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MECHANISM OF BIOMIMETIC OXIDATION OF CYCLOHEXANE TO CYCLOHEXANONE BY HYDROGEN PEROXIDE

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The process of gas-phase oxidation of cyclohexane was studied in the presence of a heterogeneous biomimetic catalyst (per-FTPhPFe(III)OH/Al₂O₃), at 130–250°C, in which high yields of cyclohexanone and cyclohexanol were obtained up to 25.2% with a selectivity of ~80% at a cyclohexane conversion of 34%. The mechanism of the conversion of cyclohexane to cyclohexanone has been studied in detail, and the coherently synchronized character of the reaction proceeding is shown.

Keywords: cyclohexane, oxidation, biomimetic catalysts, cyclohexanone, hydrogen peroxide.

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Introduction

The oxidation of cyclohexane to cyclohexanol and cyclohexanone is one among the important industrial processes. Both oxidation products are the main industrial precursors of respectively, caprolactam and adipic acid, the building blocks of polymers nylon-6 and nylon-6,6 [1, 2]. In addition, cyclohexanone is in particular also a starting material in the synthesis of insecticides, herbicides and pharmaceuticals [2].

The most promising raw material for the production of cyclohexanol, cyclohexanone and adipic acid is cyclohexane and its derivatives, which are isolated from the gasoline fractions of some oils. During the liquid-phase oxidation of cyclohexane homologues (methyl-, ethyl-, isopropyl-, and dimethylcyclohexanes) with air mixtures of mono- and dibasic acids C₁–C₄ are formed. Currently, the main industrial process for the oxidation of naphthenes is the oxidation of cyclohexane to cyclohexanone and adipic acid [3].

The initiation of the oxidation reaction of cyclohexane can be carried out by various methods with application catalysts – soluble salts of metals of variable valence (mainly cobalt salts) and initiating additives (hydrogen bromide, nitrogen dioxide, cyclohexanone), as well as thermally and photochemically [3].

The industrial method for the production of cyclohexanol, cyclohexanone and adipic acid is based on the liquid-phase oxidation of cyclo-

hexane with molecular oxygen in the presence of cobalt naphthenate at a temperature of 433–453 K, air pressure of 9–13 atm [4–6]. However, under these industrial conditions, the maximum selectivity of the process does not exceed 70% at the conversion of cyclohexane up to 9%.

Most of the known oxidation processes of cyclohexane in the presence of various catalysts – MnO, FeZSM, copper pyrophosphate and in the biomimetic iron-porphyrin system FeP/O₂/Zn/AcOH/CH₃CN are also carried out in the liquid phase [7–9].

The creation of heterogeneous biomimetic catalysts made it possible to carry out some well-known oxidation processes, including the process of oxidation of cyclohexane to cyclohexanol and cyclohexanone in the gas phase, that led to the elimination of the disadvantages existing in liquid-phase oxidation.

Heterogenized biomimetic catalysts based on iron porphyrin complexes have been developed, on which the oxidation processes were carried out in the gas phase. One of the main properties of these catalysts is functional specificity, which is characteristic of enzymes associated with the special properties of protein molecules. The synthesized catalysts mimic the main physicochemical properties of the cytochrome P-450 monooxygenase enzyme, such as activity and selectivity [10, 11].

In contrast to the well-known studies on biomimetic oxidation of cyclohexane, carried

out mainly in the liquid phase, the gas-phase oxidation of cyclohexane on heterogeneous biomimetic, as was shown in [12, 13], has significant advantages: the process is carried out in a flow system with a fixed catalyst layer through more simplified technology, where reaction products are not mixed with the catalyst and after the reaction their separation is not required and no additional costs are required.

Experimental part

The process of monooxidation of cyclohexane was carried out on heterogeneous biomimetic catalysts such as hemin – protoporphyrin iron(III) ($\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$) and perfluorotetraphenylporphyrin iron(III) ($\text{per-FTPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$), which were synthesized in several stages [14]. The primary stage in the synthesis of biomimetic is the dissolution of iron porphyrin complexes in appropriate solvents. Immobilization of active centers on a solid support Al_2O_3 was carried out by extracting them from solvents.

Experimental study of the oxidation of cyclohexane on synthesized biomimetic catalysts was carried out in the gas phase in a flowing quartz reactor with reaction zone volume of 3.0 cm^3 at the temperature of $130\text{--}230^\circ\text{C}$ and atmospheric pressure in the presence of biomimetic catalyst with the active part of perfluorinated iron tetraphenylporphyrin backed on a solid Al_2O_3 support. As an oxidizing agent were used aqueous solutions of hydrogen peroxide of various concentrations (20–40%).

