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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**Synthesis, structure and properties of 3d transition metals
complex compounds with molecular oxygen**

Speciality: 2303.01 - "Inorganic chemistry"

Field of science: Chemistry

Applicant: **Zehra Elxan Bayramova**

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The work was performed at Azerbaijan State Oil and Industry University, laboratory of "Chemistry and technology of inorganic substances" department

Scientific supervisor: D.Sci.Chem, professor
Minira Mahammad Ali Aghahuseynova

Official opponents: Academician of ANAS
Ajdar Akber Madjidov
D.Sci.Chem., professor
Sevindj Rafiq Gadjiyeva

Ph.D. Chem., associate professor
Asaf Jalal Quliyev

Dissertation council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at acad. M.P.Naghiyev Institute of Catalysis and Inorganic Chemistry

Chairman of the Dissertation council:



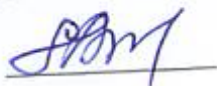
Academician
Dilgam Babir Taghiyev

Scientific secretary of the Dissertation council:



Ph. D. Chem.
Ulviyya Akhmed Mammadova

Chairman of the scientific seminar:



D.Sci.Chem., professor
Akif Shikhan Allyev

GENERAL CHARACTERISTICS OF THE WORK

Relevance and degree of development of the topic: The topic of oxygen activation and homogeneous catalytic oxidation with metal complexes has been in the spotlight for the last 20 years. Complex compounds of transition metals with organic ligands that bind molecular oxygen have extremely important properties. These types of complex compounds are very promising in terms of their use as oxidizing agents in oxidation reactions.

There is a great interest in the presentation of this topic in international conferences and symposia from various aspects of bioorganic and coordination chemistry, as well as catalysis. The number of scientific studies on the activation of molecular oxygen is constantly growing.

Complex formation of molecular oxygen, a number of heterogeneous catalytic oxidations can occur in the processes of autooxidation of complex compounds, as well as in biochemical processes. In such processes, the mechanism and functions of the action of oxygen carriers are often clarified with the help of homogeneous models. Complexes of transition metals which can bind molecular oxygen are often used as a model object. Coordinated compounds capable to bind and activate oxygen can serve as catalysts for obtaining of important industrial products.

Along with linear catalysts, cyclic biocatalysts - metalporphyrine compounds that imitate the properties of natural enzymes are of great interest. The use of metalporphyrins as a catalyst in petrochemical processes is gaining great scientific and technical relevance. Synthetic metalporphyrins have been obtained over the last 25 years and their various properties have been studied. Unlike synthetic metal-porphyrin complexes, metal-porphyrins separated from oil are very soluble in hydrocarbons and in the hydrocarbon fraction of oil.

Such oxygenated complex compounds are being intensively studied and of great interest. An analysis of the literature sources shows that there is very little information on the activation of oxygen. The properties of these complex compounds in solution have not been studied at all.

Object and subject of research: in the presented dissertation two types of linear and cyclic oxygen complex compounds with organic ligands based on 3d-transition metals have been synthesized, their structure and catalytic properties in the reaction of liquid phase oxidation of unsaturated hydrocarbons have been studied.

Thus, linear and cyclic molecular oxygen complex compounds of 3d-transition metals have been identified as effective and selective catalysts for the oxidation reaction of hydrocarbons.

Aim and objectives of the research: The main purpose of the dissertation is to select the optimal conditions for the synthesis of new complex compounds of 3d-transition metals with molecular oxygen, study the structures of complexes using various physicochemical methods, study of physicochemical properties, testing of catalytic activity in oxidation reactions, to determine their areas of application.

Research methods: Linear and cyclic complex compounds of 3d-transition metals have been synthesized with molecular oxygen. Modern methods of physical and chemical analysis (element analysis, IR-, electron absorption spectroscopy, EPR, NMR) have been used to identify the obtained complex compounds and study their structure.

The main provisions of the defense: The following issues have been resolved in order to achieve the set goal.

- Methods for the synthesis of molecular oxygen complex compounds of 3d-transition metals have been developed.
- The composition, structure and physicochemical, as well as spectroscopic properties of the synthesized oxygen complex compounds have been determined.

