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KINETICS OF THE REACTION OF OXIDATIVE DEHYDROGENATION OF METHYLCYCLOHEXANOL TO METHYLCYCLOHEXANONE OVER MODIFIED CLINOPTILOLITE

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Abstract

The catalytic activity of modified natural clinptilolite zeolite has been studied in the oxidative dehydrogenation of methylcyclohexanol to methylcyclohexanone. On the basic of experimental studies it was found that natural clinoptilolite modified with Cu^{2+} and Pd^{2+} cations exhibit high activity and selectivity in the reaction under con-sideration. Clinoptilolite containing 0.15 wt.% Pd^{2+} and 0.5 wt.% Cu^{2+} is the most ac-tive for the studied reaction. It was studied the kinetic regularities of the reaction over the selected catalyst. Based on literature material and own experimental data was suggested the stage scheme of the mechanism of the reaction and developed theoretically based kinetic model of the process.

Keywords:
Methylcyclohexanol;
Methylcyclohexanone;
Oxidation;
Zeolite;
Mechanism;
Kinetic model.

Methylcyclohexanone is widely used as a solvent for cellulose nitrates and acetates, fats, waxes, natural resins, polyvinyl chloride, etc. Also, methylcyclohexanone is the main raw material in the asymmetric synthesis of optically active substances, plasticizers and enanthic acid.

For the first time, the production of methylcyclohexanone was realized by alkylation of cyclohexanone [1]. The resulting dimethyl derivatives reduce the efficiency of the process Methylcyclohexanone is obtained by oxidation of available 2-methylcyclohexanol, which is obtained by hydrogenation of o-cresol. The process is carried out in the liquid phase at relatively high pressures in the presence of homogeneous catalysts - soluble cobalt salts, and air oxygen is used as an oxidizing agent [2]. The main disadvantage of liquid-phase processes is the difficulty of separating the catalyst from the liquid catalyzate, therefore, on an industrial scale, gas-phase processes are mainly used for the oxidative dehydrogenation of methylcyclohexanol to methylcyclohexanone using metals such as nickel, cobalt, iron, copper, zinc, chromium, ruthenium, rhodium as a catalyst. The process of oxidative dehydrogenation on these catalysts proceeds in the temperature range of 220-550 ^oC [3]. The most effective of the proposed catalysts is activated carbon containing 1.0 wt.% Pt or 2.0 wt.% Pd [4]. The process proceeds at a temperature of 200-230 ^oC with the participation of hydrogen. In this case, the conversion of methylcyclohexanol is 55.0%. The participation of hydrogen reduces the efficiency of the process.

In the present work, the results of studying the reaction of oxidative dehydrogenation of 4-methylcyclohexanol to 4-methylcyclohexanone on a highly efficient metal zeolite catalyst, natural clinoptilolite, containing 0.5 wt.% Cu^{2+} and 0.15 wt.% Pd^{2+}, are presented.

Experimental part

The natural clinoptilolite with a silicate module, λ=8.68 of the Azerbaijan deposit, has been used. The catalysts were synthesized by ion exchange in aqueous solutions of $CuCl_2$ and $[Pd(NH_3)_4]Cl_2$ followed by drying (80-120 ^oC, 5 h) and calcination in an air stream at a temperature of 300 ^oC, space velocity 2400 h^{-1} for 30 min.

Studies of the catalytic activity of synthesized catalysts were performed in a flow reactor, the U-shape. The catalyst loading was 2 ml graining 0.4-0.63 mm. The reactor was placed in an electric furnace, the temperature of which was measured with a thermocouple and recorded with a microelectronic thermostat «MICROMAX». Feed raw material is carried out automatically. The evaporation of raw materials took place in temperature-controlled

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Table 1

The results of experiments to determine the active composition of the cata-lytic system, clinoptilolite - Pd^{2+} - Cu^{2+}

