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A STUDY OF THE KINETICS AND MECHANISM OF THE SELECTIVE OXIDATIVE DEHYDROGENATION REACTION OF CYCLOPENTANE TO CYCLOPENTADIENE-1,3 OVER MODIFIED ZEOLITE CATALYSTS

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The reaction of cyclopentane has been studied on HY zeolite at 380°C. Cyclopentene and cyclopentadiene formed a stable initial product by the dehydrogenation of the raw material, although molecular hydrogen was not found as the primary product. The catalytic activity of the clinoptilolite in the reaction of selective oxidative dehydrogenation of cyclopentane to cyclopentadiene have been measured experimentally and modelled theoretically at several temperatures. It was revealed that when using of clinoptilolite with these cations { Cu²⁺ (0.5 mas.%), Zn²⁺ (0.2 mas.%), Co²⁺ (0.1 mas.%), Cr³⁺ (0.1 mas.%) and CL[Co²⁺ (0.5 mas.%)] heterogenic catalysts show the more activity in this reaction and they are prepared by the ion-exchange method. The theoretical calculation also suggest that catalytic reactions of the process proceed in a highly non-synchronous or even non-consecutive fashion. The experimental data suggest that the active centers containing the components of the catalyst are grouped and the reaction pathways are described by taking into account bonding energies that exchange cations combine with dissociative adsorbed oxygen. The energy barriers and the rate constants of the catalytic systems were accurately modelled by the correlated electronic structure and calculation of the dual-level variational transition state theory.

Keywords: *clinoptilolite, cyclopentane, catalytic dehydrogenation, cyclopenten, cyclopentadiene-1,3.*

Introduction

The unsubstituted cyclopentane molecule is unique that it is relatively free of ring strain and at the same time does not convert to smaller cyclic structures, or to larger rings as is the case for substituted cyclopentanes and cyclohexanes. Consequently, the dehydrogenation behaviour of cyclopentane at high temperatures is fundamental to an overall understanding of reactions of cycloparaffins on solid acid catalysts. By using clinoptilolite most of our studies of olefins on this catalyst have been carried out in the temperature range of 300–400°C. Natural clinoptilolite can be used as an ion exchanger for removal of heavy metals because it has desirable characteristics of high ion exchange selectivity and resistance to different media [1]. Clinoptilolite is a natural microporous material possessing a versatile range of cation exchange properties that are exploited in many industrial processes. Clinoptilolite hails from the heulandite family of zeolites, which shares the same topology of eight- and ten-membered ring channels running parallel to the c-axis and an intersecting eight-membered ring channel parallel to the a-axis [2]. Clinoptilolite is used in many industrial applications,

due primarily to its abundance and cation exchangeability. We have shown that natural clinoptilolite modified with various non-transition elements and transition cations (Zn, Cu, Co, Cr, Mn, Fe, Mg, Mo, etc.). In this work, we have used a natural clinoptilolite with rich deposits in the territory of the Republic of Azerbaijan and uptake of copper(II), cobalt(II), chrome(III), zinc(II) from their single and mixed ion solutions. The mineralogical and chemical properties of the sorption material were studied by X-ray diffraction, X-ray fluorometry, scanning electron microscopy, and wet analysis. We have applied these cations Cu²⁺, Zn²⁺, Co²⁺ and Cr³⁺ by ion-exchange and indicated that this is the active catalyst for the reaction of oxidative dehydrogenation of cyclopentane. On the basis of experimental kinetic data by using Langmuir–Hinshelwood rate expression we have established that reaction of oxidative dehydrogenation of cyclopentane proceeds with the participation of the dissociative adsorbed oxygen. The purpose of the present work is to determine a role of the components of the catalytic system, in order to simplify kinetic studies of the reaction with conjugated dehydrogenation of cyclo-

pentane with metal-clinoptilolite. Including the effect of factors such as raw material volume rates, component ratio, temperature and quartz reactor surface conditions on the process running obtained in our laboratory "Catalysis over zeolites" of the Institute of Catalysis and Inorganic Chemistry NAS of Azerbaijan.

