

UDC 544.4:661.725/741.5

**KINETICS AND MECHANISM OF SELECTIVE OXIDATIVE DEHYDROGENATION OF n-AMYL ALCOHOL INTO VALERALDEHYDE ON MODIFIED ZEOLITE CATALYST CuZnPdCaA****A.M.Aliev, F.A.Agayev, V.Sh.Agayev, A.A.Saridjanov***Institute of Catalysis and Inorganic Chemistry named after Acad.M.Nagiyev  
H.Javid ave., 113, Baku AZ 1143, Azerbaijan Republic; e-mail: [itpcht@lan.ab.az](mailto:itpcht@lan.ab.az)*

*Catalytic activity of zeolite CaA synthesized from zeolite NaA and modified by cations of metals  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pd}^{2+}$  by the method of ion exchange in the reaction of partial oxidation of n-amyl alcohol into valeraldehyd, has been studied. It revealed that metal-zeolite catalyst CaA synthesized from zeolite NaA and containing 3.0 wt.%  $\text{Cu}^{2+}$ , 2.0 wt.%  $\text{Zn}^{2+}$  and 0.1 wt.%  $\text{Pd}^{2+}$  displays the highest activity and selectivity in the reaction. Also, kinetic regularities of the reaction on the said catalyst have examined. On the basis of the experimental data, a probable phasic mechanism has been suggested and a theoretically substantiated kinetic model of the reaction developed.*

**Keywords:** n-amyl alcohol, valeraldehyde, zeolite CaA, mechanism, kinetic model, kinetic constants.

**INTRODUCTION**

Valeraldehyde is a valuable raw material for food and chemical industries. It is used for the preparation of medicaments, food supplements and essences. Besides, it is used as an emulsifier, which is a part of synthetic materials and plasticizers. Note that industrially aldehydes are obtained by catalytic oxidation of aliphatic alcohols. Metals, transition metal oxides, mixed oxides and transition metal salts are used as the catalysts. Process proceeds in a temperature range (350-450<sup>0</sup>C) with a relatively low selectivity conformably to the desired product [1-4]. In the previous paper [5-10], we found that the

zeolites modified with metal cations by ion exchange display relatively high catalytic activity and selectivity in the oxidative dehydrogenation of aliphatic alcohols at relatively low temperatures (250-350<sup>0</sup>C).

The aim of this work is the synthesis of zeolite CaA from zeolite of NaA through the use of ion exchange method, its modification with cations of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pd}^{2+}$  by ion exchange, the definition of its catalytically active composition in the oxidative dehydrogenation of n-amyl alcohol conformably to valeraldehyde and the analysis of the kinetics and mechanism of the reaction.

**EXPERIMENTAL RESULTS AND DISCUSSION**

Catalysts were prepared on the basis of synthetic CaA and zeolite CaA synthesized from NaA by ion exchange method. Inoculation of indicated zeolite with metal cations; Cu, Zn, and Pd was established by ion exchange in aqueous solutions of  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$  and  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$  followed by drying (80-120<sup>0</sup>S, for 5 hours) and calcining in flowing air at a temperature of 300<sup>0</sup>C with space velocity of 2400 h<sup>-1</sup> for 30 min. The amount of metal cations introduced into the zeolite was

established by mass spectrometry analysis on ICP-MS Agilent 7700 instrument.

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

The test results in the catalytic activity of some samples, and unmodified forms of incorporation zeolites in the reaction of

oxidative dehydrogenation of n-amyl alcohol to valeraldehyde are shown in Table 1.

