



PROPYLENE OXIDATION BY HYDROGEN PEROXIDE ON THE HETEROGENEOUS BIOMIMETIC CATALYSTS

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The catalytic activity of the synthesized heterogeneous biomimetic catalysts, $PPFe^{3+}OH/Al_2O_3$ and $per-FTPhPPFe^{3+}OH/Al_2O_3$, in the reaction of propylene gas-phase oxidation by hydrogen peroxide was studied and their high catalase and monooxygenase activity, as well as resistance to the influence of oxidizer and temperature, were established. In the study of kinetic regularities of gas-phase propylene biomimetic oxidation by hydrogen peroxide the optimal conditions of maximal target products yields were determined: on the biomimetic, $PPFe^{3+}OH/Al_2O_3$, at the temperature $160^\circ C$, molar ratio $C_3H_6 : 20\%H_2O_2 = 1:1$, maximal yield of propylene oxide was 58 mol.%; on the biomimetic, $per-FTPhPPFe^{3+}OH/Al_2O_3$, at the temperature $220^\circ C$, molar ratio $C_3H_6 : 20\%H_2O_2 = 1 : 1.5$, maximal yield of propylene oxide was 33 mol.%. The selectivity based on monooxygenase products was about 100%. On the base of experimental investigations of kinetic regularities of propylene heterogeneous biomimetic monooxidation by hydrogen peroxide, it has been showed the coherent-synchronized nature of two proceeding in the system reactions, catalase and monooxygenase. The mechanism of propylene monooxidation process over the biomimetic catalyst, in which the unity of the redox and acid-base mechanisms is traced within the framework of bonds redistribution chain theory (BRC).

Keywords: biomimetic, hydrogen peroxide, propylene, coherent-synchronized, catalase, monooxygenase, propylene oxide, allyl alcohol, acetone, propionic aldehyde.

INTRODUCTION

The selective oxidation of lower hydrocarbons in the mild conditions has long attracted the attention of researchers in the field of both fundamental and applied catalysis. A lot of investigations have been done in this direction. There are a lot of works on the investigations of lower hydrocarbons selective oxidation processes, such as CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , in order to obtain their alcohols and aldehydes, industrially important and widely used compounds. One of these hydrocarbons is propylene, which used for industrial synthesis of a large number of organic products [1, 2]. At present, the demand for propylene oxide has increased from the construction industry in developed and developing countries of the world. The oxidation of propylene to acrolein has been widely studied because of the importance of acrolein as a monomer for acrylic polymers. The direct catalytic conversion of propylene to oxygenated compounds (propylene oxide, acetone, acrolein, etc.) is one of the most perspective areas of modern chemical industry [3, 4]. The main catalysts used for propylene oxidation reactions are zeolites, molybdates, Cu oxides and silver catalysts [5-8]. In recent decades, metalloporphyrin catalytic systems have been used as effective catalysts for the oxidation of a number of organic substrates, including lower hydrocarbons [9]. Significant progress has been made in investigations related to the development and synthesis of biomimetic heterogeneous catalysts based on ironporphyrin complexes that modeling the work of enzymes, in particular, cytochrome P-450, according to certain useful characteristics: selectivity, activity, active centers work mechanism, mildness of conditions and others. Most ironporphyrin biomimetic catalysts are homogeneous and operate in the liquid phase. Distinguishing feature of heterogeneous ironporphyrin-containing biomimetic catalysts of gas-phase oxidation from known



model homogeneous catalysts of cytochrome P-450 of liquid-phase oxidation is that have many technological advantages, one of which is the difficulty of separating the reaction products from reaction medium.

Carrying out the processes of epoxidation and hydroxylation in the gas phase made it possible to exclude factors, characterized of oxidation in the liquid phase, which complicate the process: the reaction medium pH creation, the solvent choice, the influence of cellular effects, etc. In addition to all this, the high selectivity of the processes carried out in these works is also ensured by the use of hydrogen peroxide as an oxidizer in its qualities that meets the requirements of the “green chemistry” concept and is called the “green oxidizer”.

The use of such high-effective heterogeneous biomimetic catalysts in the process of monooxidation by hydrogen peroxide has been of great interest, which is the basis for the implementation of this work, investigation of propylene oxidation process by hydrogen peroxide in the presence of heterogeneous biomimetic catalysts [10, 11].

