Study of the kinetics and mechanism of the oxidative conversion of ethyl alcohol to acetic acid over the modified natural zeolite catalyst clinoptilolite

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In this study, we aimed to investigate the kinetic laws of the vapor-phase oxidation of ethyl alcohol into acetic acid over natural clinoptilolite modified by ion exchange method and containing 0.25% wt. Cu^{2+}, 0.05% wt. Mn^{2+} and 0.05% wt. Pd^{2+} ions. Experimental studies were carried out in the temperature range of 180-230^{0}C, partial pressure of C_2H_5OH – 0.05÷0.25 atm and of O_2 – 0.3÷0.55 atm, space velocity of the mixture 3600-5400 h^{-1}. Based on the experimental data the total kinetic scheme of the reaction mechanism, as well as kinetic stage schemes for product formation were proposed, and a theoretically grounded kinetic model of the process was developed. The numerical values for the constants of the kinetic model were calculated using the Matlab software package. The results of the studies showed that the developed kinetic model satisfactorily describes the experimental kinetic data.

Keywords: Ethyl alcohol, Acetic acid, Zeolites, Mechanism, Kinetic model

INTRODUCTION

Acetic acid is one of the main products of organic synthesis and is widely used in the textile and food industries. It is also used for the synthesis of ethyl acetate.

On an industrial scale organic acids are obtained *via* heterogeneous catalytic oxidation of aliphatic alcohols. The catalysts are metals (e.g., Cu, Ag, Au, Fe, and Mo), transition metal oxides (e.g., $CuO+Cu_2O$, V_2O_5, Cr_2O_3, MoO_3, etc.), mixed oxides, and salts of transition metals (e.g., vanadates, tungstates, stannates, and molybdates of zinc, cobalt, and bismuth). These processes occur in the temperature range of 350-450^{0}C and have relatively low selectivity toward the target product [1-4].

In our previous works [5-8] we showed that zeolites modified with metal cations *via* ion exchange exhibit fairly high catalytic activity and selectivity in the oxidative conversion of aliphatic alcohols at relatively low temperatures (250-350^{0}C).

Based on a study of experimental data in the literature and on physicochemical methods of analysis, it was established that – like the liquid-phase variant of the process, which is performed in an acid medium, includes protons, and proceeds through the formation of an intermediate compound (chromate ester) – the heterogeneous vapor-phase partial oxidation of aliphatic alcohols on metal-zeolite catalysts also yields surface alkoxides that form during the interaction of medium-strength Brønsted acid sites with molecules of aliphatic alcohols adsorbed on the catalyst's surface. The heterogeneous partial oxidation of aliphatic alcohols on the surfaces of metal-zeolite catalysts occurs as a result of the interaction between these alkoxide compounds and the surfaces' nucleophilic oxygen [9].

In [10] we have shown that natural zeolite – clinoptilolite (crystallinity 80-85%, SiO_2/Al_2O_3 = 8.68) of the Aydag deposit of Azerbaijan modified *via* ion exchange with cations Cu^{2+}(0.25% wt.), Mn^{2+}(0.05% wt.) and Pd^{2+}(0.05% wt.) possesses high activity and selectivity in the reaction of vapor-phase oxidation of ethyl alcohol to acetic acid.

In the present paper, the results of the investigation of the kinetic laws for the vapor-phase process of oxidation of ethyl alcohol into acetic acid on the catalyst described above are given and a theoretically grounded kinetic model of the process is developed, which takes a central place in the mathematical model serving as the basis for its optimal design.

EXPERIMENTAL

Catalysts were prepared from natural clinoptilolite (from Azerbaijan deposit) with silicate modulus λ=SiO_2/Al_2O_3 = 8.68 and crystallinity of 80-85%. The zeolite's type and crystallinity were determined *via* X-ray diffraction on a D-2 diffractometer (Bruker). The original samples of natural zeolites were converted into the hydrogen form in two ways: decationization with 1 N NH$_4$Cl solution and dealumination with 0.5 N hydrochloric acid solution for 60 min at 85-90^{0}C. By dealumina-

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tion in a solution of 0.5 N HCl, the silicate modulus of the zeolite was adjusted to $\lambda = 10.8$. Dealuminated samples were subjected to decationization by treatment with a solution of NH_4Cl. Then the samples were washed with distilled water until the absence of Cl^- ions, dried at a temperature of 80-120^{0}C (3 hours), and annealed at a temperature of 400^{0}C (4 hours) and 550^{0}C (3 hours). Then 50 grams of a fraction with 0.25-0.63 mm grain size were taken and poured into a 1 L flask, where it was treated with a 0.1 N HCl solution at a temperature of 95-98^{0}C 3 times for 2 hours each time, then the samples were washed, dried and thermally treated.