From the data shown in Table 1, it follows that the unmodified forms of synthetic CaA and CaA zeolite synthesized from NaA show a lower catalytic activity in the reaction of oxidative dehydrogenation of n-amyl alcohol of the valeraldehyde. Over these zeolites the reaction of n-amyl alcohol into amylenes proceeded (exp. №1,9) with precedence dehydration reaction of n-amyl alcohol into amylenes, and the yields of amylenes over CaA zeolite synthesized from NaA were relatively higher than over synthetic CaA. For this reason, there is a relatively high catalytic activity of CaAzeolite synthesized from NaA and modified metal cations as compared to the synthetic CaA (exp. №2-8 and №10-16). Note that cation concentration varied in a wide range of values (4.1 wt.%). Table 1 shows the concentrations of those cations which are of interest from industrial practicability standpoint. It should also be

added that the yield of the products is dependent on distribution of acid sites; concentration and nature of the cation. Incorporation of copper cations in CaA (synthesized from NaA) raises the concentration of dissociatively adsorbed oxygen molecules, which leads to increased catalytic activity of the zeolite in the reaction (exp. №2, 10). As the concentration of copper cations rises from 1.0 wt.% to 3.0 wt.%, the yield of valeraldehyde increases from 53.3% to 58.9% (exp. №2, 3) for synthetic CaA, and from 56.6% to 61.1% for CaA zeolite synthesized from NaA. Subsequent rise in the concentration of copper cation (up to 4.0 wt.%) has an insignificant influence on the yield of valeraldehyde (exp. №4,12). It might be explained as being due to changes in the distribution of acid centres over the catalyst surface toward reducing the Bronsted acid centres average force at relatively high concentrations of copper cations.

**Table 1.** Test results of the catalytic activity of the synthetic CaA and zeolite CaA are synthesized by ion exchange method from a zeolite NaA, modified metal cations  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pd}^{2+}$  in the oxidative dehydrogenation of n – amyl alcohol in valeraldehyde at a temperature  $320^{\circ}\text{C}$ , a space velocity  $V = 1600 \text{ h}^{-1}$  and a molar ratio of reactants alcohol:  $\text{O}_2$ :  $\text{N}_2 = 1: 0.75:2.9$

№	Zeolite	Composition in wt.%			Conversion, X, %	Yield A%		
		$\text{Cu}^{2+}$	$\text{Pd}^{2+}$	$\text{Zn}^{2+}$		Valeraldehyde, $A_1$	Amilenes, $A_2$	$\text{CO}_2$ , $A_3$
1	CaA (synth.)	-	-	-	45.9	39.6	5.1	1.2
2	-	1.0	-	-	57.8	53.3	2.7	1.8
3	-	3.0	-	-	64.8	58.9	3.5	2.4
4	-	4.0	-	-	64.2	57.1	4.2	2.9
5	-	3.0	0.1	-	80.3	70.1	5.9	4.3
6	-	3.0	0.2	-	79.4	68.4	6.2	4.8
7	-	3.0	0.1	2.0	85.7	76.8	5.3	3.6
8	-	3.0	0.1	3.0	83.5	72.3	6.9	4.3
9	CaA (synth-ed. from NaA)	-	-	-	50.4	43.2	5.6	1.6
10	-	1.0	-	-	62.1	56.6	3.4	2.1
11	-	3.0	-	-	67.7	61.1	3.9	2.7
12	-	4.0	-	-	68.2	60.4	4.6	3.2

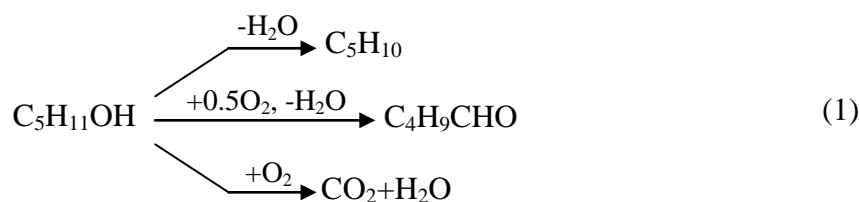
13	-	3.0	0.1	-	85.1	73.8	6.4	4.9
14	-	3.0	0.2	-	84.4	72.4	6.7	5.3
15	-	3.0	0.1	2.0	92.7	82.7	5.8	4.2
16	-	3.0	0.1	3.0	90.4	78.4	7.2	4.8

Incorporation of small amounts of palladium cations (0.1 wt.%) and zinc (1.0-2 wt.%) contributes to favorable distribution of acid centres on the surface of the catalyst in the reaction (exp. №5-8 and №13-16) and, moreover, the increased concentration of cations dissociatively adsorbed oxygen molecules.