Experimental part

We applied catalysts prepared by the ion-exchange method, using Azerbaijan natural clinoptilolite (crystallinity, 84.0%) and the different metal cations. Modification of zeolites with metal cations was performed by treatment of their initial forms into a solution of chloride salts of the corresponding cations. Before ion exchange, the clinoptilolite was treated by 0.5 N HCl. The number of the cations incorporated into the clinoptilolite was determined by ICP-MS Agilent 7700 and it amounted to (0.1–2)% by weight of the clinoptilolite. The reaction was carried out at 360–400°C and atmospheric pressure. Before the reaction, the catalyst was activated in the air (15 mL/min) at 300°C for 3 h. For Clinoptilolite, the catalysts were typically reduced at 300°C for 2 h in a flow of H₂ (10 mL/min). It was noted that H₂ was required in this reaction to prevent coke accumulation. At reaction temperature (typically at 380°C), saturated vapour of cyclopentane (Aldrich, 99.5%) was carried by hydrogen (total flow of 15 mL/min) through a fixed bed U-shaped flow reactor made with a quartz tube (outside diameter D – 8 mm). We used the catalysts with particle size in (0.25–0.63) mm. The reactor is placed in an air electric oven with automatic temperature control. Cyclopentane vapours and air mixed with oxygen in the mixer located in a thermostat doven, enter the reactor for the catalysis. The temperature stability is maintained in the oven with a contact thermometer. The temperature in the middle of the catalyst bed is measured with a thermocouple and recorded with the potentiometer. The reaction unit is directly connected to the analysis system through six-way valve what allows the analysis of the reaction mixture without loss. The mixture exiting from the reactor gradually passes through the sample loop and is collected in the cooled

trap. 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 obtained cyclopentadiene was determined by chromatography, IR spectroscopy and spectra are shown in Figures 1 and 2.

The selectivities and conversion in the fraction of cyclopentane molecules leading to a given product, are shown explicitly in Table 1. A reaction temperature of 380±20°C was used for the comparison of Cu²⁺, Zn²⁺, Co²⁺, Cr³⁺ and another transition cations. From the table, we can see natural clinoptilolite and natural clinoptilolite with modified cations, Zn²⁺ (exp. 1, 2) show lower catalytic activity in the reaction. After we add natural clinoptilolite cations; Cr³⁺, Cu²⁺ and Co²⁺ is relatively higher than above mentioned ones (exp. 3–5). Combination of two cations in natural clinoptilolite; Cu²⁺, Cr³⁺ and Co²⁺, Cr³⁺ increase the efficiency of cyclopentadiene from oxidative dehydrogenation of cyclopentane reaction. (exp. 7, 8). When we add third cation Zn²⁺ in this catalytic system we saw that it causes a considerable increase in the yields of cyclopentadiene (exp. 12, 13).

Deep dehydrogenation is faster on Zn than on the other two metals. After examining more catalysts we have arrived at a conclusion that Cu²⁺, Cr³⁺, Co²⁺ and Zn²⁺ (exp. 19, 20), cations with modified clinoptilolite system show more catalytic activity and relatively Fe, Mn, Sn, Mo and Ni cations show lower catalytic activity in the reaction of oxidative dehydrogenation of cyclopentane (exp. 9–11, 16–18).

From the data of Table 1, it has been concluded that the natural clinoptilolite containing cations, mas %: Cu²⁺ – 0.5, Zn²⁺ – 0.2, Co²⁺ – 0.1 and Cr³⁺ – 0.1 is the active catalyst for reaction of oxidative dehydrogenation of cyclopentane into cyclopenten and cyclopentadiene.

The activity of the zeolite catalysts in different reactions depends on; crystal structure, nature of cations, method of preparation and distribution of metal cations on a surface of the zeolite.

Fig.1. Chromatography spectrum of the 1,3-cyclopentadiene.