MATERIALS AND METHODS

The investigation of propylene monooxidation process by hydrogen peroxide was conducted with applying synthesized heterogeneous biomimetic catalysts, $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (hemin) and $\text{per-FTPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$. The synthesis of these catalysts is multi-stage process, in which primary stage is the synthesis of active centers (PPFe^{3+} and per-FTPhPFe^{3+}), that describes in [11, 12]. Hemin from BDH containing 8.64% iron was taken as Fe^{3+} protoporphyrin active center. The solid matrix on which active centers were immobilized was an activated, neutral Al_2O_3 in the form of spherical particles 3.0 mm in diameter with a specific surface no less than $230\text{m}^2/\text{g}$.

Active centers of biomimetic catalysts, hemin and per-FTPhPFe^{3+} , were applied to the Al_2O_3 surface by developed by us methods. Hemin adsorption on the carrier surface was conducted using water-alcohol solution with $\text{pH}=7.8$ [13]. Obtained hemin-containing biomimetic, $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ contained 3.48mg of hematin per gram of carrier.

Immobilization of $\text{per-FTPhPFe}^{3+}\text{OH}$ on Al_2O_3 in quantity of 1.58g was realized from its solution in dimethylformamide by adsorption [14]. After that, the immobilized catalyst with the content of the active mass in the carrier 30.0 mg/g (or 3.0mas.% per-FTPhPFe(III)) and in quantity of 3 sm^3 successively was subjected to drying and calcination.

To analyze reaction products gas-liquid chromatograph from LKhM-80 with a packed column (length 200 sm, diameter 0.3 sm) filled by adsorbent «Paropak Q», was used. The analysis of products was performed under the following conditions: for gaseous substances, the column and detector temperature was 100°C and evaporator, 110°C ; for liquids, the column and evaporator temperature was 150°C and detector, 140°C ; the flow rate of carrier-gas, helium, was 0.5 kgf/sm^2 . Analysis of the gaseous and liquid products was also carried out on Agilent 7820A GC Systems chromatograph with ZB-FFAB column 30m long.

RESULTS AND DISCUSSION

As known, oxidation processes, conducted with hydrogen peroxide are coherently-synchronized, consisting of two occurring in the system reactions, catalase (primary) and monooxygenase (secondary), which are in chemical conjugation due to inducing action of hydrogen peroxide [10, 11]. That's why, previously, before monooxygenation, the synthesized catalysts tested for catalase activity in liquid phase.

The investigation of catalase activity, i.e. reaction ability of synthesized heterogeneous biomimetic catalysts, $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ and $\text{per-FTPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ in the decomposition reaction of hydrogen peroxide (primary reaction) was conducted in liquid phase in static mode under the following conditions: the volume of hydrogen peroxide was 20 ml, concentration, 5-30 mas.%, sample weighing, 0.005 g, experiment temperature, 25°C .

At the investigation of biomimetics catalase activity, previously, the catalase activity of carrier, Al_2O_3 , which is basis mass of biomimetic, was investigated and its insignificant catalase activity was observed. In the case of testing of $\text{PPFe}^{3+}\text{OH}$, adsorbed on Al_2O_3 , along with the manifestation of high catalase activity, hemin was unstable to action of oxidizer, but synthesized biomimetic, per-FTPhPFe³⁺OH/ Al_2O_3 , showed notable catalase activity and high stability to the effect of oxidizer and its intermediates, as well as heat. Perfluorinated biomimetic, in addition, was tested to the action of high concentrations of oxidizer, H_2O_2 [11]. During a long time this biomimetic catalyst exhibited stable catalase activity in 30% solution of hydrogen peroxide, thereby demonstrating the unique resistance to action of high-active oxidizer intermediates.

The gas-phase propylene biomimetic monooxygenation reaction with hydrogen peroxide over the synthesized biomimetic catalysts, $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ and per-FTPhPFe³⁺OH/ Al_2O_3 in the system of $\text{C}_3\text{H}_6 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$, were experimentally studied at atmospheric pressure, in a flow quartz reactor integral type, whose design provided the undecomposed H_2O_2 introduction to the reaction zone with volume of 3.5 sm^3 .

