The kinetic model of the combined heterogeneously catalyzed condensation and esterification of propionic acid and methyl propionate with formaldehyde and methanol

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In this work we aim for developing a kinetic model for the methyl methacrylate and methacrylic acid synthesis by the combined condensation and esterification of methyl propionate and propionic acid with formaldehyde and methanol in the presence of the silica-supported boron-phosphorus-oxide catalyst promoted by oxides of tungsten and zirconium. The dependencies of the formation rates of methyl methacrylate, methacrylic acid and diethyl ketone from the concentrations of methyl propionate, propionic acid, formaldehyde and methanol were studied, and reaction orders of every product formation with respect to each reagent were determined. Methacrylic acid is formed predominantly by condensation of methyl propionate with formaldehyde, and methyl methacrylate hydrolysis is insignificantly. The methyl methacrylate formation reaction rate is limited by the methyl propionate adsorption rate on the catalyst surface, and both reactions of methyl methacrylate and methacrylic acid formation are inhibited due to adsorption of formaldehyde, propionic acid and methanol. Based on obtained data, the reaction scheme was offered, which includes formation of intermediates such as 3-hydroxy-2-methylpropanoic acid, its methyl ester and 3,3-dihydroxy-2-methylpentanoic acid. From this reaction scheme the kinetic model was derived using steady state approximation. The reaction rate constants and their activation energies for this model were calculated from experimental data. Validity of the model was experimentally confirmed by the correlation between experimental and theoretically calculated data. Therefore, the developed kinetic model satisfactorily describes the process of the combined condensation and esterification of methyl propionate and propionic acid with formaldehyde and methanol as well as partial cases of condensation of methyl propionate with formaldehyde and propionic acid with formaldehyde, and is suitable for process optimization and technological calculations.

Keywords: heterogeneous catalysis, kinetics, condensation, acrylates, esterification

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Introduction

The condensation processes of carbonyl compounds occupy a prominent place in the organic synthesis industry, since they allow to produce a multitude of valuable products, among which methyl methacrylate (MMA) and methacrylic acid (MAA) are especially important. These compounds are easily polymerized, and therefore are widely used for the production of various polymeric materials with valuable properties. The wide scope of acrylate monomers usage causes a significant annual growth of world demand for them, and as result the need for a new and improved methods for their production [1-3]. Combined condensation and esterification of methyl propionate (MP) and propionic acid (PA) with formaldehyde (FA) and methanol (M) is a prospective method for acrylates production since it allows to use either MP or PA or their mixture as raw materials depending on the market availability, and to produce both MMA and MAA with variable ratio depending on the market demand [4-5]. In the previous research t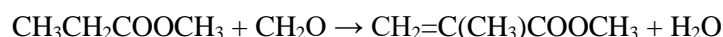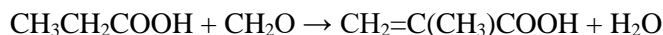he B–P–Zr–W–O$_x$/SiO$_2$ catalytic system was found to be efficient for this process, with total MMA + MAA yield up to 96.3 %, with the sole by-product being diethyl ketone (DEK) which is also valuable product [5]. Further research is needed to establish the process kinetics. Previously we have developed kinetic models for a simpler cases of individual condensation reactions of PA with FA [6] and MP with FA [7]. The aim of this work is to develop a kinetic model for a more complex case of combined condensation and esterification of MP and PA with FA and methanol, suitable for process optimization and technological calculations.

Experiment

The catalyst was prepared by impregnating the silica support with the solutions of boron acid, diammonium hydrogen phosphate, phosphotungstic acid and zirconium oxychloride, with further drying at 423 K for 8 h and calcinating at 673 K for 6 h. Atomic ratio B:P:Zr:W = 3:1:0.15:0.15 was used as it was previously determined as the optimum by the yield and

selectivity of acrylates [5]. Specific surface area of the catalyst was 348 m²/g.

