Coherently synchronized reaction of methane oxidation by green oxidizer–hydrogen peroxide – over the biomimetic catalyst iron pentafluorotetraphenylporphyrin deposited on alumina

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Abstract

The activity of penta- FTPhPFe(III)/Al₂O₃ biomimetic catalyst in the reaction of methane direct conversion into methanol by green oxidant hydrogen peroxide was studied at T = 150–350 °C and atmospheric pressure, where methanol yield was 19.2% with methane conversion of 28%. Based on the results of the structural analysis of the Al₂O₃ support and the biomimetic catalyst sample the mesoporosity of support with pore size in the range of dₚ = 2.4–22.2 nm in the cylindric shape with an open end and the synthesized biomimetic nanostructure were determined. The data on the definition of the nature and quantitative assessment of Al₂O₃ support acid–base centers are given that made possible to describe probable mechanism of methane coherent-synchronized oxidation into methanol on the biomimetic.

Keywords Methane · Methanol · Hydrogen peroxide · Biomimetic catalyst · Coherently synchronized reaction

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Introduction

An interest in the development of processes for the direct conversion of methane into liquid one-carbon oxygen-containing compounds is growing in connection with the world’s tremendous proven reserves of natural gas. Consequently, methane is a cheap and ideal raw material for the chemical industry, from which many organic compounds can be obtained. However, high thermodynamic stability (chemical inertness) of the CH$_4$ molecule, in which the breaking energy of the C–H bond is equal to 440 kJ/mol, complicates its activation in oxidation processes.

One of the main products of methane oxidation is methanol—a product of methane hydroxylation, which is used as an intermediate product in a number of chemical industries, and is also an excellent fuel, including for internal combustion engines.

The main industrial method for producing methanol is still based on initial high-temperature conversion of methane into synthesis gas (CO + H$_2$), followed by its catalytic conversion into methanol and other high pressure products. Despite the constant improvement of this production, it is a complex staged technological process that requires vast energy and capital costs. Therefore, the search for new ways of one-stage direct conversion of methane with the use of effective catalysts within the framework of “green technologies” which make it possible to oxidize methane with high selectivity at relatively low temperatures and pressures is becoming more and more urgent.

There are numerous studies in the field of direct oxidation of methane to methanol by oxygen or air in the presence of various high-temperature metal oxide catalysts, which have low-selectivity due to the formation of CO$_2$ more than 10–15% at a low conversion of CH$_4$ [1–4].

At the same time, it became known that in nature, methane is directly oxidized by aerobic bacteria to methanol under normal conditions [5]. In this regard, it is of great interest to create such effective biomimetic catalysts, similar to methane monoxygenases, which can convert methane to methanol under mild conditions [6, 7].

The discovery of the structure of the active center and the mechanism of functioning of the main class of oxygenases, the cytochrome P-450 family, the mononuclear heme iron-containing enzymes, made it possible to create their models for the activation of the C–H bond of hydrocarbons, including methane, which is difficult to activate [8]. The developed biomimetic catalysts based on heme complex, which are the active part of cytochrome P-450, exhibited high activity in hydrocarbon monooxidation reactions. For example, the heme-containing biomimetic catalyst PPF $^{3+}$OH/AlMgSi exhibited high activity in the methane-to-methanol conversion reaction, where the methanol yield was higher than 40% with its 56% conversion [9, 10]. However, this catalyst was very unstable due to the breaking of heme bridging when exposed to temperature and an oxidizing agent.

The aim of our study is the synthesis of such porphyrin complexes which will make biomimetic catalysts resistant to temperature and effect of an oxidizing agent in the gas phase [11, 12], as well as, to carry out such process that would correspond to carbon neutralization from the perspective of environmental protection and ecological problems.
The presented work is devoted to the synthesis and study of the activity of this kind of biomimetic catalyst in the direct conversion of methane by a green oxidant $\text{H}_2\text{O}_2$, into one-carbon oxygen-containing compounds.

**Experimental part**

**Synthesis of biomimetic catalyst**

The synthesized biomimetic catalysts are heterogeneous and their active sites consist of modified iron porphyrin complexes: iron pentafluorotetraphenylporphyrin—penta-FTPhPFe (III) (tetrakis) and iron tetraphenylporphyrin—TPhPFe (III). Preparation of the catalysts was carried out by adsorption of these complexes on mesoporous solid carriers of an acid–base nature—$\text{Al}_2\text{O}_3$ and NaX. The adsorption of tetrakis on these supports was carried out using a solvent of dimethylformamide, the adsorption of iron tetraphenylporphyrin from a solution in benzene. The number of adsorbed active complexes was determined using photoelectrocalorimetry (PEC) [13].