- The catalytic properties of the synthesized oxygen complexes in the oxidation reaction of alkenes have been studied.
- Cyclic complex compounds with linear molecular oxygen complexes of 3d-transition metals have been synthesized and their catalytic activity has been studied.
- 3d-transition metals are immobilized on inorganic (SiO₂) and organic (copolymer of styrene-divinylbenzene) carriers of complex compounds.

Scientific novelty of the research: 2 types of systems based on 3d-transition metals have been developed for selective liquid phase oxidation of unsaturated hydrocarbons with environmentally friendly oxidants under mild conditions. The 1 type system is based on linear metal complexes of transition metals, the 2 type metalporphyrin is based on catalysts, and these compounds are effective catalysts in the oxidation of alkenes by molecular oxygen. New methods of obtaining oxygen containing products-ketons and oksirans based on the use of these systems have been developed.

For the first time, the synthesis of molecular oxygen complex compounds of 3d-transition metals has been carried out, the composition and structure of the complexes obtained using various physicochemical methods have been studied, and their catalytic activity in oxidation reactions has been determined. On the basis of the case patent of the Republic of Azerbaijan No. 2018 0032 has been obtained. Optimal conditions for the synthesis of new 19 linear complex compounds of 3d-transition metals and 7 cyclic metalporphyrine complexes with molecular oxygen have been developed. The fact of activation of molecular oxygen has been determined during coordination.

It has been established that the redistribution of electron density during the transition of an oxygen molecule from a free to a coordinate state causes a change in the reaction ability of the molecule.

Along with linear metal complexes, cyclic porphyrin complexes have been obtained, their oxygen complexes have been studied. A highly effective method for the separation of heavy oil concentrate and metal porphyrins from petroleum products has been developed.

Obtaining porphyrin complexes of individual transition metals by metal on the basis of oil concentrate has been developed in 2 ways: based on interfacial catalysis and based on the reaction of the change of metal with a hydrogen atom in the porphyrin cycle. Unlike linear metal complexes, cyclic complexes have the ability to combine molecular oxygen. A perfect feature of these compounds is their ability to adsorb molecular oxygen, which can then pass into the supramolecular anion O_2^{2-} in the inner sphere. Anion with high activity oxidizes hydrocarbons at low temperature to suitable alcohol, ketones, etc. oxygen-retaining organic compounds.

The catalytic activity of molecular oxygen complexes of 3d-transition metals in the oxidation reactions of olefins (ethylene, propylene and butylene) has been studied and their high activity in the oxidation of alkenes has been observed. Experiments and results have shown that these compounds are new, effective, efficient and selective catalysts.

Theoretical and practical significance of the research: As a result of the research, the oxidation of alkenes in the presence of coordination compounds of molecular oxygen transition metals has been determined. Active catalysts have been proposed that allow the oxidation reaction of butene to methyl ethyl ketone with high yield $\alpha = 96-98\%$, mild conditions (low temperature $t=60-80^\circ\text{C}$, atmospheric pressure) and product selectivity $S=98-99\%$. Oxygenated complex compounds of linear and cyclic ligand 3d-transition metals can be oxygen carriers, and these compounds can be used as an effective catalyst in the oxidation of olefins, allowing the reaction to be carried out under mild conditions.

Approbation and application: The main results of the dissertation have been presented and discussed at the following National and International conferences. Третья Всероссийская Научная конференция (с международным участием): «Успехи синтеза и комплексообразования».(Москва, 2014), «Менделеев-2014» VIII Всероссийская конференция с международным участием молодых ученых по химии (Санкт-Петербург, 2014), Ümummilli Lider Heydər Əliyevin anadan olmasının 91-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların “Kimyanın aktual problemləri” VIII Respublika Elmi Konfransı (Bakı, 2014), Professor A.Ə.Verdizadənin 100 illik yubileyinə həsr olunmuş “Üzvi reagentlər analitik kimyada” II Respublika konfransının materialları (Bakı, 2014), XXVI Международная Чугаевская конференция по координационной химии (Казань, 2014), 12th European Congress on Catalysis – EuropaCat-XII (Russia, 2015), Akademik T.N.Şahtaxtinskiyin anadan olmasının 90 illik yubileyinə həsr olunmuş elmi konfrans, Akad. M.F.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu (Bakı, 2015), International Congress on Heterocyclic Chemistry «Kost -2015» dedicated to 100 years anniversary of professor Alexei Kost., Lomonosov Moscow State University (Moscow, 2015), XXIX Научно-техническая конференция «Химические реактивы, реагенты и процессы малотоннажной химии». «РЕАКТИВ–2015» (Новосибирск, 2015), “Koordinasion birləşmələr kimyası” adlı VI Respublika elmi konfransının materialları, Bakı Dövlət Universiteti (Bakı, 2015), Актуальные проблемы развития нефтегазового комплекса России (Москва, 2016), International Conference “Global Science and Innovation” (USA.Chicago, 2016), Международная научно-практическая конференция, Евразийский Союз Ученых (ЕСУ) (Москва, 2016), XII Международная научно-практическая конференция “Advances in Science and Technology” (Москва, 2018), Beynəlxalq elmi konfrans “Müasir təbiət və iqtisad elmlərinin aktual problemləri” (Gəncə, 2018), Abstracts of scientific conference “Nagiyev readings” dedicated to the 110th anniversary of academician M.Nagiyev (Bakı,