As a result of data analysis as shown in Table 1, it may be concluded that the catalyst, CaA, synthesized by ion exchange on the basis of zeolite NaA and containing 3.0 wt.%  $\text{Cu}^{2+}$ , 2.0 wt.%  $\text{Zn}^{2+}$  and 0.1 wt.%  $\text{Pd}^{2+}$  shows relatively high activity in the reaction of oxidative dehydrogenation of n-amyl alcohol in valeraldehyde (exp. №9).

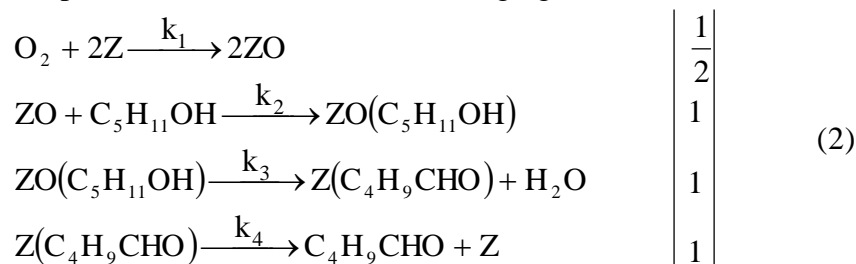
Kinetic regularities of the reaction were investigated over metal-zeolite catalyst CuZnPdCaA in the absence of diffusion inhibition. The kinetics of the reaction was carried out in a temperature range 280-340°C, space velocities of 1600-2400 h<sup>-1</sup>, partial pressures of reactants  $P_{n\text{-amyl}} = 0,2-0,3$  atm and  $P_{\text{O}_2} = 0,1-0,20$  atm under conditions that allow the flow reaction in the kinetic area. The purity of the n – amyl alcohol of the brand is 99.8%.

On the basis of the experimental data the following kinetic scheme of reactions during the partial oxidation of n – amyl alcohol over catalyst CuZnPdCaA was suggested:



By means of the analysis of literary materials [9] the following stepwise mechanism of the formation of valeraldehyde (2) may be suggested. Adsorbed molecules on n-amyl alcohol were protonated with surface

Brensted acid sites to eliminate water and form a surface alkoxide. Decomposition of surface alkoxide into valeraldehyde proceeds with nucleophilic oxygen. A simplified diagram of the staging mechanism is as follows:



All the stages are practically irreversible. Assuming their simplicity, we find the following expressions for stage rates:

$$r_1 = k_1 P_{\text{O}_2} \theta_1^2; \quad r_2 = k_2 P_{n\text{-amyl}} \theta_2; \quad r_3 = k_3 \theta_3; \quad r_4 = k_4 \theta_4 \quad (3)$$

where  $\theta_1, \theta_2, \theta_3, \theta_4$  are fractions of catalyst surface; sites with the ability to adsorb atomic oxygen; sites with adsorbed atoms oxygen;

sites with adsorbed atom oxygen and molecules of n-amyl alcohol; sites with

adsorbed molecules of aldehyde; where  $k_1, k_2, k_3, k_4$  are rate constants of the respective stages of the index;  $P_{n-amy}, P_{O_2}$  partial pressures of the index;  $r_1, r_2, r_3, r_4$  are rates corresponding to index steps.

In stationary conditions it is as follows:  $r = r_1 = r_2 = r_3 = r_4$  (4)

where the above is total rate of the process. Based on these equations and total permanence of surface portions  $\theta_1 + \theta_2 + \theta_3 + \theta_4 = 1$ , one can find the concentration of intermediates  $\theta_i$  and the rate of formation valeraldehyde as shown below:

$$r_{v.ald}: \theta_1 = \sqrt{\frac{k_4 \theta_4}{k_1 P_{O_2}}}; \theta_2 = \frac{k_4 \theta_4}{k_2 P_{n-amy}}; \theta_3 = \frac{k_4 \theta_4}{k_3} \quad (5)$$