**Study of the structure and physicochemical properties of supports and catalysts**

Specific surface area, adsorption capacity, structure, nature and pore sizes of the supports, which play an important role in the synthesis and activity of biomimetic catalysts, are determined from the data of numerous adsorption, measured as a function of relative or absolute pressure using a fully automated analyzer of the 3Flex device. The adsorption was carried out with liquid nitrogen at a temperature of 77.3 K.

The initial study was to determine the specific surface area of the carriers by the BET method using the adsorption data obtained on a modern 3Flex device. The specific surface area was determined by isotherms of adsorption depending on relative or partial pressure, as well as by the one-point BET method. It was found that the

![Fig. 1 Isotherms of adsorption and desorption on the $\text{Al}_2\text{O}_3$ surface depending on the relative pressure](image-url)
specific surface area of the Al₂O₃ support is 239 m²/g, while that of the catalyst is 216.9 m²/g.

Fig. 1 demonstrates the isotherms of adsorption and desorption of N₂ at 77 K on a Al₂O₃ sample. As can be seen from the presented curves, there is a discrepancy between the adsorption and desorption isotherms in the range of p/p₀ = 0.597–0.951, where the adsorption is 4.653–14.105 mmol/g, which leads to the formation of a hysteresis loop.

This indicates the occurrence of capillary condensation and the presence of mesopores. Isotherms of adsorption and desorption with hysteresis loops (adsorption and desorption follow different paths) show that the solid support (Al₂O₃) is mesoporous, and its pore size ranges from 2 to 50 nm. The area of hysteresis on the isotherm curve indicates a cylindrical shape of mesopores with an open end in the form of a bottle or gaps between parallel places (slits). In such pores, during capillary condensation, a meniscus in the “paths” of adsorption and desorption differ in shape, which creates a hysteresis loop. The data on the isotherms of adsorption depending on the relative pressure (p/p₀) show that the maximum amount of adsorption Nₐd = 0.771–14.198 mmol/g at p/p₀ = 0.6–0.98 corresponds to the hysteresis region, meaning that it occurs in the mesopores. The maximum adsorption (14.198 mmol/g) occurs at p/p₀ = 0.98, which is 2.84 wt% of the total amount of nitrogen (adsorbate).

Similar results are also observed on the adsorption and desorption isotherms depending on the partial or absolute pressure (Fig. 2). The maximum amount of adsorption 14.21 mmol/g occurs at Pₐₚ = 99.38 kPa in the mesopores in the hysteresis region Pₐₚ = 67.395–96.333 kPa.

Another main task of the analysis of mesoporous materials is the calculation and construction of pore volume distribution curves for the Al₂O₃ support. Calculation of the pore sizes is based on determination of radius, diameter and volumes by the method of Harkins and Jura [14].

The calculation results are shown in Fig. 3, where the distribution of pore volumes by their diameters is demonstrated. In addition, using the automatic sorption
It follows from the analysis data (Fig. 3) that the maximum total volume \( V = 0.35–0.49 \text{ cm}^3/\text{g} \) refers to the pores with the average diameter of \( d = 2.42–8.29 \text{ nm} \), while the mesopores with diameters of 8.75–11.26 nm have a total volume of 0.327–0.132 cm\(^3\)/g. At the same time the mesopores with diameters of 12.00–22.22 nm have a total volume of 0.0135 cm\(^3\)/g.

The adsorption of active complexes—2,3,4,5,6-pentafluor-TPhPFe(III) (tetrakis) and TPhPFe(III) apparently occurs in these mesopores, the size and structure of which correspond to the size and structure of iron porphyrin complexes (16–18 nm).

This is confirmed by the data obtained by the adsorption method of analysis, which indicate the difference in the amounts of the adsorbed agent (nitrogen) in the mesopores with diameters \( d = 12.00–22.22 \text{ nm} \) of the pure support and the tetrakis/
Al₂O₃ catalyst. With an increase in the pore diameters, this difference becomes more pronounced (Fig. 4).

Thickness of the adsorption layer was also determined depending on the amount of adsorption on the surface of the Al₂O₃ support and the tetrakis/Al₂O₃ catalyst (Fig. 5).

