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THE KINETICS OF THE GAS PHASE ALDOL CONDENSATION REACTION OF PROPIONIC ACID WITH FORMALDEHYDE ON B_2O_3-P_2O_5-WO_3/SiO_2 CATALYST

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Abstract. The basic kinetic regularities of aldol condensation reaction of propionic acid with formaldehyde on the B_2O_3-P_2O_5-WO_3/SiO_2 catalyst in gas phase have been investigated. The kinetic equations of the process have been proposed and the kinetic parameters have been calculated. The created kinetic model fairly well describes the condensation reaction of propionic acid with formaldehyde on the developed catalyst.

Keywords: heterogeneous catalysts, gas phase, aldol condensation, reaction rate, kinetic model, acrylic monomers, methacrylic acid.

1. Introduction

Acrylates take a prominent place in the organic synthesis industry. The main field of their application is obtaining of polymeric materials with valuable technical properties. Methacrylic acid (MAA) and its derivatives are of particular importance among acrylic monomers, because of being the main components for most acrylic polymeric and composite materials.

Nowadays different feedstock for acrylic monomers production can be used [1-4]. The main criteria of raw materials selection are their price and availability in the particular region, and technological feasibility of their use, namely the simplicity of technological process design and high yield of the final product. From this point of view use of ethylene as the feedstock for acrylic monomers obtaining is cost-effective and technologically reasonable decision. Ethylene is the available feedstock in the organic synthesis industry. Its world production capacity is nearly 140 million t/year [5].

Nowadays the investigations, aimed at industrial implementation of the method of methacrylic acid and methylmethacrylate (MMA) obtaining by the following scheme are actively carried out [4, 6]:
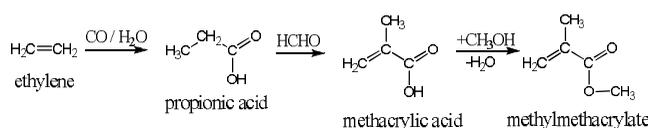
The main problem of industrial implementation of this MMA production method is lack of efficiency of the catalysts in the aldol condensation of propionic acid (PA) with formaldehyde (FA). Our previous research has shown that the B_2O_3-P_2O_5-WO_3/SiO_2 catalyst is very effective in the aldol condensation of PA with FA to MAA in gas phase in terms of yield and selectivity [7, 8]. The purpose of this paper is to create the kinetic model of the aldol condensation reaction of PA with FA to MAA in gas phase in the presence of aforementioned catalyst. This is necessary for optimization and technological designing of the process.

2. Experimental

The kinetic research of the condensation reaction of PA with FA was carried out in the presence of the B_2O_3-P_2O_5-WO_3/SiO_2 catalytic system with the components atomic ratio B:P:W = 3:1:0.3, that has been previously found to be the optimum catalyst composition in terms of MAA yield [9].

AR grade chemicals were used for the kinetic studies and for the catalyst preparation. As a source of FA the formalin with formaldehyde content of 36 wt % was used. The formalin was prepared from polyformaldehyd immediately before the research.

2.1. Catalyst Preparation

The catalyst was prepared by the impregnation method. The silica KSS-3 was used as a carrier. To introduce the catalyst active phase (B_2O_3-P_2O_5-WO_3) boron acid

H_3BO_3, ammonium hydrogenphosfate $(NH_4)_2HPO_4$ and phosphorus-tungsten heteropolyacid $H_7[P(W_2O_7)_6]\cdot H_2O$ were used. The catalyst was dried for 8 h at 423 K. Afterwards the catalyst was calcinated for 6 h at 673 K.

2.2. The Kinetic Studies

The kinetic studies were carried out in the flow reactor with the impulse feeding of the reaction mixture at low conversion of the initial reagents. The process is not limited by the diffusion factors, which has been proved by carrying out the reaction at different linear flow rates and different catalyst pellet sizes at constant contact time (τ_c).

The kinetic studies were carried out at four different temperatures: 563, 593, 623, and 653 K. The effect of reagents and water concentrations on the reagents conversion rate and the reaction products formation rate has been studied. When varying the concentration of one of the reagents, the concentration of the others was maintained to be constant by supplying helium into the reaction mixture.

The analysis was performed by chromatography.