№	Content of catalyst, weight %		T, °C	Space ve-locity, h^{-1}	Molar ratio $n^0_{alcohol} : n_{air}$	Conversion of methylcyclo-hexanol, %	Yield of methyl-cyclohexanone, %
	Cu^{2+}	Pd^{2+}					
1	0.5	-	210	1590	0.36:2.64	62.0	62.0
2	0.5	0.1	210	1590	0.36:2.64	97.0	97.0
3	0.5	0.15	210	1590	0.36:2.64	100	100
4	0.5	0.15	200	1590	0.36:2.64	98.0	98.0
5	0.5	0.15	180	1590	0.36:2.64	93.0	93.0
6	0.5	0.15	190	1590	0.36:2.64	95.0	95.0
7	0.5	0.15	210	3000	0.36:5.18	96.0	96.0
8	0.5	0.15	230	3000	0.36:5.18	98.0	98.0
9	0.5	0.15	200	2000	0.36:3.88	97.0	97.0
10	0.5	0.15	210	2000	0.36:3.88	98.0	98.0
11	0.5	0.15	210	3500	0.36:5.21	97.0	97.0
12	0.5	0.15	220	3500	0.36:5.21	98.2	98.2
13	0.5	0.15	210	1000	0.36:2.45	100	100
14	0.5	0.15	230	3500	0.36:5.21	97.5	97.5
15	0.5	0.15	210	1500	0.36:2.56	98.2	98.2

Table 2

The results of studying the kinetics of the reaction of oxidative dehydrogenation of methyl-cyclohexanol on a catalyst, clinoptilolite (0.5% Cu^{2+}, 0.15% Pd^{2+})

№	V, h^{-1}	T, °C	P_{cn}, atm	P_{O_2}, atm	Yield, %
1	1000	180	0.06	0.17	89.1
2	1500	180	0.09	0.17	89.9
3	2000	180	0.12	0.17	91.1
4	2500	180	0.15	0.17	92.3
5	3000	180	0.20	0.17	95.1
6	3500	180	0.25	0.17	91.2
7	1000	200	0.12	0.06	93.1
8	1500	200	0.12	0.12	94.7
9	2000	200	0.12	0.16	95.6
10	2500	200	0.12	0.20	96.1
11	3000	200	0.12	0.25	90.6
12	3500	200	0.06	0.12	91.5
13	1000	210	0.09	0.12	93.5
14	1500	210	0.15	0.12	91.7
15	2000	210	0.20	0.12	91.5
16	2500	210	0.25	0.12	94.1
17	3000	210	0.18	0.06	93.8
18	3500	210	0.18	0.12	94.1
19	1000	230	0.18	0.18	96.8
20	1500	230	0.18	0.20	98.5
21	2000	230	0.18	0.25	99.7
22	2500	230	0.18	0.30	100
23	3000	230	0.18	0.35	100
24	3000	260	0.18	0.35	95.6
24	3500	230	0.18	0.12	95.4

cabinet. Temperature stability is maintained in an incubator with a contact thermometer. The temperature in the middle of the catalyst bed was measured and recorded by a thermocouple potentiometer. The reaction products together with unreacted raw materials received in a cooled receiver. The separation of the reaction products were carried out in columns packed Paropak - T, in a linear programmed rise of temperature up 50 to 200 °C. Analysis of the reaction products is also carried out on the apparatus GC Agilent 7890 with Agilent 5975 MS detector using a column packed with HP-5-MS (length 30 m).

Results and discussion

In order to determine the active composition of the catalytic system and the range of variation of technological parameters, a series of experiments was carried out. The results of this study are presented in table. 1. As can be seen from the results, clinoptilolite containing 0.15 wt.% $Pd^{2+}$and 0.5 wt.% Cu^{2+} is the most active composition in all studied technological regimes. The reaction proceeds with a selectivity of 100%.

The reaction kinetics was studied in the temperature range 180÷230 °C, space velocities 1500-3000 h^{-1} and partial pressures of reagents =0.05-0.25 atm, under conditions that ensure the reaction proceeds in the kinetic region over the CuPd-clinoptilolite, containing 0.15 wt.% Pd^{2+} and 0.5 wt.% Cu^{2+}. The results of kinetic experiments are shown in table 2.