At the relative nitrogen pressure (p/p₀) = 0.685 and the amount of adsorption of 5.826 mmol/g, the thickness of the adsorption layer formed on the support surface is 0.84 nm (t-Plot data, Harkins and Jura method). The thickness of the adsorption layer on the catalyst surface at a relative nitrogen pressure (p/p₀) = 0.682 and the amount of adsorption of 5.793 mmol/g is 0.83 nm.

Fig. 5 Dependence of the amount of adsorption and the thickness of the adsorption layer on the relative pressure; a Al₂O₃, b tetrakis/Al₂O₃

Fig. 6 The total volume of slit-pores of the Al₂O₃ support depending on their width

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During the adsorption analysis, slit-pores on the surface of the support were recorded, the width of which was 0.448–1.566 nm with a total volume of 0.01–0.08 cm³/g. As can be seen from the data, they are micropores and have no role in the adsorption process (Fig. 6).

Fig. 7 shows the values of the specific surface area of the support. As can be seen from the figure, the main part of the active surface area refers to the mesopores with the diameters up to 20 nm, the specific surface of which is up to 236 m²/g.

It is known that the solid supports used as a matrix for a biomimetic catalyst have acid–base centers, which play an essential role in the mechanism of the formation of monooxygenase products [15].

Therefore, it is important to study qualitative and quantitative characteristics of the surface acid–base centers of an inorganic matrix (Al₂O₃) and a heterogeneous bioimitator [15]. To determine these characteristics, the methods of programmed thermal desorption were used under the following conditions: adsorption temperature 25 °C, temperature programming rate 35 °C/min in the temperature range of 25–600 °C.

The presence of the main centers was determined by thermal desorption spectra of carbon dioxide, while the presence of the acid sites—by thermal desorption of NH₃. For the initial untreated Al₂O₃ support, “weak” Bronsted, “moderate” and “strong” Lewis acid sites were determined from the thermal desorption peaks.

As a result of the introduction of the active mass of the bioimitator into the composition of the carrier, two peaks are observed in the thermal desorption spectrum of a fresh sample of the bioimitator, corresponding to the “weak” (Bronsted center) and “strong” (Lewis center) acid centers. In addition, the “weak” and “strong” main centers appear. Comparison of these data for the fresh bioimitator and the initial support shows that the adsorption of the active complex on the Al₂O₃ support leads to the appearance of a new “strong” basic center and to the disappearance of “moderate” Lewis acid sites. This suggests that, obviously, the adsorption of the active iron porphyrin complex occurs precisely in the “moderate” acid sites of the carrier.

![Fig. 7 Specific surface of the carrier depending on the pore diameters](image-url)
After adsorption of the active complex on the “moderate” Lewis acid sites, the free basic and “weak” Bronsted acid sites remain on the surface of the support. Thus, a structural model of iron porphyrin-containing enzymes is obtained. The reactions carried out in the presence of this model will be similar processes occurring in biochemical systems, i.e. H⁺ dependent redox processes.

As a result of investigations of the structure and acid–base centers of the Al₂O₃ support, the design of bioimitator tetrakis/Al₂O₃ catalytic domain is presented (Fig. 8):

As can be seen from Fig. 8., the redox active site of the catalytic domain is the penta-FTPhPFe(III) complex, whose structure is stabilized by the coordination of the matrix base (Al–O:) with hematin functional groups, for example, due to axial ligands.

The investigation of resonance Raman spectra of catalase or monooxygenase bioimitators, PPFe³⁺OH/Al₂O₃ and penta-FTPhPFe³⁺OH/Al₂O₃ showed that the frequencies ν₄, ν₃, ν₂, ν₃⁴, ν₁₀ correspond to the values 1372, 1491, 1574, 1593 and 1631 cm⁻¹ [10, 12], which are characteristic of iron porphyrin catalase [16],
and that the high-spin heme ion Fe$^{3+}$ is present in the fifth coordination position (Fig. 9).

The decrease in the frequency $\nu_4$ of the complex to a value of 1361 cm$^{-1}$ during the reduction of the complex indicates the involvement of the $\pi$-donor axial ligand of the iron ion in the form of Fe$^{3+}$–O–Al. Thus, a pronounced analogy with the sixth coordination high-spin heme ion Fe$^{3+}$ associated with tyrosine in catalase is revealed [12, 16].