The zeolites were modified with Cu^{2+}, Mn^{2+}, Pd^{2+} metal cations *via* ion exchange in aqueous solutions of $CuCl_2$, $MnCl_2$, and $[Pd(NH_3)_4]Cl_2$, respectively. Upon completion of the exchange, the catalyst was washed from Cl^- ions with distilled water, dried at a temperature of 120-150^{0}C (3-5 hours) and thermally treated at a temperature of 350-400^{0}C for 30 min in a stream of air at a volumetric flow rate of 2400 h^{-1}.

The mixture was stirred until the complete input of ions into the composition of the zeolite. To establish the completeness of the exchange of inputted cations a qualitative analysis procedure was used. To determine the number of cations, in addition to the above analytical method, elemental analysis was performed on the ICP-MS Agilent 7700 X (method of mass spectrometry with inductively coupled plasma in elemental analysis) and X-ray phase analysis on a D-2 diffractometer (Bruker).

Experiments were performed on a flow-through unit connected directly to the DB-624 column of an Agilent 7820A gas-liquid chromatography system at a gas (He) flow rate of 1.5 mL/min. The separation of reaction products was carried out under conditions of linearly programmed rising temperature of the chromatograph thermostat with a gas carrier velocity (N_2) – 3.6 liter per hour. Into the reactor made of Pyrex glass with an inner diameter d_{in}=20 mm, with zones for preheating of the initial reaction mixture 3 cm^3 of the catalyst with a particle size 0.25-0.63 mm was loaded and then was activated for 2 hours in an air stream at temperature 450°C and then the temperature was lowered to the reaction temperature and the reaction mixture was supplied at a certain volumetric rate. The reactor was placed in an air electric oven with automatic temperature control. The raw material was fed with a pump. Using a ME-1600 microdoser, the initial materials were supplied to a mixer in a thermostated cabinet equipped with an electric heater and a fan. A stable temperature in the thermostat was maintained using a MICROMAX temperature microcontroller. During the tests, a certain temperature was individually set and maintained for each experiment. The mixture of vapors of ethyl alcohol, together with oxygen and nitrogen was fed to one of the knees of the reactor with a catalyst bed. The temperature in the middle of the catalyst layer with granulated Pyrex (2÷3 mm) was measured with a thermocouple and recorded with a potentiometer. The composition of the reaction mixture was determined at various intervals by gas chromatography, taking samples from the reaction zone directly through a six-way crane mounted on the output of the reactor. In experiments ethyl alcohol with purity of 96% was used. The reaction products together with unreacted raw materials were fed to a cooled receiver. Runs performed at several feed rates and using granules of the catalyst with different sizes (0.3÷1.0) showed that external and internal mass transfer effects were negligible under the studied experimental conditions, so the process was carried out under conditions allowing the reaction to proceed in the kinetic range. To determine the effect of water on the process of oxidative conversion of ethyl alcohol into acetic acid, a series of additional experiments were carried out. It was established that the addition of water to ethyl alcohol does not affect the course of the reaction. During the experiments no traces of carbon monoxide were detected on the chromatograms.

The experimental studies of the kinetic laws of vapor-phase oxidation of ethyl alcohol into acetic acid were carried out in a U-shaped flow reactor directly connected to a column of a gas-liquid chromatography system in the temperature range of 180-230ºC, with partial pressures of C_2H_5OH – 0.05÷0.25 atm and O_2 – 0.3÷0.55 atm, and space velocity of the mixture – 3600-5400 h^{-1}.