Influence of temperature and space velocity on the reaction rate was studied under optimal $P_{alcohol}$ and P_{O_2}. From table 2, it follows that with increasing temperature from 180 to 230 °C the yield of methylcyclohexanone increases and reaches a maximum (100%) and and further raising the temperature to 260 °C reduces yield 95.6%). Conversion of alcohol in the whole studied temperature range is continuously growing.

Based on the analysis of literary materials it has been suggest the probable stage mechanism for the formation of methylcyclohexanone. A simplified diagram of the staging mechanism is as follows:

$$\begin{array}{l|c|}
O_2 + 2Z \xrightarrow{k_1} 2ZO & \frac{1}{2} \\
ZO + CH_3C_6H_{10}OH \xrightarrow{k_2} ZO(CH_3C_6H_{10}OH) & 1 \\
\underline{ZO\cdot(CH_3C_6H_{10}OH) \xrightarrow{k_3} Z + CH_3C_6H_9O + H_2O} & 1
\end{array}$$

$$\frac{1}{2}O_2 + CH_3C_6H_{10}OH = CH_3C_6H_9O + H_2O$$

Assuming simplicity of these stages, we find the following expressions for the rates of stages:

$$r_1 = k_1 \cdot P_1 \cdot \theta_1^2\,, \quad r_2 = k_2 \cdot P_2 \cdot \theta_2\,, \quad r_3 = k_3 \cdot \theta_3 \qquad (1)$$

In steady-state conditions:

$$r_1 = r_2 = r_3 \qquad (2)$$

Based on these equations and the constancy of the total number of surface areas of formations, the reaction rate of the formation of 4-methylcyclohexanone can be represented as a function of the concentration of reagents:

$$\theta_1 + \theta_2 + \theta_3 = 1 \qquad (3)$$

$$k_1 \cdot P_1 \cdot \theta_1^2 = k_2 \cdot P_2 \cdot \theta_2\,, \quad \theta_2 = \frac{k_1 \cdot P_1}{k_2 P_2} \cdot \theta_1^2$$

$$k_1 \cdot P_1 \cdot \theta_1^2 = k_3 \cdot \theta_3\,, \quad \theta_3 = \frac{k_1 \cdot P_1}{k_3} \cdot \theta_1^2$$

Substituting the expressions θ1 and θ3 into equation (3), we obtain:

$$\left(\frac{k_1 \cdot P_1}{k_2 P_2} + \frac{k_1 \cdot P_1}{k_3}\right)\theta_1^2 + \theta_1 = 0$$

$$\theta_1 = \frac{-1 + \sqrt{1 + 4\left(\frac{k_1 \cdot P_1}{k_2 P_2} + \frac{k_1 \cdot P_1}{k_3}\right)}}{2\left(\frac{k_1 \cdot P_1}{k_2 \cdot P_2} + \frac{k_1 \cdot P_1}{k_3}\right)} \qquad (4)$$

Taking into account the expression θ_1, we obtain the following equation for the rate of formation of 4-methylcyclohexanone:

$$r_{MC} = r_3 = k_3 \frac{k_1 P_1}{k_3}\theta_1^2 = k_1 P_1 = \left[\frac{-1 + \sqrt{1 + 4\left(\frac{k_1 P_1}{k_2 P_2} + \frac{k_1 P_1}{k_3}\right)}}{2\left(\frac{k_1 P_1}{k_2 P_2} + \frac{k_1 P_1}{k_3}\right)}\right]^2 \qquad (5)$$