The kinetic was studied in the gas-phase flow tubular reactor (200 mm × 16 mm) with fixed catalyst bed at low (under 30%) reagents conversion to maintain concentrations at quasi-stationary values. Catalyst load was 16 g. Analytical research grade methyl propionate, propionic acid, methanol and paraformaldehyde were used. 36 wt.% formaldehyde water solution was prepared from paraformaldehyde immediately before the experiments. MP, PA and methanol concentrations in the gas phase were varied in the range $3.74 \cdot 10^{-3}$ – $7.48 \cdot 10^{-3}$ mol/l, while FA $1.25 \cdot 10^{-2}$ – $2.49 \cdot 10^{-2}$ mol/l to account for its double stoichiometric consumption. While varying the initial concentration of one reactant, initial concentrations of others were kept constant. Analysis was done on Agilent 5890 SII gas chromatograph equipped with FID and TCD detectors, using Supelcowax 10 column (30 m × 0.53 mm) and helium as carrier gas.

Results and discussion

Generally, the investigated process can be described by the following reactions:

$$CH_3CH_2COOH + CH_2O \rightarrow CH_2=C(CH_3)COOH + H_2O$$

$$CH_3CH_2COOH + CH_2O + CH_3OH \rightarrow CH_2=C(CH_3)COOCH_3 + 2\ H_2O$$

$$CH_3CH_2COOCH_3 + CH_2O \rightarrow CH_2=C(CH_3)COOCH_3 + H_2O$$

$$2\ CH_3CH_2COOH \rightarrow (CH_3CH_2)_2CO + H_2O + CO_2$$