RESULTS AND DISCUSSION

The effect of the partial pressure of ethyl alcohol on the course of the reaction was studied in the range of 0.05-0.25 atm at a temperature of 220ºC, space velocity of 4800 h^{-1}, and partial pressure of oxygen of 0.4 atm. Along with the main product – acetic acid, acetaldehyde, ethyl acetate, and carbon dioxide were formed in the reaction. Figure 1 shows the curves of the conversion of ethyl alcohol and the yield of reaction products as a function of the partial pressure of ethanol at 220ºC. As can be seen from the figure increasing the partial pressure of alcohol from 0.05 atm to 0.25 atm leads to decreasing conversion from 97.4 to 22.2%, wherein the yield of acetic acid and carbon dioxide decreases, the yield of acetaldehyde increases, and that of ethyl acetate passes through a maximum. The change in the course of the curves can be explained as follows. At

partial pressures of ethanol less than 0.1 atm, the process occurs in an excess of oxygen, which provides relatively high oxidation rates of alcohol to acetaldehyde and acetaldehyde to acetic acid, while the lack of alcohol inhibits the esterification reaction leading to the formation of ethyl acetate. The maximum yield of ethyl acetate is observed at the partial pressure of alcohol, approximately equal to 0.1 atm. Increasing the partial pressure of ethyl alcohol above 0.1 atm leads to obstruction of the coordination of oxygen on the active sites of the metal-zeolite catalyst, which reduces the conversion and yields of all reaction products except acetaldehyde.
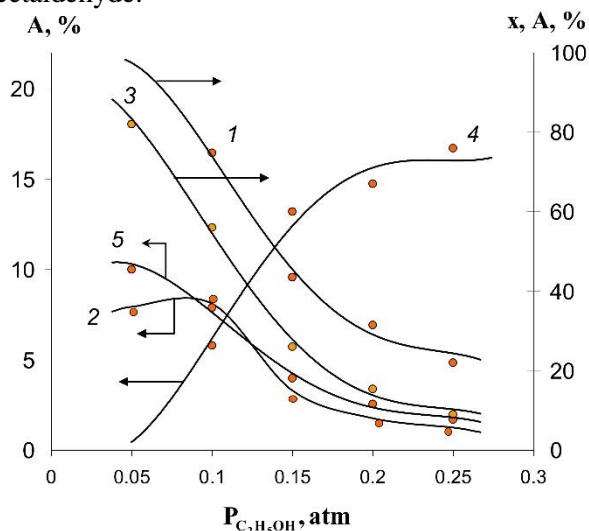

Fig. 1. Effect of the partial pressure of ethyl alcohol on the course of the reaction at a temperature of 220ºC, space velocity of 4800 h⁻¹, and partial pressure of oxygen of 0.4 atm. x – conversion, A – yields of reaction products. 1 –alcohol; 2 – ethyl acetate; 3 – acetic acid; 4 – acetaldehyde; 5 – carbon dioxide.

The effect of the partial pressure of oxygen on the yield of the products of the reaction at a space velocity of 4800 h⁻¹, partial pressure of ethyl alcohol of 0.1 atm, and temperature of 220ºC ls shown in Fig. 2. The partial pressure of oxygen was varied in the range of 0.3-0.55 atm. The figure shows that with increasing the partial pressure of oxygen, there is an increase in the degree of conversion of ethyl alcohol. In the entire studied range of the partial pressure of oxygen, a decrease of the yield of acetaldehyde and an increase of the yields of all other reaction products is observed.

The yield of ethyl acetate is stabilized at ethanol partial pressures above 0.4 atm. The course of the curves can be explained by the sequential mechanism of the formation of acetaldehyde, acetic acid, and carbon dioxide and the sequentially parallel mechanism of the formation of ethyl acetate from ethyl alcohol and acetic acid.
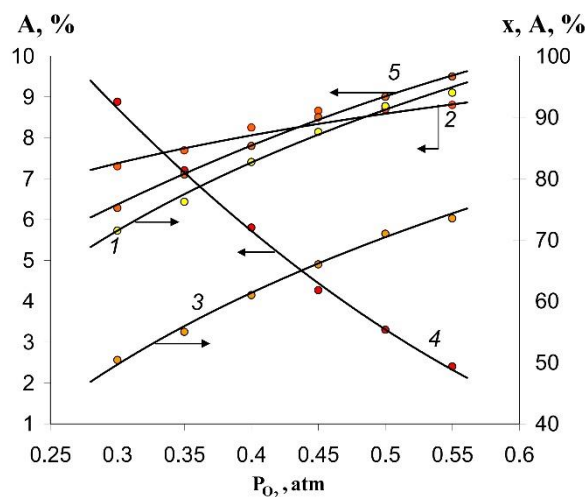

Fig. 2. Effect of the partial pressure of oxygen on the course of the reaction at a temperature of 210ºC, space velocity of 4800 h⁻¹, and partial pressure of ethyl alcohol of 0.1 atm. x – conversion, A – yields of reaction products. 1 – alcohol; 2 – ethyl acetate; 3 – acetic acid; 4 – acetaldehyde; 5 – carbon dioxide.

