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USE OF METAL-ZEOLITES AS A CATALYST IN REACTION OF OXIDATIVE DEHYDROGENATION OF NAPHTHENES**A.M.Aliyev, Z.A.Shabanova, A.I.Kerimov, M.F.Bahmanov, F.V.Aliyev, U.M.Najaf-Guliyev***M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**zumrud-042425-@mail.ru*

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Oxidative dehydrogenation of cyclohexane into 1,3-cyclohexadiene and methylcyclohexane into 1-methyl-1,3-cyclohexadiene has been found possible by use of clinoptilolite (CL) {Cu²⁺ (0.5 mas. %), Zn²⁺ (0.2 mas. %), Co²⁺ (0.1 mas. %), Cr³⁺ (0.1 mas. %)} and CL {Co²⁺ (0.5 mas. %), Cr³⁺ (0.25 mas. %)} heterogenic catalysts, prepared by ion-exchange, accordingly. By analyzing experimental data and taking into account bonding energies of exchange cations with dissociative adsorbed oxygen the active centers consisting of components of the catalyst have been grouped and reaction paths have been elucidated. The kinetic model worked out by taking into account these active centers, is presented.

Keywords: *cyclohexane, 1,3-cyclohexadiene, methyl cyclohexane, 1-methyl-1,3-cyclohexadiene.*

Introduction

Zeolites modified with metal cations have been widely used in practice as a catalyst and they are an object of the intensive investigation in fundamental catalysis. Very important problem is a development of procedures of preparation of modified zeolite catalysts with maximum achieved degree of using the active component. One of the procedures of preparation of this type of catalysts is the modifying of zeolites with metal cations by ion-exchange [1, 2]. Having used this method we synthesized active ultra-dispersion metal-zeolite catalysts for the reactions of oxidation of lower olefin hydrocarbons into carbonyl compounds, partial oxidation of lower parafin hydrocarbons, oxidative conversion of aliphatic alcohols, oxidative coupling of methane and oxidative dehydrogenation of naphthenic hydrocarbons [3–9]. All these catalysts show high activity and selectivity at relatively lower temperatures. In early published works we have shown that natural clinoptilolite modified with cations Cu²⁺, Zn²⁺, Co²⁺ and Cr³⁺ by ion-exchange is the active catalyst for reaction of oxidative dehydrogenation of cyclohexane into 1,3-cyclohexadiene [7, 8]. On the basis of experimental kinetic data by using Langmuir–Hinshelwood rate expression we have established that reaction of oxidative dehydrogenation of cyclohexane proceeds with participation of the dissociative adsorbed oxygen. We have also studied influence of separate components of the

catalyst system on selectivity of the process [7, 8].

The purpose of the present work is to determine a role of the components of the catalytic system in reaction of oxidative dehydrogenation of naphthenic hydrocarbons taking into account the new experimental data on oxidative dehydrogenation of methyl cyclohexane [11] obtained in the laboratory "Catalysis over zeolites" of the Institute of Catalysis and Inorganic Chemistry NAS of Azerbaijan.

Experimental

The catalysts were prepared by the method of ion-exchange using Azerbaijan natural clinoptilolite (crystallinity, 89.0%) and cations of the different metals [8]. After incorporating of the cations, all of the specimens of the metal-zeolite catalysts were activated by air at temperature, 350⁰C and space velocity, 2400 h⁻¹ during 30 minutes.

The test of the activity of the prepared metal-zeolite catalysts and a study of the kinetic regularities of the reactions was carried out in a flow apparatus with the quartz tube reactor connected directly to the gas chromatograph. The reactor was placed inside a thermostatic chamber. Small stainless-steel balls of a 0.2 cm diameter were placed before the catalyst bed in order to obtain plug flow conditions. No catalytic activity was shown by these nonporous balls. A fraction of granulated metal-zeolites of about 0.25–0.63 cm of equivalent diameter was used as the catalyst. The analyses of the product of

reactions were performed by gas chromatography (GC), using a column filled with Paropack-T (length, 3 m), helium as the carrier gas, hot wire detector and program control of the temperature (from 50 to 200°C). Runs performed at several feed rates and using granules of catalyst of different sizes showed that external and internal mass transfer effects were negligible under the studied conditions.

Before incorporating the cations, natural clinoptilolite ($\text{SiO}_2/\text{Al}_2\text{O}_3=8.68$) was treated with 0.5 N HCl solution. Amount of incorporating cations was determined by ion spectral analysis using ICP-MS "Agilent 7700". Purity of using cyclohexane and methyl cyclohexane was 99.5% and 99.0% accordingly. The analyses of the product of the reactions were also performed by gas chromatography using GC "Agilent 7890" with "Agilent 5975" MS and capillary column HP-5MS (length, 30 m).

Results and discussion

The results of a testing of a catalytic activity of the prepared metal-zeolites in the reaction of oxidative dehydrogenation of cyclohexane into 1,3-cyclohexadiene are presented in Table 1. It can be seen from the data of Table 1, natural cli-

noptilolite and its modified form with cations, Zn^{2+} (exp. 1, 2) show lower catalytic activity in the reaction. The activity of the specimens of natural clinoptilolite modified with cations; Cr^{3+} , Cu^{2+} and Co^{2+} is relatively higher than above mentioned ones, particularly in course of aromatization of cyclohexane (exp. 3–5), yields of benzene are 15.5%, 12.5 and 9.8% accordingly, and 1,3-cyclohexadiene forms with lower yields. Incorporating of two cations in natural clinoptilolite; Cu^{2+} , Cr^{3+} and Co^{2+} , Cr^{3+} is led to insignificant increasing yields of 1,3-cyclohexadiene in dominating reaction of cyclohexane aromatization (exp. 7, 8). Incorporating in these catalytic system of the third cation, Zn^{2+} is led to significant increasing in the yields of 1,3-cyclohexadiene and decreasing in the yields of benzene (exp. 12, 13).

Relatively high yields, of 1,3-cyclohexadiene is achieved on the catalytic systems containing cations Cu^{2+} , Cr^{3+} , Co^{2+} and Zn^{2+} (exp. 19, 20). Natural clinoptilolite modified with cations; Fe, Mn, Sn, Mo and Ni shows relatively low catalytic activity in reaction of oxidative dehydrogenation of cyclohexane into 1,3-cyclohexadiene (exp. № 9–11, 16–18).

