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CONSTRUCTION OF A KINETIC MODEL FOR THE OXIDATION OF C₃-C₄-ALDEHYDES ON HETEROPOLY COMPOUNDS

Abstract. The kinetic regularities of oxidation of unsaturated aldehydes acrolein and methacrolein into corresponding acids have been studied on modified phosphormolybdenum heteropoly acid catalysts. It was found that methacrylic acid is formed according to the sequential scheme, and deep oxidation products according to the parallel-sequential scheme. The analysis of experimental data shows that the acetic acid yield on heteropolyacetic acid catalysts is high enough and can reach 30%. Therefore, it is incorrect to neglect the route of acetic acid formation when assessing the kinetics of the process. Differential equations were made to process the experimental data on the kinetics of aldehyde oxidation. The developed kinetic model can be used to model the reaction apparatus.

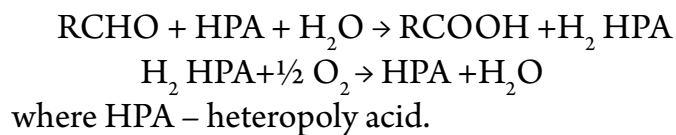
Keywords: kinetics, heteropolyacids, acrolein, methacrolein, acrylic, and methacrylic acid.

There are almost no data in the literature on the kinetics of acrolein or methacrolein oxidation on hetero compounds. For example, [1] provides only brutto-equations for the rate of formation of methacrylic acid (MAA) and the rate of consumption of methacrolein (MACR).

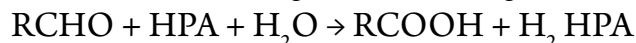
$$-\frac{d[\text{MA}]}{dt} = K_1 P_{\text{MACR}}^{0,6-1} \times P_{\text{O}_2}^{0,2} P_{\text{H}_2\text{O}}^0 P_{\text{O}_2}^{0-0,2} P_{\text{H}_2\text{O}}^0$$

$$\frac{d[\text{MAK}]}{d\tau} = K_2 P_{\text{MACR}}^{0,5-1} \times P_{\text{O}_2}^{0,1-0,2} P_{\text{H}_2\text{O}}^0$$

In [2], it is pointing out that the reaction proceeds by the redox mechanism through the following stages:



It follows from the following kinetic equations that the next stage is the limiting one:



As can be seen from the equations, the rate of methacrylic acid formation and methacrolein consumption weakly depend on oxygen concentration, the order of methacrolein changes from 1 to 0,5, and this agrees with our experimental data.

In [3], some kinetic regularities of the oxidation of methacrolein into methacrylic acid on a modified phosphoromolybdenum catalyst are

also given. The research work shows that the conversion of methacrolein increases markedly with increasing temperature and does not depend on the initial concentration of methacrolein in the contact time interval studied, and this is also following the results of our studies.

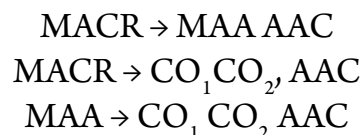
An analysis of the literature data showed different points of view on the mechanism of acetic acid formation. In [4], it is shown that the afterburning of methacrylic acid leads to the formation of the same products as in the case of heteropoly acid catalyst. However, this conclusion is based on kinetic data, but there are no experiments on the direct attainment of methacrylic acid in this work.

To determine the mechanism of acetic acid formation during the oxidation of methacrolein into methacrylic acid, the authors of [2] performed a qualitative experiment on a modified phosphoromolybdenum heteropoly acid catalyst to transform methacrolein in an empty reactor.

It turned out that methacrolein is pre-oxidized in the presence of air at $t = 330$ °C into acetic acid, acrylic acid, and carbon oxides. The same products are formed during the pre-oxidation of methacrylic acid.

Thus, according to the authors [2], sequential products of deep oxidation form methacrylic acid by a parallel-sequential scheme. The yield of acetic acid formed during the oxidation of methacrolein in the desired temperature range was < 5%. Therefore, specially staged schemes of acetic acid formation in work [3] are not reflected.

Based on the data on the oxidation of methylacrolein and afterburning of methacrylic acid, as well as on the dependence of the selectivity of methacrylic acid formation on the degree of aldehyde transformation, the general scheme of the methacrolein oxidation process appears as follows:



Analysis of the kinetic data allows us to show that the following equations describe the process rates for routes 1–3:

$$\begin{aligned} R_1 &= \frac{K_1 P_{\text{MACR}} P_{\text{O}_2}}{(1 + \alpha P_{\text{O}_2})} \\ R_2 &= \frac{K_2 P_{\text{MACR}} P_{\text{O}_2}}{(1 + \alpha P_{\text{O}_2})} \\ R_3 &= \frac{K_3 P_{\text{MACR}} P_{\text{O}_2}}{(1 + \alpha P_{\text{O}_2})} \end{aligned}$$

Expressions for the rate of consumption of methacrolein (W_{MACR}), the rate of formation of methacrylic acid (W_{MAA}), and the rate of formation of deep oxidation products (W_{PDO}) in excess oxygen are as follows:

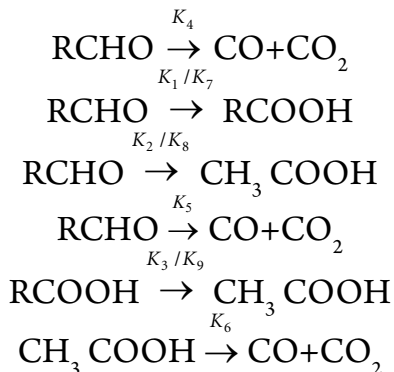
$$\begin{aligned} W_{\text{MACR}} &= (K_1 + K_2) P_{\text{MACR}} \\ W_{\text{MAA}} &= K_1 P_{\text{MACR}} - K_3 P_{\text{MAA}} \\ W_{\text{PDO}} &= K_2 P_{\text{MACR}} + K_3 P_{\text{MAA}} \end{aligned}$$

The values of constants $K_1 - K_2$ were determined from experimental data as the angular coefficients of the corresponding linear anamorphoses W_{MAA} from P_{MACR} and W_{MACR} from P_{MAA} at different temperatures. The values of the constants (C^{-1}), also determined by the experiment, were equal:

$$\begin{aligned} K_1 &= 5.8 \cdot 10^7 \text{ EXP}(-22000/\text{RT}) \\ K_2 &= 1.4 \cdot 10^5 \text{ EXP}(-18000/\text{RT}) \\ K_3 &= 8.0 \cdot 10^{13} \text{ EXP}(-40000/\text{RT}) \end{aligned}$$

Analysis of experimental data [4] shows that the yield of acetic acid on heteropoly acid catalysts is high enough and can be up to 30%. Therefore, it is incorrect to neglect the route of acetic acid formation when assessing the kinetics of the process. In this connection, it becomes evident that a parallel-sequential scheme can describe the set of reactions occurring during the oxida-

tion of methacrolein on modified heteropolyacid catalysts.



Based on the above, the following differential equations were made to process the experimental data on the kinetics of aldehyde oxidation:

$$\frac{dP_{\text{AAD}}}{d\tau} = -\frac{K_1 P_{\text{AAD}}}{1 + K_7 P_{\text{acid}}} - \frac{K_2 P_{\text{AAD}}}{1 + K_8 P_{\text{AAC}}} - K_4 P_{\text{AAD}}$$

$$\frac{dP_{\text{acid}}}{d\tau} = \frac{K_1 P_{\text{AAD}}}{1 + K_7 P_{\text{acid}}} - \frac{K_3 P_{\text{acid}}}{1 + K_9 P_{\text{AAC}}} - K_5 P_{\text{acid}}$$

$$\frac{dP_{\text{AAC}}}{d\tau} = \frac{K_2 P_{\text{AAD}}}{1 + K_8 P_{\text{AAC}}} + \frac{K_3 P_{\text{acid}}}{1 + K_9 P_{\text{AAC}}} - K_6 P_{\text{AAC}}$$

Initial conditions:

$$\text{With } \tau = 0 \quad P_{\text{AAD}}(0) = P_{\text{AAD}}^0, \quad P_{\text{acid}}(0) = P_{\text{acid}}^0 \quad \text{и} \quad P_{\text{AAC}}(0) = P_{\text{AAC}}^0$$

An optimization criterion of the species was formulated to determine the kinetic parameters of $K_1 - K_9$:

$$F = \sum_{i=1}^M \cdot \sum_{j=1}^N \left(\frac{P_{ij}^E - P_{ij}^C}{P_{ij}^E} \right)^2$$

where E – experimental, C – calculated and constraints on the kinetic parameters in the form of $K_{oi} > 0$

$$a_i \leq E_i \leq C_i$$

where K_i – the rate constant of chemical reactions, $i = 1, 9$,

E_i – activation energy,

K_{oi} – pre-exponential factor,

a_i and c_i – respectively lower and upper limits of changes in the activation energies,

P_{ij}^E – experimental process data,

P_{ij}^C – accounting data,

M and N – number of temperatures and experimental points.

The system and initial conditions together constitute the Cauchy problem for the first order ordinary differential equations. The problem was solved by the Runge-Kutta-Merson method with automatic selection of the integration step. The optimization criterion $a_i \leq F_i \leq C_i$ is an additive function that depends on the input and output variables of the states and the kinetic parameters of the process.

To determine the kinetic parameters $K_1 - K_9$, the following problem of optimization conditions was set: it is required to find such equations K_{oi} , $F_i (i = \overline{1,9})$, that satisfy the constraints $a_i \leq F_i \leq C_i$, at which the target function F takes a minimum value.

We used the sliding acceptance and Powell methods to determine the kinetic parameters. These methods are optimization methods based on a direct comparison of function values at neighboring points.

Calculated isotherms, compared with experimental data, showed that there is a good correspondence between them.

Based on the above, the following conclusions can be made: the developed kinetic model can be the basis for modeling the reaction apparatus.

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