sum_{j=1}^m \sum_{i=1}^n \left(\frac{A_{ji}^{tec} - A_{ji}^{hes}}{A_{ji}^{tec}} \right)^2 \quad (17)$$

A_{ji}^{tec} , A_{ji}^{hes} – experiments vø i- component, j–experiment, m– number of experiments, n– indicates the number of components.

The numerical values of the parameters of the kinetic model are listed in the table below.

Table 4.
Numerical values of the parameters of the kinetic model

Kinetic model of the oxidative dehydrogenation reaction of cyclopentane			
$\ln k_1^0$ ($\ln K_1^0$)		$E_i(Q_i)$, kcal / mole	
$\ln k_1^0$	32.13	E_1	14.77
$\ln k_2^0$	73.63	E_2	24.25
$\ln k_3^0$	43.90	E_3	58.28
$\ln k_4^0$	53.16	E_4	59.48
$\ln k_5^0$	54.35	E_5	20.29
$\ln K_1^0$	12.06	Q_1	28.51
$\ln K_2^0$	95.45	Q_2	46.34
$\ln K_3^0$	25.61	Q_3	-
$\ln K_4^0$	47.55	Q_4	50.88
$\ln K_5^0$	81.55	Q_5	23.42

Based on the calculations, it was found that the relative error of the experiments does not exceed 10%.

Based on the results of the research, it can be concluded that

the parameters of the kinetic model fully reflect the mechanism of the reaction in the studied interval and it is possible to apply it in the development of a mathematical model for the optimal design of the process.

Study of kinetic regularities in the oxidative dehydrogenation reaction of methylcyclopentane to methylcyclopentadiene: Different activation energies of selective C-C and C-H bonds cause the reaction pathway of the methylcyclopentane molecule to be in different directions. Table 5 details the effects of temperatures, partial pressures, and volume velocity studied for the oxidative dehydrogenation reaction of methylcyclopentane to methylcyclopentadiene. Thus, it was found that natural clinoptilolite modified with cations in percentage proportions {Cu²⁺(0.5 wt.%), Zn²⁺(0.2 wt.%), Co²⁺(0.1 wt.%), Cr³⁺(0.1 wt.%)} forms active catalytic system in the oxidative dehydrogenation of methylcyclopentane. From the results given in Table 5, it is clear that the yield of methylcyclopentadiene increases from 18.8 to 42.3%, when partial pressure of oxygen increases from 0.1438 to 0.1659 atm over selected active catalyst at all investigated temperatures [11].

It can be explained as the formation of partial oxidation products at higher values of oxygen partial pressure. When the partial pressure of cyclopentane and methylcyclopentane increases, we can say that, decrease in the percentage of the target reaction products (cyclopentadiene and methylcyclopentadiene) is related to obstruction at a constant value of the partial pressure of oxygen for coordination of molecular oxygen to active centers of metal zeolite catalysts in a high partial pressures of cyclopentane and methylcyclopentane[15,16].

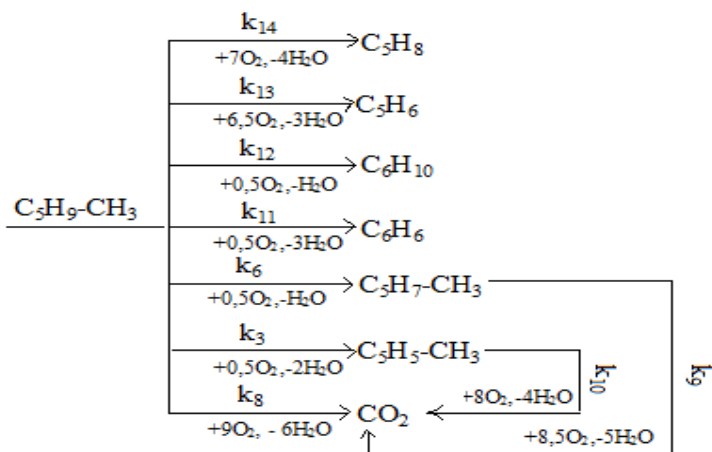
When conducting a process on the prepared catalyst, it is found that in the temperature range of 300-400⁰ C, the molar ratio of (C₅H₉CH₃:O₂:N₂=1.74:1:3.72) and the contact time of 1.8-7.2 seconds shows highest catalytic activity for the oxidative dehydrogenation of methylcyclopentane with air. Partial pressure of reagents C₅H₉CH₃=0.2196-0.3199 atm; O₂=0.1438-0.1659 atm; the mass of the catalyst is G_{kat}=1.78 gr.