3. Results and Discussion

3.1. The Kinetic Studies

It is known that reactions of carbonyl compounds condensation are based on increased reactivity of hydrogen atoms in the α-position relative to the carbonyl group, which enables the active methylene compound formation due to the catalyst effect. During the condensation of PA with FA the molecules of PA are able to react both as carbonyl and methylene compounds, and the molecules of FA are able to react only as the carbonyl compounds due to the absence of hydrogen atoms in the α-position relative to the carbonyl group in the molecules of FA. So, 3 cases are theoretically possible: 1) The PA and FA molecules are sorbed on the neighbor active sites of the catalyst and then activated molecules interact with one another. 2) The PA molecules are sorbed on the active sites of the catalyst and then activated molecules interact with PA and FA molecules from reaction volume. 3) Combined case.

In order to determine the scheme of aldol condensation reaction of PA with FA in the presence of the investigated catalyst the effect of the initial reagents concentration on the reaction products formation rate was studied.

First of all the effect of PA and FA concentration on the rate of MAA formation in the presence of the B_2O_3-P_2O_5-WO_3/SiO_2 catalytic system (the acid type catalyst) has been determined (Figs. 1 and 2). By linearization of this data in the $\ln(C_{PA})$ *vs* $\ln(W_{MAA})$ and $\ln(C_{FA})$ *vs* $\ln(W_{MAA})$ coordinates, respectively, it has been calculated that the rate of MAA formation has the order

with respect to PA approximately 1 (0.95 ± 0.04) and the fractional order with respect to FA (0.56–0.65).

The fractional order with respect to FA in the gas phase heterogeneous catalytic condensation of PA with FA indicates the inhibition of the reaction by FA. FA competes with the PA for the active sites of the catalyst surface.

Based on the obtained experimental data we can exclude the possibility of interaction between activated methylene and carbonyl compounds formed in the first stage of the process. Such interaction is possible only in case of the adsorption of methylene and carbonyl compounds on the neighboring active sites. But in this case, taking into account the equivalent chemisorption of PA and FA on the catalysts surface [10] they would equally inhibit the process. But it is not observed – only FA inhibits the process. Therefore it can be assumed that the PA molecules, activated in the first stage (active methylene compound), are attacked by the molecules of FA and PA from the reaction volume (carbonyl compound), and the FA, adsorbed on the catalytic surface does not take part in the reaction. As it is known, the carbonyl compounds interact with the activated methylene compounds due to the partially positive charge on the carbon atom of carbonyl group. In case of the PA and FA molecules interaction the MAA is formed and in case of two molecules of PA interaction diethylketone (DEK) is formed.

Then the effect of PA and FA concentration on the rate of DEK formation in the presence of the B_2O_3-P_2O_5-WO_3/SiO_2 catalyst has been determined (Figs. 3 and 4). By linearization of this data in the $\ln(C_{PA})$ *vs* $\ln(W_{DEK})$ coordinates it has been calculated that the rate of DEK formation has the order with respect to PA approximately 2 (1.91–1.99). This indicates that DEK formation reaction is limited by the interaction of the activated PA molecule adsorbed on the surface with a PA molecule from the reaction volume. The rate of adsorbed PA molecule interaction with free PA molecule is comparatively low because the ability of carbonyl compound interaction with methylene compound in the aldol condensation processes reduces in the range:

$$CH_2OH < R–CHO < R–C(O)–R < R–C(O)–OH < R–C(O)–O–R$$

By linearization of the data (Fig. 4) in the $\ln(C_{FA})$ *vs* $\ln(W_{DEK})$ coordinates it has been calculated that the rate of DEK formation with respect to FA has the order slightly less than zero -0.39 ± 0.05. So, FA does not take part in the DEK formation, and besides it inhibits this process as well as the MAA formation. Based on the analysis of the results shown in Figs. 1-4 it has been determined that the rate of PA consumption is equal to the sum of the rate of MAA formation and double rate of DEK formation. At the same time the rate of FA consumption is equal to the rate of MAA formation. This confirms that only PA takes part in the process of the side product formation, *i.e.* DEK is the product of two PA molecules condensation.
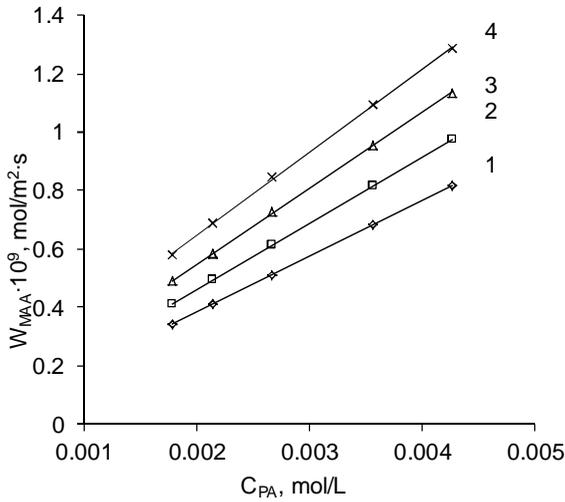
Fig. 1. The effect of PA concentration on the rate of MAA formation at 563 (1), 593 (2), 623 (3) and 653 (4) K. $\tau_c = 6$ s, $C_{FA} = 0.0892$ mol/l
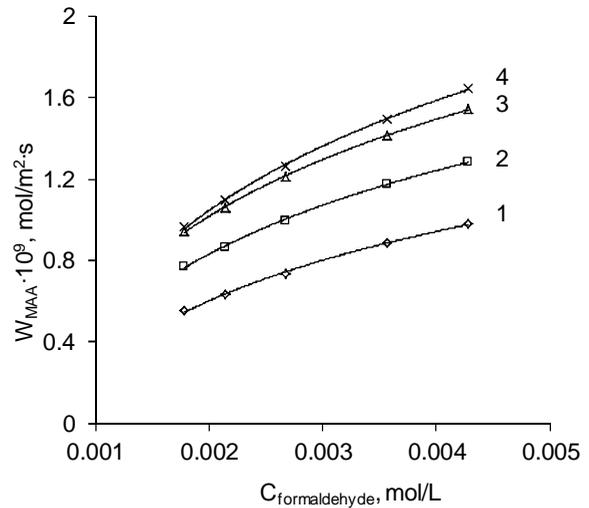

Fig. 2. The effect of FA concentration on the rate of MAA formation at 563 (1), 593 (2), 623 (3) and 653 (4) K. $\tau_c = 6$ s, $C_{PA} = 0.0892$ mol/l
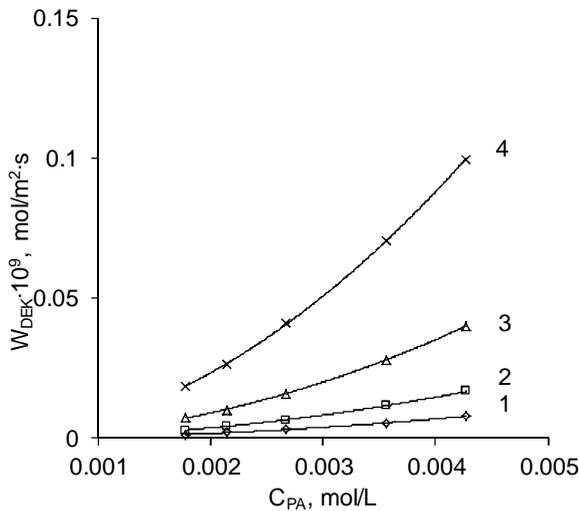

Fig. 3. The effect of PA concentration on the rate of DEK formation at 563 (1), 593 (2), 623 (3) and 653 (4) K. $\tau_c = 6$ s, $C_{FA} = 0.0892$ mol/l
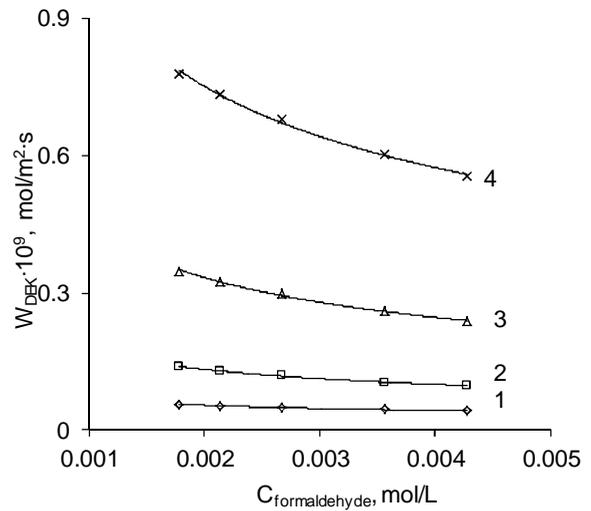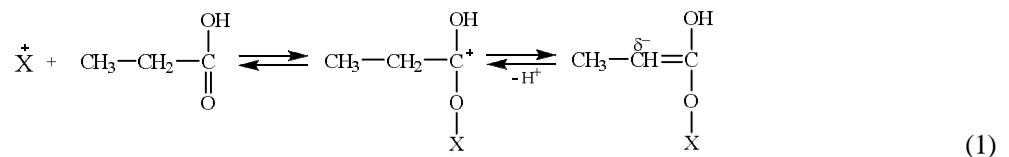