The dependencies of the products (MMA, MAA and DEK) formation rates from the reagent (MP, PA, FA and methanol) concentrations were studied in the temperature range 593 – 683 K. The results at 653 K are shown in the Fig. 1.
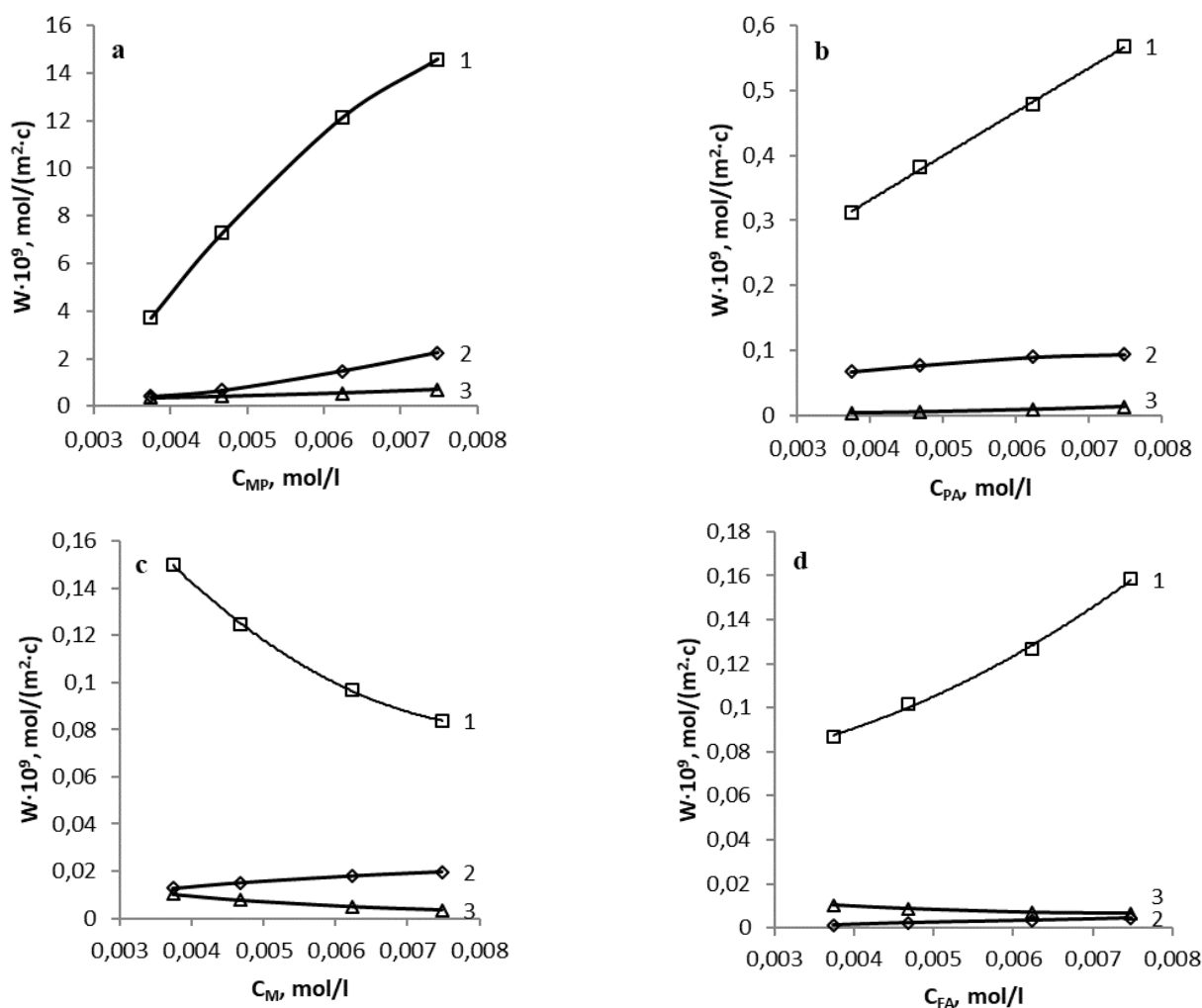
Fig. 1. Dependence of the initial formation rate of methacrylic acid (1), methyl methacrylate (2) and diethyl ketone (3) from each individual reagent initial concentration: methyl propionate (a), propionic acid (b), methanol (c) and formaldehyde (d) at reaction temperature 653 K
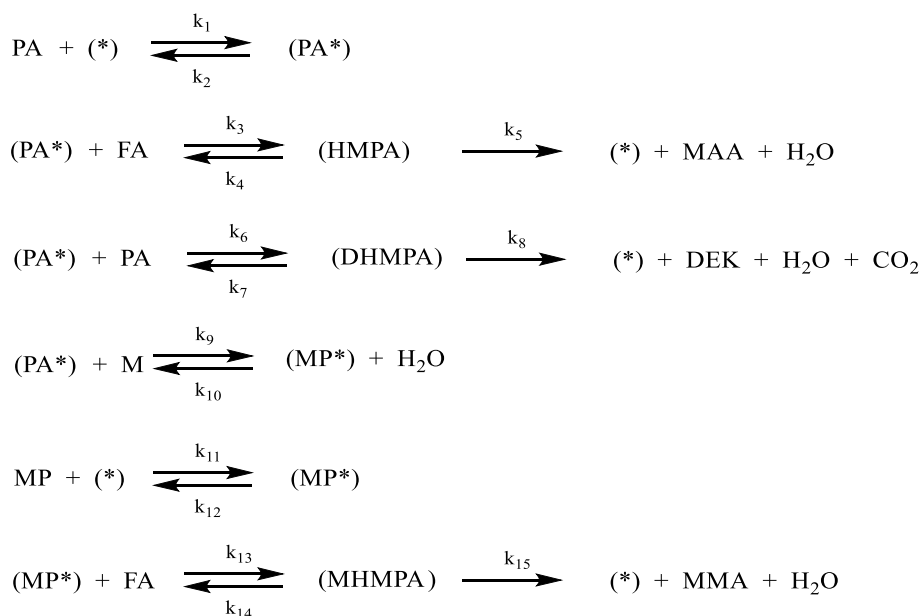
From experimental data, it has been established that the MMA formation reaction in the presence of the B–P–Zr–W–O$_x$/SiO$_2$ catalytic system has the order close to first (0.93 – 1) with respect to MP and a bit less than one (0.8 – 0.9) with respect to PA (Fig. 1a–1b, curve 1). The order of the MMA formation is significantly lower than one and is 0.3 – 0.5 (Fig. 1c, curve 1), which indicates the limiting of the MMA formation reaction rate by the MP adsorption rate on the surface of the catalyst, similar to the individual condensation reaction of MP with FA [7]. The order of MMA formation with respect to methanol is also substantially smaller than one and is 0.2 – 0.4 (Fig. 1d, curve 1).