Table 5.
Effects of partial pressures and mole ratios of reagents on the production of methylcyclopentadiene

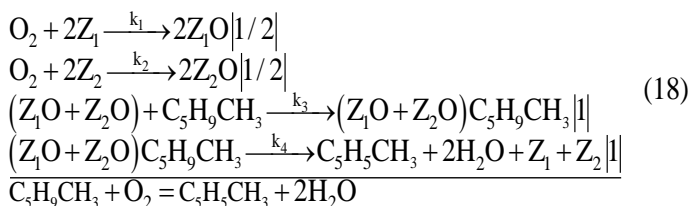
Partial pressure of reactants ,atm		Moles of reactants , (mol/hours).			Volume Velocity, h ⁻¹	Temperature, °C	Conversion % C ₅ H ₉ CH ₃	Percentage of reaction products, %						
C ₅ H ₉ CH ₃	O ₂	C ₅ H ₉ CH ₃	O ₂	N ₂				C/Pent en	CPD	MCP	MCPD	C/Hek sene	Ben zen e	CO ₂
0,2675	0,1533	0,0178	0,00987	0,0367	500	300	31,5	-	8,1	12,8	5,8	0,7	4,1	
						320	34,9	0,3	9,0	14,6	6,0	-	5,0	
						340	42,7	0,9	10,5	15,7	6,3	4,2	4,7	
						360	48,1	1,4	13,7	17,5	7,4	1,9	5,6	
0,3199	0,1438	0,0356	0,016	0,0597	1000	300	47,5	2,7	12,4	18,5	5,4	2,4	3,7	
						320	50,8	3,1	13,9	18,8	5,9	3,4	3,0	
						340	53,5	4,1	15,9	19,4	5,9	3,7	2,9	
						360	58	2,4	16,3	22,7	6,3	3,0	3,5	
0,2836	0,1512	0,045	0,024	0,0897	1500	300	54,8	3,8	12	25,9	2,7	3,5	4,3	
						320	60,5	5,2	14,4	27,2	4,5	2,6	2,7	
						340	70,6	3,1	15,8	36,0	2,3	4,0	4,5	
						360	74,6	1,5	17,0	42,3	4,3	2,0	3,9	
0,2196	0,1659	0,045	0,034	0,126	2000	300	40,9	2,7	10,7	14,7	3,3	1,9	3,4	
						320	43,7	1,9	13,2	15,9	4,6	2,7	2,7	
						340	50,7	2,9	15,5	17,0	4,9	4,1	4,8	
						360	58,4	3,4	15,8	20,4	5,5	4,9	6,3	

The kinetic regularities of the reaction (the effect of the partial pressures of reactants, the volume velocity of the reaction mixture, the temperature of the reaction on the way of the reaction) were studied in detail based on experimental results. It was found that the yield of methylcyclopentadiene on the appropriate catalyst is 42.3%, and selectivity of the process for methylcyclopentadiene is 56.7% at a temperature of 360°C and a volume speed of 1500h⁻¹.

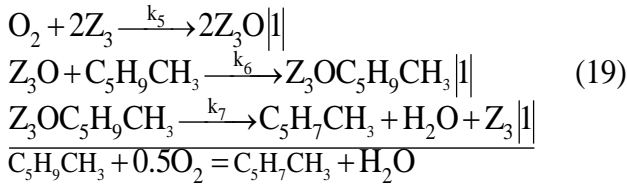
Based on experimental evidence, the kinetic scheme of the oxidative dehydrogenation reaction of methylcyclopentane molecule on the catalyst formed by modified clinoptilolite (0.5% Cu²⁺, 0.2% Zn²⁺, 0.1% Co²⁺ and 0.1% Cr³⁺) cations can be given as follows [14].



The following stepwise mechanism can be proposed for obtaining the reaction of methylcyclopentadiene (18) [18].



The following stepwise mechanism can be proposed for obtaining of the methylcyclopentene reaction (19).