Fig.2. Infrared spectrum of the 1,3-cyclopentadiene.

Table 1. The results of the activity of modified natural clinoptilolite (CL) catalyst in the reaction of oxidative dehydrogenation of cyclopentane ($T=380^{\circ}\text{C}$, $V=2000\text{ h}^{-1}$, $\text{C}_5\text{H}_{10}:\text{O}_2:\text{N}_2=2:1:3.7$)

No	Catalyst	Conversion of C_5H_{10} , x , %	Selectivity s , %	Yield, A , %		
				C_5H_8	C_5H_6	CO_2
1	CL	8.2	7.3	7.5	0.6	0.1
2	CLZn (0.2*)	1.7	17.7	0.9	0.3	0.5
3	CLCr (0.1)	15.4	19.5	6.7	3.0	5.7
4	CLCu (0.5)	7.1	22.5	3.1	1.6	2.4
5	CLCo (0.1)	16.4	19.5	7.6	3.2	5.6
6	CLZnNi (0.2:0.2)	10.2	17.6	4.9	1.8	3.5
7	CLCuCr (0.5:0.1)	13.4	16.4	3.6	2.2	7.6
8	CLCoCr (0.1:0.1)	22.3	23.8	8.8	5.3	8.2
9	CLCuSn (0.5:0.5)	8.8	21.6	2.6	1.9	4.3
10	CLCuMn (0.5:0.5)	13.7	21.2	4.2	3.0	6.5
11	CLCuFe (0.5:0.5)	10.9	22.9	1.8	2.5	6.6
12	CLZnCoCr (0.2:0.1:0.1)	24.7	24.3	9.9	6.0	8.8
13	CLZnCuCr (0.2:0.5:0.1)	20.5	27.3	9.3	5.6	6.6
14	CLCuCoCr (0.5:0.1:0.1)	20.8	27.9	7.9	5.8	7.1
15	CLCuZnCo (0.5:0.2:0.1)	22.2	28.3	10.1	6.3	5.8
16	CLCoMnCu (0.1:0.1:0.5)	22	25	8.9	5.5	7.6
17	CLCoMnCr (0.1:0.5:0.1)	18.4	25.5	9.9	4.7	3.8
18	CLCoMnCr (0.1:0.1:0.1)	16.5	21.8	8.5	3.6	4.4
19	CLCuZnCoCr (0.5:0.2:0.1:0.1)	25.3	34.8	2.5	8.8	14.0
20	CLCuZnCoCr (2:2:1:0.5)	20.6	33.0	10.9	6.8	2.9

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

The naturally occurring Heulandite-type zeolites, including heulandite (Heu) and clinoptilolite (CPT), are the most abundant minerals on earth, exhibiting a zeolite structure. Large, easily accessible surface deposits mainly of volcanoclastic origin, enables clinoptilolite low-cost production by simple excavation [3, 4]. The crystal structure shows the existence of three types of structural channels confined by ten- and eight-membered tetrahedral ring systems (Figure 1). From the crystal-chemistry point of view, aluminosilicate framework possesses a negative charge that is equilibrated by cations located in the channels (simplified formula: $([\text{Me}^+, \text{Me}^{2+}, \text{N}_x\text{H}_2\text{O}]^{6+}[\text{Al}_6\text{Si}_{30}\text{O}_{72}]^{6-})$). Detailed structural investigations on complete and partially ion-exchanged on Na, K, Rb, Cs, Cd, Ag, Mn, Cu, Pb, Sr, Er, La clinoptilolite have been carried out and summarizing the results some typical positions for cation placement in the channels have been assigned [5, 6]. However, no detailed single crystal structural studies for Zn ion-exchanged clinoptilolite (ZnCL) have been undertaken. The studies conducted by us revealed that CL tolerates li-

imited to complete Zn ion-exchange. The ion-exchange and reduction processes for Co^{2+} reduction mechanism is complex, indirect and sensitive to reduction temperature; consequently, Co_n^+ states intermediate between Co^{2+} and Co^0 should be present in the reduced samples. We know from the literature a crystal lattice of clinoptilolite consist of three open channels; A, B and C. In Figure 3 the polyhedron model of clinoptilolite, has a fragment of the structure with exchange cations is shown. A and B channels are parallel to axis, C and consist of tencyclic and octocyclic rings.