The reaction of MAA formation has the order of 0.7 – 0.95 with respect to MP and 0.9 – 0.97 with respect to PA, while the order with respect to FA is around 0.7 – 0.8 (Fig. 1a–1c, curve 2). Similarly, to the individual condensation reaction of MP with FA [7], an increase in the FA concentration inhibits the MMA formation rate, but increases MAA formation rate, which indicates that MAA is formed predominantly by condensation of PA with FA, and MMA hydrolysis is insignificant. With respect to methanol, MMA formation has the order a bit under zero (-0.1 – -0.2), since methanol does not participate in the MAA formation and inhibits this reaction (Fig. 1d, curve 2). It should be noted that both reactions of MMA and MAA formation are inhibited due to adsorption of FA, PA and methanol on the surface of the catalyst.

The reaction of the formation of DEK has an order of somewhat less than 2 with respect to MP (1.4 – 1.8) and PA (1.8 – 1.94) (Fig. 1a–1b, curve 3), which confirms that the rate of DEK formation is limited by the rate of interaction of PA molecules adsorbed on the catalyst surface with free PA molecules from the reaction volume, and in addition is slightly inhibited by MP due to its adsorption on the catalyst surface. Also the reaction of the DEK formation has the order a bit under zero with respect to FA (-0.05 – -0,015) and with respect to methanol (-0.1 – -0.2), and hence is inhibited by both reagents (Fig. 1c–1d, curve 3).

Based on this data, the following reaction scheme can be derived for the process of combined condensation and esterification of MP and PA with FA and methanol. PA molecules are adsorbed on active sites of the catalyst surface with the formation of activated methylene component, which are next attacked by FA molecules from the reaction volume with the formation of adsorbed 3-hydroxy-2-methylpropanoic acid, which is next dehydrated to MAA. In the case of the interaction of an adsorbed PA molecule with another PA molecule, 3,3-dihydroxy-2-methylpentanoic acid is formed, which is next converted into DEK due to the splitting out of CO$_2$ and water. In the case of interaction of an adsorbed molecule of PA with methanol from reaction volume, the formation of an activated MP molecule occurs. Also activated MP molecules are formed as a result of adsorption of MP from reaction volume on free active sites on the catalyst surface. Interaction of activated MP molecules with FA molecules from reaction volume leads to the formation of adsorbed methyl ester of 3-hydroxy-2-methylpropanoic acid, which due to dehydration is next transformed into MMA. Taking into account the practical irreversibility of dehydration reactions in the reaction conditions [6, 7], the following scheme was used to derive the kinetic model:

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

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

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

$$(PA*) + M \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} (MP*) + H_2O$$

$$MP + (*) \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} (MP*)$$

$$(MP*) + FA \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} (MHMPA) \overset{k_{15}}{\rightarrow} (*) + MMA + H_2O$$

where (*) – free active site on the catalyst surface, (MP*) – adsorbed activated MP, (PA*) – adsorbed activated PA, (MHMPA) – adsorbed methyl ester of 3-hydroxy-2-methylpropanoic acid, (HMPA) – adsorbed 3-hydroxy-2-methylpropanoic acid, M – methanol, (DHMPA) – adsorbed 3,3-dihydroxy-2-methyl pentanoic acid.

Based on the above reaction scheme and using steady state approximation, the following equations for

$$d\Theta_1/dt = k_1 \cdot C_{PA} \cdot (1 - \Theta_1 - \Theta_2 - \Theta_3 - \Theta_4 - \Theta_5) - k_2 \cdot \Theta_1 - k_3 \cdot C_{FA} \cdot \Theta_1 + k_4 \cdot \Theta_2 - k_6 \cdot C_{PA} \cdot \Theta_1 + k_7 \cdot \Theta_3 + k_{10} \cdot \Theta_4 - k_9 \cdot \Theta_1 \cdot C_M = 0$$
$$d\Theta_2/dt = k_3 \cdot C_{FA} \cdot \Theta_1 - k_4 \cdot \Theta_2 - k_5 \cdot \Theta_2 = 0$$
$$d\Theta_3/dt = k_6 \cdot C_{PA} \cdot \Theta_1 - k_7 \cdot \Theta_3 - k_8 \cdot \Theta_3 = 0$$
$$d\Theta_4/dt = k_{11} \cdot C_{MP} \cdot (1 - \Theta_1 - \Theta_2 - \Theta_3 - \Theta_4 - \Theta_5) - k_{12} \cdot \Theta_4 - k_{13} \cdot C_{FA} \cdot \Theta_4 + k_{14} \cdot \Theta_5 - k_{10} \cdot \Theta_4 + k_9 \cdot \Theta_1 \cdot C_M = 0$$
$$d\Theta_5/dt = k_{13} \cdot C_{FA} \cdot \Theta_4 - k_{14} \cdot \Theta_5 - k_{15} \cdot \Theta_5 = 0$$