Table 1. The results of the test of activity of modified natural clinoptilolite (CL) catalyst in reaction of oxidative dehydrogenation of cyclohexane ($T=380^\circ\text{C}$, $v=2000\text{ h}^{-1}$, $\text{C}_6\text{H}_{12}:\text{O}_2:\text{N}_2=1:1:5.3$)

№	Catalyst	Conversion of C_6H_{12} , X, %	Selectivity, S, %	Yield, A, %					
				C_6H_{10}	C_6H_8	C_6H_6	$\text{C}_6\text{H}_{10}\text{OH}$	$\text{C}_6\text{H}_{10}\text{O}$	CO_2
1	CL	14.8	6.1	10.8	0.9	1.7	0.3	0.8	0.3
2	CL Zn (0.2)*	14.3	2.8	0.7	0.4	0.3	12.1	–	0.8
3	CLCr (0.1)	49.3	9.5	8.8	4.7	15.5	7.9	10.5	1.9
4	CLCu (0.5)	49.7	5.8	3.6	2.9	12.5	10.5	17.7	2.5
5	CLCo (0.1)	41.6	9.4	6.9	3.9	9.8	6.5	10.6	3.9
6	CLZnNi (0.2:0.1)	18.2	2.7	0.8	0.5	0.9	14.8*	–	1.2
7	CLCuCr (0.5:0.1)	39.3	13.9	0.9	5.5	9.8	7.9	8.6	6.6
8	CLCoCr (0.1:0.1)	44.1	18.6	5.4	8.2	9.9	10.8	5.5	4.1
9	CLCuSn (0.5:0.1)	34.1	9.6	2.2	3.3	1.3	6.1	15.3	5.9
10	CLCuMn (0.5:0.1)	33.9	12.1	3.8	4.1	7.5	–	13.8	4.7
11	CLCuFe (0.5:0.25)	14.6	54.1	0.6	7.9	1.7	3.7	–	0.7
12	CLZnCoCr (0.2:0.1:0.1)	39.2	30.3	4.8	12.5	4.9	8.5	2.2	6.3
13	CLZnCuCr (0.2:0.5:0.1)	35.5	21.8	0.5	8.4	4.5	6.7	7.9	7.5
14	CLCuCoCr (0.5:0.1:0.1)	47.9	21.5	4.5	10.3	6.4	11.5	8.4	6.8
15	CLCuZnCo (0.5:0.2:0.1)	45.6	25.8	16.7	11.8	2.1	7.2	6.5	1.3
16	CLCoMnCu (0.1:0.5:0.5)	16.3	41.7	3.5	6.8	1.3	–	3.8	0.9
17	CLCoMnCr (0.1:0.5:0.5)	43.1	20.6	11.3	8.9	16.7	–	4.9	1.3
18	CLCoMoCr (0.1:0.5:0.1)	41.4	7.97	7.8	3.3	2.9	13.7	9.3	4.4
19	CLCuZnCoCr (0.5:0.2:0.1:0.1)	35.8	65.1	–	23.3	0.5	7.1	–	4.9
20	CLCuZnCoCr (2:2:1.0:0.5)	54.4	29.7	2.5	16.2	3.9	16.9	13.5	1.4

* – the figures in brackets indicate the containing exchange cations in mas. %

From the data of Table 1, it has been concluded that the natural clinoptilolite containing $\text{Cu}^{2+} - 0.5$ mas. %, $\text{Zn}^{2+} - 0.2$ mas. %, $\text{Co}^{2+} - 0.1$ mas. % and $\text{Cr}^{3+} - 0.1$ mas. % is the active catalyst for reaction of oxidative dehydrogenation of cyclohexane into 1,3-cyclohexadiene.

The results of the experimental investigation on a selection of the catalyst for reaction of oxidative dehydrogenation of methyl cyclohexane into 1-methyl-1,3-cyclohexadiene are presented in Table 2. It can be seen from data in Table 2 that natural clinoptilolite modified with cations Zn^{2+} , Cu^{2+} , Cr^{3+} , Fe^{2+} and Ni^{2+} shows relatively low catalytic activity in reaction of oxidative dehydrogenation of methyl cyclohexane into 1-methyl-1,3-cyclohexadiene (exp. 1–6). The natural clinoptilolite modified with cations Co^{2+} and Cr^{3+} shows relatively high catalytic activity in this reaction (exp. 11–15). Incorporating in composition of these catalytic systems of cation Zn^{2+} decreases their catalytic activity in the reaction (exp. 16, 17). Natural clinoptilolite containing cations Cu^{2+} , Zn^{2+} , Co^{2+} and Cr^{3+} has relatively low catalytic activity in the reaction as compared with the clinoptilolite containing cations Co^{2+} and Cr^{3+} (exp. 14, 18). Analysis of the data given in Table 2 shows that the clinoptilolite

containing cations $\text{Co}^{2+} - 0.5$ and $\text{Cr}^{3+} - 0.25$ mas.% is the active catalyst for reaction oxidative dehydrogenation of methyl cyclohexane into 1-methyl-1,3-cyclohexadiene.

It is known that an activity of the zeolite catalysts in different reactions depends on; crystal structure, nature of cations, method preparation and distribution of cations of metals on a surface of zeolite. In our previous work [8], it was shown that the crystal structure of clinoptilolite is optimum for preparation of the catalyst for reaction of oxidative dehydrogenation of naphthenic hydrocarbons. It is known that a crystal lattice of clinoptilolite consists of three open channels; A, B and C [12]. In Figure 1 it is presented the polyhedron model of clinoptilolite, reflecting a fragment of the structure with exchange cations. A and B channels are parallel to axis, C and consist of tencyclic and octocyclic rings. They cross with the third octocyclic channel parallel to axis, a . Hexagonal planers in structure of clinoptilolite are surrounded with channels A, B and C in which the exchange cations are localized. Planar molecule of cyclohexane is hexacyclic which is solidly adsorbed on the hexagonal planers surrounded exchange cations in the structure of clinoptilolite.

Table 2. The results of the test of the activity of modified natural clinoptilolite catalysts in reaction of oxidative dehydrogenation of methyl cyclohexane ($T=380^{\circ}\text{C}$, $v=2000\text{h}^{-1}$, $\text{C}_6\text{H}_{11}\text{CH}_3:\text{O}_2:\text{N}_2=1:1:5.3$)

№ exp.	Catalyst	Conversion of $\text{C}_6\text{H}_{11}\text{CH}_3$, X, %	Selectivity, S, %	Yield, A, %			
				$\text{C}_6\text{H}_9\text{CH}_3$	$\text{C}_6\text{H}_7\text{CH}_3$	$\text{C}_6\text{H}_5\text{CH}_3$	CO_2
1	Zn (0.2)*	7.6	7.9	0.9	0.6	5.2	0.9
2	Cu (0.5)	28.9	1.03	3.8	0.3	8.5	16.3
3	Cr (0.1)	21.4	21.02	5.9	4.5	9.5	1.5
4	Co (0.1)	19.4	19.6	6.2	3.8	7.4	2.0
5	Fe (0.25)	21.4	–	1.5	–	6.7	13.2
6	Ni (0.1)	50.2	–	–	–	40.3	9.9
7	CuFe (0.5:0.25)	34.6	6.4	3.2	2.2	10.3	18.9
8	CuCo (0.5:0.1)	32.5	10.8	5.8	3.5	15.7	7.5
9	CuCr (0.5:0.1)	28.6	7.7	3.9	2.2	19.8	2.7
10	ZnCr (0.2:0.1)	18.8	4.3	1.9	0.8	14.5	1.6
11	CoCr (0.1:0.1)	32.7	30.3	3.6	9.9	13.9	5.3
12	CoCr (0.5:0.1)	37.4	28.9	5.8	10.8	12.3	8.5
13	CoCr (1.0:0.1)	41.1	23.4	5.2	9.6	13.8	12.5
14	CoCr (0.5:0.25)	49.8	28.9	7.2	14.4	15.6	12.6
15	CoCr (0.5:0.5)	53.9	12.1	1.9	6.5	35.7	9.8
16	ZnCoCr (0.2:0.5:0.25)	45.9	23.3	12.5	10.7	10.9	11.8
17	ZnCoCr (0.2:0.5:0.5)	49.4	13.9	13.5	6.9	21.5	7.5
18	CuZnCoCr (0.5:0.2:0.1:0.1)	37.4	22.7	5.3	8.5	9.9	13.7