The effect of temperature of the process on the activity of the catalytic system at partial pressures of ethyl alcohol – 0.1 atm, oxygen – 0.4 atm, and space velocity of 4800 h⁻¹ js shown in Figure 3. The figure shows that on increasing the temperature of the process, the degree of conversion of ethyl alcohol also increases. A sharp increase of the conversion of alcohol is observed with increasing temperature up to 210ºC. The observed change in the course of the curves of the yields of reaction products depending on temperature is explained by the formation of acetic acid and carbon dioxide by the oxidation of acetaldehyde.

The effect of the space velocity on the course of the reaction was studied in the range of 3000-5400 h⁻¹ at a temperature of 220ºC. Figure 4 shows the dependence of the activity of the catalyst on the space velocity at the temperature of 220ºC. It follows from the figure that with increasing the space velocity, the conversion of ethyl alcohol decreases. Increasing yield of acetaldehyde and decreasing conversion of ethyl alcohol is explained by shortening of the contact time.
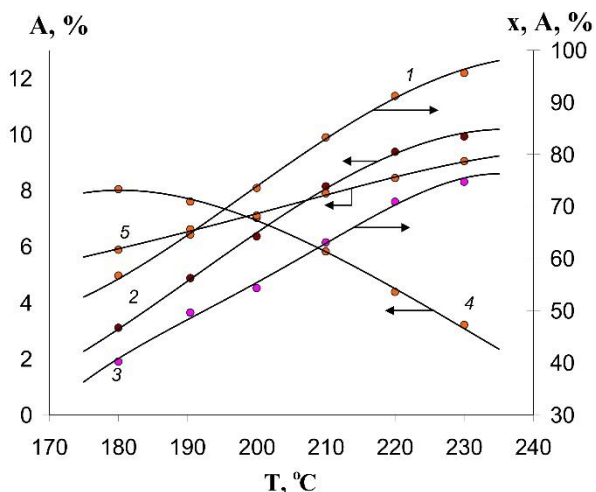
Fig. 3. Effect of the temperature on the course of the reaction at a space velocity of 4800 h⁻¹ and partial pressures of ethyl alcohol of 0.1 atm, and oxygen of 0.4 atm. x – conversion, A – yields of reaction products. 1 – alcohol; 2 – ethyl acetate; 3 – acetic acid; 4 – acetaldehyde; 5 – carbon dioxide.

Increasing the yield of acetaldehyde over the entire studied range of space velocities and decreasing the yields of the remaining products confirms the formation of acetic acid and carbon dioxide by the oxidation of acetaldehyde and the sequentially parallel mechanism of formation of ethyl acetate.

Based on the above analysis and literature data the following hypothesis about the reaction mechanism was proposed: acetaldehyde is formed by the interaction of adsorbed ethanol molecules with dissociatively adsorbed oxygen molecules. Acetic acid is formed by the interaction of adsorbed acetaldehyde molecules with dissociatively adsorbed oxygen molecules. Ethyl acetate is formed by the interaction of strongly adsorbed acetic acid molecules with weakly adsorbed molecules of ethyl alcohol. Carbon dioxide is formed by the interaction of adsorbed acetaldehyde molecules with oxygen molecules from the gas phase.