The investigations of activity of synthesized biomimetic catalyst $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ in propylene monooxidation reaction by hydrogen peroxide were conducted at the temperature range of $120-220^\circ\text{C}$, concentration of H_2O_2 aqueous solution, 20 mas.%, molar ratio, $\text{C}_3\text{H}_6 : 20\% \text{ H}_2\text{O}_2 = 1:1$. The Figure 1 shows the temperature dependence of the yields of propylene biomimetic monooxygenation by hydrogen peroxide, from which it follows that, along with propylene oxide, its isomers, propionic aldehyde, allyl alcohol and acetone, are also formed. At the temperature 160°C the maximum yield of propylene oxide (53mol.%) was observed. Temperature increasing up to 220°C leads to a noticeable decrease in the yield of propylene oxide and sharp increase in the yield of propionic aldehyde (above 45mol.%). At further temperature increasing, isomerization of propylene oxide was observed with acetone formation in small amounts. Propylene conversion in the studied temperature range was more than 90%. However, during these investigations, we encountered difficulties related to the fact that ironporphyrin catalyst, $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$, eventually lost its activity and its action duration in the propylene monooxidation by H_2O_2 was 30-40 minutes. As it was found in the investigation of biomimetic catalysts catalase activity, per-FTPhPFe³⁺OH/ Al_2O_3 , showed high stability and resistance to oxidizer (H_2O_2) action. This explained by the substitution of hydrogen atoms by phenyl radicals in porphyrin ring, which gives stability to the bridge between the pyrrole fragments, and perfluorination brings it to an absolutely stable state [15]. These properties of biomimetic catalyst, per-FTPhPFe³⁺OH/ Al_2O_3 , gave us the opportunity to study for a long time its catalytic activity and selectivity in the reaction of propylene monooxidation with hydrogen peroxide to a number of products of practical importance.

The investigation of kinetic regularities of propylene oxidation monooxygenase reaction over the biomimetic, per-FTPhPFe³⁺OH/ Al_2O_3 , was conducted in the range of temperatures $180-320^\circ\text{C}$; molar ratios, $\text{C}_3\text{H}_6:\text{H}_2\text{O}_2$ in the range from 1:0.5 to 1:2; concentrations of hydrogen peroxide aqueous solutions, 5-35mas.%; contact times, equaled $0.7-2.8\text{s}$.

Figure 2 shows the temperature dependence of the products yields of propylene oxidation reaction by hydrogen peroxide at $\text{C}_3\text{H}_6:20\%\text{H}_2\text{O}_2 = 1:1.2$ and $\tau = 1.4\text{s}$. It is seen from figure, that the curves for the accumulation of propylene oxide, propionic aldehyde and allyl alcohol pass through a maximum, and the greatest yields of the monooxygenase products are observed at 220 , 300 and 260°C for propylene oxide (33 mol.%), propionic aldehyde (25 mol%) and allyl alcohol (8 mol%), respectively. The temperature increasing to 320°C results in a noticeable decrease in the yield propylene oxide, allyl alcohol and to a somewhat lesser extent, propionic aldehyde. On the contrary, for acetone, a regular growth of the yield to 25mol.% is observed.

Notice, that observed kinetic regularities of monooxygenase products accumulation similar in nature to those of biomimetic, $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$; the only difference is that for the biomimetic, per-FTPhPFe³⁺OH/ Al_2O_3 the temperature range is shifted towards higher temperatures. During the

process of propylene oxidation, no formation of products of the propylene destructive transformation, as well as CO and CO₂, was observed in almost the entire temperature range; that's, the process practically proceeds with 100% selectivity based on monooxygenase products.

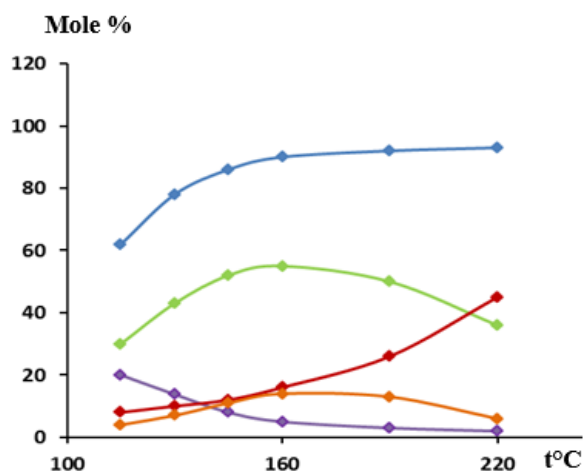


Fig.1. Temperature dependence of yields of propylene monooxidation by hydrogen peroxide on biomimetic, PPhFe³⁺OH/Al₂O₃ (C₃H₆: 20%H₂O₂ = 1:1, τ = 1.86 s, V_{C₃H₆} = 800 ml/h).