* – the figures in brackets indicate the containing exchange cations in mas. %

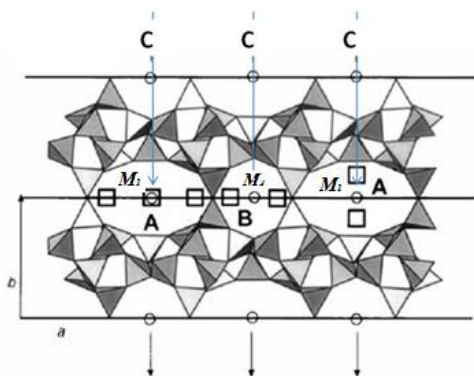


Fig. 1. Polyhedron model of clinoptilolite, reflected fragment of structure with exchange cations.

In clinoptilolite there are four types of places in localization of exchange cations; they are M_1 in channel A, M_2 in channel B, M_3 in C arranged along axis of a near center of the hexacyclic ring and M_4 – place arranged in channel A in center of inversion. Their quantity is not great. M_3 is arranged near M_1 [13, 14].

A role of components of the catalytic system in the reaction of oxidative dehydrogenation of cyclohexane can be explained by analysis of surrounding of the adsorbed molecules of cyclohexane with the exchange cations bonded with dissociative adsorbed oxygen, taking into account their bonding energies which can be found by expression [15]:

$$q_0 = \frac{1}{2}(q_{\text{ads}} + 500), \quad (1)$$

where 500 kJ/mole – energy of dissociation of molecule oxygen, q_{ads} – heat of adsorption of oxygen on the pure surfaces of the polycrystal specimens of transient metals [16]; $q_{\text{ads}}(\text{Cu}) = 478$ kJ/mole, $q_{\text{ads}}(\text{Zn}) = 240$ kJ/mole, $q_{\text{ads}}(\text{Co}) = 418$ kJ/mole, $q_{\text{ads}}(\text{Cr}) = 753$ kJ/mole. Bonding energies of the components of catalyst with oxygen may be calculated by using formula, (1); $q_0(\text{Cu}) = 489$ kJ/mole, $q_0(\text{Zn}) = 370$ kJ/g-atom, $q_0(\text{Co}) = 459$ kJ/g-atom, $q_0(\text{Cr}) = 612$ kJ/g-atom.

Depending on solidity of these bonds driving force of hydrogen atoms of cyclohexane changes. The most driving force of hydrogen atoms of cyclohexane is displayed by the oxygen atoms bonded with the component of the catalyst, Cr^{3+} .

On the basis of the experimental data presented in Table 1 and with taking regard to the bonding energies of the components of the catalyst with oxygen atom it is possible to group the active centers of components of the catalyst for reaction of oxidative dehydrogenation of cyclohexane which are responsible for formation of 1,3-cyclohexadiene, cyclohexene and benzene. Total scheme of oxidative dehydrogenation of cyclohexane on these active centers is presented in Figure 2.

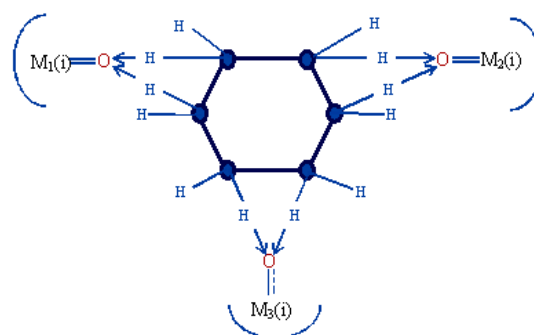


Fig. 2. Schematic representation of the reaction of oxidative dehydrogenation on an active center of modified clinoptilolite catalyst, CL-CuCrCoZn. i – exchange cation, $i=1-4$; 1 – Cr^{3+} , 2 – Cu^{2+} , 3 – Zn^{2+} , 4 – Co^{2+} .

There are two types of active centers for reaction of oxidative dehydrogenation of cyclohexane into 1,3-cyclohexadiene; $\{M_1(1), M_2(2), M_3(3)\}$ and $\{M_1(1), M_2(4), M_3(3)\}$. Because of the solidity of bonds of cations; Cr^{3+} , Cu^{2+} and Co^{2+} with oxygen atoms they have very strongly driving force of hydrogen atoms of cyclohexane, forming molecules of 1,3-cyclohexadiene stabilized with $\text{Zn}=0$ which has relatively lower bonding energy (Figure 3).

By means of analysis of the experimental data and bonding energies of the components of the catalyst with oxygen atoms three types of active centers may be suggested for reaction oxidative dehydrogenation cyclohexane into benzene; $\{M_1(1), M_2(1), M_3(1)\}$, $\{M_1(2), M_2(2), M_3(2)\}$ and $\{M_1(4), M_2(4), M_3(4)\}$ as well three types of active centers for reaction oxidative dehydrogenation of cyclohexane into cyclohexene; $\{M_1(1), M_2(3), M_3(3)\}$, $\{M_1(2), M_2(3), M_3(3)\}$ and $\{M_1(4), M_2(3), M_3(3)\}$.

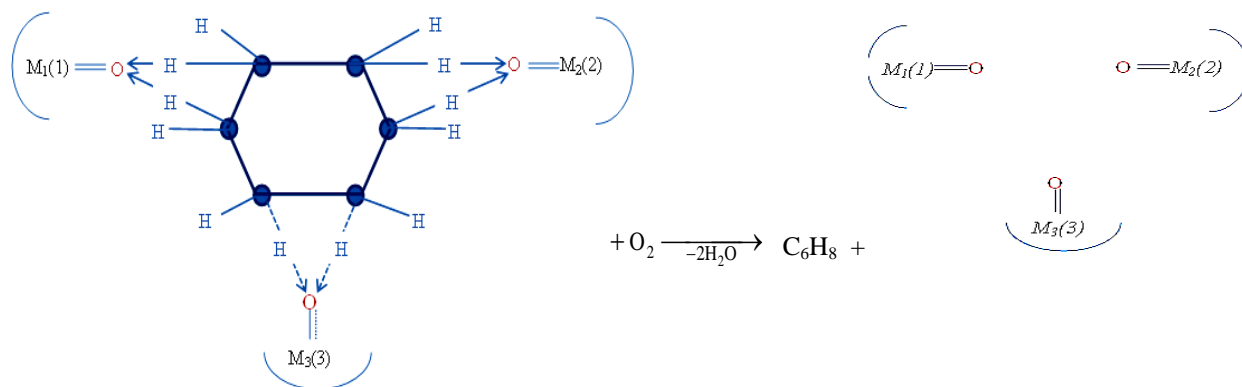


Fig. 3. Schematic representation of formation of 1,3-cyclohexadiene on an active center, $\{M_1(1), M_2(2), M_3(3)\}$ of modified clinoptilolite catalyst CL-CuCrCoZn.

