THE SYNTHESIS OF NEW MONOOXYGENASE BIOMIMETIC CATALYSTS AND OXIDATION IN THE THEIR PRESENCE OF HYDROCARBONS BY HYDROGEN PEROXIDE TO CHEMICALLY IMPORTANT COMPOUNDS

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Heterogeneous ironporphyrin-containing biomimetic catalysts were investigated for their selectivity in relation of determined compound in the cyclohexane gas-phase oxidation process and mixture of the latter with its derivatives by hydrogen peroxide. On the basis of experimental investigations of the cyclohexane monooxidation process it was investigated that the complex reaction, consisting of parallel-consecutive monooxidation reactions and oxidative dehydrogenation, which are the coherent-synchronized reactions were proceed on the biomimetic catalyst. The probable mechanisms of cyclohexane biomimetic transformation to desired products, in which there is a unity of mechanisms of acid-base catalysis and the redox system by the principle of BRC (bonds redistribution chain) typical for enzymatic catalysis, were presented. The direct oxidation of methane to methanol by hydrogen peroxide also was investigated in the presence of biomimetic catalyst.

**Keywords:** cyclohexane, cyclohexanol, cyclohexanone, coherent-synchronized reactions, biomimetic catalysts, enzymatic catalysis, methane, methanol.

Monooxidation of cyclohexane by hydrogen peroxide on biomimetic catalyst

Heterogeneous biomimetic catalysts on the base of ironporphyrin complexes being an active part of enzyme cytochrome P-450 allow us to realize coherent-synchronized oxidation of a number of hydrocarbons by hydrogen peroxide in gas phase in the most mild conditions with high selectivity [1, 2].

One of the important processes of the oil chemistry is the oxidation of cyclohexane, which oxidation products have a wide application. Application of biomimetic catalyst in this process, investigation of its activity, selectivity, also study of its action mechanism is the one of priority directions of our investigation.

The wide experimental investigation of gas-phase monooxidation of cyclohexane by hydrogen peroxide was performed in the presence of biomimetic catalyst – perfluorinated iron(III)tetraphenylporphyrin [3–12].

The first stage of the investigations was the investigation of the biomimetic catalytic system for the selective nature of their actions by using as a raw material the mixtures of cyclohexane with some derivatives.

The results of investigations by using of raw material with the composition (%) 88.85 C₆H₁₂, 6.25 C₆H₁OH and 2.53 CH₃C₆H₁₁ were showed that during the oxidation process, mainly cyclohexane undergoes transformation, but quantity of methylcyclohexane presented in the composition of the raw material remains practically unchanged.

With the aim to establish selective action of used by us ironporphyrin-containing biomimetic catalysts in the oxidation of complex mixtures, as a raw material there was taken artificially prepared mixture with a content, %: 45.4 C₆H₁₂, 38.64 CH₃C₆H₁₁, 1.91 C₆H₁₁OH.

The investigation results of the oxidation process of this mixture by 20% hydrogen peroxide at various raw material supplying rates and different temperatures on the biomimetic PPFe(III)/Al₂O₃ were shown in Table 1. From the data of Table 1 an unambiguous conclusion follows about the selective action of the catalytic biomimetic in relation of cyclohexane oxidation in the mixture that have a significant quantity of methylcyclohexane (38.6%).

On the base of obtained results the mechanism of the coherent-synchronized biomimetic oxidation reaction of cyclohexane is presented. Kinetic regularities of the cyclohexane transformation on the biomimetic catalyst per-FTPPFe(III)OH/Al₂O₃ in dependence of temperature (Figure 1) show that at temperature of 150–180°C with the greatest speed proceed the oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol.
Table 1. The results of cyclohexane oxidation process in the mixture on the biomimetic, PPFε(III)/Al₂O₃ by hydrogen peroxide: \( C_{\text{H}_2\text{O}_2} = 20\% \), \( V_{\text{H}_2\text{O}_2} = 1.41 \text{ ml/h} \), \( V_{\text{C}_6\text{H}_{12}} = 0.9 \text{ ml/h} \)

| \( t, ^\circ\text{C} \) | Composition of raw material | Reaction products | Conversion, % | \( \text{O}_2 \) yield in catalase reaction, % |
|---------------------|---------------------------|-------------------|-------------|----------------------------------|
| 150                 | \( \text{C}_6\text{H}_{12} \) | \( \text{C}_6\text{H}_{12} \) | 37.1        | 6.771                            | 8.34  | 91     |
| 180                 | \( \text{C}_6\text{H}_{12} \) | \( \text{C}_6\text{H}_{12} \) | 33.19       | 7.078                            | 12.2  | 88     |
| 200                 | \( \text{C}_6\text{H}_{12} \) | \( \text{C}_6\text{H}_{12} \) | 29.34       | 7.165                            | 16.0  | 84     |
| 220                 | \( \text{C}_6\text{H}_{12} \) | \( \text{C}_6\text{H}_{12} \) | 24.85       | 6.7                              | 20.5  | 79     |

By temperature increasing the yield of cyclohexene dramatically increases and discretely cyclohexadiene, due to the increase in the reaction rate of oxidative dehydrogenation of cyclohexane in these conditions. The yield of cyclohexanol with temperature is decreased, but the yield of cyclohexanone at 180\(^\circ\text{C}\) passes through a maximum (10.34\%).