2018), Международная научно-практическая конференция «Инновативные перспективы развития нефтепереработки и нефтехимии» (Баку, 2018), Beynəlxalq elmi konfrans international scientific conference “Müasir təbiət və iqtisad elmlərinin aktual problemləri” (Gəncə, 2019), XX Международная научно-практическая конференция «Российская наука в современном мире» (Москва, 2019), Ümummilli lider Heydər Əliyevin anadan olmasının 96-cı ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların “Kimyanın aktual problemləri” XIII Beynəlxalq elmi konfransı (Bakı, 2019), The international Scientific Conference “Actual problems of modern chemistry” (Baku, 2019).

36 scientific works on the topic of the dissertation have been published, including 1 invention patent, 15 scientific articles (10 foreign and 5 local) and theses of 20 conference-symposium reports. Based on the results of the dissertation, 3 articles have been published individually.

Name of the organization where the dissertation work has been carried out: The dissertation work has been carried out in the laboratory of the "Chemistry and Technology of Inorganic Compounds" department of the Azerbaijan State Oil and Industry University.

MAIN CONTENT OF THE WORK

The introductory part of the dissertation shows the relevance and degree of development of the topic, the object and subject of research, goals and objectives, research methods, the main provisions of the defense, scientific novelty, theoretical and practical significance of research, approbation and application of the work.

The first chapter compares the literature sources on the activation of oxygen, the existing molecular oxygen coordination compounds, their structure and properties, oxidation reactions in the presence of dioxide-metal complexes, the oxidation of hydrocarbons.

Studies have shown that complex compounds of 3d-transition metals with molecular oxygen, both linear and cyclic, are more promising catalysts in the oxidation reaction of alkenes. Although molecular oxygen (dioxide O₂), a naturally regenerating and favorable oxidant, in many cases a natural product leading to the formation of water, is considered ideal compared to all oxidizing agents, the triplet nature prevents the widespread use of molecular oxygen as an oxidant in industrial processes. Very high potential barriers are formed during the interaction with most reducers that are single.

One way to increase the reactivity of oxygen is to "chemically activate" it. As a special case, it is fixed in transition metal complexes.

It is assumed that due to the large valence potential of the complexes, the activated molecule may have a certain selectivity in relation to the substrate, in addition to its ability to react under mild conditions. Analysis of the literature information shows that there are studies on the binding of molecular oxygen, the activation of small molecules, the catalytic properties of coordination compounds, the catalytic oxidation of hydrocarbons and the reactivity of oxygen complexes. However, the principles of molecular oxygen fixation and activation have not yet been fully elucidated.

Complex formation of molecular oxygen can occur in a number of heterogeneous catalytic oxidations, autooxidation of complex compounds, as well as in biochemical processes. In such processes, the impact mechanism and functions of oxygen carriers are clarified with the help of homogeneous models. In such cases, complexes of transition metals that can bind molecular oxygen are taken as the model object.

The dissertation provides information on the synthesis of oxygen complexes of 3d-transition metals, their structure and the ability to react in the oxidation reactions of hydrocarbons.

The second chapter provides brief information about the primary reagents, their properties, experimental techniques, research methods used (element analysis, IR-, UV-, electron and EPR

spectroscopy, NMR) and methods of synthesis of molecular oxygen compounds of 3d-metal complexes. Optimal conditions have been developed for the synthesis of 19 new 3d-transition metals of complex compounds having linear structure with molecular oxygen.