Fig.3. Polyhedron model of clinoptilolite reflected of structure with exchange cations.

They cross with the third octocyclic channel parallel to the, a. Hexagonal planers in the structure of clinoptilolite are surrounded by channels A, B and C in which the exchange cations are localized. A planar molecule of cyclopentane is pentagonal planers surrounded exchange cations in the structure of clinoptilolite.

In clinoptilolite there are four types of places in the 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 [7, 8].

A role of components of the catalytic system in the reaction of oxidative dehydrogenation of cyclopentane can be explained by analysis of surrounding of the adsorbed molecules of cyclopentane with the exchange cations bonded with dissociative adsorbed oxygen, taking into account their bonding energies which can be found by expression [9].

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

where 500 kJ/mole – energy of dissociation of molecule oxygen, q_{ads} – heat of adsorption of oxygen the pure surfaces of the polycrystal specimens of transient metals, q_{ads} , kJ/mole for [10]; Cu=478 Zn=240, Co=418, Cr=753. Bonding energies of the components of catalyst with oxygen can be calculated by using cited above formula; $q_0(\text{Cu})=489$ 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.

The maximum propellant force of hydrogen atoms of cyclopentane is indicated by the oxygen atoms bonded with the component of the catalyst.

The source of the cyclopentane oxidative decomposition reaction products depends on the amounts and the concentration of effective centres for the reaction and the combination of ion exchange cations. On obtaining 1,3-cyclopentadiene the optimum succession incorporating of cation in clinoptilolite is Cu^{2+} (0.5 mas %) $\rightarrow$ Zn^{2+} (0.2 mas %) $\rightarrow$ Co^{2+} (0.2 mas %) $\rightarrow$ Cr^{3+} (0.2 mas %) $\rightarrow$ CL. From experimental data it

was confirmed that the kinetic scheme of the considered reactions over the active catalytic system does not proceed on a consecutive mechanism. As well from these experimental data, it can be concluded that on the surface of the catalyst there are different active centres obtained, which are responsible for the formation of the products of the reaction. The mechanism of oxidative dehydrogenation cyclopentane on above mentioned active centres may be presented as following stage scheme:

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

$$\begin{aligned} r_1 &= k_1\theta_1^2 P_{\text{O}_2}, & r_2 &= k_2\theta_2^2 P_{\text{O}_2}, & r_3 &= k_3\theta_3 P_{\text{C}_5\text{H}_{10}}, \\ r_4 &= k_4\theta_4. \end{aligned}$$

$$\theta_1 + \theta_2 + \theta_3 + \theta_4 = 1,$$

$$\begin{aligned} \theta_1 &= \sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_1 P_{\text{O}_2}}} \cdot \sqrt{\theta_3}, & \theta_2 &= \sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_2 P_{\text{O}_2}}}, \\ \theta_4 &= \frac{k_3 \theta_3 P_{\text{C}_5\text{H}_{10}}}{k_4}, \end{aligned}$$

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

In stationary conditions

$$r = r_1 = r_2 = r_3 = r_4.$$

$$\begin{aligned} \frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_4} \theta_3 + \theta_3 + \left(\sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_2 P_{\text{O}_2}}} \right) \times \\ \times \sqrt{\theta_3} - 1 = 0. \end{aligned}$$

Assuming:

$$\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_4} = A, \quad \left(\sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_2 P_{\text{O}_2}}} \right) = B,$$

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

We'll receive:

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

$$\theta_3 = x^2 = \left(\frac{-B \pm \sqrt{B^2 + 4A}}{2A} \right)^2.$$

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

$$r = r_{C_5H_6}^1 = k_3 P_{C_5H_{10}} \cdot \left(\frac{-B \pm \sqrt{B^2 + 4A}}{2A} \right)^2 \quad (1)$$

$$r = r_{C_5H_6}^1 = k_3 P_{C_5H_{10}} \left[\frac{- \left(\sqrt{\frac{k_3 P_{C_5H_{10}}}{k_1 P_{O_2}}} + \sqrt{\frac{k_3 P_{C_5H_{10}}}{k_2 P_{O_2}}} \right)}{2 \frac{k_3 P_{C_5H_{10}}}{k_4}} + \sqrt{\left(\sqrt{\frac{k_3 P_{C_5H_{10}}}{k_1 P_{O_2}}} + \sqrt{\frac{k_3 P_{C_5H_{10}}}{k_2 P_{O_2}}} \right)^2 + 4 \frac{k_3 P_{C_5H_{10}}}{k_4}} \right]^2 \quad (2)$$

Stage scheme of oxidative dehydrogenation of cyclopentane into cyclopentene may be presented as

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

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

Here $\theta_5, \theta_6, \theta_7$ are fractions of catalyst surface; sites with the ability to adsorb atom oxygen sites with atom oxygen and sites adsorbed molecules of cyclopentane.

In stationary conditions

$$r = r_5 = r_6 = r_7$$

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

$$\theta_7 = \frac{k_6 P_{C_5H_{10}}}{k_7} \theta_6, \quad \theta_5 = \sqrt{\frac{k_6 P_{C_5H_{10}} \theta_6}{k_5 P_{O_2}}},$$

$$\frac{k_6 P_{C_5H_{10}}}{k_7} \theta_6 + \theta_6 + \sqrt{\frac{k_6 P_{C_5H_{10}}}{k_5 P_{O_2}}} \sqrt{\theta_6} - 1 = 0.$$

Assuming:

$$\frac{k_6 P_{C_5H_{10}}}{k_7} + 1 = c, \quad \sqrt{\frac{k_6 P_{C_5H_{10}}}{k_5 P_{O_2}}} = d, \quad \theta_6 = x^2, \quad \sqrt{\theta_6} = x.$$

We'll obtain

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

$$\theta_6 = x^2 = \left(\frac{-d + \sqrt{d^2 + 4c}}{2c} \right)^2.$$

Then equation of formation rate of cyclopentene appears as

$$r = r_{C_5H_8}^1 = k_6 \theta_3 P_{C_5H_{10}} \left(\frac{-d + \sqrt{d^2 + 4c}}{2c} \right)^2, \quad (3)$$

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

Results of experimental investigation of kinetic regularities of the reaction of oxidative dehydrogenation of cyclopentane over metal-clinoptilolite catalyst CL-CuCrCoZn are given in Table 2. Kinetic tests were performed in the temperature range of 350–390°C, at a space velocity of 500–2500 h⁻¹, partial pressure of reagents $P_{C_5H_{10}} = 0.273$ – 0.5641 atm, $P_{O_2} = 0.0768$ – 0.1540 atm, $G_{cat} = 1.78$ g, $V_{cat} = 3$ cm³.

Table 2. The results of kinetic runs

Partial pressure of reagents, atm		Moles of substance, mol/h	Moles of substance, mol/h	Moles of substance, mol/h	Space velocity, ν , h ⁻¹	Temperature, T , °C	Conversion, X , %	Yields of products of reaction, A , %		
$P_{C_3H_{10}}$	P_{O_2}	$n_{C_3H_{10}}^0$	$n_{O_2}^0$	$n_{N_2}^0$				A_1 (C ₃ H ₈)	A_2 (C ₅ H ₆)	A_3 (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	380	13.6	3.7	6.3	3.6
0.2738	0.1540	0.0654	0.0368	0.1367	2000	390	25.3	2.5	8.8	14.0
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	400	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	390	13.4	3.8	6.6	3.0
0.2980	0.1489	0.0368	0.0184	0.0683	1000	380	9.4	2.5	5.7	1.2
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

Assuming that carbon dioxide is formed as a result of interaction of adsorbed molecules; cyclopentane, cyclopentene and cyclopentadiene with adsorbed molecules of oxygen it can be written the following kinetic equations corresponding to these mechanisms.