The influence of the aqueous solution of hydrogen peroxide concentration on the process of monooxidation and oxidative dehydrogenation of cyclohexane is presented in Figure 2.
Increasing of H₂O₂ concentration leads to marked decreasing of the speed of oxidative dehydrogenation of cyclohexane and considerable increasing of cyclohexanone yield. Kinetic curves of monooxidation products formation — cyclohexanone and cyclohexanol, show that the yield of cyclohexanone increases from 10% to 14%, while the cyclohexanol yield passes through a maximum (7.6%).

The complex nature of these kinetic curves (Figures 1 and 2) does not give an unambiguous answer to the key question: whether cyclohexanone is formed from cyclohexanol. In this regard, the reaction of cyclohexanol oxidation (97.52% in original C₆H₁₁OH) was investigated under identical conditions.

From the kinetic curves of Figure 3 it follows that the peroxidase reaction of cyclohexanol, i.e., the formation of cyclohexanone is practically not observed, there basically goes on dehydration of cyclohexanol to cyclohexene.

![Fig.3. Yields of cyclohexanol transformation reaction products on biomimetic per-FTPPhPFe(III)/Al₂O₃ by hydrogen peroxide in dependence of temperature: 1 — conversion of C₆H₁₂OH, 2 — cyclohexene, 3 — 1,2-cyclohexanediol, 4 — 1,3 cyclohexadiene, 5 — other oxygen-containing compounds, 6 — O₂;
C₆H₁₂O = 20%, V₉₃,₅₈ = 1.41 ml/h, V₅₆₈OH = 0.9 ml/h.](image)

It should be noted that the temperature increasing from 150°C to 230°C the conversion of cyclohexanol increases to the side of cyclohexene formation.

The experimental data of Figure 3 unambiguously show that in the reaction system the reaction of cyclohexanol dehydration to cyclohexene occurs. Thus, the kinetic data of Figures 1 and 3 shed light on the mechanism of cyclohexanol and cyclohexene formation. Really, the kinetic data of Figure 1 show that at temperatures up to 150–180°C, mainly, the reaction of cyclohexane monooxidation proceeds, and above 180°C the reaction of oxidative dehydrogenation of cyclohexanol to cyclohexene (curve 4, Figure 1) is accelerates, the yields of cyclohexanol and cyclohexanone decrease, respectively. Sharp increase in cyclohexene yield in parallel with decreasing of the cyclohexanone yield indicates that at 230°C and at lower concentrations of H₂O₂ in the reaction system cyclohexanol converts into cyclohexene. Such conclusion unambiguously is confirmed by the experimental data of C₆H₁₂OH oxidation on biomimetic catalyst, at 200–230°C: cyclohexanol fully subjected to dehydration (Figure 3) with obtaining a high yield of cyclohexene (16–30%).

Thus, from the experimental data of Figures 1–3 we can conclude that the process of cyclohexene formation proceeds via the consecutive-parallel mechanism, which can be represented in the following scheme:

\[
\begin{align*}
C₆H₁₂ + & H₂O₂ \xrightarrow{[230°C]} C₆H₁₁OH & \rightarrow & C₆H₁₀ + H₂O. & (1) \\
C₆H₁₂ & \rightarrow C₆H₁₀ + 2H₂O \\
C₆H₁₁OH & \rightarrow C₆H₁₀ + H₂O \\
C₆H₁₂ & \rightarrow C₆H₁₀ + 2H₂O \\
\end{align*}
\]

Comparing the kinetic curves of cyclohexene formation in Figures 1–3 it can be concluded that at temperatures above 180°C and at the lowest concentration of H₂O₂, the main part of cyclohexene is formed by oxidative dehydrogenation of cyclohexane by the reaction of 4 (scheme 1). Of course, this does not exclude the possibility of cyclohexene formation via the consecutive reactions 2 and 3. The formation of cyclohexanone takes place by direct conversion of cyclohexane (reaction 1). The coherent-synchronized reactions of cyclohexane mono-
oxidation by hydrogen peroxide is described by the following generalized scheme [1, 2]:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{ImtOH/Al}_2\text{O}_3 & \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{ImtOH} \\
\text{H}_2\text{O}_2 + \text{ImtOOH/Al}_2\text{O}_3 & \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{ImtOH}
\end{align*}
\]

(2)

From this scheme it follows that the primary reaction of H₂O₂ decomposition forms the highly reactive hydroperoxide active center, which interacts in the system both with H₂O₂ molecules and molecules of cyclohexane.

