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Kinetics and catalysis**KINETICS AND MECHANISM OF SELECTIVE OXIDATIVE DEHYDROGENATION
OF 2-BUTANOL TO METHYLETHYLKETONE ON A MODIFIED ZEOLITE
CATALYST CuZnPdCaA****Academician of ANAS A.M.Aliyev, F.A.Agayev**

It has been found that metal zeolite catalyst CuZnPdCaA, containing 3.0 wt.% Cu²⁺, 2.0 wt.% Zn²⁺ and 0.1 wt.% Pd²⁺, shows the highest activity and selectivity in this reaction.

Keywords: 2-butanol, oxidative dehydrogenation, zeolite catalyst, methylethylketone, kinetics, ion exchange

Methylethylketone (MEK) is used as solvent and extractant in some cases superior to acetone - less volatile and safer to fire relation. On an industrial scale methylethylketone prepared by oxidation of butylenes on PdCl₂ and a two-step method, which consists of n-butene hydration in 2-butanol with a catalyst in a sulfuric acid and oxidative dehydrogenation of sec-butanol in MEK on mixed oxide catalysts [1-3].

For the production of methyl ethyl ketone increasingly used by oxidative dehydrogenation of sec-butyl alcohol [1]. However, due to these disadvantages, this method has low economic efficiency.

The aim of this work is the selection of an active and selective catalyst for the reaction of partial oxidation of 2-butanol in one of the most important products of the chemical industry, methylethylketone and the study of kinetics and mechanism of reactions involving active metal zeolite catalyst.

Catalysts were prepared on the basis of CaA zeolite synthesized by the method of ion exchange from NaA. Inoculation of said zeolite with metal cations; Cu, Zn, and Pd were determined by ion exchange in aqueous solutions of CuCl₂, ZnCl₂ and [Pd(NH₃)₄]Cl₂ followed by drying (80-120⁰S, 5 hours) and calcining in flowing air at a temperature of 300⁰C, space velocity 2400 h⁻¹ for 30 min. The amount of metal cations introduced into the zeolite was determined by mass spectrometry analysis instrument ICP-MS Agilent 7700.

Experiments were carried out on flow unit directly connected to the gas-liquid chromatograph Agilent 7820A with column DB-624 at a rate of carrier gas (He) 1,5 ml/min and a pressure 0,51 atm.

Based on zeolite CaA and metal cations Cu²⁺, Zn²⁺ and Pd²⁺ ion-exchange the catalysts synthesized samples containing different amounts of these cations. The test results of the catalytic activity of some of these samples, as well as unmodified zeolite CaA in oxidative dehydrogenation of 2-butanol (B-2) in methylethylketone (MEK) are presented in table 1. From the data presented in table 1 shows that the reaction of oxidative dehydrogenation of 2-butanol to methyl ethyl ketone in these catalysts is accompanied by extensive oxidation and dehydration of 2-butanol to form carbon dioxide and butylenes. The output of individual products are significantly affected by the distribution of acid sites (administered metal cations into the zeolite acid site distribution changes on the surface), the concentration and the nature of the cation. From table 1 it follows that the reaction of oxidative dehydrogenation of 2-butanol in methyl ethyl ketone on a zeolite, CaA flows with relatively low conversion (experiment №1), which can be attributed to insufficient concentration dissociatively adsorbed oxygen molecules. Introduction copper cations in the zeolite increases the yield of methylethylketone (experiments №2-4). With increasing concentration of copper cations with 0.5 wt.% to 3.0 wt.% Yield of methylethylketone is substantially increased from 45.0% to 58.0% further increase in the concentration of the cations of copper (up to 4.0 wt.%) (Experiment number 5) has little effect on the output of IEC. This can be explained with the change of the distribution of the acid sites on the catalyst surface in the direction of reducing the number of Bronsted acid sites average force at relatively high concentrations of copper cations.