**Investigation of the catalytic activity of the synthesized biomimetic catalysts in the reaction of methane monooxidation**

The process of methane monooxidation was carried out in a flow-through quartz reactor with a volume of 3.5 cm$^3$ in ideal displacement mode at atmospheric pressure with varying process parameters—temperature, volumetric feed rate of initial reagents, and oxidant concentration. A “green oxidant”—hydrogen peroxide—was used as an oxidizing agent. Referring to [8–13], we can say that hydrogen peroxide, having redox properties and an inducing effect, as will be shown below, promotes the selective oxidation of the studied compounds under very moderate conditions. The process was carried out in a flow-through reactor with a special design, which provides introduction of H$_2$O$_2$ into the reaction zone in a non-decomposed form.

The inductive effect of H$_2$O$_2$ is associated with its catalase reaction under the effect of a bioimitator, which provokes a secondary reaction in the system—the reaction of substrate monooxidation. Under such conditions of chemical interference, the reaction of monooxidation of the substrate is accompanied by the occurrence of two interrelated and interacting—coherent reactions: catalase and monooxygenase [8].

In addition, the use of a biomimetic catalyst that mimics the basic properties of the cytochrome P-450 oxidoreductase enzyme in the presence of the H$_2$O$_2$ oxidant made it possible to activate methane to methanol at a temperature of 150–350 °C and atmospheric pressure.

Since aqueous solutions of hydrogen peroxide of various concentrations (15–35%) were used as an oxidizing agent, the unconditionally obtained liquid reaction products also consist of aqueous solutions, which include methanol, dimethyl ether and formaldehyde with different contents depending on the condition reactions.

Chromatographic analysis of these mixtures was carried out on an AGILENT-7820 chromatograph on a ZB-FFAP (USA) capillary column (length = 30 m, ID = 0.25 nm, Film Thickness = 0.25 μm) with a flame ionization detector, which gives the percentage ratio of the obtained components with the exception of water (Fig. 10).

Determining the methane conversion by chromatographic analysis with a packed column with Porapak Q, which shows the amount of unreacted methane and from the analysis of liquid products, the yields of the reaction products were determined: CH$_3$OCH$_3$; CH$_2$O; CH$_3$OH and CO$_2$ (Fig. 11.).

The results of the experimental study of direct oxidation of methane on a tetrakis/Al$_2$O$_3$ bioimitator depending on temperature are shown in Fig. 12.
From the kinetic curves shown in Fig. 12, it can be seen that at higher temperatures, the yield of methanol increases. However, at the same time, a decrease in the yield of formaldehyde is observed, which can be explained by its transformation into deep oxidation products—CO₂. According to the data in Fig. 12, as the temperature rises, the yields of dimethyl ether also increase along with methanol, which is associated with the catalytic interaction of two methanol molecules. A further increase in temperature leads to a decrease in dimethyl ether, which is reflected in the yields of by-products.

Experiments carried out at a constant temperature (250 °C) and a molar ratio of CH₄: H₂O₂ = 1: 1 with 30% H₂O₂, depending on the contact time, showed that with an increase in the contact time, the yields of methanol and dimethyl ether increase (Fig. 13).
Fig. 12  Temperature dependence of the product yields of the biomimetic oxidation of methane by hydrogen peroxide, reaction conditions: \( V_{\text{CH}_4} = 0.35 \) l/h; \( V_{\text{H}_2\text{O}_2} = 1.8 \) ml/h; \( C_{\text{H}_2\text{O}_2} = 30\% \); \( \text{CH}_4:\text{H}_2\text{O}_2 = 1:1 \); \( \tau = 2.45 \) s. 1—\( \text{CH}_3\text{OH} \); 2—\( \text{CH}_2\text{O} \); 3—\( \text{CH}_3\text{OCH}_3 \); 4—\( \text{CO}_2 \); 5—\( \text{CH}_4 \) conv.; 6—consumption of \( \text{H}_2\text{O}_2 \) in the catalase reaction.