Scheme 3 illustrates the principle of construction of the complex ImtOOH/Al₂O₃ on the biomimetic per-FTPhPF₃OH/Al₂O₃ by the theory of bonds redistribution chain (BRC) in catalase reaction, like the formation of the Chance complex (PPFe₃⁺OOH) under the action of the enzyme catalase. As the matrix of the acidic-basic nature in our case, Al₂O₃ is used [13].

**Primary (catalase) reaction**

\[
\text{H}_2\text{O}_2 + \text{ImtOH/Al}_2\text{O}_3 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{ImtOH}
\]

where, ImtOH/Al₂O₃ – catalytic biomimic (imitator); ImtOOH/Al₂O₃ – intermediate; + and ∙∙∙ – correspondingly breaking and formation of bonds, respectively.

High-active intermediate per-FTPhPF₃OH/Al₂O₃ interacting with cyclohexane leads to the formation of desired products (secondary reactions).

Mechanisms of cyclohexane monooxidation to cyclohexanol and oxidative dehydrogenation of it to cyclohexene on the biomimetic catalyst, according to known representations [1], can be represented as follows:

**Mechanism of cyclohexane monooxidation to cyclohexanol**

\[
\begin{align*}
\text{A} & \rightarrow \text{B} \\
\text{B} & \rightarrow \text{A}
\end{align*}
\]

(4)

where A and B are acid and base centers respectively.
Mechanism of cyclohexane oxidative dehydrogenation to cyclohexene

In the schemes of the mechanism of cyclohexane transformation to cyclohexene and cyclohexanol there is also traced the unity of the acid-base and oxidation-reduction mechanisms on the principle of BRC (scheme 4 and 5). Under the action of acid-base centers of support takes place the transfer of two or more protons from the substrate and the acid center of the substrate with the formation of cyclohexanol or cyclohexene at different stages of cyclohexane oxidation.

Methane oxidation by hydrogen peroxide on the biomimetic catalyst

The chemical transformation of low alkenes, the main products of natural and associated gases, has become one of the important trends of the modern petrochemical industry and a new industrial sector: the gas chemistry. The direct transformation of methane to methanol and other oxygen-containing compounds for many decades was the goal of the gas industry.

The main common industrial method of methanol producing from methane consists of two stages: 1) methane transformation to the synthesis-gas (2\(\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2\)) by deep oxidation; 2) transformation of synthesis-gas to methanol. Despite numerous studies in the field of direct oxidation of methane to methanol with oxygen or air in the presence of various catalysts, these processes have not found industrial application due to low yields of methanol and low selectivity. It is known that methane is difficult to convert the hydrocarbon component, and its thermic transformation occurs only at temperatures above 900°C.

A few years ago, due to induction property of hydrogen peroxide the transformation of methane was achieved without using of any catalysts at atmosphere pressure at 460–580°C by free-radical mechanism. In this process the yield of methanol was only 5–6% with low selectivity, the main product of reaction was formaldehyde [14, 15]. Conducting this process under pressure at temperature 400°C it was possible to increase the yield of methanol to 17% [16]. Last time, by using synthesized biomimetic catalyst in the process of methane oxidation by hydrogen peroxide already at a temperature of 180°C methanol with high selectivity was formed with the yield of 30–40%. As a biomimetic catalyst we use the iron protoporphyrin (hemin), immobilized on various supports – PPFe(III)OH/Al\(_2\)O\(_3\), PPFe(III)OH/AlMgSi, PPFe(III)OH/NaX. These catalysts quickly lose their activity. Even catalyst PPFe(III)OH/AlMgSi manifesting the highest activity worked only 6 hours [17].

The aim of the present work is to develop a new more resistant to temperature and oxidant biomimetic catalyst for direct, partial oxidation of methane. For the synthesis of new biomimetic catalyst we use fluorinated 5,10,15,20-tetraakis(pentafluorophenil)-21H,23H-Fe(III)Cl, in which the hydrogen atoms of phenyl groups of ironporphyrin complex substituted by fluorine. Immobilization of this complex on Al\(_2\)O\(_3\) was carried out from its solution in dimethylformamide by adsorption method. The catalysts with concen-
trations of active complex 2.92 and 1.92 mg/g were obtained.

