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Investigation of the Kinetics and the Development of a Mathematical Model for the Synthesis of Propylene Oxide in Methanol Environment

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Abstract

Kinetics of propylene epoxidation using an aqueous solution of hydrogen peroxide in the presence of titanium-containing zeolite was studied. An effect of concentration reagent and reaction product concentration and the temperature on the reaction rate was considered. Basing on the experimental data obtained, a mathematical model of the process was proposed to calculate the reaction rate constants, adsorption equilibrium and activation energy.

Key words: propylene oxide, kinetic model, epoxidation, titanium-containing zeolite

INTRODUCTION

Propylene oxide is one of the most important products of basic organic and petrochemical synthesis. With a high reactivity, it readily reacts with compounds of different classes, which allows one to obtain on its base a large amount of products. Propylene oxide is used for the production of antifreezes, solvents, plasticizers, detergents, *etc.* [1]. However, more than 80 % of the obtained propylene oxide is used for the production of hard and soft polyurethanes. Owing to a unique set of physical and mechanical properties, polyurethanes are widely used in various industries: construction, transport, *etc.*

At the present time, according to the most of researchers, the most promising way is assumed to consist in direct liquid-phase epoxidation of propylene with an aqueous solution of hydrogen peroxide in an organic solvent in the presence of a heterogeneous titanium containing catalyst [2, 3]. According to the assessments by European experts, in the future, eight among ten plants for the production of propylene oxide will be based on this technology. A distinctive feature of the process consists in the fact that it is carried out at moderate temperature values (30–60 °C), low pressure (6–8 atm), being at the same time environmentally safe, since the main by-product of the process represents water.

The aim of this work consisted in studying the kinetics and in obtaining a mathematical model for the process of propylene epoxidation using an aqueous solution of hydrogen peroxide in the environment of methyl alcohol on the surface of titanium-containing zeolite under the conditions of a cyclic reactor.

EXPERIMENTAL

In the experiments we used the following reagents: analytical (ch. d. a.) grade methyl alcohol (State Standard 2222–95), pure (ch.) grade propylene oxide (PO) (GOST 23001–88), special purity (os. ch.) grade 33–34 % hydrogen peroxide solution (engineering specifications TU 2611-069-05807977–2006), propylene (GOST 25043–87).

The oxidation of propylene (P) was performed in a thermostatic metal reactor at 30–60 °C under vigorous stirring (200–600 rpm). Reading the time was started at the moment of adding 0.38–1.96 mol/dm^3 of H_2O_2 to a reaction mixture containing 1.47–2.91 mol/dm^{3}of propylene 15.27–19.67 mol/dm^3 of methanol (M), the catalyst content being equal to 4.74–5.13 g/dm^3. The catalyst under use represented a titanium-containing zeolite powder, prepared according to the procedure described in [4] (the content of Ti as calculated for TiO_2 being equal to 3.16 %, ratio Si/Ti = 25, pore size 5.1 × 5.5 nm and 5.3 × 5.6 nm).

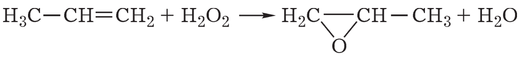
The oxidation products were identified from mass spectra thereof. The chromatography-mass spectrometry analysis was performed using a Crystal MS unit equipped with a Thermo Electron DSQ II mass spectrometric detector. The content of propylene oxide, 1-methoxy-2-propanol (1MP2), 2-methoxy-1-propanol (2MP1), and 1,2-propanediol (PD) was determined by means of GLC. For GLC analysis, we used a Chromos GC-1000 chromatograph equipped with a flame ionization detector and a stainless steel column 3 mm in diameter and 3 m long, packed with a Chromaton-N-AW carrier coated by a Carbowax 6000 adsorbent (15 % with respect to the mass of the carrier). The content of hydrogen peroxide in the reaction mixtures was monitored by means of iodometric titration.

The techniques used were evaluated according to the results of 5–7 replicates, whose mean square error did not exceed 5 %.