Designating  $\theta_4 = y^2$ , we get:

$$\left( \frac{k_4}{k_2 P_{n-amy}} + \frac{k_4}{k_3} + 1 \right) y^2 + \sqrt{\frac{k_4}{k_1 P_{O_2}}} y - 1 = 0 \quad (6)$$

$$y = \frac{-\sqrt{\frac{k_4}{k_1 P_{O_2}}} + \sqrt{\frac{k_4}{k_2 P_{O_2}} + 4 \left( \frac{k_4}{k_2 P_{n-amy}} + \frac{k_4}{k_3} + 1 \right)}}{2 \left( \frac{k_4}{k_2 P_{n-amy}} + \frac{k_4}{k_3} + 1 \right)} \quad (7)$$

$$\theta_4 = \left[ \frac{-\sqrt{\frac{k_4}{k_1 P_{O_2}}} + \sqrt{\frac{k_4}{k_2 P_{O_2}} + 4 \left( \frac{k_4}{k_2 P_{n-amy}} + \frac{k_4}{k_3} + 1 \right)}}{2 \left( \frac{k_4}{k_2 P_{n-amy}} + \frac{k_4}{k_3} + 1 \right)} \right]^2 \quad (8)$$

Substituting  $\theta_4$  in the corresponding rate equation, we get:  
- for the rate of formation of valeraldehyde

$$r_4 = r_{v.a.} = k_4 \left[ \frac{-\sqrt{\frac{k_4}{k_1 P_{O_2}}} + \sqrt{\frac{k_4}{k_2 P_{n-amy}} + 4 \left( \frac{k_4}{k_2 P_{n-amy}} + \frac{k_4}{k_3} + 1 \right)}}{2 \left( \frac{k_4}{k_2 P_{n-amy}} + \frac{k_4}{k_3} + 1 \right)} \right]^2 \quad (9)$$

Carbon dioxide is formed through the reaction of weakly adsorbed molecules of n-amy alcohol adsorbed oxygen molecules according to the Langmuir-Hinshelwood mechanism. Then the kinetic equation corresponding to this mechanism is as follows:

$$r_{CO_2} = \frac{k_6 K_1 K_2 P_{O_2} P_{n-amy}}{(1 + K_1 P_{O_2} + K_2 P_{n-amy})^2} \quad (10)$$

where  $k_6$  - constant of forming reaction rate of carbon dioxide;  $K_1$ ,  $K_2$  - constants of adsorption of oxygen molecules and  $n$  - amyl alcohol at the active centers of the catalyst surface for reaction.

Note that amylenes are formed by dehydration of  $n$  - amyl alcohol, which is a reversible reaction. The observed rate of the reaction is as follows:

$$r = \bar{r} - \bar{r} = \bar{r} \left( 1 - \frac{\bar{r}}{\bar{r}} \right) \quad (11)$$

Where

$$1 - \frac{\bar{r}}{\bar{r}} = 1 - \frac{P_{C_5H_{10}} \cdot P_{H_2O}}{K_P P_{n-amyl}} = \gamma \quad (12)$$

$\gamma$  - irreversibility criterion, then:

$$r = \bar{r} \gamma \quad (13)$$

$\bar{r}$  - can be expressed by:

$$\bar{r} = K P_{n-amyl} \quad (14)$$

Substituting (12) and (14) into (13) we have the following:

$$r = k P_{n-amyl} \left( 1 - \frac{P_{C_5H_{10}} \cdot P_{H_2O}}{K_P P_{n-amyl}} \right) = k \left( P_{n-amyl} - \frac{1}{K_P} P_{C_5H_{10}} \cdot P_{H_2O} \right) \quad (15)$$