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

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

$$r_{\text{CO}_2}^3 = \frac{k_{10} K_4 P_4}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2}, \quad (7)$$

$$r_{\text{C}_5\text{H}_8} = r_{\text{C}_5\text{H}_8}^1 - r_{\text{CO}_2}^2, \quad (8)$$

$$r_{\text{C}_5\text{H}_6} = r_{\text{C}_5\text{H}_6}^1 - r_{\text{CO}_2}^3, \quad (9)$$

$$\frac{dA_1}{d \frac{G_{\text{cat}}}{n_{\text{C}_5\text{H}_{10}}^0}} = K_6 P_{\text{C}_5\text{H}_{10}} \left\{ \frac{-\sqrt{\frac{k_6 P_{\text{C}_5\text{H}_{10}}}{k_5 P_{\text{O}_2}}} + \sqrt{\left(\sqrt{\frac{k_6 P_{\text{C}_5\text{H}_{10}}}{k_5 P_{\text{O}_2}}}\right)^2 + 4 \left(\frac{k_6 P_{\text{C}_5\text{H}_{10}}}{k_7} + 1\right)}}{2 \left(\frac{k_6 P_{\text{C}_5\text{H}_{10}}}{k_7} + 1\right)} \right\} -$$

$$- \frac{k_9 K_3 P_3}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2}, \quad (14)$$

$$\frac{dA_2}{d \frac{G_{\text{cat}}}{n_{\text{C}_5\text{H}_{10}}^0}} = k_3 P_{\text{C}_5\text{H}_{10}} \left\{ \frac{-\left(\sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_2 P_{\text{O}_2}}}\right) + \sqrt{\left(\sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_1 P_{\text{O}_2}}} + \sqrt{\frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_2 P_{\text{O}_2}}}\right)^2 + 4 \frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_4}}}{2 \frac{k_3 P_{\text{C}_5\text{H}_{10}}}{k_4}} \right\} -$$

$$- \frac{k_{10} K_4 P_4}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2}, \quad (15)$$

$$\frac{dA_3}{d \frac{G_{\text{cat}}}{n_{\text{C}_5\text{H}_{10}}^0}} = \frac{k_8 K_1 P_1}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2} + \frac{k_9 K_3 P_3}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2} +$$

$$+ \frac{k_{10} K_4 P_4}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5\right)^2}. \quad (16)$$

$$r_{\text{CO}_2} = r_{\text{CO}_2}^1 + r_{\text{CO}_2}^2 + r_{\text{CO}_2}^3. \quad (10)$$

Equations (8)–(10) make up the kinetic model of the considered reaction, where K_i – the adsorption equilibrium constant, k_i – the reaction rate constant.

$$\left(K_i = K_i^0 \cdot e^{\frac{Q_i}{RT}} \right), \quad (11)$$

$$k_i = k_i^0 \cdot e^{\frac{E}{RT}}. \quad (12)$$

We can show the rate of formation of carbon dioxide can be represented by the following differential equation:

$$r_{\text{CO}_2}^1 = \frac{dA_1}{d \frac{G_{\text{cat}}}{n_{\text{C}_5\text{H}_{10}}^0}}, \quad r_{\text{CO}_2}^2 = \frac{dA_2}{d \frac{G_{\text{cat}}}{n_{\text{C}_5\text{H}_{10}}^0}}, \quad r_{\text{CO}_2}^3 = \frac{dA_3}{d \frac{G_{\text{cat}}}{n_{\text{C}_5\text{H}_{10}}^0}}, \quad (13)$$

The suitable stoichiometric equations for forming of the reaction products are

- 1) $C_5H_{10} + \frac{1}{2}O_2 = C_5H_8 + H_2O$,
- 2) $C_5H_{10} + O_2 = C_5H_6 + 2H_2O$,
- 3) $C_5H_{10} + 7.5O_2 = 5CO_2 + 5H_2O$,
- 4) $C_5H_8 + 7O_2 = 5CO_2 + 4H_2O$,
- 5) $C_5H_6 + 6.5O_2 = 5CO_2 + 3H_2O$.