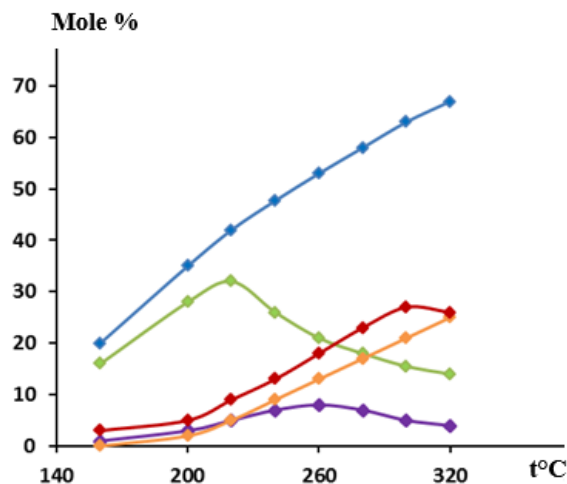
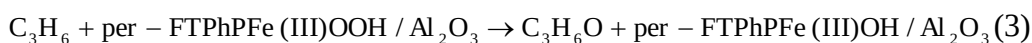
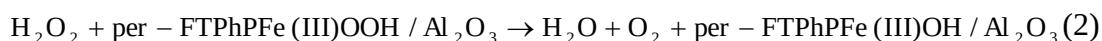
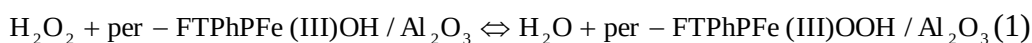


Fig.2. Temperature dependence of yields of propylene monooxidation by hydrogen peroxide on biomimetic, per-FTPhPFe³⁺OH/Al₂O₃ (C₃H₆: 20%H₂O₂ = 1:1.2, τ = 1.4 s).



It should be noted, that the process of propylene biomimetic oxidation by hydrogen peroxide is carried out in the system BioImtOH – H₂O₂ – C₃H₆ in the bifurcation mode, in which simultaneously proceeds conjugated with each other catalase (hydrogen peroxide decomposition) and monooxygenase (propylene monooxidation) reactions. These reactions proceeds via common high-active intermediate compound, intermediate, BioImtOOH, which is the carrier of the inducing effect of primary (catalase) reaction to the secondary (monooxygenase).

According to [10, 11], in catalytic monooxygenation of propylene by H₂O₂ at the presence of biomimetic catalyst, per-FTPhPFe³⁺OH/Al₂O₃, the intermediate is catalyst-substrate complex, per-FTPhPFe³⁺OOH/Al₂O₃, which forms in the interaction of biomimetic with H₂O₂ at the first stage:



The structure of activated complex of elementary reaction (1), building within the framework of the theory of bonds redistribution chains (BRC), was shown on Fig.3.

Principle of BRC is based on the breaking of existing and formation of new bonds by way of one-sided transfer of protons and electrons movement it the opposite direction between active centers atoms: ligand, acid and base centers of the carrier Al₂O₃. Heterolytic joining of hydrogen peroxide to Fe³⁺ ion carried out in such way that there is no overall change in the formal oxidation state or coordination number of the iron ion. Obtained intermediate is consumed in two reactions:

reacts with the second hydrogen peroxide molecule to form final products of catalase reaction or epoxidizes propylene to form final products of monooxygenase reaction.

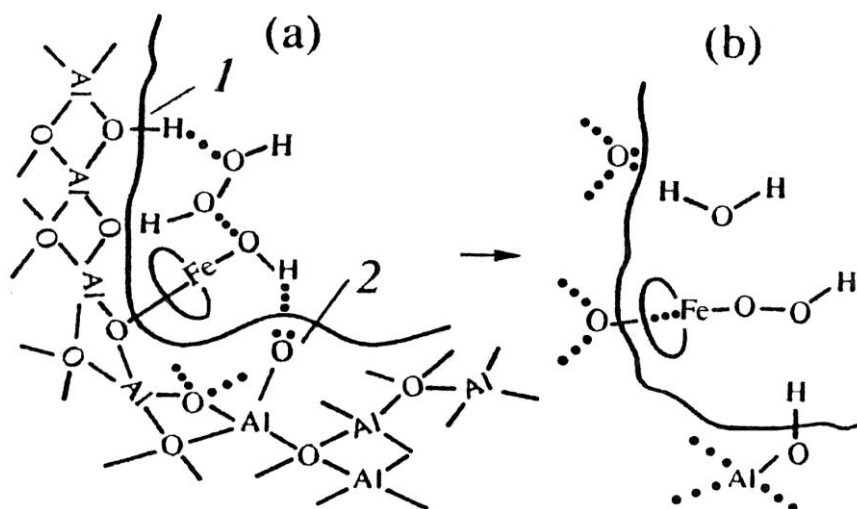


Fig. 3. The mechanism of catalyst-substrate complex formation: (a) formation of active complex with participation of acid-base centers of Al₂O₃; (b) active intermediate, catalyst-substrate complex; (1) acid center; (2) base center; points are forming bonds; solid lines are breaking bonds.