Fig. 4. The effect of FA concentration on the rate of DEK formation at 563 (1), 593 (2), 623 (3) and 653 (4) K. $\tau_c = 6$ s, $C_{PA} = 0.0892$ mol/l

Summarizing the obtained results, we can assume that the first stage of the PA with FA condensation reaction is the chemosorption of PA molecules on the free active sites (X^+) of the catalyst surface. As a result activated methylene compounds are formed (1). In the second stage of the reaction the activated methylene compounds are attacked by the FA molecules from the reaction volume (carbonyl compounds). The result of such interaction is formation of the adsorbed 3-hydroxy-2-methylpropanoic acid (2). Then water is immediately eliminated from the adsorbed molecule to form MAA (3). In case of the attack of activated methylene compound by another molecule of PA DEK is formed via intermediate formation of 3-hydroxy-2-methylpentanoic acid (4), from which water $(XOH + H^+ = X^+ + H_2O)$ and CO_2 are eliminated (5):
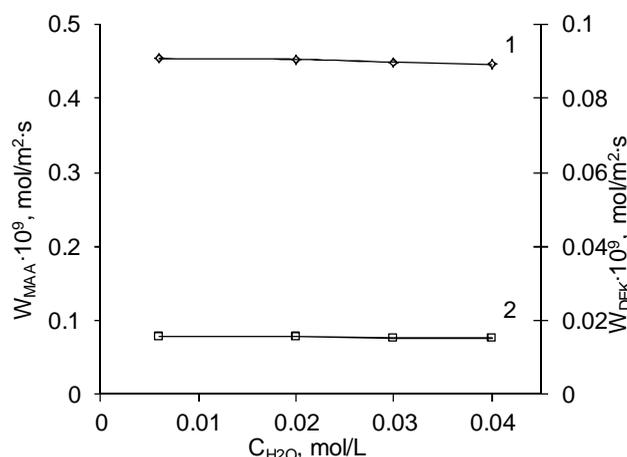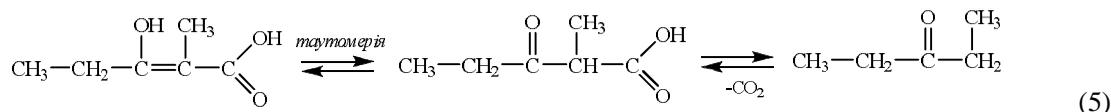
$$\overset{+}{X} \;+\; CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{C}} \;\rightleftharpoons\; CH_3{-}CH_2{-}\underset{\underset{X}{|}}{\overset{\overset{OH}{|}}{\overset{+}{C}}} \;\underset{-H^+}{\rightleftharpoons}\; CH_3{-}\overset{\delta-}{CH}{=}\underset{\underset{X}{|}}{\overset{\overset{OH}{|}}{C}}$$
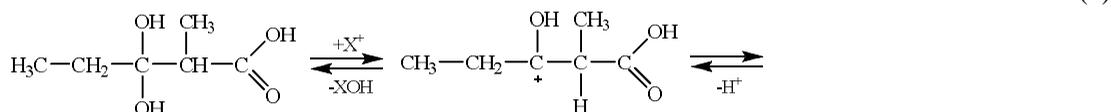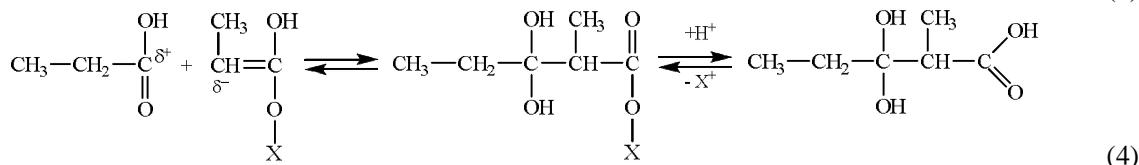
<div align="right">(1)</div>

(2)

(3)

(4)

(5)