The following gross-stoichiometric equations for the formation of acetaldehyde, acetic acid, ethyl acetate, and carbon dioxide correspond to the proposed hypothesis:
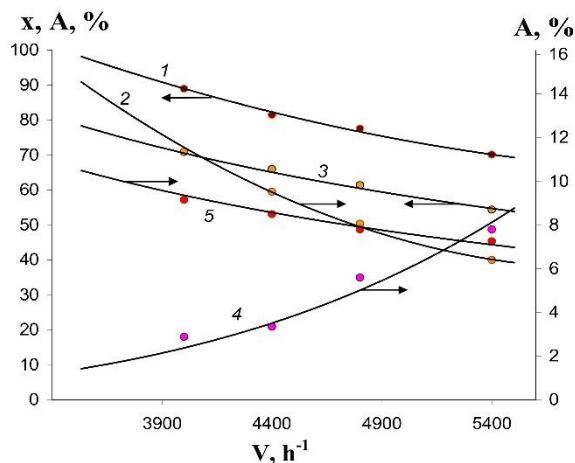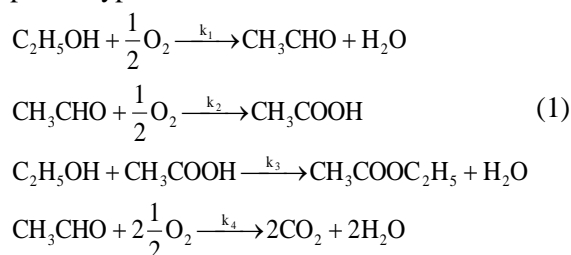
$$C_2H_5OH + \frac{1}{2}O_2 \xrightarrow{k_1} CH_3CHO + H_2O$$

$$CH_3CHO + \frac{1}{2}O_2 \xrightarrow{k_2} CH_3COOH \qquad (1)$$

$$C_2H_5OH + CH_3COOH \xrightarrow{k_3} CH_3COOC_2H_5 + H_2O$$

$$CH_3CHO + 2\frac{1}{2}O_2 \xrightarrow{k_4} 2CO_2 + 2H_2O$$

Fig. 4. The effect of the influence of the space velocity on the course of the reaction at the temperature 210⁰C and partial pressures of ethyl alcohol of 0.1 atm and oxygen of 0.4 atm. x – conversion, A – yields of reaction products. 1 –alcohol; 2 – ethyl acetate; 3 – acetic acid; 4 – acetaldehyde; 5 – carbon dioxide.

In adsorption of the gas mixture components, the molecules of these components interact with the free surface of the catalyst according to the Langmuir scheme, wherein is assumed that molecules of the components are adsorbed on the same free sites on the surface. It is known that the sum of the occupied and free sites on the surface of the catalyst equal one, i.e.:

$$1 = Z + Z_{C_2H_5OH} + Z_{O_2} + Z_{CH_3COOH} + Z_{CH_3CHO}, \quad (2)$$

where Z – fraction of the free surface of the catalyst; $Z_{C_2H_5OH}$, Z_{O_2}, Z_{CH_3COOH}, Z_{CH_3CHO} – fractions of surface coverage by ethyl alcohol, oxygen, acetic acid and acetaldehyde, respectively.

The calculation of surface concentrations proposed by Langmuir is based on the concepts of equality of the processes of adsorption and desorption. Adsorption equilibrium can be described by the isotherm $\theta = f(p)_{T=const}$, which is the basis for the mathematical description of adsorption processes. Expressing surface concentrations in terms of the fraction of the free surface of the catalyst Z and the partial pressures of the corresponding components, we obtain:

$$1 = Z + b_1P_1Z + b_2\sqrt{P_2}Z + b_3P_4Z + b_4P_5Z$$

$$Z = \frac{1}{1 + b_1P_1 + b_2\sqrt{P_2} + b_3P_4 + b_4P_5}, \qquad (3)$$

where b_1, b_2, b_3, b_4 – adsorption equilibrium constants of ethyl alcohol, oxygen, acetic acid and acetaldehyde; $P_i \left(i = \overline{1,8} \right)$ partial pressures of ethyl alcohol – P_1, oxygen – P_2, ethyl acetate – P_3, acetic acid – P_4, acetaldehyde – P_5, carbon dioxide – P_6,
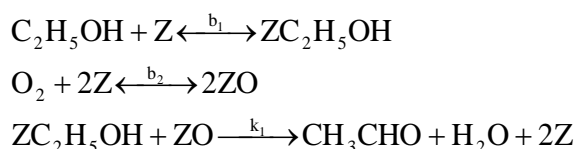
water – P_7, nitrogen – P_8; $k_i (i = \overline{1,4})$ – reaction rate constants.