RESULTS AND DISCUSSION

The development of mathematical model represents a sequence of stages involving the thermodynamic analysis of processes, charting a scheme of transformations, identifying the most important details of the mechanism, as well as constructing a kinetic model to find its parameters basing on a formal mechanism of the reactions.

The formation of target product occurs *via* the following reaction:

 (1)

$$H_3C-CH=CH_2 + H_2O_2 \longrightarrow H_2C\underset{O}{-}CH-CH_3 + H_2O \quad (1)$$

It is known [5] that the most probable mechanism of the epoxidation process is based on the interaction between hydrogen peroxide molecule and Ti-containing catalytic centers to produce an active form of the catalyst (titanium hydroperoxo complex) stabilized by a solvent molecule. A five-membered complex **I** formed in such a way is further involved in the epoxidation of propylene to form the target product such as propylene oxide (Fig. 1).

Basing on the thermodynamic analysis performed (calculating the values of isobaric-isothermal potentials) and on the experimental data obtained, we revealed that, alongside with the target reaction (1) in the system, a num-

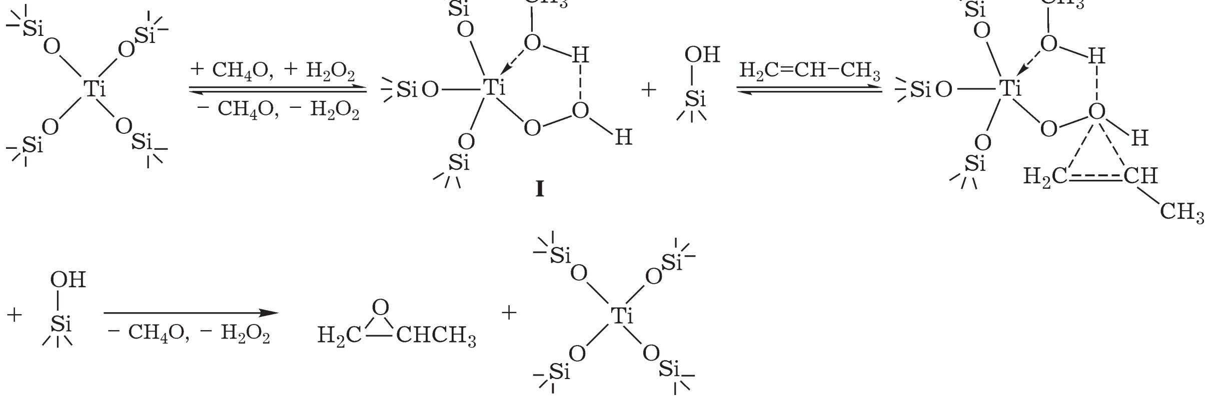
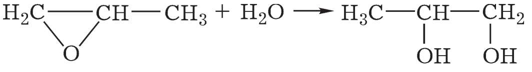


Fig. 1. Mechanism of propylene epoxidation with hydrogen peroxide in methanol environment.

ber of secondary processes takes place those lead to the formation of small amounts of propylene glycol (2), 1-methoxy-2-propanol (3), 2-methoxy-1-propanol (4), as well as the reaction of hydrogen peroxide decomposition (5):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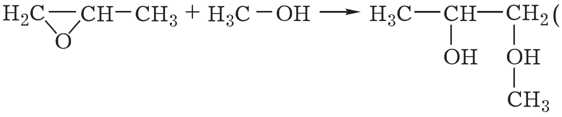
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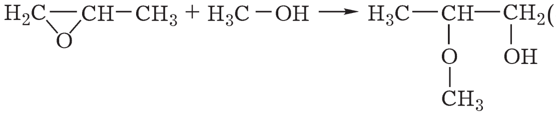
(4)

$2H_2O_2 \rightarrow 2H_2O + O_2$ (V) (5)

It was established experimentally that the propylene oxide under formation slows down the process of epoxidation. To all appearance, this could be caused by the fact that the propylene oxide is adsorbed on the active sites of the catalyst thereby reducing the fraction of free surface. We took this fact into account in the course of constructing the kinetic model.