In considering the reaction rates of inhibition adsorbed molecules of alcohol and

water, the observed rate of the reaction is as follows:

$$r_{C_5H_{10}} = k_7 \frac{P_{n-amyl} - \frac{1}{K_P} P_{C_5H_{10}} \cdot P_{H_2O}}{K_3 P_{n-amyl} + K_4 P_{H_2O}} \quad (16)$$

where  $K_p$  is an equilibrium constant dehydration  $n$  - amyl alcohol

$$\lg K_p = -A + \frac{B}{T} \quad (17)$$

where  $A$  and  $B$  are empirical constants identified from experimental data ( $A=2.39$  and  $B=2010.7$ );  $K_3$  and  $K_4$  are constants of equilibrium adsorption of molecules of water and alcohol in the active centers of the catalyst for dehydration reaction of  $n$  - amyl alcohol, respectively;  $k_7$  - constant of dehydration reaction rate. (To calculate the constants  $k$  and  $K$  in equations (9), (10) and (15) we used a

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

Note that equations (9) and (10) and (15) form a kinetic model of the  $n$  - amyl alcohol oxidation.

Statistically analyzed kinetic model of the reaction was 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 ( $Q_i^0$ ) have been carried on by methods of "rolling admission" and with the help of the Powell software system "Search".

A kinetic model of the reaction of oxidation of  $n$  - amyl alcohol to valeraldehyde provides an appropriate description of experimental data. Calculations showed that a relative error in the experimental and calculated data does not exceed 5%.

## REFERENCES

1. Braylovski S.M., Temkin O.N., Trofimova I.V. Oxidation of alcohols on the metals of copper subgroup. *Problemi kinetiki i kataliza - Kinetics and Catalysis Problem*. 1985, V.19, pp.146-175. (In Russian).
2. Lazareva T.V., Osipova H.A., Kurina L.N. The study of methanol oxidation reactions on the vanadium-molybdenum oxide catalyst by thermal desorption. *Izvestia vysshykh uchebnykh zavedeniy. Khimia i khimicheskaya tekhnologiya - Chemistry and Chemical Technology*. 1990, V.33, no. 4, pp.49-52. (In Russian).
3. Kurina L.N., Davudov A.A., Osipova N.A. Surface interaction of ethylenglicol with silver. / V International Symposium Relations between Homogenous and Heterogenous Catalysis: Novosibirsk. 1986, pp. 140-145. (In Russian).
4. Wong G.S., Kragten D.D., Vohs J.M. Temperature-programmed desorption study of the oxidation of methanol to formaldehyde on  $TiO_2(110)$  - supported vanadia monolayers. *J. Phys. Chem. B*. 2001, 105(7), pp. 1366-1373.
5. Aliyev A.M., Medjidova S.M., Saridjanova A.A., Shabanova Z.A. et al. Oxidative dehydrogenation of lower aliphatic alcohols  $C_1-C_4$  over natural and synthetic zeolites modified by cations of transition metals. 6ya Vserossiyskaya seolitnaya konferensiya "Seoliti i mezoporiyemateriali: Dostijeniya i perspektivi". Tezisi dokladov. Zvenigorod, 2011, pp.177-179. (In Russian).
6. Alixanova Z.A., Aliyev A.M., Saridjanov A.A., Bahmanov M.F. Kinetics of the oxidative dehydrogenation of ethyl alcohol over the bimetal zeolite catalyst CuPdNaY. *Izvestia vysshykh uchebnykh zavedeniy. Khimia i khimicheskaya tekhnologiya - Chemistry and Chemical Technology*. 2009, no. 11, pp.106-110. (In Russian).
7. Aliyev A.M., Shabanova Z.A., Aliyev F.V. Oxidative dehydrogenation of hydrocarbons and the partial oxidation of aliphatic alcohols on modified zeolites. *European Applied Sciences*. 2015, no.5, pp. 67-79.
8. Aliyev A.M., Medjidova S.M., Shabanova Z.A. et al. Selection of metalzeolite catalyst and reaction kinetics of oxidative dehydrogenation of lower aliphatic alcohols // Rossiyski kongress katalizu "ROSKATALIZ". Sbornik tezisov. Novosibirsk, 2011, V.2, pp.186-192. (In Russian).
9. Aliyev A.M., Medjidova S.M., Saridjanov A.A., Matiev K.I. et al. The ion exchange method of modifying of zeolites with metal cations as the ultimate model of a supported catalyst. *Azerb. Kimya Jurnalı - Azerbaijan Chemical Journal*. 2011, no.4, pp. 9-25. (In Azerbaijan).
10. Shakhtakhtinskiy T.N., Aliyev A.M., Kuliye A.R., Medjidova S.M., Matiev K.I., Kasum-Zade A.Y. Selection of an active catalyst and reaction kinetics of partial oxidation of isoamyl alcohol. *Kinetika i kataliz - Kinetics and Catalysis*. 1996, V.37, no. 2, pp. 286-293. (In Russian).