The reaction mechanism of propylene monooxidation, shown in Fig.4, is that the oxygen atom of hydrogen peroxide is transferred to the propylene molecule by attaching the OH group to it, in which the proton enters into partial interaction with the basic center of the surface and thus prevents the complete transition of the substrate proton to the matrix, Al₂O₃.

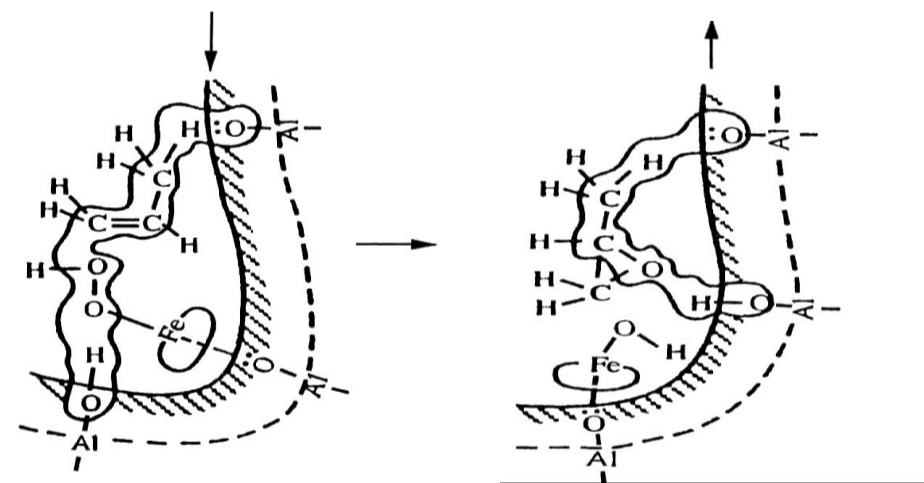
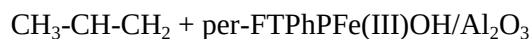


Fig. 4. The mechanism of propylene oxide formation on the per-FTPhPFe(III)OH/Al₂O₃.



In the conditions of our experiments, biomimetic catalysts, $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ and per- $\text{FTPhPPe(III)OH}/\text{Al}_2\text{O}_3$, has an exceptional epoxidizing ability resulting in a high yield of propylene oxide (58 and 33 mol.%, correspondingly).

CONCLUSION

At the investigation of catalase activity of the synthesized ironporphyrin-containing heterogeneous biomimetic catalysts, high catalase activity and resistance to the effect of an oxidizer of biomimetic, per- $\text{FTPhPPe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$, were established.

On the base of experimental investigation of kinetic regularities of propylene heterogeneous biomimetic monooxidation by hydrogen peroxide on the biomimetics, $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ and per- $\text{FTPhPPe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$, the coherent-synchronized nature of two proceeding in the system reactions, catalase and monooxygenase, was shown.

At the process of propylene oxidation on the biomimetic $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ at the temperature 160°C , molar ratio $\text{C}_3\text{H}_6:20\%\text{H}_2\text{O}_2 = 1:1$, maximal yield of propylene oxide was 58 mol.%; on the biomimetic per- $\text{FTPhPPe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ at the temperature 220°C , molar ratio $\text{C}_3\text{H}_6:20\%\text{H}_2\text{O}_2 = 1:1.5$, maximal yield of propylene oxide was 33 mol.%. The selectivity based on monooxygenase products was about 100%.

The experimental research data revealed the fact that during the reaction of propylene biomimetic monooxidation per- $\text{FTPhPPe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ proved to be more stable under the influence of oxidizer and temperature than $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$.

The probable mechanism of propylene coherent-synchronized biomimetic oxidation by hydrogen peroxide over the biomimetic catalyst, per- $\text{FTPhPPe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$, in which the unity of the redox and acid-base mechanisms is traced within the framework of bonds redistribution chain theory (BRC).