where:
Θ_1 – surface concentration of activated PA molecules;
Θ_2 – surface concentration of 3-hydroxy-2-methylpropanoic acid;
Θ_3 – surface concentration of 3,3-dihydroxy-2-methylpentanoic acid;
Θ_4 – surface concentration of activated MP molecules;
Θ_5 – surface concentration of methyl ester of 3-hydroxy-2-methylpropanoic acid;

intermediates formation rates can be formulated:

$(1 - \Theta_1 - \Theta_2 - \Theta_3 - \Theta_4 - \Theta_5)$ – concentration of free active catalytic sites;
C_{MP} – concentration of MP in reaction volume;
C_{PA} – concentration of PA in reaction volume;
C_{FA} – concentration of FA in reaction volume;
C_M – concentration of methanol in reaction volume.

Considering that total concentration of catalyst's active sites is constant, and assuming Θ_1, Θ_2, Θ_3, Θ_4, $\Theta_5 \ll 1$, we can simplify these equations:

$$d\Theta_1/dt = k_1 \cdot C_{PA} - k_2 \cdot \Theta_1 - k_3 \cdot C_{FA} \cdot \Theta_1 + k_4 \cdot \Theta_2 - k_6 \cdot C_{PA} \cdot \Theta_1 + k_7 \cdot \Theta_3 + k_9 \cdot C_{MP} - k_{10} \cdot \Theta_1 \cdot C_M = 0$$
$$d\Theta_2/dt = k_3 \cdot C_{FA} \cdot \Theta_1 - k_4 \cdot \Theta_2 - k_5 \cdot \Theta_2 = 0$$
$$d\Theta_3/dt = k_6 \cdot C_{PA} \cdot \Theta_1 - k_7 \cdot \Theta_3 - k_8 \cdot \Theta_3 = 0$$
$$d\Theta_4/dt = k_{11} \cdot C_{MP} - k_{12} \cdot \Theta_4 - k_{13} \cdot C_{FA} \cdot \Theta_4 + k_{14} \cdot \Theta_5 - k_9 \cdot \Theta_4 + k_{10} \cdot \Theta_1 \cdot C_M = 0$$
$$d\Theta_5/dt = k_{13} \cdot C_{FA} \cdot \Theta_4 - k_{14} \cdot \Theta_5 - k_{15} \cdot \Theta_5 = 0$$

from where we can derive Θ_1, Θ_2, Θ_3, Θ_4, Θ_5 via reagents concentrations and rate constants.
Based on the reaction scheme the following equations can be formulated for the formation rates of MMA, MAA, PA and DEK:

$$W_{MMA} = k_{15} \cdot \Theta_5;$$
$$W_{MAA} = k_5 \cdot \Theta_2;$$
$$W_{PA} = k_1 \cdot C_{PA} - k_2 \cdot \Theta_1 + k_6 \cdot C_{PA} \cdot \Theta_1 - k_7 \cdot \Theta_3;$$
$$W_{DEK} = k_8 \cdot \Theta_3.$$

Substituting here the values of Θ_1, Θ_2, Θ_3, Θ_4, Θ_5, with the values derived from steady state equations, and simplifying the resulting equations by designating specific expressions of rate constants $k_1 - k_{15}$ as effective rate constants $k^{ef}_1 - k^{ef}_{10}$, we get the following final kinetic model of combined condensation and esterification of MP and PA with FA and methanol:

$$W_{MMA} = \frac{K^{ef}_5 \cdot C_{MP} \cdot C_{FA} + K^{ef}_7 \cdot C_{PA} \cdot C_{FA} \cdot C_M}{1 + K^{ef}_6 \cdot C_{FA} + K^{ef}_2 \cdot C_{PA} + K^{ef}_8 \cdot C_M} \quad (1)$$