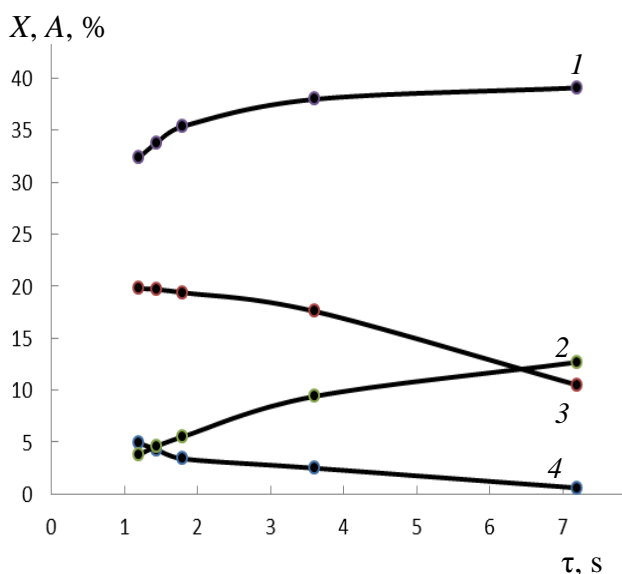


Fig. 4. Dependence of oxidative dehydrogenation of cyclohexane on the average residence time, τ : 1 – conversion of cyclohexane, X , %; 2 – yield of cyclohexene, A_1 , %; 3 – yield of 1,3-cyclohexadiene, A_2 , %; 4 – yield of benzene, A_3 , %; $T=380^\circ C$, $C_6H_{12}:O_2:N_2=1:1:5.3$.

It should be noted that an advantage formation of that or the other product of reaction of oxidative dehydrogenation of cyclohexane depends on amount of active centers for corresponding reaction which depends on concentration and sequence of incorporating of cations by ion-exchange. With the purpose of obtaining of 1,3-cyclohexadiene the optimum succession incorporating of cation in clinoptilolite is

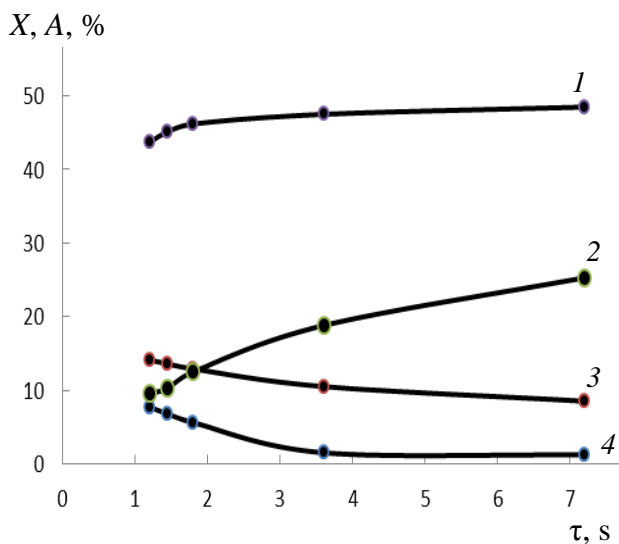
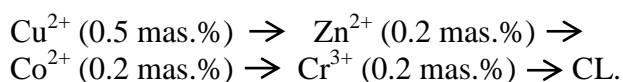


Fig. 5. Dependence of oxidative dehydrogenation of methyl cyclohexane on the average residence time, τ : 1 – conversion of methyl cyclohexane, X , %; 2 – yield of methyl cyclohexadiene, A_2 , %; 3 – yield of methyl cyclohexene, A_1 , %; 4 – yield of toluene, A_3 , %; $T=380^\circ C$, $C_6H_{11}CH_3:O_2:N_2=1:1:5.3$.

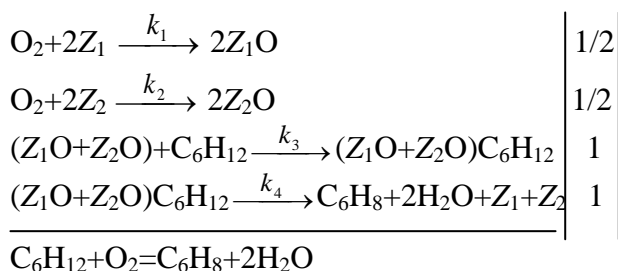
Experimental data on a study of the kinetic regularities of the considered reactions over the active catalytic system testified to that these reactions don't proceed on a consecutive mechanism.

In Figures 4 and 5 there is presented an influence of average resident time on proceeding of reactions of oxidative dehydrogenation of cyclohexane over CL-CuCrCoZn and methyl cyclohexane over CL-CoCr catalysts accordingly.

If the reactions proceed on a consecutive mechanism with formation of end products; benzene and toluene, then cyclohexene, 1,3-cyclohexadiene and methyl cyclohexene, 1-methyl-1,3-cyclohexadiene are the intermediate products of the reactions of oxidative dehydrogenation of cyclohexane and methyl cyclohexane accordingly. It can be seen in Figures 4 and 5 the character of curves of dependence of yields of intermediate and end-products on average resident time not corresponded to consecutive mechanism of proceeding of these reactions.

Thus on the basis of these experimental data it has been concluded that on the surface of the catalyst there are different active centers consisting of their components which are responsible for formation of the products of the reaction that is agreed with above mentioned hypothesis about structure of active centers.

Stage scheme of mechanism of oxidative dehydrogenation of cyclohexane on above mentioned active centers may be presented as follows:



The following expression can be written for rates of the stages:

$$r_1 = k_1 \theta_1^2 P_{\text{O}_2}, \quad r_2 = k_2 \theta_2^2 P_{\text{O}_2}, \quad r_3 = k_3 \theta_3 P_{\text{C}_6\text{H}_{12}},$$

$$r_4 = k_4 \theta_4.$$

In stationary conditions

$$r = r_1 = r_2 = r_3 = r_4,$$

where θ_1 , θ_2 , θ_3 and θ_4 are fractions of catalyst surface; the sites with the ability to adsorb atom oxygen, the sites with two near arranged adsorbed atom oxygen on different exchange cations and the sites with adsorbed molecules of cyclohexane.

$$\theta_4 = \frac{k_3 \theta_3 P_{\text{C}_6\text{H}_{12}}}{k_4}, \quad \theta_1 = \sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_1 P_{\text{O}_2}}} \sqrt{\theta_3},$$

$$\theta_2 = \sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_2 P_{\text{O}_2}}} \sqrt{\theta_3}, \quad \theta_1 + \theta_2 + \theta_3 + \theta_4 = 1,$$

$$\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_4} \theta_3 + \left(\sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_2 P_{\text{O}_2}}} \right) \sqrt{\theta_3} - 1 = 0.$$