For convenience of calculations, marking $Z_{C_2H_5OH}$, Z_{O_2}, Z_{CH_3COOH}, Z_{CH_3CHO} over θ_1, θ_2, θ_3, θ_4 and using (3), we obtain the dependences of surface concentrations through their partial pressures:

$$\theta_1 = b_1 P_1 Z = \frac{b_1 P_1}{1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5}$$

$$\theta_2 = b_2 \sqrt{P_2} Z = \frac{b_2 \sqrt{P_2}}{1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5} \quad (4)$$

$$\theta_3 = b_3 P_4 Z = \frac{b_3 P_4}{1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5}$$

$$\theta_4 = b_4 P_5 Z = \frac{b_4 P_5}{1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5}$$

Kinetic staged schemes for the formation of reaction products can be presented as follows:

For acetaldehyde:

$$C_2H_5OH + Z \xleftrightarrow{b_1} ZC_2H_5OH$$

$$O_2 + 2Z \xleftrightarrow{b_2} 2ZO$$
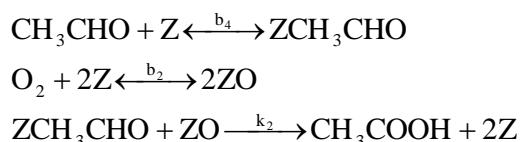
$$ZC_2H_5OH + ZO \xrightarrow{k_1} CH_3CHO + H_2O + 2Z$$

The rate of formation of acetaldehyde, according to this scheme takes the form:

$$r_1 = k_1 \theta_1 \theta_2 \quad (5)$$

For acetic acid:

$$CH_3CHO + Z \xleftrightarrow{b_4} ZCH_3CHO$$

$$O_2 + 2Z \xleftrightarrow{b_2} 2ZO$$

$$ZCH_3CHO + ZO \xrightarrow{k_2} CH_3COOH + 2Z$$
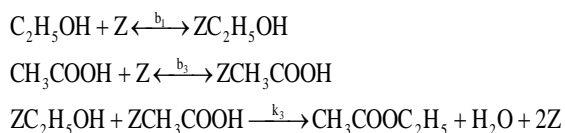
The rate of formation of acetic acid, according to this scheme takes the form:

$$r_2 = k_2 \theta_4 \theta_2 \quad (6)$$

For ethyl acetate:

$$C_2H_5OH + Z \xleftrightarrow{b_1} ZC_2H_5OH$$

$$CH_3COOH + Z \xleftrightarrow{b_3} ZCH_3COOH$$

$$ZC_2H_5OH + ZCH_3COOH \xrightarrow{k_3} CH_3COOC_2H_5 + H_2O + 2Z$$
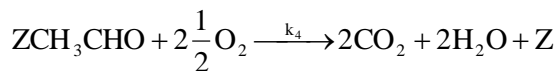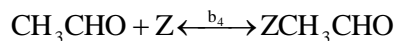
The kinetic equation corresponding to this scheme can take the form:

$$r_3 = k_3 \theta_1 \theta_3 \quad (7)$$

For carbon dioxide:

$$CH_3CHO + Z \xleftrightarrow{b_4} ZCH_3CHO$$

$$ZCH_3CHO + 2\frac{1}{2}O_2 \xrightarrow{k_4} 2CO_2 + 2H_2O + Z$$

The kinetic equation corresponding to this scheme takes the form:

$$r_4 = k_4 \theta_4 P_2 \quad (8)$$

Expressing the rate of formation of each component through the rates of the stages in which this component is involved and taking into account the corresponding stoichiometric coefficients, we obtain:

$$
\begin{cases}
\dfrac{dn_1}{dG_{kat}} = -r_1 - r_3 \\[2mm]
\dfrac{dn_2}{dG_{kat}} = -\dfrac{1}{2}r_1 - \dfrac{1}{2}r_2 - \dfrac{5}{2}r_4 \\[2mm]
\dfrac{dn_3}{dG_{kat}} = r_3 \\[2mm]
\dfrac{dn_4}{dG_{kat}} = r_2 - r_3 \\[2mm]
\dfrac{dn_5}{dG_{kat}} = r_1 - r_2 - r_4 \\[2mm]
\dfrac{dn_6}{dG_{kat}} = 2r_4 \\[2mm]
\dfrac{dn_7}{dG_{kat}} = r_1 + r_3 + 2r_4 \\[2mm]
\dfrac{dn_8}{dG_{kat}} = 0,
\end{cases} \quad (9)
$$

where n_1 – ethyl alcohol, mol/h; n_2 – oxygen, mol/h; n_3 – ethyl acetate, mol/h; n_4 – acetic acid, mol/h; n_5 – acetaldehyde, mol/h; n_6 – carbon dioxide, mol/h; n_7 – water, mol/h; n_8 – nitrogen, mol/h.