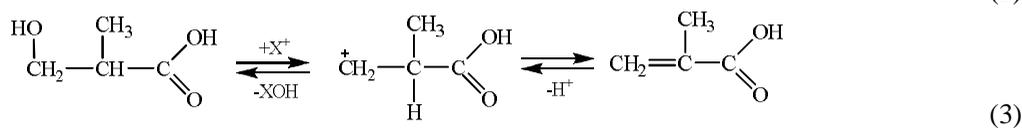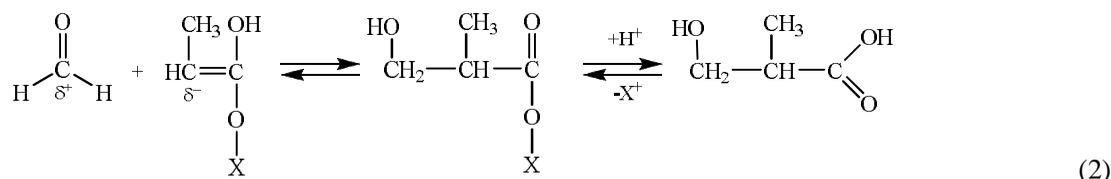**Fig. 5.** The effect of water concentration on the rate of MAA (1) and DEK (2) formation.
$T = 593$ K, $\tau_c = 6$ s, $C_{PA} = 0.002$ mol/l, $C_{FA} = 0.002$ mol/l

Fig. 6. The $1/W_{MAA}$ (1–4) dependence on $1/C_{PA}$ at 563, 593, 623 and 653 K, respectively

As is shown in Fig. 5, the concentration of water slightly affects the rates of MAA and DEK formation. This can be due to the fact that elimination of water from the hydroxy acid formed in the process proceeds very easily in the presence of the acid catalyst, and the dehydration stage is almost completely irreversible at the reaction conditions. Based on the thermodynamic data it has been calculated that the equilibrium conversion of the initial reagents in the condensation process of PA with FA is over 97 %. Taking into account this results and the fact that kinetic research was carried out at low conversion of initial reagents in order
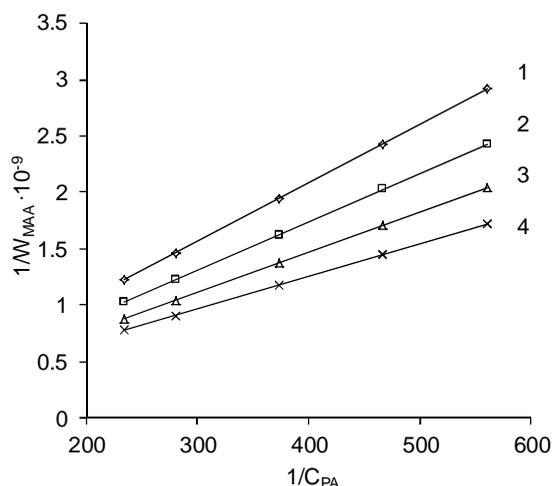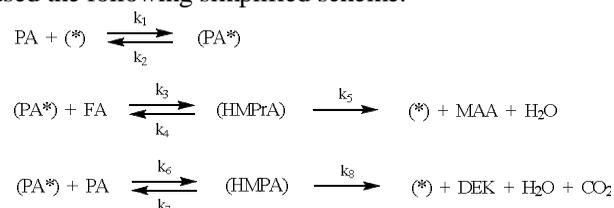
to simplify the kinetic model of investigated reaction, we neglected the effect of water concentration and the reversibility of the dehydration stage.

Therefore, in order to derive the kinetic model we used the following simplified scheme:

$$PA + (*) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (PA*)$$

$$(PA*) + FA \underset{k_4}{\overset{k_3}{\rightleftharpoons}} (HMPrA) \overset{k_5}{\longrightarrow} (*) + MAA + H_2O$$

$$(PA*) + PA \underset{k_7}{\overset{k_6}{\rightleftharpoons}} (HMPA) \overset{k_8}{\longrightarrow} (*) + DEK + H_2O + CO_2$$

where (*) – free active site of the catalyst surface, (PA*) – adsorbed activated PA molecule (methylene compound), (HMPrA) – adsorbed 3-hydroxy-2-methylpropanoic acid, (HMPA) – adsorbed 3-hydroxy-2-methylpentanoic acid.