Assuming

$$\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_4} = A, \quad \left(\sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_2 P_{\text{O}_2}}} \right) = B,$$

$$\theta_3 = x^2, \quad \sqrt{\theta_3} = x, \quad Ax^2 + Bx - 1 = 0,$$

we'll receive

$$x = \frac{-B + \sqrt{B^2 + 4A}}{2A},$$

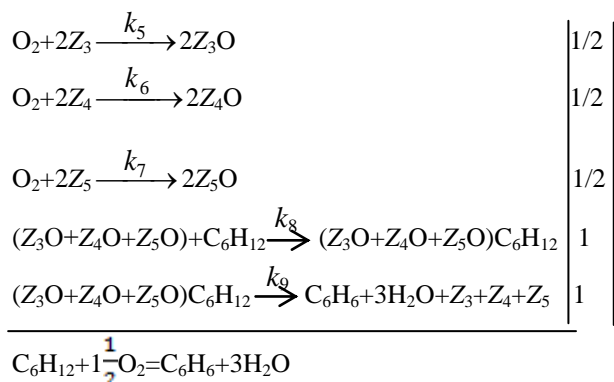
$$\theta_3 = x^2 = \left\{ \frac{-B + \sqrt{B^2 + 4A}}{2A} \right\}^2,$$

Then, the equation of rate of the formation 1,3-cyclohexadiene appears as

$$r = r_{\text{C}_6\text{H}_8}^1 = k_3 P_{\text{C}_6\text{H}_{12}} \cdot \left\{ \frac{-B + \sqrt{B^2 + 4A}}{2A} \right\}^2, \quad (1)$$

$$r = r_{\text{C}_6\text{H}_8}^1 = k_3 P_{\text{C}_6\text{H}_{12}} \left\{ \frac{- \left(\sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_2 P_{\text{O}_2}}} \right) + \frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_4}}{2 \frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_4}} + \frac{\left(\sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_2 P_{\text{O}_2}}} \right)^2 + 4 \frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_4}}{2 \frac{k_3 P_{\text{C}_6\text{H}_{12}}}{k_4}} \right\}^2 \quad (2)$$

Stage scheme of mechanism of oxidative dehydrogenation of cyclohexane into benzene on the above-mentioned active centers may be presented as



Expressions for rates of stages:

$$r_5 = k_5\theta_5^2 P_{\text{O}_2}, \quad r_6 = k_6\theta_6^2 P_{\text{O}_2}, \quad r_7 = k_7\theta_7^2 P_{\text{O}_2},$$

$$r_8 = k_8\theta_8 P_{\text{C}_6\text{H}_{12}}, \quad r_9 = k_9\theta_9,$$

$$\theta_5 + \theta_6 + \theta_7 + \theta_8 + \theta_9 = 1,$$

where θ_5 , θ_6 , θ_7 , θ_8 and θ_9 are fractions of catalyst surface; the sites with the ability to adsorb atom oxygen, the sites with three near arranged by adsorbed atom oxygen on different exchange cations and the sites with adsorbed molecules of cyclohexane.

In stationary conditions

$$r = r_5 = r_6 = r_7 = r_8 = r_9,$$

$$\theta_9 = \frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_9} \theta_8, \quad \theta_5 = \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_5 P_{\text{O}_2}}} \sqrt{\theta_8},$$

$$\theta_6 = \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_6 P_{\text{O}_2}}} \sqrt{\theta_8}, \quad \theta_7 = \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_7 P_{\text{O}_2}}} \sqrt{\theta_8},$$

$$\begin{aligned}
 & \frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_9} \theta_8 + \left(\sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_5 P_{\text{O}_2}}} + \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_6 P_{\text{O}_2}}} + \right. \\
 & \left. + \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_7 P_{\text{O}_2}}} \right) \sqrt{\theta_8} - 1 = 0.
 \end{aligned}$$

Assuming

$$\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_9} = a,$$

$$\left(\sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_5 P_{\text{O}_2}}} + \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_6 P_{\text{O}_2}}} + \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_7 P_{\text{O}_2}}} \right) = b,$$

$$\theta_8 = x^2, \quad \sqrt{\theta_8} = x,$$

we'll obtain

$$ax^2 + bx - 1 = 0,$$

$$x = \frac{-b + \sqrt{b^2 + 4a}}{2a},$$

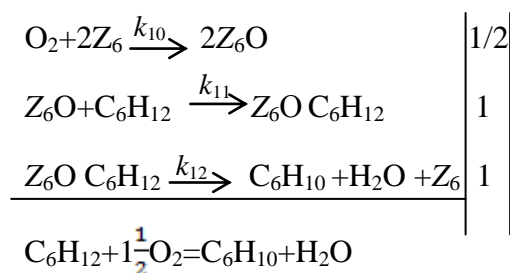
$$\theta_8 = x^2 = \left\{ \frac{-b + \sqrt{b^2 + 4a}}{2a} \right\}^2.$$

Then equation of rate of formation benzene will appear as

$$r = r_{\text{C}_6\text{H}_6}^1 = k_8 P_{\text{C}_6\text{H}_{12}} \cdot \left\{ \frac{-b + \sqrt{b^2 + 4a}}{2a} \right\}^2,$$

$$\begin{aligned}
 r = r_{\text{C}_6\text{H}_6}^1 = k_8 P_{\text{C}_6\text{H}_{12}} & \left\{ \frac{- \left(\sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_5 P_{\text{O}_2}}} + \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_6 P_{\text{O}_2}}} + \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_7 P_{\text{O}_2}}} \right)}{2 \frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_9}} + \right. \\
 & \left. + \sqrt{\frac{\left(\sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_5 P_{\text{O}_2}}} + \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_6 P_{\text{O}_2}}} + \sqrt{\frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_7 P_{\text{O}_2}}} \right)^2 + 4 \frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_9}}{2 \frac{k_8 P_{\text{C}_6\text{H}_{12}}}{k_9}}} \right\}. \quad (3)
 \end{aligned}$$

Stage scheme of mechanism of oxidative dehydrogenation of cyclohexane into cyclohexene may be presented as



Expressions for rates of stages

$$r_{10} = k_{10}\theta_{10}^2 P_{\text{O}_2}, \quad r_{11} = k_{11}\theta_{11} P_{\text{C}_6\text{H}_{12}}, \quad r_9 = k_{12}\theta_{12}.$$

In stationary conditions

$$r = r_{10} = r_{11} = r_{12},$$

where θ_{10} , θ_{11} and θ_{12} are fractions of catalyst surface; sites with the ability adsorb atom

oxygen, sites with atom oxygen and sites adsorbed molecules of cyclohexane

$$\theta_{10} + \theta_{11} + \theta_{12} = 1,$$

$$\theta_{12} = \frac{k_{11}P_{C_6H_{12}}}{k_{12}} \theta_{11}, \quad \theta_{10} = \sqrt{\frac{k_{11}P_{C_6H_{12}} \cdot \theta_{11}}{k_{10}P_{O_2}}},$$

$$\frac{k_{11}P_{C_6H_{12}}}{k_{12}} \theta_{11} + \theta_{11} + \sqrt{\frac{k_{11}P_{C_6H_{12}}}{k_{10}P_{O_2}}} \sqrt{\theta_{11}} - 1 = 0.$$