$$W_{MAA} = \frac{K^{ef}_3 \cdot C_{PA} \cdot C_{FA}}{1 + K^{ef}_1 \cdot C_{FA} + K^{ef}_2 \cdot C_{PA} + K^{ef}_8 \cdot C_M} \quad (2)$$

$$W_{DEK} = \frac{K^{ef}_4 \cdot C_{PA}^2}{1 + K^{ef}_1 \cdot C_{FA} + K^{ef}_2 \cdot C_{PA} + K^{ef}_8 \cdot C_M} \quad (3)$$

$$W_{MP} = K^{ef}_9 \cdot C_{MP} - K^{ef}_{10} \cdot \frac{W_{MMA}}{C_{FA}} \quad (4)$$

$$W_{PA} = W_{MMA} + W_{MAA} + 2 \cdot W_{DEK} - W_{MP} \quad (5)$$

$$W_{FA} = W_{MMA} + W_{MAA} \quad (6)$$

$$W_M = W_{MMA} - W_{MP} \quad (7)$$

Effective rate constants K^{ef}_1, K^{ef}_2, K^{ef}_3, K^{ef}_4 were calculated from experimental data by linearization of equation (2) in the coordinates $1/W_{MAA} - 1/C_{PA}$ with stationary concentrations of FA and methanol (Fig. 2a):

$$\frac{1}{W_{MAA}} = \frac{K^{ef}_1 \cdot C_{FA} + K^{ef}_8 \cdot C_M + 1}{K^{ef}_3 \cdot C_{FA}} \cdot \frac{1}{C_{PA}} + \frac{K^{ef}_2}{K^{ef}_3 \cdot C_{FA}}$$

and by linearization of equation (3) in the coordinates $1/W_{DEK} - C_{FA}$ with stationary concentrations of PA and methanol (Fig. 2b):

$$\frac{1}{W_{DEK}} = \frac{K^{ef}_1}{K^{ef}_4 \cdot C_{PA}^2} \cdot C_{FA} + \frac{K^{ef}_2 \cdot C_{PA} + K^{ef}_8 \cdot C_M + 1}{K^{ef}_4 \cdot C_{PA}^2}$$

Constants K^{ef}_5, K^{ef}_6, K^{ef}_7, K^{ef}_8 were calculated from the equation (1), and constants K^{ef}_9, K^{ef}_{10} – from the equation (4) using data fitting by the least squares method.