3.2. The Kinetic Model Derivation

Based on the reaction scheme using the stationary concentrations method we can write the following equations:

$$\frac{d\Theta_1}{dt} = k_1 \cdot C_{PA} \cdot (1 - \Theta_1 - \Theta_2 - \Theta_3) - k_2 \cdot \Theta_1 -$$

$$- k_3 \cdot C_{FA} \cdot \Theta_1 + k_4 \cdot \Theta_2 - k_6 \cdot C_{PA} \cdot \Theta_1 + k_7 \cdot Q_3 = 0$$

$$\frac{d\Theta_2}{dt} = k_3 \cdot C_{FA} \cdot \Theta_1 + k_4 \cdot \Theta_2 - k_5 \cdot Q_2 = 0$$

$$\frac{d\Theta_3}{dt} = k_6 \cdot C_{PA} \cdot \Theta_1 - k_7 \cdot Q_3 - k_5 \cdot Q_2 + k_8 \cdot Q_3 = 0$$

where Θ_1 – the activated PA molecules surface concentration; Θ_2 – the 3-hydroxy-2-methylpropanoic

acid surface concentration; Θ_3 – the 3-hydroxy-2-methylpentanoic acid surface concentration; $(1 - \Theta_1 - \Theta_2 - \Theta_3)$ – free active sites of catalyst surface concentration; C_{PA} – PA concentration; C_{FA} – FA concentration.

Taking into account the constant value of the active sites concentration (quantity) of solid catalyst surface and assuming that $\Theta_1, \Theta_2, \Theta_3 \ll 1$, the obtained equation system is simplified:

$$\frac{d\Theta_1}{dt} = k_1 \cdot C_{PA} - k_2 \cdot \Theta_1 - k_3 \cdot C_{FA} \cdot \Theta_1 +$$

$$+ k_4 \cdot \Theta_2 - k_6 \cdot C_{PA} \cdot \Theta_1 + k_7 \cdot Q_3 = 0$$

$$\frac{d\Theta_2}{dt} = k_3 \cdot C_{FA} \cdot \Theta_1 + k_4 \cdot \Theta_2 - k_5 \cdot Q_2 = 0$$

$$\frac{d\Theta_3}{dt} = k_6 \cdot C_{PA} \cdot \Theta_1 - k_7 \cdot Q_3 - k_5 \cdot Q_2 + k_8 \cdot Q_3 = 0$$

Hence we obtain:

$$\Theta_1 = \frac{k_1 \cdot C_{PA} \cdot (k_7 + k_8) \cdot (k_4 + k_5)}{k_5 \cdot k_3 \cdot (k_7 \cdot C_{FA} + k_8 \cdot C_{FA}) + k_8 \cdot k_6 \cdot (k_4 \cdot C_{PA} + k_5 \cdot C_{PA}) + (k_7 \cdot k_4 \cdot k_2 + k_7 \cdot k_2 \cdot k_5 + k_8 \cdot k_2 \cdot k_4 + k_8 \cdot k_2 \cdot k_5)}$$

$$\Theta_2 = \frac{k_1 \cdot k_3 \cdot C_{PA} \cdot C_{FA} \cdot (k_7 + k_8)}{k_5 \cdot k_3 \cdot (k_7 \cdot C_{FA} + k_8 \cdot C_{FA}) + k_8 \cdot k_6 \cdot (k_4 \cdot C_{PA} + k_5 \cdot C_{PA}) + (k_7 \cdot k_4 \cdot k_2 + k_7 \cdot k_2 \cdot k_5 + k_8 \cdot k_2 \cdot k_4 + k_8 \cdot k_2 \cdot k_5)}$$

$$\Theta_3 = \frac{k_1 \cdot k_6 \cdot C_{PA}^2 \cdot (k_4 + k_5)}{k_5 \cdot k_3 \cdot (k_7 \cdot C_{FA} + k_8 \cdot C_{FA}) + k_8 \cdot k_6 \cdot (k_4 \cdot C_{PA} + k_5 \cdot C_{PA}) + (k_7 \cdot k_4 \cdot k_2 + k_7 \cdot k_2 \cdot k_5 + k_8 \cdot k_2 \cdot k_4 + k_8 \cdot k_2 \cdot k_5)}$$

Let us write the equations of MAA and DEK formation rate and PA and FA consumption rate as follows:

$$W_{MAA} = k_5 \cdot \Theta_2;$$
$$W_{DEK} = k_8 \cdot \Theta_3;$$
$$W_{PA} = k_1 \cdot C_{PA} - k_2 \cdot \Theta_1 + k_6 \cdot C_{PA} \cdot \Theta_1 - k_7 \cdot \Theta_3;$$
$$W_{FA} = k_3 \cdot C_{FA} \cdot \Theta_1 - k_4 \cdot \Theta_3.$$