Assuming

$$\frac{k_{11}P_{C_6H_{12}}}{k_{12}} + 1 = c, \quad \sqrt{\frac{k_{11}P_{C_6H_{12}}}{k_{10}P_{O_2}}} = d, \quad \theta_{11} = x^2,$$

$$\sqrt{\theta_{11}} = x,$$

we'll obtaine

$$cx^2 + dx - 1 = 0,$$

$$x = \frac{-d + \sqrt{d^2 + 4c}}{2c},$$

$$\theta_{11} = x^2 = \left\{ \frac{-d + \sqrt{d^2 + 4c}}{2c} \right\}^2.$$

Then equation of formation rate of cyclohexene appears as

$$r = r_{C_6H_{10}}^1 = k_{11}P_{C_6H_{12}} \left\{ \frac{-d + \sqrt{d^2 + 4c}}{2c} \right\}^2 + \frac{k_{11}P_{C_6H_{12}}}{k_{10}P_{O_2}} \left\{ \frac{-d + \sqrt{d^2 + 4c}}{2c} \right\} + \frac{\left(\sqrt{\frac{k_{11}P_{C_6H_{12}}}{k_{10}P_{O_2}}} + 4 \left(\frac{k_{11}P_{C_6H_{12}}}{k_{12}} + 1 \right) \right)^2}{2 \left(\frac{k_{11}P_{C_6H_{12}}}{k_{12}} + 1 \right)}. \quad (4)$$

The results of experimental investigation of kinetic regularities of the reaction of oxidative dehydrogenation of cyclohexane over metal-zeolite catalyst CL-CuCrCoZn are given in Table 3. Kinetic tests were performed in the range of temperature, 320–380°C, at space velocity of 500–3000 h⁻¹, partial pressure of reagents, P_{C₆H₁₂} = 0.05–0.14 atm, P_{O₂} = 0.07–0.25 atm.

Table 3. The results of kinetic runs

Partial pressure of reagents, atm		Space velocity, v, h ⁻¹	Temperature, T, °C	Conversion, X, %	Yields of products of reaction, A, %				
P _{C₆H₁₂}	P _{O₂}				C ₆ H ₁₀	C ₆ H ₈	C ₆ H ₆	C ₆ H ₁₀ OH	CO ₂
0.12	0.07	2000	320	22.2	4.6	2.1	1.4	0.7	0.1
0.12	0.07	2000	340	10.9	2.7	5.9	1.8	0.3	0.2
0.12	0.07	2000	380	19.6	1.6	12.2	2.8	1.4	1.6
0.12	0.14	2000	340	23.2	4.3	11.7	4.3	1.1	1.8
0.12	0.25	2000	340	31.8	5.2	13.3	6.9	3.2	3.2
0.12	0.09	2000	380	28.6	1.8	17.1	4.1	2.5	3.1
0.05	0.18	2000	380	47.5	16.5	1.2	0.5	5.4	2.9
0.12	0.25	2000	380	44.8	2.8	23.3	7.2	4.4	7.1
0.05	0.14	2000	340	27.1	0.8	4.1	6.5	6.8	8.9
0.10	0.14	2000	340	24.6	3.4	9.9	5.3	2.5	3.5
0.12	0.14	2000	340	23.2	4.3	11.7	4.3	1.1	1.8
0.14	0.07	2000	360	15.6	2.3	9.6	2.2	0.8	0.7
0.25	0.17	2000	360	38.8	3.8	20.2	7.5	2.9	4.4
0.3	0.25	2000	360	47.6	4.5	21.5	10.6	5.4	5.6
0.12	0.14	500	380	47.5	0.2	12.2	13.7	10.5	10.9
0.12	0.14	1000	380	46.4	1.9	21.1	8.2	7.1	8.1
0.12	0.14	2500	320	12.5	5.8	4.1	1.2	0.5	0.9
0.12	0.14	3000	340	20.9	5.7	12.4	1.5	0.6	0.7
0.12	0.14	3000	360	31.7	4.9	19.8	3.3	1.5	2.2

Assuming that carbon dioxide is formed as a result of interaction of adsorbed molecules; cyclohexane, cyclohexene and 1,3-cyclohexadiene with adsorbed molecules of oxygen and formation of cyclohexanol proceeds at interaction of adsorbed molecules of cyclohexene with adsorbed molecules of water it can be written the following kinetic equations corresponding to these mechanisms

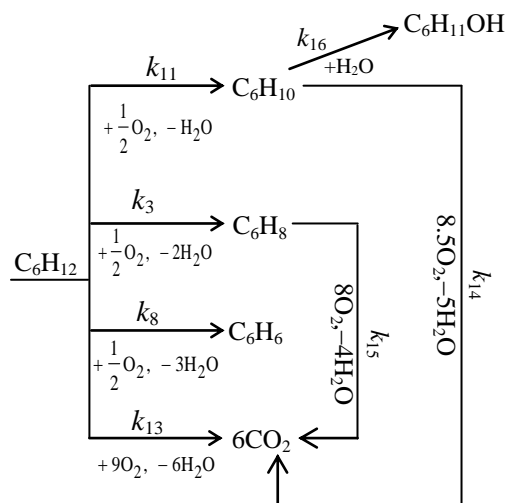
$$r_{\text{CO}_2}^1 = \frac{k_{13}K_1P_1K_6P_2}{(1 + K_1P_1 + \sqrt{K_2P_2} + K_3P_3 + K_4P_4 + K_5P_5 + K_6P_2)^2}, \quad (5)$$

$$r_{\text{CO}_2}^2 = \frac{k_{14}K_3P_3K_6P_2}{(1 + K_1P_1 + \sqrt{K_2P_2} + K_3P_3 + K_4P_4 + K_5P_5 + K_6P_2)^2}, \quad (6)$$

$$r_{\text{CO}_2}^3 = \frac{k_{15}K_4P_4K_6P_2}{(1 + K_1P_1 + \sqrt{K_2P_2} + K_3P_3 + K_4P_4 + K_5P_5 + K_6P_2)^2}, \quad (7)$$

$$r_{\text{C}_6\text{H}_{11}\text{OH}}^1 = \frac{k_{16}K_3P_3P_6}{(1 + K_1P_1 + \sqrt{K_2P_2} + K_3P_3 + K_4P_4 + K_5P_5 + K_6P_2)}. \quad (8)$$

Thus we can suppose the following kinetic scheme of proceeding of reaction of oxidative dehydrogenation of cyclohexane over above mentioned metal-zeolite catalyst:



$$r_{\text{C}_6\text{H}_{10}} = r_{\text{C}_6\text{H}_{10}}^1 - r_{\text{CO}_2}^2 - r_{\text{C}_6\text{H}_{11}\text{OH}}^1, \quad (9)$$

$$r_{\text{C}_6\text{H}_8} = r_{\text{C}_6\text{H}_8}^1 - r_{\text{CO}_2}^3, \quad (10)$$