Hydrogen peroxide is an affordable and cheap "green oxidizer", according to the principles of the "Green Chemistry" concept and is increasingly used in hydrocarbons oxidation processes [15, 16].

Analysis of reaction products was carried out on chromium-mass spectrometer 5975 MSD + 7820 GC System and gas-liquid chromatograph 7820A GC System from Agilent Technology and on the chromatograph JIXM-80.

Results and discussion

Experimental studies of the activity of $\text{per-FTPhPFe(III)OH}/\text{Al}_2\text{O}_3$ catalyst depending on the temperature, concentration of hydrogen peroxide and contact time made it possible to

obtain data indicative of its high activity in the process of cyclohexane monooxidation.

Kinetic regularities of cyclohexane conversion over $\text{per-FTPhPFe(III)OH}/\text{Al}_2\text{O}_3$ biomimetic catalyst as a function of temperature are presented in Figure 1. As shown in figure, oxidation of cyclohexane to cyclohexanol and cyclohexanone at the temperature range of $150\text{--}180^\circ\text{C}$ proceeds at the highest rate. With an increase in temperature, the yield of cyclohexene sharply increases and the yield of cyclohexadiene slightly increases, which is explained by the increase of the reaction rate of oxidative dehydrogenation of cyclohexane under these conditions ($200\text{--}230^\circ\text{C}$).

While the yield of cyclohexanol decreases with temperature, the yield of cyclohexanone at 180°C reaches its maximum (10.34%).

It can be concluded from the nature of the kinetic curves 2 and 3 (Figure 1) that the formation of cyclohexanone probably does not pass through the formation of an intermediate product of cyclohexanol. The temperature dependence of the kinetic curves shows that, starting from 200°C H_2O_2 decomposition into molecular oxygen stabilizes, that indicates full expenditure of hydrogen peroxide in the system for carrying out of two interrelated reactions. This undoubtedly affects the processes of monooxidation and hydroxylation of cyclohexane. This experimental fact indicates that the processes of monooxidation and hydroxylation are interrelated with the reaction of H_2O_2 decomposition and proceed in a coherent manner with it. It is shown in [17] that such reaction system is effectively realized in a coherently synchronized regime. In this context, the kinetic data obtained in Figure 1 are consistent with the theory and practice of coherently synchronized reactions [18].

Since cyclohexanone has been the dominant (target) product in our study (from Figure 1), and its maximum yield (10%) has been observed at 180°C , the effect of contact time on the cyclohexane oxidation has been investigated at this temperature.

Kinetic curves in Figure 2 show that the increase in the contact time (τ) in cyclohexane monooxidation reaction up to 10 seconds the yield of cyclohexanone increases (up to 12.1%), and then the yield varies insignificantly.

Fig. 1. Temperature dependence of the products yields of cyclohexane oxidative conversion by hydrogen peroxide in a mixture with 6.25% of $C_6H_{11}OH$ and 2.53% of $CH_3C_6H_{11}$ on per-FTPhPFe(III)/ Al_2O_3 biomimetic: $c_{H_2O_2} = 25\%$, $V_{H_2O_2} = 1.41$ ml/h, $V_{C_6H_{12}} = 0.9$ ml/h, $C_6H_{12}:H_2O_2 = 1: 1.5$. 1 – conversion of C_6H_{12} , 2 – cyclohexanol, 3 – cyclohexanone, 4 – cyclohexene, 5 – cyclohexadiene, 6 – O_2 .

Fig. 2. Dependence of the product yields of cyclohexane oxidation in a mixture with 6.25% of $C_6H_{11}OH$ and 2.53% of $CH_3C_6H_{11}$ on per-FTPhPFe(III)/ Al_2O_3 biomimetic by hydrogen peroxide on contact time: $c_{H_2O_2} = 25\%$, $t = 180^\circ C$, $C_6H_{12}:H_2O_2 = 1:1$. 1 – conversion of C_6H_{12} , 2 – cyclohexanol, 3 – cyclohexanone, 4 – cyclohexene, 5 – O_2 .

The rate of cyclohexene production process also increases, while the yield of cyclohexanone increases insignificantly. In this case, conversion of cyclohexane increases with increasing contact time. Kinetic regularities from Figure 2 lead us to the conclusion that cyclohexanone is probably not formed from cyclohexanol. It should be noted that in the absence of cyclohexane, H_2O_2 at these contact times has been completely decomposed.