Based on this mechanism, the rate equation for the formation of methylcyclopentene was formulated in the form of equation (20), taking into account that the process proceeds under stationary conditions.

$$r = r_{\text{C}_5\text{H}_7\text{CH}_3}^1 = k_6 P_{\text{C}_5\text{H}_9\text{CH}_3} \left\{ \frac{-\sqrt{\frac{k_6 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_5 P_{\text{O}_2}}} + \sqrt{\left(\sqrt{\frac{k_6 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_5 P_{\text{O}_2}}}\right)^2 + 4\left(\frac{k_6 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_7} + 1\right)}}{2\left(\frac{k_6 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_7} + 1\right)} \right\}^2 \quad (20)$$

Accordingly, the rate equation for the formation of methylcyclopentadiene is formulated based on the proposed probabilistic stepwise mechanism considering the steady state process and can be written as the following equations (21).

$$r = r_{\text{C}_5\text{H}_5\text{CH}_3}^1 = k_3 P_{\text{C}_5\text{H}_9\text{CH}_3} \left\{ \frac{\left(\sqrt{\frac{k_3 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_2 P_{\text{O}_2}}} \right) + \sqrt{\left(\sqrt{\frac{k_3 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_2 P_{\text{O}_2}}} \right)^2 + 4\frac{k_3 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_4}}}{2\frac{k_3 P_{\text{C}_5\text{H}_9\text{CH}_3}}{k_4}} \right\}^2 \quad (21)$$

According to the Hinshelwood–Langimur mechanism, the kinetic equation for the formation of methylcyclopentene from methylcyclopentane and methylcyclopentadiene from methylcyclopentene with the presence of a dissociative adsorbed oxygen molecule can be described as follows (22), (23):

$$r_1 = \frac{k_6 K_1 P_1 \sqrt{K_2 P_2}}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_2\right)^2} \quad (22)$$

$$r_4 = \frac{k_3 K_3 P_3 \sqrt{K_2 P_2}}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_2\right)^2} \quad (23)$$

The numerical values of the parameters of the kinetic model are listed in the following figure.

According to the calculations, the relative error of experiments did not exceed 15%.

Table 6.
Numerical values of the parameters of the kinetic model

A kinetic model of the oxidative dehydrogenation of methylcyclopentane.			
$\ln k_i^0$ ($\ln K_i^0$)		$E_i(Q_i)$, kcal / mole	
$\ln k_1^0$	17.28	E_1	78.42
$\ln k_2^0$	11.88	E_2	31.82
$\ln k_3^0$	84.93	E_3	76.41
$\ln k_4^0$	37.98	E_4	72.81
$\ln k_5^0$	18.59	E_5	55.37
$\ln k_6^0$	64.12	E_6	93.55
$\ln k_7^0$	94.88	E_7	30.18
$\ln k_8^0$	-10.91	E_8	30.39
$\ln k_9^0$	-48.37	E_9	56.98
$\ln k_{10}^0$	19.06	E_{10}	30.27
$\ln k_{11}^0$	14.63	E_{11}	20.17
$\ln k_{12}^0$	96.07	E_{12}	15.24
$\ln k_{13}^0$	20.54	E_{13}	27.69
$\ln k_{14}^0$	16.26	E_{14}	25.43
$\ln K_1^0$	97.61	Q_1	73.54
$\ln K_2^0$	11.53	Q_2	20.13
$\ln K_3^0$	11.19	Q_3	84.11
$\ln K_4^0$	13.61	Q_4	10.41
$\ln K_5^0$	14.42	Q_5	83.88
$\ln K_6^0$	35.72	Q_1	88.54

CONCLUSION

1. As a result of the work, were synthesized multicomponent metal zeolite catalysts, which is formed by natural and synthetic zeolites with transition metal cations and their catalytic activity was determined under the presence of air and atmospheric pressure in the oxidative dehydrogenation reaction of cyclopentane to cyclopentadiene and methylcyclopentane to methylcyclopentadiene [4,5,6,7].
2. It was determined that natural clinoptilolite with silicate modulus $\text{SiO}_2/\text{Al}_2\text{O}_3=8.68$, containing $\text{Cu}^{2+}-0.5\% : \text{Zn}^{2+}-0.2\% : \text{Co}^{2+}-0.1\% : \text{Cr}^{3+}-0.1\%$ metal cations shows relatively high catalytic activity and selectivity for oxidative dehydrogenation of cyclopentane and methylcyclopentane. For cyclopentane, yield of cyclopentadiene was 12.1%, the selectivity of the process for cyclopentadiene was 39.4%, and the conversion was 30.7%, is arranged at temperature of 390°C, a volume velocity 2000h⁻¹ and a molar ratio of $\text{C}_5\text{H}_{10}:\text{O}_2:\text{N}_2=2:1:3,7$. For methylcyclopentane, the yield of methylcyclopentadiene is 42.3%, the selectivity of the process is 56.7%, and the conversion is 74.6 % is arranged at temperature 360°C, a volume velocity 1500h⁻¹ and a molar ratio of $\text{C}_5\text{H}_9-\text{CH}_3:\text{O}_2:\text{N}_2=1,74:1:3,72$ [5,9,11,12,14].
3. Experimental kinetic regularities of cyclopentane was determined ($\text{Cu}^{2+}-0.5\% ; \text{Zn}^{2+}-0.2\% ; \text{Co}^{2+}-0.1\% ; \text{Cr}^{3+}-0.1\%$) over a metal zeolite catalyst at temperature of 320–390°C, a volume velocity 500–2500 h⁻¹ and partial pressures of cyclopentane 0.273–0.5641 atm and 0.0768–0.1540 atm for oxygen [4,16].
4. The kinetic regularities of methylcyclopentane were determined experimentally at temperature of 300-380⁰ C, a volume velocity of 500-2000h⁻¹ and partial pressures of methylcyclopentane of 0.2196-0.3199atm and oxygen of 0.1438-0.1659atm [13,14,15,16].
5. The scheme of the possible stepwise mechanism of the reaction of oxidative dehydrogenation of cyclopentane and methylcyclopentane molecules on the modified ($\text{Cu}^{2+}-0.5\% ; \text{Zn}^{2+}-0.2\% ; \text{Co}^{2+}-0.1\% ; \text{Cr}^{3+}-0.1\%$) metal zeolite catalyst was