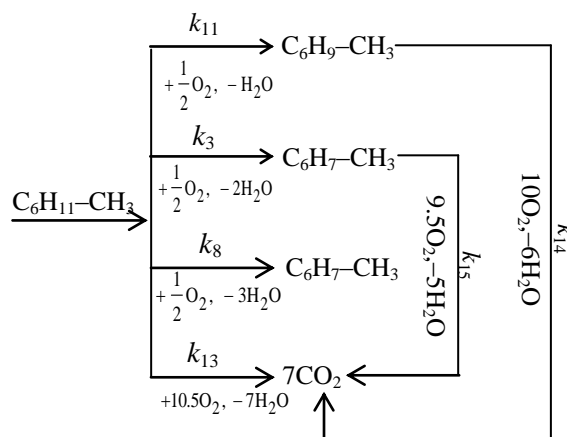
$$r_{\text{C}_6\text{H}_6} = r_{\text{C}_6\text{H}_6}^1, \quad (11)$$

$$r_{\text{CO}_2} = r_{\text{CO}_2}^1 + r_{\text{CO}_2}^2 + r_{\text{CO}_2}^3, \quad (12)$$

$$r_{\text{C}_6\text{H}_{11}\text{OH}} = r_{\text{C}_6\text{H}_{11}\text{OH}}^1. \quad (13)$$

Equations (9)–(13) make up the kinetic model of the considered reaction.

Similar investigation was carried out for reaction of oxidative dehydrogenation of methyl cyclohexane into 1-methyl-1,3-cyclohexadiene. On the basis of experimental data kinetic scheme of the reaction has been established.



The kinetic model of the reaction is form

$$r_{\text{C}_7\text{H}_{12}}^1 = k_{11}P_{\text{C}_7\text{H}_{14}} \left\{ \frac{-\sqrt{\frac{k_{11}P_{\text{C}_7\text{H}_{14}}}{k_{10}P_{\text{O}_2}}}}{2\left(\frac{k_{11}P_{\text{C}_7\text{H}_{14}}}{k_{12}} + 1\right)} + \frac{\sqrt{\left(\sqrt{\frac{k_{11}P_{\text{C}_7\text{H}_{14}}}{k_{10}P_{\text{O}_2}}}\right)^2 + 4\left(\frac{k_{11}P_{\text{C}_7\text{H}_{14}}}{k_{12}} + 1\right)}}{2\left(\frac{k_{11}P_{\text{C}_7\text{H}_{14}}}{k_{12}} + 1\right)} \right\}^2$$

$$r_{C_7H_{10}}^1 = k_3 P_{C_7H_{14}} \left\{ \frac{- \left(\sqrt{\frac{k_3 P_{C_7H_{14}}}{k_1 P_{O_2}}} + \sqrt{\frac{k_3 P_{C_7H_{14}}}{k_2 P_{O_2}}} \right)^2}{2 \frac{k_3 P_{C_7H_{14}}}{k_4}} + \right. \quad r_{C_7H_{10}} = r_{C_7H_{10}}^1 - r_{CO_2}^3, \quad (15)$$

$$r_{C_7H_8} = r_{C_7H_8}^1, \quad (16)$$

$$r_{CO_2} = r_{CO_2}^1 + r_{CO_2}^2 + r_{CO_2}^3. \quad (17)$$

$$+ \left. \frac{\sqrt{\left(\sqrt{\frac{k_3 P_{C_7H_{14}}}{k_1 P_{O_2}}} + \sqrt{\frac{k_3 P_{C_7H_{14}}}{k_2 P_{O_2}}} \right)^2 + 4 \frac{k_3 P_{C_7H_{14}}}{k_4}}}{2 \frac{k_3 P_{C_7H_{14}}}{k_4}} \right\}^2$$

$$r_{C_7H_8}^1 = k_8 P_{C_7H_{14}} \left\{ \frac{- \left(\sqrt{\frac{k_8 P_{C_7H_{14}}}{k_5 P_{O_2}}} + \sqrt{\frac{k_8 P_{C_7H_{14}}}{k_6 P_{O_2}}} + \sqrt{\frac{k_8 P_{C_7H_{14}}}{k_7 P_{O_2}}} \right)^2}{2 \frac{k_8 P_{C_7H_{14}}}{k_9}} + \right.$$

$$+ \left. \frac{\sqrt{\left(\sqrt{\frac{k_8 P_{C_7H_{14}}}{k_5 P_{O_2}}} + \sqrt{\frac{k_8 P_{C_7H_{14}}}{k_6 P_{O_2}}} + \sqrt{\frac{k_8 P_{C_7H_{14}}}{k_7 P_{O_2}}} \right)^2 + 4 \frac{k_8 P_{C_7H_{14}}}{k_9}}}{2 \frac{k_8 P_{C_7H_{14}}}{k_9}} \right\}^2$$

$$r_{CO_2}^1 = \frac{k_{13} K_1 P_1 K_6 P_2}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_2 \right)^2}$$

$$r_{CO_2}^2 = \frac{k_{14} K_3 P_3 K_6 P_2}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_2 \right)^2}$$

$$r_{CO_2}^3 = \frac{k_{15} K_4 P_4 K_6 P_2}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_2 \right)^2}$$

$$r_{C_7H_{12}} = r_{C_7H_{12}}^1 - r_{CO_2}^2 \quad (14)$$

Equations (14)–(17) present the kinetic model of the reaction of oxidative dehydrogenation of methyl cyclohexane over CL-CoCr catalyst. Here K_i – the adsorption equilibrium constants ($K_i = K_i^0 \cdot e^{\frac{Q_i}{RT}}$), k_i – the reaction rate constants ($k_i = k_i^0 \cdot e^{-\frac{E}{RT}}$), P_i – partial pressure of i -component ($P_i = \frac{n_i}{\sum n_i} P$)

The results of investigation of kinetic regularities of the reaction are given in Table 4.

Both models, (9)–(13) and (14)–(17) have been subjected to statistical analysis on the basis of the data of Tables 3 and 4 separately. The objective function was

$$F(X) = \sum_i^N \left(\frac{A_{\text{exp}} - A_{\text{cal}}}{A_{\text{exp}}} \right)^2$$

where X – signifies the set of parameters of the considered model. The kinetic parameters obtained for the two models are presented in Table 5. According to these results, the models satisfactorily describe the experimental data of the reactions.

Thus, the kinetic method supports an existence on the surface of the metal-zeolite catalysts for reaction of oxidative dehydrogenation of cyclohexane into 1,3-cyclohexadiene and methyl cyclohexane into 1-methyl-1,3-cyclohexadiene the different active centers consisted of above mentioned group of exchange cations which responsible for formation of the products of reactions.