Thus, the process of epoxidation conventionally involves the following stages to consider: hydrogen peroxide adsorption onto the active centers of the catalyst, surface reaction and propylene oxide desorption. Moreover, each of these stages can be a rate-determining one. Basing on the set of the data obtained one could suggest the following mechanism of propene oxidation by aqueous hydrogen peroxide (HP) in the presence of titanium catalyst:

$$\mathrm{Cat} + \mathrm{CH_4O} + \mathrm{HP} \xrightleftharpoons{b_{HP}} \mathrm{Cat} \cdot \mathrm{CH_4O} \cdot \mathrm{HP}$$

$$\mathrm{Cat} \cdot \mathrm{CH_4O} \cdot \mathrm{HP} + \mathrm{P} \xrightarrow{k_1} \mathrm{Cat} \cdot \mathrm{CH_4O} \cdot \mathrm{PO}$$

$$\mathrm{Cat} \cdot \mathrm{CH_4O} \cdot \mathrm{PO} \xrightleftharpoons{b_{PO}} \mathrm{Cat} + \mathrm{CH_4O} + \mathrm{PO} + \mathrm{H_2O}$$

To describe the material balance of the isothermal reactor operating in a periodical mode employed for the synthesis of propylene oxide we used the following set of differential equations:

$$dC_P/dt = -r_1$$
$$dC_{HP}/dt = -r_1 - 2r_5$$
$$dC_{PO}/dt = r_1 - r_2 - r_3 - r_4$$
$$dC_W/dt = r_1 - r_2 + 2r_5$$
$$dC_{PD}/dt = r_2$$
$$dC_M/dt = -r_3 - r_4$$
$$dC_{1MP2}/dt = r_3$$
$$dC_{2MP1}/dt = r_4$$
$$dC_{O_2}/dt = r_5$$

Basing on the above listed scheme of converting the substances, we developed a kinetic model for the process of propylene epoxidation with the aqueous solution of hydrogen peroxide in the medium of methanol. The mathematical model describing the rate of product formation taking into account the assumptions imposed (the rate-determining stage of the process presented by the surface reaction occurring between H_2O_2 adsorbed on the catalyst surface, and propylene in the dissolved state) could be expressed in the following form:

$$r_1 = \frac{k_1 b_{HP} C_{HP} C_P}{1 + b_{HP} C_{HP} + b_{PO} C_{PO}} (m/V)$$
$$r_2 = k_2 C_{PO} C_W m/v$$
$$r_3 = k_3 C_{PO} C_M m/v$$
$$r_4 = k_4 C_{PO} C_M m/v$$
$$r_5 = k_5 C_{HP} m/v$$

where r_1 is the rate of target reaction (1) mol/(L · s); r_2, r_3, r_4, r_5 are the rates of side reactions (2)–(5), mol/(L · s); k_1, k_5 are the rate constants of the target and side reactions, L/(s · g); k_2, k_3, k_4 are the rate constants of side reactions, L^2/(mol · s · g); b_{HP} and b_{PO} are adsorption equilibrium constants for hydrogen peroxide and propylene oxide, L/mol; m is the mass of the catalyst, g; V is the volume of the reaction mixture, dm^3.

The temperature dependence of the rate constants i for reactions (1)–(5) and the adsorption equilibrium constants b_{HP}, b_{PO} for hydrogen peroxide and propylene oxide were described using the Arrhenius and Van't Hoff equations, respectively:

$$k_i = k_{0i} \exp(-E_i/RT)$$
$$b_{HP} = b_{0HP} \exp(Q_{HP}/RT)$$
$$b_{PO} = b_{0PO} \exp(Q_{PO}/RT)$$

where k_{0i}, b_{0HP}, b_{0PO} are pre-exponential factors; E_i is the activation energy of the i-th reaction, kJ/mol; Q_{HP}, Q_{PO} is the heat of adsorption for hydrogen peroxide and propylene oxide, respectively, J/mol.