The creation of catalytic systems that combine the activity of homogeneous metal complexes with the reusability characteristic of heterogeneous catalysts is of particular interest. One of the ways to create catalysts reusable, with high-activity and high-efficiency is the immobilization of homogeneous metal complex catalysts in solid carriers. For this reason, a number of samples have been synthesized in order to heterogeneize the molecular oxygen complex compounds of the synthesized 3d-transition metals (Table 1).

Table 1

Yield of MEK in the presence of heterogeneous catalyst

№	The amount of catalyst, %	Carrier volume, ml	Yield of MEK, %
1	17,8	80	83,6
2	20	70	85,5
3	23	60	85
4	28,5	50	87
5	35	40	69

The third chapter describes the mechanism of activation of molecular oxygen through the complex formation of 3d-transition metals. There are reports that the obtained complex compounds play the role of effective catalysts in the oxidation reaction of olefins. The synthesis of molecular oxygen compounds of 3d-transition metals and the study of the catalytic properties of methyl ethyl ketone (MEK) in the production reaction have been presented here.

The purpose of the research is the synthesis of complex compounds of transition metals with molecular oxygen, the determination of the nature of the compounds involved in the formation of the complex, as well as the study of the reversible binding capacity of molecular oxygen, the possible applications of

the obtained complexes. Complexes of transition metals with molecular oxygen have been taken as catalysts in the oxidation reactions of direct hydrocarbons as the object of research.

Strict environmental and economic requirements dictate the creation of new technologies that replace the existing multi-stage processes leading to the generation of large amounts of waste in the acquisition of the MEK. Methods based on the use of n-butene as a more suitable raw material and molecular oxygen or hydrogen peroxide as an environmentally friendly oxidizer are of greater interest in this field. If to consider that MEK is a valuable industrial product, there is an urgent need for efficient catalytic systems that ensure the obtaining of environmentally safe and economically viable a single-stage selective MEK.

The existing methods of obtaining the MEK are characterized by the following significant shortcomings:

- multi-stage;
- low operating efficiency of the synthesis junction, low efficiency of reactors, high energy costs;
- during the development of methods for condensation of spent sulfuric acid, certain difficulties arise due to the corrosive activity of evaporated solutions, the formation of sulfuric acid mist, as well as the decomposition of sulfuric acid;
- formation of a large number of difficult-to-dispose products (polymers);
- with a complex separation system of methyl ethyl ketone.

There is a great demand for MEK in modern industry. MEK is an excellent solvent in oil refining and petrochemical industry, deparaffinization of oil fractions, is widely used in the manufacture for printing, audio and video cassettes, etc. The annual production of the MEK in the world in 2020 is 5.2 million tons. Demand for it is growing and it is annually 7%. At present, MEK is not produced in Russia and Azerbaijan, and the demand for MEK is met through imports. The lack of industrial production of the MEK is primarily explained by the lack of effective obtaining technology.

Complex compounds of 3d-transition metals with organic ligands have very important properties. These complex compounds have great potential for use as oxidizing agents in oxidative reactions of organic substances. That is why the idea of activating molecular oxygen appeared to increase the reactivity. The idea of activated molecular oxygen occurred in nature, and many scientists are now working in this field.

Currently, in many countries ketones are obtained by oxidation of alkenes using the Wacker-Schmidt method in the presence of an aqueous solution of d-element chlorides. During the reaction, chlorinated compounds are obtained as an additional product that complicates the technology of obtaining ketones from the reaction product. This is a highly selective, one-step and promising method that works in mild conditions. An effective catalyst for the oxidation of propylene are aqueous solutions of phosphoric acid and heteropolytic acid with phosphorolybden vanadium, which increase the yield of acetone to 90%.

Unfortunately, the oxidation of butene-1 and high alkenes in these catalytic systems is accompanied by an unsatisfactory product yield due to the low adsorption of alkenes in water. In this regard, our research is aimed at finding simple catalytic systems that are similar to the properties of macrocyclic ligand metal complexes, allowing the selective oxidation of higher alkenes with high product yields. Therefore, we have conducted research to find simple catalytic systems that increase the yield of basic products, allow the selective oxidation of high alkenes, and imitation properties of natural metal complexes.