This system of differential equations takes into account the changes of all components of the process. Such a system is quite difficult for solving. Therefore, we transform it. We select the following substances as the key components (linearly independent components): ethyl acetate (n_3); acetic acid (n_4); acetaldehyde (n_5); carbon dioxide (n_6). The remaining components will be expressed through these key components. Thus, after some mathematical transformations, as well as expressing the ratio of the current amount of the component to the initial amount of ethyl alcohol through the dimensionless quantity A, i.e.: $A_i = n_i / N_1^0$, $i = 3, 4, 5, 6$, we obtain the following kinetic model of the process:

$$
\begin{cases}
\dfrac{dA_1}{d\left(\dfrac{G_{kat}}{N_1^0}\right)} = \dfrac{k_3 b_1 b_3 P_1 P_4}{\left(1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5\right)^2} \\[4ex]
\dfrac{dA_2}{d\left(\dfrac{G_{kat}}{N_1^0}\right)} = \dfrac{k_2 b_2 \sqrt{P_2} b_4 P_5 - k_3 b_1 b_3 P_1 P_4}{\left(1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5\right)^2} \\[4ex]
\dfrac{dA_3}{d\left(\dfrac{G_{kat}}{N_1^0}\right)} = \dfrac{k_1 b_1 b_2 P_1 \sqrt{P_2} - k_2 b_2 \sqrt{P_2} b_4 P_5 - k_4 P_2 b_4 P_5 \left(1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5\right)}{\left(1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5\right)^2} \\[4ex]
\dfrac{dA_4}{d\left(\dfrac{G_{kat}}{N_1^0}\right)} = \dfrac{2 k_4 b_4 P_5 P_2}{1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5},
\end{cases}
\tag{10}
$$

where $k_i = \exp(\ln k_{0i} - E_i / RT)$, $b_i = \exp(\ln K_{0i} + Q_i / RT)$, $(i = \overline{1,4})$; $A_i (i = \overline{1,4})$ – yields of ethyl acetate, acetic acid, acetaldehyde and carbon dioxide, respectively; T – reactor temperature, $^\circ$C; G_{kat} – catalyst mass, kg; Q_i – heat of adsorption of the *i*-th component.

Using the gross-stoichiometric equations (1), yields of reaction products and initial molar amounts of input reagents have determined the current molar amounts of all components in the stream. So, the conversion of ethyl alcohol is determined by the following expression:

$$X = 2A_1 + A_2 + A_3 + 0.5A_4 \tag{11}$$

The current number of moles of all components was determined by the following balance equations:

$$n_1 = N_1^0 (1 - X)$$
$$n_2 = N_2^0 - N_1^0 (A_1 + A_2 + 0.5A_3 + 1.5A_4)$$
$$n_3 = N_1^0 A_1$$
$$n_4 = N_1^0 A_2$$
$$n_5 = N_1^0 A_3$$
$$n_6 = N_1^0 A_4$$
$$n_7 = 2n_3 + n_4 + n_5 + 1.5n_6$$
$$n_8 = N_8^0,$$

where N_1^0, N_2^0, N_8^0 – input reagents of ethyl alcohol, oxygen, nitrogen, respectively, mol/h.

The partial pressures of the components are determined as follows:

$$P_i = \dfrac{n_i}{\sum_{i=1}^{8} n_i} P, \tag{12}$$

where P – total pressure of the system (P=1 atm).

The results of the experimental study of the kinetic laws of this process are shown in Table 1.