In order to find the parameters of the equation we performed several series of experiments with different initial conditions. In

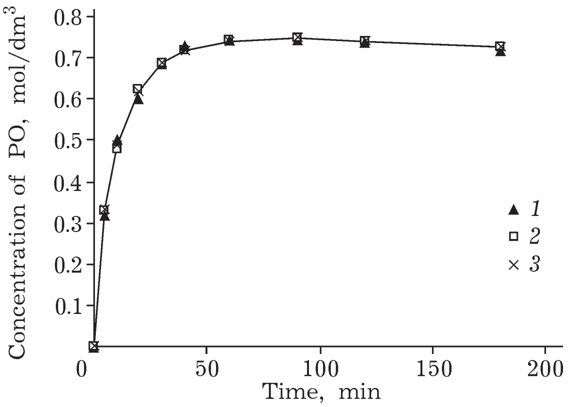

Fig. 2. Concentration of propylene oxide depending on time at different stirring frequency (C_{0P} = 1.68 mol/dm^3, C_{0HP} = 0.79 mol/dm^3, C_{0M} = 7.19 mol/dm^3, temperature 40 °C, the content of catalyst 4.82 g/L). Rotational frequency of the stirrer (min^{-1}): 200 (*1*), 400 (*2*), 600 (*3*).

the course of investigations, we varied the reaction temperature (30–60 °C), the initial concentration of hydrogen peroxide (0.63–1.90 mol/dm^3), the initial concentration of propylene (1.68–3.52 mol/dm^3), propylene oxide concentration at the initial time (0–1.64 mol/dm^3), methanol concentration (14.09–19.07 mol/dm^3) and the catalyst content (4.74–5.13 g/dm^3). At the temperature of 60 °C we performed an experiment with no catalyst added. Within 30 min, the conversion level of hydrogen peroxide exhibited changing less than 0.5 %, whereby we concluded that there is not occurring any non-catalytic reaction.

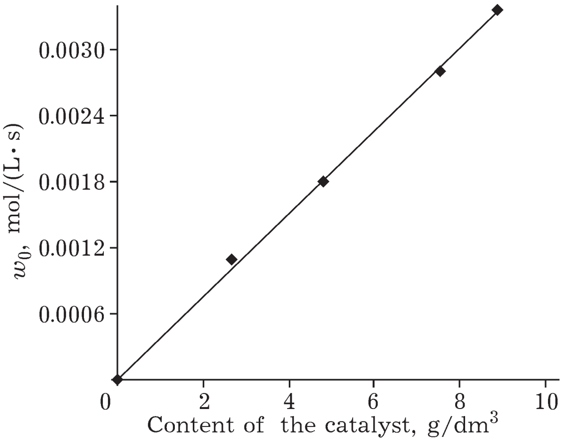

Fig. 3. Initial rate of propylene oxide formation (w_0) depending on the content of the catalyst in the reaction mixture. C_{0P} = 1.68 mol/dm^3, C_{0HP} = 0.79 mol/dm^3, C_{0M} = 7.19 mol/dm^3; temperature 40 °C.

In order to determine the conditions of occurring the reaction of propylene epoxidation by the aqueous solution of hydrogen peroxide using a titanium-containing zeolite as catalyst in a periodical mode reactor we performed a series of experiments with different stirrer rotation frequency as well as with an identical initial content of reagents and catalyst (Fig. 2). It can be seen that providing the chosen values stirrer rotation frequency (200–600 min^{-1}), the concentration of propylene oxide in the reaction mixture, under other equal terms and conditions, does not depend on the stirring frequency, *i. e.* the reaction occurs in the kinetic mode. Further experiments were carried out at stirrer rotation frequency equal to 200 min^{-1}. Furthermore, the initial rate of the epoxidation process depends on the content of the catalyst in a linear manner (Fig. 3), which also indicates the reaction to occur in the kinetic mode. Thus, the epoxidation of propylene is not rate-determined by diffusion hindrances.

The optimality criterion for finding the values of effective rate constants and adsorption equilibrium constants was determined from the condition for minimal values of function *F*, defined *via* the relationship

$$F = 1/n\sum_{j}\sum_{i}[(C_{ij}^{\text{exp}} - C_{ij}^{\text{calc}})/C_{ij}^{\text{exp}}]^2 v_{ij}$$

where n is the number of experimental points; C_{ij}^{exp} and C_{ij}^{calc} are the experimental and calculated values of the molar concentrations of components, respectively; v_{ij} is the mass coefficient. The summation was performed over all the components (index i) and for all the experimental points for each experiment (index j).