Table 4. The result of kinetic runs

Partial pressure of reagents, atm		Space velocity, V , h^{-1}	Temperature, T , $^{\circ}C$	Conversion, X , %	Yields of products of reaction, A, %			
$P_{C_7H_{14}}$	P_{O_2}				$C_6H_9CH_3$	$C_6H_7CH_3$	$C_6H_5CH_3$	CO_2
0.11	0.04	2000	340	11.4	4.2	2.2	3.8	0.06
0.11	0.09	2000	340	36.3	4.4	4.5	5.9	0.2
0.11	0.14	2000	340	44.8	4.5	6.9	7.2	0.4
0.11	0.14	2000	360	49.9	6.02	9.9	10.4	0.6
0.11	0.20	2000	360	22.6	5.9	13.6	11.8	1.1
0.17	0.14	2000	320	35.1	4.5	4.8	4.8	0.2
0.25	0.14	2000	320	48.4	4.5	3.7	3.6	0.1
0.17	0.14	2000	360	30.8	8.0	10.8	7.8	4.2
0.25	0.14	2000	360	27.4	8.7	8.5	6.9	3.3
0.17	0.14	2000	380	43.2	9.1	15.5	10.3	8.2
0.25	0.14	2000	380	39.1	9.9	12.8	10.2	6.2
0.11	0.14	2500	340	21.2	4.4	6.5	7.0	3.3
0.11	0.14	2500	380	46.6	7.2	15.7	12.2	11.5
0.11	0.14	3000	360	31.7	10.1	11.3	6.1	4.2
0.11	0.14	3000	380	43.7	12.0	15.9	9.6	6.2

Table 5. The kinetic parameters of the kinetic models

For kinetic model of reaction of oxidative dehydrogenation of cyclohexane				For kinetic model of reaction of oxidative dehydrogenation of methyl cyclohexane			
$\ln k_i^0 (\ln K_i^0)$		$E_i(Q_i)$, kcal/mole		$\ln k_i^0 (\ln K_i^0)$		$E_i(Q_i)$, kcal/mole	
$\ln k_1^0$	15.71	E_1	8.30	$\ln k_1^0$	40.93	E_1	7.84
$\ln k_2^0$	4.56	E_2	11.0	$\ln k_2^0$	7.06	E_2	14.62
$\ln k_3^0$	-0.16	E_3	10.99	$\ln k_3^0$	11.44	E_3	2.25
$\ln k_4^0$	-2.63	E_4	6.73	$\ln k_4^0$	26.20	E_4	4.17
$\ln k_5^0$	7.10	E_5	4.46	$\ln k_5^0$	11.70	E_5	15.00
$\ln k_6^0$	11.9	E_6	6.06	$\ln k_6^0$	27.97	E_6	11.07
$\ln k_7^0$	29.72	E_7	7.67	$\ln k_7^0$	8.63	E_7	14.74
$\ln k_8^0$	3.93	E_8	4.00	$\ln k_8^0$	24.41	E_8	2.37
$\ln k_9^0$	-2.39	E_9	3.99	$\ln k_9^0$	5.81	E_9	14.54
$\ln k_{10}^0$	12.44	E_{10}	8.39	$\ln k_{10}^0$	9.43	E_{10}	13.04
$\ln k_{11}^0$	16.37	E_{11}	4.00	$\ln k_{11}^0$	5.70	E_{11}	13.09
$\ln k_{12}^0$	6.94	E_{12}	7.37	$\ln k_{12}^0$	16.16	E_{12}	10.18
$\ln k_{13}^0$	20.86	E_{13}	35.15	$\ln k_{13}^0$	22.0	E_{13}	32.15
$\ln k_{14}^0$	-10.51	E_{14}	39.79	$\ln k_{14}^0$	-9.2	E_{14}	35.49
$\ln k_{15}^0$	41.52	E_{15}	21.55	$\ln k_{15}^0$	42.5	E_{15}	20.09
$\ln k_{16}^0$	23.17	E_{16}	17.82	-	-	-	-
$\ln K_1^0$	23.16	Q_1	2.49	$\ln K_1^0$	20.1	Q_1	2.00
$\ln K_2^0$	1.02	Q_2	11.00	$\ln K_2^0$	0.99	Q_2	10.12
$\ln K_3^0$	8.75	Q_3	8.57	$\ln K_3^0$	7.81	Q_3	7.85
$\ln K_4^0$	6.84	Q_4	11.00	$\ln K_4^0$	7.04	Q_4	9.81
$\ln K_5^0$	25.48	Q_5	3.19	$\ln K_5^0$	26.11	Q_5	2.72
$\ln K_6^0$	3.027	Q_6	2.49	$\ln K_6^0$	3.24	Q_6	1.99

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NAFTENLƏRİN OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏ REAKSİYALARINDA METAL-SEOLİTLƏRİN TƏTBİQİ

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İon mübadilə üsulu ilə sintez olunmuş klinoptilolit (KL) {Cu²⁺ (0.5 küt.%), Zn²⁺ (0.2 küt.%), Co²⁺ (0.1 küt.%), Cr³⁺ (0.1 küt.%)} və KL {Co²⁺ (0.5 küt.%), Cr³⁺ (0.25 küt.%)} katalizatorlarının uyğun olaraq tsikloheksanın 1,3-tsikloheksadienə və metiltsikloheksanın 1-metil-1,3-tsikloheksadienə oksidləşdirici dehidrogenləşmə reaksiyalarında tətbiqinin mümkünlüyü müəyyən olunmuşdur. Təcrübi məlumatların təhlili və dissosiativ adsorbsiya olunmuş oksigen ilə mübadilə kationların rabitə enerjilərini nəzərə almaqla katalizatorun komponentlərindən ibarət aktiv mərkəzlər qruplaşdırılmış və reaksiya yolları aydınlaşdırılmışdır. Bu aktiv mərkəzlərin nəzərə alınması ilə işlənilib hazırlanmış kinetik model təqdim olunmuşdur.

Açar sözlər: tsikloheksan, 1,3-tsikloheksadien, metiltsikloheksan, 1-metil-1,3-tsikloheksadien.

ИСПОЛЬЗОВАНИЕ МЕТАЛЛ-ЦЕОЛИТОВ В КАЧЕСТВЕ КАТАЛИЗАТОРОВ В РЕАКЦИЯХ ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ НАФТЕНОВ

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Установлена возможность использования гетерогенных катализаторов: клиноптилолит (Кл) {Cu²⁺ (0.5 мас.%), Zn²⁺ (0.2 мас.%), Co²⁺ (0.1 мас.%), Cr³⁺ (0.1 мас.%)} и Кл. {Co²⁺ (0.5 мас.%), Cr³⁺ (0.25 мас.%)}, полученных методом ионного обмена в реакции окислительного дегидрирования циклогексана в 1,3-циклогексадиен и метилциклогексана в 1-метил-1,3-циклогексадиен соответственно. На основе анализа экспериментальных данных и с учетом энергий связи обменных катионов с диссоциативно адсорбированным кислородом были сгруппированы активные центры, состоящие из компонентов катализатора, и выяснены реакционные пути. Представлены кинетические модели, разработанные с учетом этих активных центров.

Ключевые слова: циклогексан, 1,3-циклогексадиен, метилциклогексан, 1-метил-1,3-циклогексадиен.