proposed. Based on these mechanisms, a theoretically based kinetic model of the processes was constituted [4,13,18].

6. The numerical values of the parameters of the developed kinetic models were determined on the basis of experimental evidence, and according to the calculations, it was determined that the relative error of the experiments did not exceed for cyclopentane - 10% and methylcyclopentane -15% [4,13,18].
7. The parameters of the kinetic model were determined fully reflect the mechanism of the reaction in the studied interval, and it is possible to apply it in the development of a mathematical model for the optimal design of the process. [4,7,13].
8. Time-dependent changes of catalytic activity of (0.5%Cu²⁺, 0.2%Zn²⁺, 0.1%Co²⁺ and 0.1%Cr³⁺) clinoptilolite catalyst were determined in the oxidative dehydrogenation reaction of cyclopentane and methylcyclopentane and it was found that catalytic activity of the catalyst not change during 400 hours practically. Based on experimental results, it can be concluded that these catalysts can be used in the implementation of large industrial processes [14].

The main content of the thesis is published in the following articles and abstracts:

1. Aliyev, A.M., Shabanova, Z.A., Kerimov, A.I., Najaf-Guliyev U.M., Abbasov, M.Y. Selective oxidative dehydrogenation of methylcyclohexane on modified zeolite catalysts // International scientific and technical conference "Petrochemical synthesis and catalysis in complex condensed systems", devoted to the 100th anniversary of academician B.K. Zeynalov, - Baku: -29-30 June, - 2017, - p. 187.
2. Aliyev, A.M., Shabanova, Z.A., Ali-zadeh, G.A., Najaf-Guliev U.M., Abbasov, M.Y. Mechanism of oxidative dehydrogenation of cyclohexane on modified clinoptilolite // International scientific and technical conference "Petrochemical synthesis and catalysis in complex condensed systems" devoted to the 100th anniversary of Academician B.K. Zeynalov, - Baku: -29-30 June, -2017, -c .176.

3. Aliyev, A.M., Shabanova, Z.A., Najaf-Quliyev, U.M., Huseynova, T.I., Abbasov, M.Y. Mechanism of oxidative dehydrogenation of cyclopentane on modified clinoptilolite // Proceedings of the "Nagiyev Readings" scientific conference dedicated to the 110th anniversary of Academician M. Nagiyev, - Baku:-2017, -p.207.
4. Aliyev, A.M. A Study of the kinetics and mechanism of the selective oxidative dehydrogenation reaction of cyclopentane to cyclopentadiene-1,3 over modified zeolite catalysts/ A.M.Aliyev, M.Y.Abbasov, Z.A.Shabanova // Azerbaijan Chemical Journal, - Baku: -2018. No. 3, p. 11-20.
5. Aliyev, A.M., - Method of obtaining 1.3-Cyclopentadiene, Invention i2020 0068, Republic of Azerbaijan / Aliyev A.M., Abbasov M.Y., Najaf-Guliyev U.M. [etc.].
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10. Aliyev, A.M., Abbasov, M.Y. Study of oxidative dehydrogenation of methylcyclopentane on a clinoptilolite catalyst / A.M. Aliyev., M.Y.Abbasov // XVIII International scientific and practical

conference “perspective directions for the development of science and practice”, – Athens, Greece: – June 14 – 16, – 2021, – pp. 24–25.

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