As a catalyst, trisdimethylamine phosphine oxide complexes, known as hmfa-hexamethylphosphoramidate, phosphoric compounds of transition metals Cu (I) and Pd (II) are considered to be derivatives of phosphoric acid. The rate of oxygen absorption of amide complexes of chlorides of synthesized d-transition metals has been studied (Figure 1).



(com.1)

M = Cu(I), Cr(II), Fe(II),Co(II),V(III).

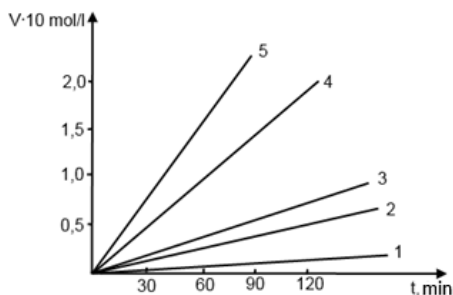
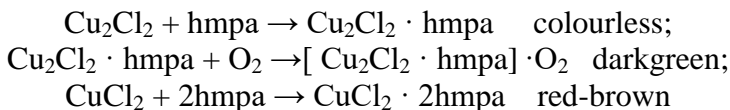


Fig.1. Absorption of oxygen (V,mol/l) by $MCl_n \cdot hmpa$ complexes at $T=20^{\circ}C$: 1-Cr (II); 2-V(III); 3- Co(II); 4- Fe(II); 5- Cu(I).

It has been found that the monovalent copper salt $CuCl$ is compatible with $CuCl$ capable of forming a stable oxygen complex $(CuCl \cdot hmpa)_2 \cdot O_2$ by coordinating oxygen in solution ($t_{melt}=7^{\circ}C$, $t_{boil}=230^{\circ}C$, 760 mm.m.c.) $CuCl$ forms the hmfa complex.



The spectra of the Cu (I) complex solution (curve 1) and the oxygen-absorbed complex solution (curve 2) differ sharply from the spectra of the Cu (II) complex solution (curve 3). The maximum absorption at 265 nm proves the formation of an oxygen complex (Figure 2).

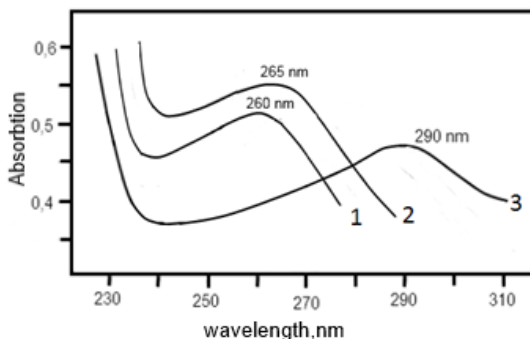
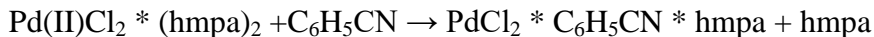


Fig. 2. UV absorption spectrum of copper complex solutions

The peculiarity of this oxygen complex is that even when heated, the coordinated oxygen does not break away from the complex, ie absorption is irreversible.

Methylethylketone (MEK) is obtained from the oxidation of butene-1 by direct contact with oxygen activated by the formation of an oxygen complex, and if butene-1 is activated by the formation of the butene-1 (B-1) complex, it will be possible to carry out the oxidation reaction at low temperatures and pressures. Therefore, studies have been conducted with complexes of transition metals of different palladium groups. The absorption capacity of B-1 complexes synthesized has been studied. The study of the kinetic patterns of absorption of butene-1 by Zn (II) Cl₂, Cu (II) Cl₂ and Pd (II) Cl₂ complexes showed that the absorption rate of the complex formed by palladium with aprotic solvents such as hexamethylphosphoramide-hmpa and benzonitrile was the highest (Figure 3).