By using these equations, the reaction yield and the initial molar amounts of the reactants we can determine the current velocity in the molar flow of cyclopentane, cyclopentene, cyclopentadiene, carbon dioxide, oxygen and water accordingly by the following equations:

$$\left. \begin{aligned} n_{C_5H_{10}} &= n_{C_5H_{10}}^0 - (A_1 n_{C_5H_{10}}^0 + A_1 n_{C_5H_{10}}^0 + A_1 n_{C_5H_{10}}^0) / 100 \\ n_{C_5H_8} &= A_1 n_{C_5H_{10}}^0 / 100 \\ n_{C_5H_6} &= A_2 n_{C_5H_{10}}^0 / 100 \\ n_{CO_2} &= 5A_3 n_{C_5H_{10}}^0 / 100 \\ n_{O_2} &= n_{O_2}^0 - \left(\frac{1}{2} A_1 n_{C_5H_{10}}^0 + A_2 n_{C_5H_{10}}^0 + 7.5 A_3 n_{C_5H_{10}}^0 \right) / 100 \\ n_{H_2O} &= (A_1 n_{C_5H_{10}}^0 + 2A_2 n_{C_5H_{10}}^0 + 5A_3 n_{C_5H_{10}}^0) / 100 \\ n_{N_2} &= n_{N_2}^0 \end{aligned} \right\}, (17)$$

The partial pressure of the reactants expressed by the equation:

$$P_i = \frac{n_i}{\sum n_i} P. \quad (18)$$

Here A_1, A_2, A_3 – yield of cyclopentene, cyclopentadiene and carbon dioxide respectively. P_1, P_2, P_3, P_4, P_5 – partial pressure of cyclopentane, oxygen, cyclopentene, cyclopentadiene and water, accordingly.

A kinetic model of the reaction subjected to statistical analysis on the basis of kinetic data. Calculation of pre-exponential factors of the reaction constants, activation energies and heats of adsorption conducted by methods of "rolling admission" and Paelusing software system "Search" [11], where the objective function has the form:

$$F = \min \sum_{j=1}^m \sum_{i=1}^n \left\{ \frac{A_{ji}^{\exp} - A_{ji}^{\text{calc}}}{A_{ji}^{\exp}} \right\}^2, \quad (19)$$

$A_{ji}^{\exp}, A_{ji}^{\text{calc}}$ – the experimental and calculated values of outputs i -th component in the j -experiment, m – the number of experiments, n – the number of components.

Numerical values of the constants of a kinetic model presented in the Table 3. Calculations showed that the relative error of experimental and calculated data did not exceed 10–15%.

Table 3. The kinetic parameters of kinetic models

For kinetic model of reaction of oxidative dehydrogenation of cyclopentane			
$\ln k_i^0 \quad (\ln K_i^0)$		$E_i(Q_i)$, kcal/mole	
$\ln k_1^0$	53.89	E_1	20.62
$\ln k_2^0$	86.76	E_2	19.76
$\ln k_3^0$	3.62	E_3	23.48
$\ln k_4^0$	20.81	E_4	20.56
$\ln k_5^0$	61.88	E_5	19.88
$\ln K_1^0$	–16.43	Q_1	5.05
$\ln K_2^0$	–49.30	Q_2	4.50
$\ln K_3^0$	–21.34	Q_3	7.25
$\ln K_4^0$	–61.23	Q_4	10.0
$\ln K_5^0$	–33.49	Q_5	2.26

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TSİKLOPENTANIN 1,3-TSİKLOPENTADIENƏ SELEKTİV OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏSİ REAKSİYASININ MEXANİZM VƏ KİNETİKASININ MODİFİKASIYA OLUNMUŞ SEOLİT KATALİZATORU ÜZƏRİNDƏ ÖYRƏNİLMƏSİ