Activation energy of effective rate constants $K^{ef}_1 - K^{ef}_{10}$, were determined from the Arrhenius equation linearization in the coordinates $\ln(K) - 1/T$ (Fig. 3).
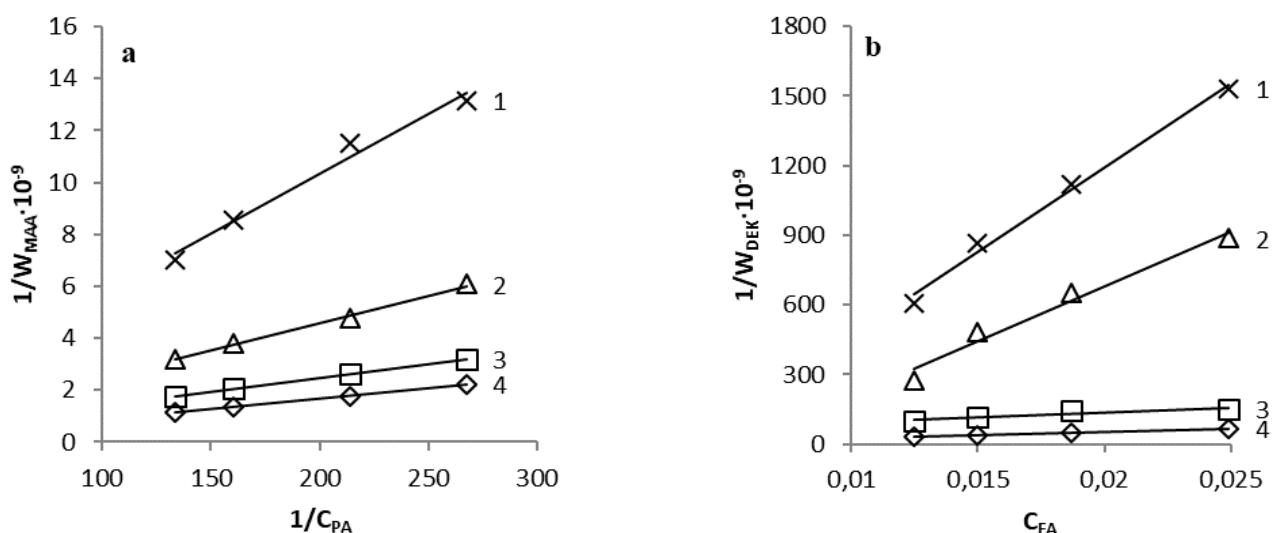
Fig. 2. Linearization of equation (2) in the coordinates $1/W_{MAA} - 1/C_{PA}$ (a) and equation (3) in the coordinates $1/W_{DEK} - C_{FA}$ (b).
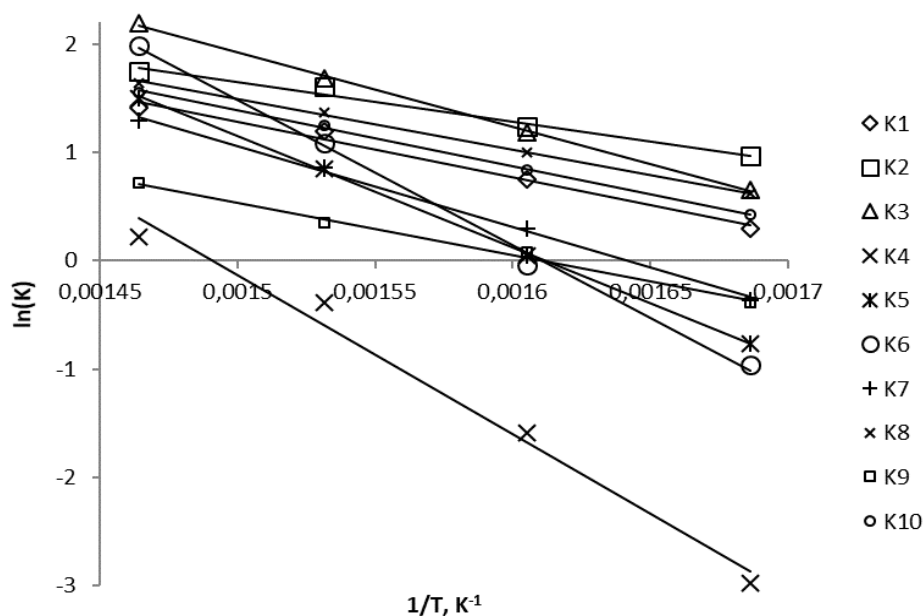
Fig. 3. Linearization of the Arrhenius equation in the coordinates $\ln(K) - 1/T$.

Resulting values of effective rate constants and their activation energies are shown in the Table 1. The correlation coefficient between the experimental data of the reaction rates dependencies on the reagents concentrations and theoretically calculated data from the kinetic equations (1) – (7) is 0.95 – 0.99. Thus, we can conclude that the developed kinetic model well describes the process of gas-phase combined condensation and esterification of MP and PA with FA and methanol in the presence of a B–P–Zr–W–O_x/SiO_2 catalyst, and can be used for technological calculation.

The kinetic model (1) – (7) also can be used for the partial cases of the studied process. By equating concentrations of methanol and MP to zero ($C_M = 0$, $C_{MP} = 0$), the kinetic model transforms in the one for the condensation of PA with FA to MAA described in [6]. Similarly, by equating only the methanol concentration to zero ($C_M = 0$), the model describes the process of condensation of MP with FA to MAA and MMA [7]. Therefore, the kinetic model (1) – (7) can be used as a general model for kinetics of various cases of acrylic monomer synthesis by aldol condensation reactions.

Table 1. **Rate constants of the equations (1) – (7) and their activation energies**.