Table 1

Test results of the catalytic activity of the zeolite CaA modified metal cations Cu^{2+} , Zn^{2+} and Pd^{2+} in the oxidation of 2-butanol in methylethylketone at a temperature of 300°C , a space velocity $V = 2500 \text{ h}^{-1}$ and a molar ratio of the reactants alcohol: O_2 : $\text{N}_2 = 1: 0.69:2.5$

№	Zeolite	Composition in wt.%			Conversion, X, %	Yield A%		
		Cu^{2+}	Pd^{2+}	Zn^{+2}		MEK, A_1	Butylenes, A_2	CO_2 , A_3
1.	CaA	-	-	-	18,4	12,1	6,0	0,3
2.		0,5	-	-	48,1	45,0	2,5	0,6
3.		1,0	-	-	58,5	54,6	3,0	0,9
4.		3,0	-	-	63,8	58,0	4,3	1,5
5.		4,0	-	-	64,1	57,6	4,6	1,9
6.		0,5	0,1	-	80,4	74,7	3,7	2,0
7.		3,0	0,1	-	84,9	78,8	4,0	2,1
8.		3,0	0,1	1,0	88,0	82,4	3,4	2,2
9.		3,0	0,1	2,0	91,1	86,9	2,0	2,2
10.		3,0	0,1	4,0	87,2	80,0	4,4	2,8
11.		3,0	1,0	4,0	95,3	81,8	9,1	4,4

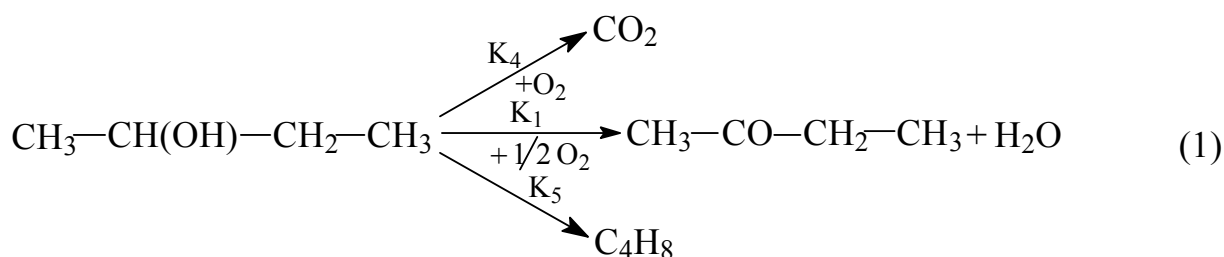
The introduction of small amounts of palladium cations (0.1 wt.%) and zinc (1.0-2.0 wt.%) creates a favorable distribution of the acid sites on the catalyst for the reaction (experiments № 6-9). Further increasing the concentration of these cations dissociatively adsorbed oxygen molecules.

A result of analysis the data presented in table 1 it can be concluded that the catalyst synthesized based CaA zeolite by ion exchange comprising 3.0 wt.% Cu^{2+} , 2.0 wt.% Zn^{2+} and 0.1 wt.% Pd^{2+} , exhibits the highest activity in the reaction, oxidative dehydrogenation of 2-butanol to methyl ethyl ketone.

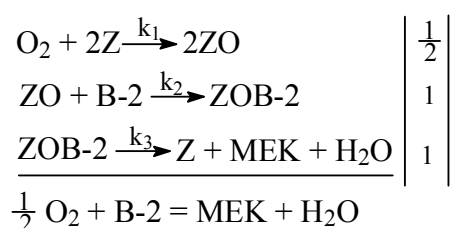
Kinetic regularities of this reaction were

investigated for the metal-zeolite catalyst CuZnPdCaA said composition in the absence of diffusion inhibition. The kinetics of the reaction was investigated in the temperature range $280-340^\circ\text{C}$, space velocities of $2000-4000 \text{ h}^{-1}$, the partial pressures of reactants $P_{\text{B-2}} = 0,12-0,36 \text{ atm}$ and $P_{\text{O}_2} = 0,12-0,24 \text{ atm}$ under conditions allowing the flow reaction in the kinetic region. The purity of the 2-butanol (B-2) of the brand "a.g" is 99.5%.