Fig. 13  Influence of the contact time on the yield of the reaction products of biomimetic monooxidation of methane on tetrakis/\( \text{Al}_2\text{O}_3 \) by hydrogen peroxide under the following conditions: \( C_{\text{cat}} = 0.64 \) mg/g, \( T = 250 \) °C, \( C_{\text{H}_2\text{O}_2} = 30\% \). 1—\( \text{CH}_3\text{OH} \); 2—\( \text{CH}_2\text{O} \); 3—\( \text{CH}_3\text{OCH}_3 \); 4—\( \text{CO}_2 \); 5—\( \text{CH}_4 \) conv.; 6—consumption of \( \text{H}_2\text{O}_2 \) in the catalase reaction.
The effect of the concentration of hydrogen peroxide in water on the course of the reaction is shown in Fig. 14, from which it can be seen that an increase in the concentration of \( \text{H}_2\text{O}_2 \) increases the conversion of methane, while the yield of methanol also increases. By varying the process parameters, a highly selective (100%) formation of liquid oxygen-containing one-carbon compounds with carbon neutralization was achieved; at \( T = 200 \) °C, yield \( \text{CH}_3\text{OH} = 7.8\% \), \( \text{CH}_2\text{O} = 7\% \) and \( \text{CH}_3\text{OCH}_3 = 5.5\% \), with \( \text{CH}_4 \) conversion = 20.3, where \( \text{CO}_2 = 0 \) is practically not formed.

As can be seen from the experimental results, the formation of methanol leads to the appearance of dimethyl ether in the reaction system and high yields of methanol contributes to the increase in the rate of formation of dimethyl ether. Such a kinetic regularity is unambiguously observed in the results of additional experiments carried out with methanol over the same bioimitator under the same conditions (Fig. 15).

The experimental results show that, under the indicated conditions, methanol is converted into dimethyl ether with 100% selectivity (Fig. 15).

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**Fig. 14** Influence of \( \text{H}_2\text{O}_2 \) concentration on the course of methane monooxidation reaction under the following conditions: tetrakis/\( \text{Al}_2\text{O}_3 \); Cat. = 0.64 mg/g; \( T = 300 \) °C; \( \text{V}_{\text{CH}_4} = 0.51 \, \text{l/h} \); \( \text{V}_{\text{H}_2\text{O}_2} = 1.25 \, \text{ml/h} \). 1—\( \text{CH}_3\text{OH} \); 2—\( \text{CH}_2\text{O} \); 3—\( \text{CH}_3\text{OCH}_3 \); 4—\( \text{CO}_2 \); 5—\( \text{CH}_4 \) conv

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**Fig. 15** Conversion of methanol to dimethyl ether under the conditions of the reaction of \( \text{CH}_4 \) monooxidation on tetrakis/\( \text{Al}_2\text{O}_3 \). 1—\( \text{CH}_3\text{OH} \); 2—\( \text{CH}_3\text{OCH}_3 \)
Mechanism and kinetics

On the basis of the experimental study, it is possible to present a scheme for the direct conversion of methane into one-carbon oxygen-containing compounds with their subsequent transformations (Scheme 1).

However, curves 5 and 6 in Figs. 12 and 13, which represent the amount of H$_2$O$_2$ consumed in the catalase reaction (the rate of O$_2$ formation) and the rate of methane conversion, respectively, show coherently synchronized nature of these reactions: catalase (the reaction of H$_2$O$_2$ decomposition with the formation of O$_2$) and monooxygenase—the reaction of CH$_4$ oxidation to methanol [8]. It can be seen from the curves in these figures that the interaction of these synchronously proceeding reactions leads to simultaneous intensification of one (monooxidation of CH$_4$) and weakening of the other reaction (catalase). At the maximum rate of the catalase reaction, the rate of methane conversion is insignificant, or vice versa (curve 1), with an increase in temperature and contact time, an increase in the rate of the methane monooxidation reaction is accompanied by a decrease in the rate of O$_2$ formation—the rate of catalase reaction. The connection between these two coherently synchronized reactions is created using ImtOOH intermediate, formed during the interaction of H$_2$O$_2$ with a catalytic biomimetic in the primary stage (1) of the catalase reaction, followed by its consumption in reactions 2 and 3 according to the following mechanism (Scheme 2):

The principle of the formation of the highly active hydroperoxide complex ImtOOH (1) under the effect of a biomimetic is presented in a scheme of mechanism of the catalase reaction (2) and biomimetic conversion of methane into methanol (3).

The mechanism of methane conversion on the surface of a biomimetic catalyst with the participation of H$_2$O$_2$, it is based on the detailed mechanisms of the
action of the enzyme catalase on the breakdown of \( \text{H}_2\text{O}_2 \) in biosystems by scientists Chance, Nagiev, Poltorak et al. [8, 12, 18, 22]

It follows from the scheme of the mechanism that under the effect of the axial group of the ligand \( \text{Fe}^{3+} + \text{OH} \), as well as with the “assistance” of the acid–base centers of the \( \text{Al}_2\text{O}_3 \) carrier, the \( \text{H}_2\text{O}_2 \) molecule is transformed into the \( \text{IntOOH} \) by the elimination of two protons from the acid center and the hydroxyl group of the ligand, along with rupture and formation of chemical bonds, according to the principle of the chain of bond redistribution (CBR) [12, 22].