Investigation of the process of methane oxidation by hydrogen peroxide in the presence of this biomimetic catalyst was carried out at temperature 200–300°C. At temperature 240°C 5.84% of methanol was obtained, at 280°C – 8.6%, on missed methane, on the catalyst with concentration 2.92 mg/g. Further temperature increasing (over 280°C) led to decrease the yield of methanol to 4.7% at 300°C, that associated with production of 4.0% CH₂O and 0.2% CO₂ (Figure 4).

The next series of experiments is dedicated to studying H₂O₂ concentration influence and biomimetic catalyst on the reaction proceeding and it is established that the temperature increasing of these concentrations has a positive effect on the yield of methanol.

The investigation of the catalyst surface was conducted by scanning electron microscope, and were determined the micro- and nanosizes of pores of Al₂O₃ support and active complexes adsorbed in those pores (Figure 5).

![Graph](image)

**Fig. 4.** Dependence of reaction products yields on temperature: 1 – CH₃OH, 2 – CH₂O, 3 – CO₂; C₁₂H₂₀ = 30%, Vₕ₂₀ = 1.01 ml/h, Vₕ₄ = 0.24 ml/h, CH₄:H₂O₂ = 1.08:1.

![Surfaces](image)

**Fig. 5.** Surfaces of support (Al₂O₃) and catalyst, filmed by scanning electron microscope.
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YENİ MONOOKSIDŁƏŞDIRİCİ BIOMİMETİK KATALİZATORLARIN SİNTEZİ VƏ ONLARIN İŞTİRAKINDA KARBOHİDROGENLƏRİN HİDROGEN PEROKSİDİNİ KİMİYƏ İƏHƏMİYYƏTLİ MƏŞHULLARA OKSIDŁƏŞMƏSI

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Tsikloheksan və onun tərəmləri ilə qarşılıqda hidrojen peroksidə oksidlaşması prosesində dəmirporfirintəkbi hərətli biomimetic katalizatorların müəyyən bir işlənməyi qarşılıq verdir. Tsikloheksanın monooxidləşdirməsini eksperimental tədqiqi əsasında müəyyən edilmişdir ki, biomimetic katalizator səthinə paralel-ardicil monooxidləşmə və oksidləşdirici dehidroenləşmə reaksiyalarından ibarət koherent-sinxronlaşdırılmış mürəkkəb reaksiya bax verir. Tsikloheksanın reaksiya məşhullarına çevriləninin fermentativ kataliz xarakterik olan rəhbərlik və xüsusiyyətlərin (RZP) ilə türşü-əsasi kataliz və redoks sistemlərinin birgə manevrazmınlarin

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daxil olduğu mehanizmləri təsvir edilmişdir. Həmçinin metanın biomimetik katalizator ətərənda hidrogen peroksidə birbaşa metanola oksidlaşması prosesinin tədqiqi aparılmışdır.

Açar sözlər: tsikloheksan, tsikloheksanol, tsikloheksanon, koherent-sinxronlaşdırılmış reaksiyalar, biomimetik katalizatorlar, fermentativ kataliz, metan, metanol.

СИНТЕЗ НОВЫХ МОНООКСИДИРУЮЩИХ БИОМИМЕТИЧЕСКИХ КАТАЛИЗАТОРОВ И ОКИСЛЕНИЕ В ИХ ПРИСУТСТВИИ УГЛЕВОДОРОДОВ ПЕРОКСИДОМ ВОДОРОДА В ХИМИЧЕСКИ ВАЖНЫЕ СОЕДИНЕНИЯ

Л.М. Гасанова

Исследованы гетерогенные железо-порофиринсодержащие биомиметические катализаторы на их избирательность в отношении определённого соединения в процессе газофазного окисления циклогексана и смеси последнего с его производными пероксидом водорода. На основе экспериментальных исследований процесса монооксидирования циклогексана было установлено, что на биомиметическом катализаторе происходит сложная реакция, состоящая из параллельно-последовательных реакций монооксидирования и окислительного дегидрирования, являющихся когерентно-синхронизированными реакциями. Представлены вероятные механизмы биомиметического превращения циклогексана в целевые продукты, в котором прослеживается единство механизмов кислотно-основного катализа и редокс-системы по принципу цепи перераспределения связей (ЦПС), характерному для ферментативного катализа. Проведено также исследование прямого окисления метана в метанол пероксидом водорода в присутствии биомиметического катализатора.

Ключевые слова: циклогексан, циклогексанол, циклогексанон, когерентно-синхронизированные реакции, биомиметические катализаторы, ферментативный катализ, метан, метанол.

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