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HETEROGEN BIOMİMETİK KATALİZATORLAR ÜZƏRİNDƏ PROPİLENİN HİDROGEN PEROKSİDLƏ OKSİDLƏŞMƏSİ

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Sintez olunmuş $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ və $\text{per-FTPhPPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ heterogen biomimetik katalizatorların propilenin hidrogen peroksidlə qazfazalı oksidləşməsi reaksiyasında katalitik aktivliklərinin tədqiqi aparılmış və nəticədə, onların yüksək katalaz və monooksigenaz aktivlikləri, həmçinin oksidləşdirici və temperatura qarşı davamlılıqları müəyyən edilmişdir.

Propilenin hidrogen peroksidlə qazfazalı biomimetik oksidləşməsi reaksiyasının kinetik qanunauyğunluqlarının tədqiqi sayəsində məqsədli məhsulların maksimal çıxımları üçün optimal şəraitlər təyin edilmişdir: $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ biomimetiki üzərində 160°C temperaturda, C_3H_6 :20% H_2O_2 =1:1 mol nisbətində propilen oksidin maksimal çıxımı 58 mol.%; $\text{per-FTPhPPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ biomimetiki üzərində 220°C -də, C_3H_6 : 20% H_2O_2 = 1 : 1.5 mol nisbətində propilen oksidin yüksək çıxımı 33 mol.%. Prosesin monooksigenaz məhsullara görə selektivliyi praktiki olaraq 100%-ə yaxın təşkil edir.

Propilenin hidrogen peroksidlə heterogen biomimetik monooksidləşməsi reaksiyasının kinetik qanunauyğunluqlarının eksperimental tədqiqi əsasında prosesin koherent-sinxronlaşdırılmış xarakterdə iki – katalaz və monooksigenaz – reaksiyadan ibarət olaraq getdiyi göstərilmişdir. Biomimetik katalizator səthində propilenin monooksidləşməsinin mexanizmi verilmişdir ki, bu mexanizmdə rabitələrin zəncirvari paylanması nəzəriyyəsi (RZP) çərçivəsində oksidləşmə-reduksiya və turşu-əsas mexanizmlərin birlikdə təsiri əks olunur.

Açar sözlər: biomimetik, hidrogen peroksid, propilen, koherent-sinxronlaşdırılmış, propilen oksid, allil spirti, aseton, propion aldehidi.



ОКИСЛЕНИЕ ПРОПИЛЕНА ПЕРОКСИДОМ ВОДОРОДА НА ГЕТЕРОГЕННЫХ БИОМИМЕТИЧЕСКИХ КАТАЛИЗАТОРАХ

Л.М. Гасанова, У.В. Мамедова, Б.Э. Агамалиева

Исследована каталитическая активность синтезированных гетерогенных биомиметических катализаторов – $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ и $\text{per-FTPhPPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ в реакции газофазного окисления пропилена пероксидом водорода и установлена их высокая каталазная и монооксигеназная активность в этой реакции, а также устойчивость к воздействию окислителя и температуры.

При исследовании кинетических закономерностей реакции газофазного биомиметического окисления пропилена пероксидом водорода определены оптимальные условия для максимальных выходов целевых продуктов процесса: на биомиметике $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ при температуре 160°C , мольном соотношении $\text{C}_3\text{H}_6 : 20\% \text{H}_2\text{O}_2 = 1 : 1$, максимальный выход пропиленоксида составил 58 мол.%; на биомиметике $\text{per-FTPhPPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ при температуре 220°C , мольном соотношении $\text{C}_3\text{H}_6 : 20\% \text{H}_2\text{O}_2 = 1 : 1.5$, наибольший выход пропиленоксида составил 33 мол.%. Селективность в расчёте на монооксигеназные продукты составила практически 100%.

На основе экспериментального исследования кинетических закономерностей реакции гетерогенного биомиметического монооксидирования пропилена пероксидом водорода показан когерентно-синхронизированный характер двух протекающих в системе реакций – каталазной и монооксигеназной. Предложен механизм процесса монооксидирования пропилена на поверхности биомиметического катализатора, в котором прослеживается единство окислительно-восстановительных и кислотно-основных механизмов в рамках теории цепи перераспределения связей (ЦПС).

Ключевые слова: биомиметик, пероксид водорода, пропилен, когерентно-синхронизированный, оксид пропилена, аллиловый спирт, ацетон, пропионовый альдегид.