Based on previous studies on coherently synchronized oxidation reactions by hydrogen peroxide [16, 18] and the nature of the kinetic curves according too of the experimental results

of this process, we can say that the biomimetic oxidation of cyclohexane with hydrogen peroxide is a complex reaction consisting of two coherently synchronized reactions: 1) catalase and 2) monooxygenase. The coherently synchronized nature of the process is associated with the inducing ability of hydrogen peroxide, which contributes to the formation of a highly active intermediate complex, similar to the enzyme-substrate complex. The generalized scheme of coherently synchronized biomimetic oxidation of cyclohexane by hydrogen peroxide is described as follows [10, 16, 18–20]:

Scheme

It follows from the scheme that a highly active intermediate (ImtOOH) obtained as a result of the interaction of hydrogen peroxide with a bioimitator at the first stage of the primary (catalase) reaction, interacts with the second H_2O_2 molecule and with cyclohexane in the secondary (monooxygenase) reaction leads to the formation of final reaction products [18].

The Al_2O_3 we used as a matrix, possessing acid-base properties, has Brensted and Lewis acid and basic centers, which play a key role in the formation of reaction products. Aluminum oxide acts as an electron donor and acceptor, thereby facilitating the cleavage and formation of bonds.

A detailed study of the characteristics of

these centers gives a complete understanding of the mechanism of the redox action of a biomimetic catalyst and the possibility of selective transformation of the substrate into target products [21].

Since, according to our experimental data, the peroxidase reaction does not proceed, the probable mechanism of the formation of cyclohexanone from cyclohexane can be presented in the following form according to Scheme I, which shows the electronic mechanism of the catalase reaction with the preparation of the active intermediate complex ImtOOH (1) and the mechanism of its interaction with cyclohexane, which leads to the formation of cyclohexanone on the surface of the biomimetic (2) and (3).

Mechanism of catalase reaction

Mechanism of formation of cyclohexanone

According to the results of studies and the presented schemes (2 and 3), the direct conversion of cyclohexane to cyclohexanone occurs through the formation of an intermediate biomimetic-substrate complex $\text{Imt-O-C}_6\text{H}_{11}$, which is formed by the interaction of the intermediate (ImtOOH) with cyclohexane (2). The interaction of this complex with another H_2O_2 molecule leads to oxidation-reduction transformation of the complex into cyclohexanone, water and original biomimic (3). This mechanism agrees with the fact that cyclohexanone is formed precisely under usage the most concentrated H_2O_2 (30% or more) and a lower temperature (150–180°C).

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**TSİKLOHEKSANIN TSİKLOHEKSANONA HİDROGEN PEROKSİDLƏ BİOMİMETİK OKSİDLƏŞMƏSİ
MEXANİZMİ****S.Ə.Ağaməmmədova**

Heterogen biomimetik katalizator (per-FTPhPFe(III)OH/Al₂O₃) iştirakında 130–250⁰C temperaturda tsikloheksanın qaz fazada oksidləşməsi prosesi öyrənilmiş, tsikloheksanın 34% konversiyasında tsikloheksanon və tsikloheksanolun ~80% selektivliklə 25.2%-ə qədər yüksək çıxımı müəyyən olunmuşdur. Tsikloheksanın tsikloheksanona çevrilmə mexanizmi dəqiqliklə öyrənilmiş və reaksiyanın koherent-sinxronlaşdırılmış xüsusiyyəti göstərilmişdir.

Açar sözlər: tsikloheksan, oksidləşmə, biomimetik katalizatorlar, tsikloheksanon, hidrogen peroksid.

**МЕХАНИЗМ БИОМИМЕТИЧЕСКОГО ОКИСЛЕНИЯ ЦИКЛОГЕКСАНА В ЦИКЛОГЕКСАНОН
ПЕРОКСИДОМ ВОДОРОДА****С.А.Агамамедова**

Изучен процесс газофазного окисления циклогексана в присутствии гетерогенного биомиметического катализатора (per-FTPhPFe(III)OH/Al₂O₃) при 130–250⁰C, в котором были получены высокие выходы циклогексанона и циклогексанола до 25.2% с селективностью ~80% при конверсии циклогексана 34%. Подробно изучен механизм превращения циклогексана в циклогексанон, показан когерентно-синхронизированный характер протекания реакции.

Ключевые слова: циклогексан, окисление, биомиметические катализаторы, циклогексанон, пероксид водорода.