The experiments allow us to offer the following kinetic scheme of reactions in the process of partial oxidation of 2-butanol on the catalyst CuZnPdCaA :



Based on the analysis of literary materials [4-6] can suggest the following mechanism of the MEK. In the adsorption of 2-butanol is its protonation with Brønsted acid sites of the catalyst to the further elimination of water and formation of a surface alkoxide. Conversion of surface alkoxide MEK occurs when it interacts with the surface through the formation of a nucleophilic oxygen ketones like surface compound. Then there is the collapse ketones like surface connection to the MEK and restores the initial state of the catalyst. A simplified diagram of the staging mechanism is as follows:



All these stages are almost irreversible. Assuming their simplicity, we find the following expressions for the rates of stages:

$$\begin{aligned} r_1 &= k_1 P_{\text{O}_2} \theta_1^2 ; r_2 = k_2 P_{\text{B-2}} \theta_2 ; \\ r_3 &= k_3 \theta_3 \end{aligned} \quad (2)$$

where $\theta_1, \theta_2, \theta_3$ - the proportion of vacant lots modified zeolite-coated atomic oxygen molecules of 2-butanol and ketones like surface intermediates; k_1, k_2, k_3 - the rate constants of the respective stages of the index; $P_{\text{O}_2}, P_{\text{B-2}}$ partial pressures of the respective index components; r_2, r_1, r_3 - speed corresponding to index steps.

In stationary conditions:

$$r = r_1 = r_2 = r_3 \quad (3)$$

where, r - total rate of formation of MEK.

Based on these equations and the total surface of constant education sector θ_i and the overall reaction rate as a function of concentration of reactants:

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

$$k_1 P_{\text{O}_2} \theta_1^2 = k_2 P_{\text{B-2}} \theta_2 ; \theta_2 = \frac{k_1 P_{\text{O}_2}}{k_2 P_{\text{B-2}}} ; \quad (4)$$

$$k_1 P_{\text{O}_2} \theta_1^2 = k_3 \theta_3 ; \theta_3 = \frac{k_1 P_{\text{O}_2}}{k_3} \theta_1^2$$

Substituting expression θ_2, θ_3 , in the equation (4) we get:

$$1 - \frac{\bar{r}}{\bar{r}} = 1 - \frac{P_{\text{C}_4\text{H}_8} \cdot P_{\text{H}_2\text{O}}}{K_p P_{\text{B-2}}} = \gamma \quad (5)$$

Solving the equation (5) we obtain an expression for θ_1 . Substituting θ_1 in equation (2) we obtain

$$r_{\text{MEK}} = k_1 P_{\text{O}_2} \left\{ \frac{\sqrt{1 + 4 \left(\frac{k_1 P_{\text{O}_2}}{2 k_2 P_{\text{B-2}}} + \frac{k_1 P_{\text{O}_2}}{2 k_3} \right)} - 1}{2 \left(\frac{k_1 P_{\text{O}_2}}{2 k_2 P_{\text{B-2}}} + \frac{k_1 P_{\text{O}_2}}{2 k_3} \right)} \right\}^2 \quad (6)$$

Carbon dioxide is formed by reacting weakly adsorbed molecules of 2-butanol adsorbed oxygen molecules according to the Langmuir-Hinshelwood mechanism. Kinetic equation corresponding to this mechanism is as follows:

$$r_{\text{CO}_2} = \frac{k_4 K_1 K_2 P_{\text{O}_2} P_{\text{B-2}}}{(1 + K_1 P_{\text{O}_2} + K_2 P_{\text{B-2}})^2} \quad (7)$$

where k_4 - forming reaction rate constant of carbon dioxide, K_1, K_2 - constant of adsorption of oxygen molecules and 2-butanol at the active centers of the catalyst surface for reaction.