At the first stage of determining the unknown parameters of the model, we found constants k_{01}, b_{0HP}, E_1, Q_{HP}. The calculation was

TABLE 1

Arrhenius equation parameters

Reactions	k_{0i}	E_i, 10^3 J/mol
(1)	(4.87±0.24) · 10^2 L/(s · g)	(35.95±1.8)
(2)	(4.95±0.25) · 10^2 L^2/(mol · s · g)	(59.42±3.0)
(3)	(5.31±0.27) · 10 L^2/(mol · s · g)	(56.74±2.8)
(4)	(6.41±0.32) · 10 L^2/(mol · s · g)	(56.03±2.8)
(5)	(2.93±0.15) · 10 L/(s · g)	(50.86±2.5)

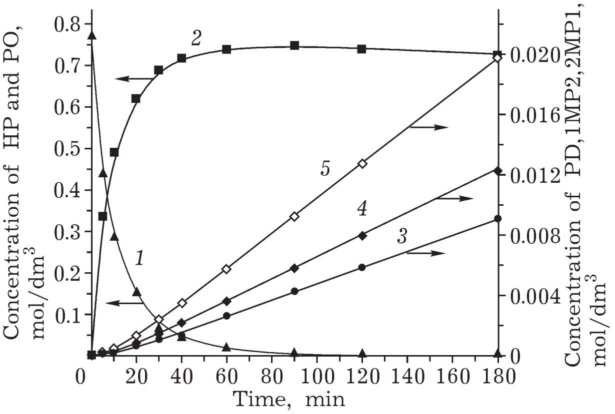

Fig. 4. Kinetic curves for the epoxidation of propylene with 30 % H_2O_2 solution (C_{0P} = 2.24 mol/L, C_{0HP} = 0.74 mol/L, C_{0M} = 17.95 mol/L, $T = 40$ °C, the content of catalyst 4.83 g/L): *1* – HP, *2* – PO, *3* – PD, *4* – 1MP2, *5* – 2MP1; points stand for the experimental values, lines denote calculated values.

performed for the initial parts of the kinetic curves of hydrogen peroxide consumption in the experiments carried out at different initial hydrogen peroxide concentrations and at different temperature values. This approach allows one to neutralize the influence of propylene oxide formed and side reactions. In the course of further processing of the kinetic data, we used the constants obtained to determine the values of remaining unknown parameters. We calculated the values of pre-exponential factors k_{02}, k_{03}, k_{04}, k_{05}, b_{0PO}, effective activation energy values E_2, E_3, E_4, E_5 and the heat of propylene oxide adsorption of $Q_{PO.}$

The results of mathematical processing are demonstrated in Table 1. The following parameters of the Van't Hoff equation: b_{0HP} = $(2.41\pm0.12)\cdot10^{-3}$ L/mol, $b_{0PO} = (1.99\pm0.1)\cdot10^{-3}$ L/mol, Q_{HP} = $(15.76\pm0.79)\cdot10^{3}$ J/mol, Q_{PO} = $(18.39\pm0.92)\cdot10^{3}$ J/ mol.

Figure 4 demonstrates the calculated and experimental data for the current concentration the initial reagents and reaction products. It can be seen that the data are in a good agreement between each other.

CONCLUSION

The kinetic model obtained allows one to perform predictive calculations of the reaction mixture at different temperature values and initial reagent ratio to determine the influence of the process conditions upon the selectivity. A good agreement between the calculated and the experimental data indicate that the system of differential equations to a most complete extent reflects a real process of the liquid-phase epoxidation of propylene using an aqueous solution of hydrogen peroxide in the presence of titanium-containing heterogeneous catalyst. The kinetic data obtained as the result of mathematical modelling of propylene epoxidation process could be used in the engineering calculations for a reactor of propylene epoxidation using an aqueous solution of hydrogen peroxide.

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