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{IntOH} & \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O} + \text{IntOH} \\
& \rightarrow \text{H}_2\text{O} + \text{CH}_4
\end{align*}
\]

The interaction of the catalytic intermediate with the initial substrate (\( \text{CH}_4 \)), leading to the formation of the target product (\( \text{CH}_3\text{OH} \)), also proceeds according to a mechanism similar to that of cytochrome P-450 [17, 19].

The condition of coherence between the synchronously proceeding above mentioned reactions: (2) catalase and (3) monooxygenase reaction of methane oxidation to methanol is quantitatively estimated using the determinant equation [8, 20, 21]:

\[
D = \nu \left( \frac{f_1}{f_{\text{acc}}} + \frac{f_2}{f_{\text{acc}}} \right)^{-1}
\]

Used as an oxidizing agent, hydrogen peroxide plays the role of an actor and an inductor in this reaction system. And as can be seen from the scheme of the mechanism, it is consumed in the form of an intermediate in these two coherently synchronized reactions: in the primary catalase in the amount of \( f_1 \) (2) and in the secondary monooxygenase (3) in the amount of \( f_2 \); \( f_{\text{acc}} \) —methane consumption (acceptor), \( \nu \) is the stoichiometric coefficient of the actor.

Calculated values of the determinant and data on the fulfilment of the coherence relation according to the equation.
### Table 1

Determinants of the reaction of methane monooxidation and the amount of H₂O₂ consumed in these reactions: CH₂O₂ =30%, V₇H₂O₂=1.8 ml/h, V₇CH₄=0.35 l/h

| № | t, °C | CH₂O₂, % | CH₄:H₂O₂, | N⁰CH₄, mol/h | f⁰H₂O₂, mol/h | conversion, CH₄, % | CH₃OH, % | CH₃O+CH₃OCH₃, % | f₁, mol/h | f₂, mol/h | f₃, mol/h | D     |
|---|------|----------|-----------|--------------|---------------|-------------------|-----------|-----------------|-----------|-----------|-----------|-------|
| 1 | 130  | 30       | 1:1       | 0.0157       | 0.0177        | 9.2               | 2.1       | 7.1             | 0.0163    | 0.0014    | 0.0014    | 0.08  |
| 2 | 150  | 30       | 1:1       | 0.0157       | 0.0177        | 13.3              | 3.8       | 9.5             | 0.0156    | 0.0021    | 0.0021    | 0.12  |
| 3 | 200  | 30       | 1:1       | 0.0157       | 0.0177        | 20.3              | 7.8       | 12.5            | 0.0145    | 0.0032    | 0.0032    | 0.18  |
| 4 | 250  | 30       | 1:1       | 0.0157       | 0.0177        | 24.3              | 12.4      | 11.95           | 0.0138    | 0.0039    | 0.0039    | 0.22  |
| 5 | 300  | 30       | 1:1       | 0.0157       | 0.0177        | 27                | 16        | 11              | 0.0134    | 0.0043    | 0.0043    | 0.24  |
| 6 | 350  | 30       | 1:1       | 0.0157       | 0.0177        | 27.7              | 19.2      | 8.5             | 0.0133    | 0.0044    | 0.0044    | 0.25  |
are given in Table 1, which unambiguously indicates that the considered reactions are indeed coherently synchronized.

Values \(0 < D < 1\) are consistent with the chemical interference condition.

**Conclusion**

The activity of the penta-FTPhPFe\(^{3+}\)OH/Al\(_2\)O\(_3\) biomimetic in the conversion of methane by the green oxidant \(\text{H}_2\text{O}_2\) and its stability under reaction conditions were investigated.

Based on the results of the structural analysis of the Al\(_2\)O\(_3\) support and the biomimetic catalyst sample, the nature, size and shape of their mesopores were identified, which allows us to call the biomimetic catalyst nanocatalyst.

The ways and mechanisms of the formation of reaction products of coherent synchronized monooxidation of methane by peroxide hydrogen on biomimetics were determined based on the experimental study carried out on the basis of oxidative biomimetic conversion of methanol to dimethyl ether.

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