Butylenes are formed by dehydration of 2-butanol, which is a reversible reaction. The observed rate of the reaction:

$$r = \bar{r} - \bar{r} = \bar{r} \left(1 - \frac{\bar{r}}{\bar{r}} \right) \quad (8)$$

Where

$$1 - \frac{\bar{r}}{\bar{r}} = 1 - \frac{P_{\text{C}_4\text{H}_8} \cdot P_{\text{H}_2\text{O}}}{K_p P_{\text{B-2}}} = \gamma \quad (9)$$

γ - irreversibility criterion, then:

$$r = \vec{r}\gamma \quad (10)$$

$\vec{r}$ - can be expressed:

$$\vec{r} = KP_{B-2} \quad (11)$$

Substituting (9) and (11) into (10) we have:

$$\begin{aligned} r &= kP_{B-2} \left(1 - \frac{P_{C_4H_8} \cdot P_{H_2O}}{K_p P_{B-2}} \right) = \\ &= k \left(P_{B-2} - \frac{1}{K_p} P_{C_4H_8} \cdot P_{H_2O} \right) \end{aligned} \quad (12)$$

In view of the reaction rate of inhibition adsorbed molecules of alcohol and water, the observed rate of the reaction is as follows:

$$r_{C_4H_8} = k_5 \frac{P_{B-2} - \frac{1}{K_p} P_{C_4H_8} \cdot P_{H_2O}}{K_3 P_{B-2} + K_4 P_{H_2O}} \quad (13)$$

where K_p - equilibrium constant dehydration 2-butanol

$$\lg K_p = -A + \frac{B}{T} \quad (14)$$

where A and B are empirical constants determined from experimental data; K_3 and K_4 are constants of equilibrium adsorption of molecules of water and alcohol on the active centers of the catalyst for dehydration reaction of 2-butanol, respectively; k_5 - dehydration reaction rate constant. (To calculate the constants a and K

in equations (6), (7) and (13) used the formula

$$\kappa = \kappa_0 \cdot e^{-\frac{E}{RT}}, \quad K = K_0 \cdot e^{\frac{Q}{RT}}.$$

Equations (6) and (7) and (13) form a kinetic model of the 2-butanol oxidation.

A kinetic model of the reaction subjected to statistical analysis based on kinetic data. Calculation of pre-exponential factors of reaction constants $\ln k_i^0$ ($\ln K_i^0$), activation energies (E_i^0) and heat of adsorption (Q_i^0) by the method of "rolling admission" and Powell using software system "Search".

A kinetic model of the reaction of oxidation of secondary butyl alcohol MEK adequately describes the experimental data. Calculations have shown that the relative error of the experimental and calculated data does not exceed 7%.

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**MODİFİKASIYA OLUNMUŞ CuZnPdCaA SEOLİT KATALİZATORU ÜZƏRİNDƏ
BUTANOL-2-in METİLETİLKETONA SELEKTİV OKSİDLƏŞDİRİCİ
DEHİDROGENLƏŞMƏSİNİN KİNETİKA VƏ MEXANİZMİ**

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Müəyyən olunmuşdur ki, 3,0% Cu²⁺, 2,0% Zn²⁺ və 0,1% Pd²⁺ ionları saxlayan CuZnPdCaA metallseolit katalizatoru baxılan reaksiya üçün yüksək aktivlik və selektivliyə malikdir.

Açar sözlər: butanol-2, oksidləşdirici dehidrogenləşmə, seolit katalizatoru, metiletilketon, kinetika, ion mübadiləsi

**КИНЕТИКА И МЕХАНИЗМ СЕЛЕКТИВНОГО ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ
БУТАНОЛА-2 В МЕТИЛЭТИЛКЕТОН НА МОДИФИЦИРОВАННОМ ЦЕОЛИТНОМ
КАТАЛИЗАТОРЕ CuZnPdCaA**

А.М.Алиев, Ф.А.Агаев

Установлено, что металлцеолитный катализатор CuZnPdCaA, содержащий 3,0 мас.% Cu²⁺, 2,0 мас.% Zn²⁺ и 0,1 мас.% Pd²⁺, проявляет наиболее высокую активность и селективность в рассматриваемой реакции.

Ключевые слова: бутанол-2, окислительное дегидрирование, цеолитный катализатор, метилэтилкетон, кинетика, ионный обмен