**MODİFİKASIYA OLUNMUŞ  $CuZnPdCaA$  SEOLİT KATALİZATORU ÜZƏRİNDƏ AMİL SPİRTİNİN VALERİAN ALDEHİDİNƏ SELEKTİV OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏSİNİN KİNETİKA VƏ MEXANİZMİ**

*A.M.Əliyev, F.A.Ağayev, V.Ş.Ağayev, A.A.Sarıcanov*

AMEA-nın akad. M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu  
AZ 1143, Bakı, H.Cavid pr., 113; e-mail: [itpcht@lan.ab.az](mailto:itpcht@lan.ab.az)

*NaA seoliti əsasında sintez olunmuş, ionmübadilə üsulu ilə müxtəlif metal kationları ilə (Cu, Zn və Pd) modifikasiya edilmiş CaA seolitinin amil spirtinin valerian aldehidinə oksidləşdirici dehidrogenləşməsi reaksiyasında katalitik aktivliyi öyrənilmişdir. Müəyyən olunmuşdur ki, NaA seolitindən sintez edilmiş və tərkibində 3.0%  $Cu^{2+}$ , 2.0%  $Zn^{2+}$  və 0.1%  $Pd^{2+}$  ionları saxlayan CaA metal-seolit katalizatoru baxılan reaksiya üçün yüksək aktivlik və selektivliyə malikdir. Bu*

*katalizator üzərində reaksiyanın getməsinin kinetik qanunauyğunluğu öyrənilmişdir. Təcrübi nəticələr əsasında reaksiyanın getməsinin mümkün mərhələli mexanizmi verilmiş və prosesin nəzəri əsaslandırılmış kinetik modeli hazırlanmışdır.*

*Açar sözlər: amil spirti, valerian aldehidi, CaA seoliti, mexanizm, kinetik model, kinetik sabitlər.*

**КИНЕТИКА И МЕХАНИЗМ СЕЛЕКТИВНОГО ОКИСЛИТЕЛЬНОГО  
ДЕГИДРИРОВАНИЯ *n*-АМИЛОВОГО СПИРТА В ВАЛЕРИАНОВЫЙ АЛЬДЕГИД  
НА МОДИФИЦИРОВАННОМ ЦЕОЛИТНОМ КАТАЛИЗАТОРЕ CuZnPdCaA**

**А.М.Алиев, Ф.А.Агаев, В.Ш.Агаев, А.А.Сарыджанов**

*Институт катализа и неорганической химии им. акад. М.Нагиева  
Национальной АН Азербайджана  
AZ 1143 Баку, пр.Г.Джавида, 113; e-mail:itpcht@lan.ab.az*

*Исследована каталитическая активность цеолита CaA, синтезированного из цеолита NaA и модифицированного катионами металлов (Cu, Zn, Pd) методом ионного обмена, в реакции парциального окисления *n*-амилового спирта в валериановый альдегид.*

*Установлено, что металлцеолитный катализатор CaA, синтезированный из цеолита NaA и содержащий 3.0 мас.% Cu<sup>2+</sup>, 2.0 мас.% Zn<sup>2+</sup> и 0.1 мас.% Pd<sup>2+</sup>, проявляет наиболее высокую активность и селективность в рассматриваемой реакции. Изучены кинетические закономерности протекания реакции на указанном катализаторе. На основе экспериментальных данных предложен вероятный стадийный механизм протекания реакции и разработана теоретически обоснованная кинетическая модель процесса.*

**Ключевые слова:** *n*-амиловый спирт, валериановый альдегид, цеолит CaA, механизм, кинетическая модель, кинетические константы.

*Поступила в редакцию 21.10.2016.*