Substituting the obtained expressions of $\Theta_1, \Theta_2, \Theta_3$ to the rate equations, simplifying the obtained expressions and introducing the designations:

$$\frac{k_5 \cdot k_3 \cdot (k_7 + k_8)}{k_7 \cdot k_4 \cdot k_2 + k_7 \cdot k_2 \cdot k_5 + k_8 \cdot k_2 \cdot k_4 + k_8 \cdot k_2 \cdot k_5} = K_1^{ef}$$

$$\frac{k_8 \cdot k_6 \cdot (k_4 + k_5)}{k_7 \cdot k_4 \cdot k_2 + k_7 \cdot k_2 \cdot k_5 + k_8 \cdot k_2 \cdot k_4 + k_8 \cdot k_2 \cdot k_5} = K_2^{ef}$$

we obtain the kinetic model of gas phase aldol condensation reaction of PA with FA:

$$W_{MAA} = \frac{k_1 \cdot K_1^{ef} \cdot C_{PA} \cdot C_{FA}}{1 + K_1^{ef} \cdot C_{FA} + K_2^{ef} \cdot C_{PA}} \qquad (6)$$

$$W_{DEK} = \frac{k_1 \cdot K_2^{ef} \cdot C_{PA}^2}{1 + K_1^{ef} \cdot C_{FA} + K_2^{ef} \cdot C_{PA}} \qquad (7)$$

$$W_{PA} = k_1 \cdot \frac{K_1^{ef} \cdot C_{PA} \cdot C_{FA} + 2 \cdot K_2^{ef} \cdot C_{PA}^2}{1 + K_1^{ef} \cdot C_{FA} + K_2^{ef} \cdot C_{PA}} \qquad (8)$$

$$W_{FA} = \frac{k_1 \cdot K_1^{ef} \cdot C_{PA} \cdot C_{FA}}{1 + K_1^{ef} \cdot C_{FA} + K_2^{ef} \cdot C_{PA}} \qquad (9)$$

The constants k_1, K_1^{ef} i K_2^{ef} have been calculated by linearization of Eq. (6) in the $1/W_{FA}$ *vs* $1/C_{FA}$ coordinates at the constant FA concentration (Fig. 6):

$$\frac{1}{W_{MAA}} = \frac{K_1^{ef} \cdot C_{FA} + 1}{k_1 \cdot K_1^{ef} \cdot C_{FA}} \cdot \frac{1}{C_{PA}} + \frac{K_2^{ef}}{k_1 \cdot K_1^{ef} \cdot C_{FA}}$$

and by linearization of Eq. (7) at the constant PA concentration (Fig. 7):

$$\frac{1}{W_{DEK}} = \frac{K_1^{ef}}{k_1 \cdot K_2^{ef} \cdot C_{PA}^2} \cdot C_{FA} + \frac{K_2^{ef} \cdot C_{PA} + 1}{k_1 \cdot K_2^{ef} \cdot C_{PA}^2}$$

The values of activation energy of the reactions have been determined from the graphical dependence of $\ln k_i$ on $1/T$ (Fig. 8.).
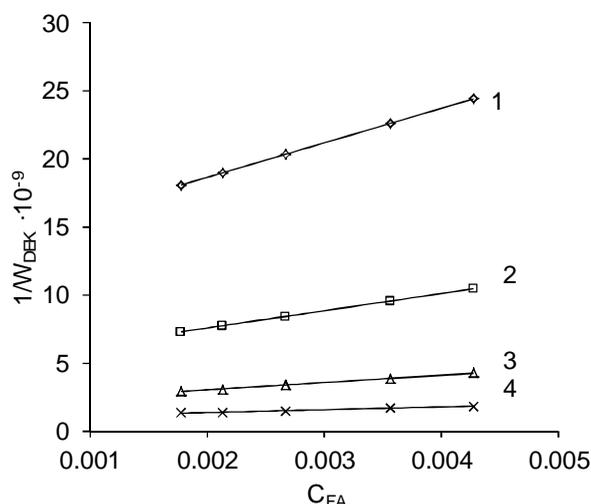
Fig. 7. The $1/W_{DEK}$ dependence on C_{FA} at 563 (1), 593 (2), 623 (3) and 653 (4) K, respectively

Fig. 8. The $\ln k_i$ dependence on $1/T$: $\ln(k_1)$ (1); $\ln(K^{ef}_1)$ (2) and $\ln(K^{ef}_2)$ (3)

The correlation coefficient of the theoretically derived kinetic equations with the experimental data is within 0.95–0.99.