Calculations of pre-exponential factors of the reaction constants ($\ln k_{0i}$, $\ln K_{0i}$), activation energies (E_i), and heats of adsorption (Q_i) were performed on the Matlab software package [11] by using the simplex search method of Nelder-Mead [12], wherein the objective function has the form:

$$F = \min \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\dfrac{\left| A_{ij}^{\exp} - A_{ij}^{\text{calc}} \right|}{A_{ij}^{\exp}} \right) \to \min, \tag{13}$$

where $A_{ij}^{\exp}$, A_{ij}^{calc} – experimental and calculated values of yields for the j-th component in the i-th experiment; m is the number of experiments; n is the number of components. The values of the found parameters of the kinetic model are shown in Table 2. The average relative error of the experimental and calculated values of the yields of the reaction products did not exceed 5-6%. All graphs in Figures (1-4) confirm the closeness of the experimental and calculated values. Here, the dots indicate the experimental data, and the solid lines are the results calculated from the kinetic model.

Table 1. Experimental kinetic data.

№	T, °C	V, hour^{-1}	Molar ratio of reagents $C_2H_5OH:O_2:N_2$	Conversion of alcohol, X, %	A_1,% Ethyl acetate	A_2, % Acetic acid	A_3, % Acetaldehyde	A_4, % Carbon dioxide
1	190	4200	1:4:5	63.5	2.2	44.5	9.5	9.1
2	200	4200	1:4:5	77.6	3.0	55.4	8.1	11.1
3	210	4200	1:4:5	92.0	4.4	71.1	4.0	12.5
4	220	4200	1:4:5	96.2	5.0	76.1	0.3	14.8
5	220	6600	1:4:5	76.1	2.1	50.8	13.1	10.1
6	220	6000	1:4:5	80.0	2.8	56.2	9.3	11.7
7	220	5400	1:4:5	90.5	3.6	67.3	6.3	13.3
8	220	4800	1:4:5	98.4	4.7	77.2	1.7	14.8
9	220	3600	1:4:5	92.6	5.0	70.3	0.3	17.0
10	220	3000	1:4:5	98.4	4.9	77.7	0.3	15.5
11	220	4800	1:5.5:3.5	93.4	4.0	72.2	0.3	16.9
12	220	4800	1:5:4	98.0	3.6	77.0	0.3	17.1
13	220	4800	1:4.5:4.5	99.1	5.4	81.4	0.3	12.0
14	220	4800	1:3.5:5.5	91.4	4.9	68.8	4.2	13.5
15	220	4800	1:3:6	87.3	4.1	64.3	6.3	12.6
16	220	4800	0.5:4.5:5	97.6	2.1	78.5	0.3	16.7
17	220	4800	1.5:4.5:4	60.0	1.9	32.7	17.1	8.3
18	220	4800	2:4.5:3.5	50.8	1.1	24.6	19.7	5.4
19	220	4800	2.5:4.5:3	40.4	0.9	15.5	21.0	3.0
20	230	4200	1:4:5	91.0	4.2	70.6	0.2	16.0
21	240	4200	1:4:5	97.5	4.0	77.0	0.2	16.3

Table 2. Values of the constants of the kinetic model.

$\ln k_{0i}(\ln K_{0i})$		$E_i(Q_i)$, kcal/mol	
$\ln k_{01}$	19.12	E_1	17.61
$\ln k_{02}$	10.77	E_2	12.15
$\ln k_{03}$	12.05	E_3	12.85
$\ln k_{04}$	9.79	E_4	13.27
$\ln K_{01}$	4.1	Q_1	1.2
$\ln K_{02}$	-4.5	Q_2	7.5
$\ln K_{03}$	2.79	Q_3	2.5
$\ln K_{04}$	5.61	Q_4	3.25

CONCLUSION

Based on natural clinoptilolite (from Azerbaijan deposit) with silicate modulus λ=SiO$_2$/Al$_2$O$_3$=8.68 and crystallinity of 80-85%, a high-efficiency catalyst for the reaction of vapor-phase oxidation of ethyl alcohol to acetic acid – clinoptilolite Cu^{2+}(0.25% wt.) Mn^{2+}(0.05% wt.) Pd^{2+}(0.05% wt.) was synthesized *via* ion exchange. The kinetic laws of vapor-phase oxidation of ethyl alcohol to acetic acid over this catalyst were studied. Based on the study of experimental data in the literature and the results of physicochemical methods of analysis, a probable stepwise mechanism and a theoretically grounded kinetic model of the process was proposed.

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