The reaction proceeds selectively on the studied catalyst, without the formation of by-products, the stoichiometric equation of the gross mechanism of formation of 4-methylcyclohexanone can be represented as follows:

$$CH_3C_6H_{10}OH + 0.5O_2 = CH_3C_6H_9O + H_2O \qquad (6)$$

Using the stoichiometric equation, the yield of the target product (A) and the initial molar amounts of the reagents, the current molar amounts of the ingredients can be determined by the following expressions:

$$\begin{cases}
n_1 = n_1^0 - n_1^0 \cdot \dfrac{A}{100}; \\
n_2 = n_1^0 \dfrac{A}{100}; \\
n_3 = n_3^0 - \dfrac{1}{2} n_1^0 \cdot \dfrac{A}{100}; \\
n_3^0 = n_{O_2}^0 + 0.21 \cdot \dfrac{V_{air}}{23.1}; \\
n_4 = n_2; \\
n_{N_2} = 0.79 \cdot \dfrac{V_{air}}{23.1}
\end{cases} \qquad (7)$$

where A - is the yield of methylcyclohexanone;

n_1, n_2, n_3, n_4 и n_{N_2} are the current molar amounts of methylcyclohexanol, methylcyclohexanone, oxygen, water, and nitrogen;

P_1, P_2, P_3, P_4 и P_{N_2} are the partial pressures of the substances;

V_{air} - volumetric air consumption.

The partial pressures of the components are determined as follows:

$$P_i = \frac{n_i}{\sum n_i} P \qquad (8)$$

where *P* is the total pressure equal to 1 atm.

Equations (5) and (7) constitute the kinetic model of this process. The indicated kinetic model of the reaction was subjected to statistical analysis based on the kinetic data given in table 2 [5].

The numerical values of the constants of the kinetic model are presented in table. 3. For these numerical values of the kinetic parameters, the relative error of the experimental and calculated data does not exceed 3%.

Table 3

Numerical values of the constants of the kinetic model

$Ln\ k^0_i$		E_i, kkal/mole	
Ln k^0_1	10.5	E_1	7.2
Ln k^0_2	1.2	E_2	3.6
Ln k^0_3	65.6	E_3	6.8

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Кинетика реакции окислительного дегидрирования метилциклогексанола в метилциклогексанон на модифицированном клиноптилолите

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Реферат

Исследована каталитическая активность модифицированного природного клинптилолита цеолита в реакции окислительного дегидрирования метилциклогекса-нола в метилциклогексанон. На основе экспериментальных исследований уста-новлено, что природный клиноптилолит, содержащий 0.15 мас.% Pd^{2+} и 0.5 мас.% Cu^{2+}, наиболее активен в исследуемой реакции. Изучены кинетические закономерности реакции на выбранном катализаторе. На основании литературных материалов и собственных экспериментальных данных предложена стадийная схема механизма реакции и разработана теоретически обоснованная кинетическая модель процесса.

Ключевые слова: метилциклогексанол; метилциклогексанон; окисление; цеолит; механизм; кинетическая модель.

Metiltsikloheksanolun metiltsikloheksanona oksidləşdirici dehidrogenləşməsi reaksiyasının kinetikası

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Xülasə

Metilsikloheksanolun metilsikloheksanona oksidləşdirici dehidrogenləşdirilməsi reaksiyasında modifikasiya olunmuş təbii klinptilolit seolitin katalitik aktivliyi tədqiq edilmişdir. Eksperimental tədqiqatlar əsasında müəyyən edilmişdir ki, 0.15 kütlə % Pd^{2+} və 0.5 kütlə % Cu^{2+} olan klinoptilolit seoliti tədqiq olunan reaksiyada yüksək aktivlik göstərir. Seçilmiş katalizator üzərində reaksiyanın kinetik qanunauyğunluqları tədqiq edilmişdir. Ədəbiyyat materialı və təcrübi nəticələr əsasında reaksiya mexanizminin mərhələ sxemi təklif edilmiş və prosesin nəzəri cəhətdən əsaslandırılmış kinetik modeli hazırlanmışdır.

Açar sözlər: metilsikloheksanol; metilsikloheksanon; oksidləşmə; seolit; mexanizm; kinetik model.