As can be seen from the Table, the activation energy of DEK formation reaction is much higher than the activation energy of MAA formation reaction. Therefore according to the created kinetic model the increase of the reaction temperature must result in decrease of the selectivity of MAA formation, which is confirmed by the experimental data [6-7].

Table

The rate constants of the kinetic equations and their activation energies

T, K	$k_1 \cdot 10^7$, l/m²·s	$K^{ef}_1 \cdot 10^{-2}$, l/m²·s	$K^{ef}_2 \cdot 10^{-2}$, l/m²·s
563	2.44	1.96	0.072
593	2.83	3.05	0.241
623	3.24	4.54	0.716
653	3.66	6.52	1.93
E_a, kJ/mol	13.8	40.8	111.6

4. Conclusions

The kinetic model of the gas phase condensation reaction of PA with FA to MAA in the presence of the B_2O_3-P_2O_5-WO_3/SiO_2 catalytic system was developed. The kinetics of the reaction is fairly well described by Eqs. (6)–(9). Therefore the created kinetic model can be used for the process optimization and technological designing.
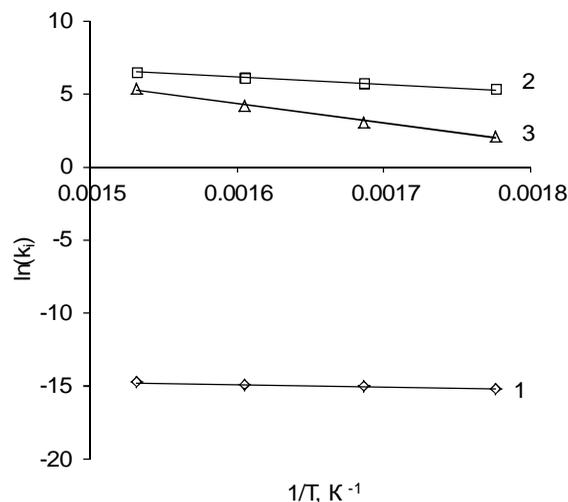
References

[1] Kida K.: Pat. EP0941984, Publ. Sept. 23, 1999.
[2] Watanabe S. and Oh-kita M.: Pat. 6346646 US, Publ. Feb. 12, 2002.
[3] Hino T. and Ogawa A.: Pat. 7304179 US, Publ. Dec. 04, 2007.
[4] Ai M., Fujihashi H., Hosoi S. and Yoshida A.: Appl. Catal. A, 2003, **252**, 185.
[5] True W.: Oil & Gas J., 2012, **110**, 14.
[6] Nagai K.: Appl. Catal. A, 2001, **221**, 367.
[7] Nebesnyi R., Ivasiv V., Zhyznevskyi V., *et al*.: Visnyk Nats. Univ. "Lvivska Polytechnika", 2012, **726**, 184.
[8] Nebesnyi R., Ivasiv V., Zhyznevskyi V., *et al*.: Visnyk Nats. Univ. "Lvivska Polytechnika", 2011, **700**, 205.
[9] Nebesnyi R., Ivasiv V., Zhyznevskyy V. and Pikh Z.: Khim. Promysl. Ukrayiny, 2012, **1**, 3.
[10] Ivasiv V., Pikh Z., Zhyznevskyi V. and Nebesnyi R.: Dop. Nats. Akad. Nauk Ukrainy, 2011, **11**, 126.

КІНЕТИКА РЕАКЦІЇ АЛЬДОЛЬНОЇ КОНДЕНСАЦІЇ ПРОПІОНОВОЇ КИСЛОТИ З ФОРМАЛЬДЕГІДОМ У ГАЗОВІЙ ФАЗІ НА B_2O_3-P_2O_5-WO_3/SiO_2 КАТАЛІЗАТОРІ

Анотація. *Встановлено основні кінетичні законо-мірності реакції альдольної конденсації пропіонової кислоти з формальдегідом у газовій фазі на B_2O_3-P_2O_5-WO_3/SiO_2 каталі-заторі. Запропоновано кінетичні рівняння та розраховано кінетичні параметри. Створена кінетична модель, яка непо-гано описує реакцію конденсації пропіонової кислоти з формальдегідом на запропонованому каталізаторі.*

Ключові слова: *гетерогенний каталіз, газова фаза, альдольна конденсація, швидкість реакції, кінетична модель, акрилатні мономери, акрилова кислота.*