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Tsiklopentanın 380°C-də HY seolitlər üzərində reaksiyası öyrənilmişdir. Əsas xammalın dehidrogenləşməsinin ilkin mərhələsində davamlı tsiklopenten və tsiklopentadien molekulu əmələ gəlmişdir, lakin əsas məhsul kimi molekulyar hidrogenə rast gəlinməmişdir. Klinoptilolit katalitik aktivliyi tsiklopentandan tsiklopentadienin alınması istiqamətində təcrübə olaraq öyrənilmiş və bir neçə temperaturda nəzəri olaraq modelləşdirilmişdir. Müəyyən olunmuşdur ki, klinoptilolit bu kationlarla {Cu²⁺ (0.5 kütl.%), Zn²⁺ (0.2 kütl.%), Co²⁺ (0.1 kütl.%), Cr³⁺ (0.1 kütl.%)} və CL{Co²⁺ (0.5 kütl.%)} daha çox katalitik aktivlik göstərir və bu katalizatorlar ion-mübadiləsi üsulu ilə hazırlanmışdır. Nəzəri hesablamalar həmçinin sübut etdi ki, bu reaksiyalar qeyri-sinxron, yəni ardıcıl olamayan şəkildə gedir. Təcrübə məlumatlarında katalizatorun tərkib hissələrini əhatə edən aktiv mərkəzlərin qruplaşdırıldığı və kationlərin dissosiativ adsorbsiyalı oksigen ilə birləşməsinə təmin edən rabitə enerjiləri nəzərə alınmaqla reaksiya yollarının təsvir olunduğu bildirilir. Enerji baryerləri və katalizə olunan sistemlərin elektron quruluşla əlaqəli sürət sabitləri və ikili səviyyəli varyasyon keçid nəzəriyyəsi hesablamalarının köməyi ilə dəqiqliklə modelləşdirilmişdir.

Açar sözlər: klinoptilolit, tsiklopentan, katalitik dehidrogenləşmə, tsiklopenten, tsiklopentadien-1,3.

ИЗУЧЕНИЕ КИНЕТИКИ И МЕХАНИЗМА РЕАКЦИИ СЕЛЕКТИВНОГО ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ ЦИКЛОПЕНТАНА В ЦИКЛОПЕНТАДИЕН-1,3 НА МОДИФИЦИРОВАННОМ ЦЕОЛИТНОМ КАТАЛИЗАТОРЕ

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Реакция окислительного дегидрирования цикlopentана изучалась на цеолите HY при 380°C. Цикlopenten и цикlopentadiен образуются в виде стабильного исходного продукта путем дегидрирования сырья, хотя молекулярный водород не был обнаружен в качестве первичного продукта. Каталитическая активность клиноптилолита в реакции селективного окислительного дегидрирования цикlopentана в цикlopentadiен-1,3 была измерена экспериментально и теоретически смоделирована при нескольких температурах. Выяснено, что клиноптилолит, модифицированный катионами {Cu²⁺ (0.5 мас.%), Zn²⁺ (0.2 мас.%), Co²⁺ (0.1 мас.%), Cr³⁺ (0.1 мас.%)} и CL{Co²⁺ (0.5 мас.%)}, показывает наибольшую активность. Катализатор получали ионообменным методом. Теоретический расчет показал, что катализируемые реакции протекали не синхронно и не последовательно. Экспериментальные данные выявили, что активные центры катализатора сгруппированы. Описаны пути реакции с учетом энергии связи, которые обмениваются катионами в сочетании с диссоциативным адсорбированным кислородом. Энергетические барьеры и константы скорости катализируемых систем были точно моделированы коррелированной электронной структурой и двухуровневым изменением теории состояния вариационного перехода.

Ключевые слова: клиноптилолит, цикlopentan, каталитическое дегидрирование, цикlopenten, цикlopentadiен-1,3.