T, K	$K^{ef}_1 \cdot 10^{-2}$, $\dfrac{dm^3}{mol}$	$K^{ef}_2 \cdot 10^{-2}$, $\dfrac{dm^3}{mol}$	$K^{ef}_3 \cdot 10^{6}$, $\dfrac{dm^6}{mol \cdot m^2 \cdot s}$	$K^{ef}_4 \cdot 10^{5}$, $\dfrac{dm^6}{mol \cdot m^2 \cdot s}$	$K^{ef}_5 \cdot 10^{5}$, $\dfrac{dm^6}{mol \cdot m^2 \cdot s}$	$K^{ef}_6 \cdot 10^{-2}$, $\dfrac{dm^3}{mol}$	$K^{ef}_7 \cdot 10^{7}$, $\dfrac{dm^9}{mol^2 \cdot m^2 \cdot s}$	$K^{ef}_8 \cdot 10^{-3}$, $\dfrac{dm^3}{mol}$	$K^{ef}_9 \cdot 10^{-2}$, $\dfrac{dm^3}{m^2 \cdot s}$	$K^{ef}_{10} \cdot 10^{-3}$, $\dfrac{mol}{dm^3}$
593	1.348	2.624	1.924	0.0457	0.464	0.384	0.694	1.853	0.678	1.527
623	2.126	3.458	3.268	0.2044	1.045	0.962	1.347	2.729	1.082	2.321
653	3.294	4.955	5.371	0.6817	2.341	2.957	2.354	3.924	1.419	3.486
683	4.118	5.725	8.983	1.2452	4.487	7.276	3.629	5.172	2.041	4.743
E_a, kJ/mol	42.7	30.3	57.4	125.6	85.5	111.4	62.1	38.7	40.2	42.7

Conclusions

In this work we developed the kinetic model for the gas-phase combined condensation and esterification of methyl propionate and propionic acid with formaldehyde and methanol in the presence of a B–P–Zr–W–O$_x$/SiO$_2$ catalyst. The kinetic model well describes the process as whole as well as partial cases of condensation of methyl propionate with formaldehyde and propionic acid with formaldehyde. Validity of the model was experimentally confirmed by the correlation between experimental and theoretically calculated data.

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Кінетична модель сумісної гетерогенно-каталітичної конденсації та естерифікації пропіонової кислоти та метилпропіонату з формальдегідом та метанолом

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Метою даної роботи є розробка кінетичної моделі синтезу метилметакрилату та метакрилової кислоти шляхом комбінованої конденсації та естерифікації метилпропіонату та пропіонової кислоти з формальдегідом та метанолом у присутності нанесеного на силікагель бор-фосфор-оксидного каталізатора, промотованого оксидами вольфраму та цирконію. Встановлено залежності швидкостей утворення метилметакрилату, метакрилової кислоти та діетилкетону від концентрацій метилпропіонату, пропіонової кислоти, формальдегіду та метанолу, а також порядки реакцій формування кожного продукту за кожним з реагентів. Результати показали, що метакрилова кислота утворюється переважно конденсацією метилпропіонату з формальдегідом, а гідроліз метилметакрилату є незначним. Швидкість реакції формування метилметакрилату лімітується швидкістю адсорбції метилпропіонату на поверхні каталізатора, а обидва реакції утворення метилметакрилату та метакрилової кислоти гальмуються через адсорбцію формальдегіду, пропіонової кислоти та метанолу на поверхні каталізатора. Виходячи з отриманих даних, запропоновано схему реакцій, яка включає утворення проміжних сполук, таких як 3-гідрокси-2-метилпропанова кислота, її метиловий ефір, та 3,3-дигідрокси-2-метилпентанова кислота. З цієї схеми реакцій була виведена кінетична модель з використанням методу стаціонарних концентрацій. Константи швидкості реакції та їх активації для цієї моделі були розраховані з експериментальних даних. Дійсність моделі експериментально підтверджено кореляцією між експериментальними та теоретично розрахованими даними. Таким чином, розроблена кінетична модель добре описує процес комбінованої конденсації та естерифікації метилпропіонату та пропіонової кислоти з формальдегідом та метанолом, а також часткові випадки конденсації метилпропіонату з формальдегідом та пропіонової кислоти з формальдегідом, і підходить для оптимізації процесу та технологічних розрахунків.

Ключові слова: гетерогенний каталіз, кінетика, конденсація, акрилати, естерифікація