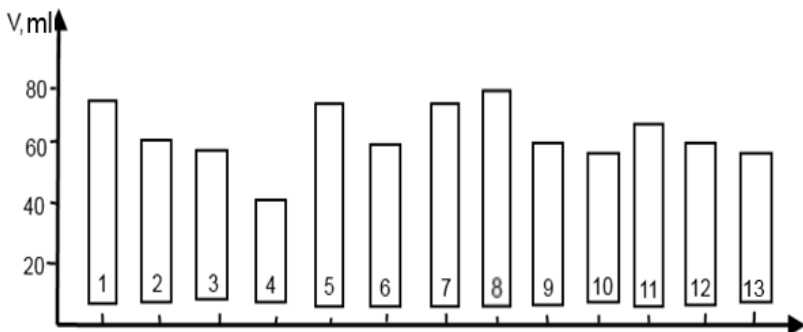
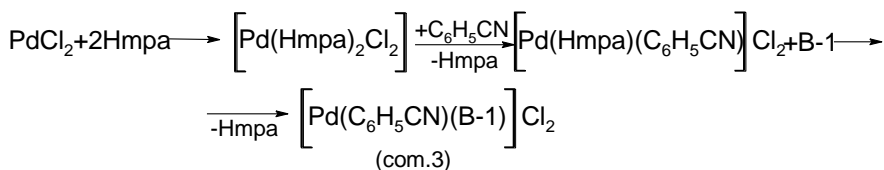


Fig.3. Histogram of B-1 absorption with various absorbents at room temperature for 120 min. 1-hmpa, 2-acetonitrile (AN), 3-propionitrile (PN), 4-benzonitrile (BN), 5-PdCl₂ · hmpa, 6-PdCl₂ · 2AH, 7- PdCl₂ · hmpa · AH, 8-PdCl₂ · hmpa · BN, 9-PdCl₂ · hmpa · PN, 10-CuCl₂ · hmpa · AN, 11-ZnCl₂ · hmpa · AN, 12-ZnCl₂ · hmpa · PN, 13-ZnCl₂ · hmpa · BN.

It is known that butene-1 dissolves well in aprotic solvents and some complexes. However, the highest absorption capacity is in hmpa and benzonitrile palladium complexes. These complexes are formed at room temperature, in the next stage it is converted to butene-1 at different temperatures and time values. As a result, the complex (Pd(C₆H₅CN)(B-1))Cl₂ is obtained from this interaction.



The study of the kinetic regularities of the absorption of the palladium complex of butene-1 showed that the absorption of B-1 increased due to raising the temperature to 60⁰C and the time of the process – to 90 minutes (Figure 4, curve 3). Experimental studies have shown that the (Pd(C₆H₅CN)(hmpa))Cl₂ complex is the best absorbent for butene-1.

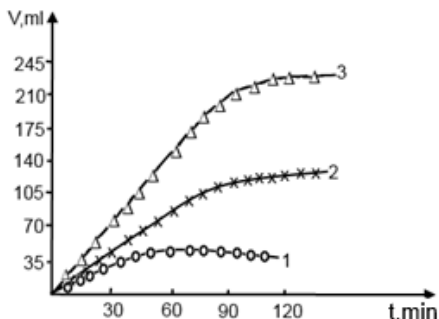
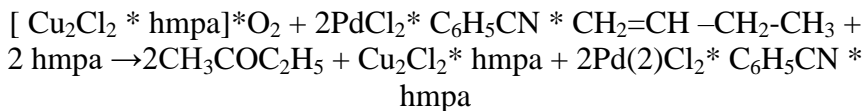


Fig.4. The kinetics of B-1 absorption by the complex $\text{PdCl}_2 \cdot \text{hmpa} \cdot \text{C}_6\text{H}_5\text{CN}$; 1-20, 2-40, 3-60°C.

Thus, the binary system of $\text{Cu(I)Cl} \cdot \text{hmpa}$ and $\text{Pd(II)Cl}_2 \cdot \text{C}_6\text{H}_5\text{CN} \cdot \text{hmpa}$ complexes is soluble in hmfa, benzonitrile- $\text{C}_6\text{H}_5\text{CN}$ and sulfolan- $\text{C}_4\text{H}_8\text{O}_2\text{S}$ solvents acting as complexing agents, then air or pure oxygen is transferred from the solution in order to receive an oxygen complex at the required concentration. A degassing process is carried out to remove the excess free oxygen remaining in the system, or B-1 as a reaction substrate obtained from the solution by the formation of an activated butene-1 complex is passed. As a result, activated butene-1 is oxidized by coordinated activated oxygen and the main product – MEK is received from the oxygenated complex. This oxidation reaction can be shown as follows:



The identification of the obtained product has been confirmed by IR spectroscopy and NMR methods. A spectrum corresponding to the ketone group ($\text{C}=\text{O}$) with a wavelength of 1715 cm^{-1} has been observed in the spectrum (Figure 5). It has been then analyzed by the NMR method to confirm the structure of the product obtained (Figure 6).

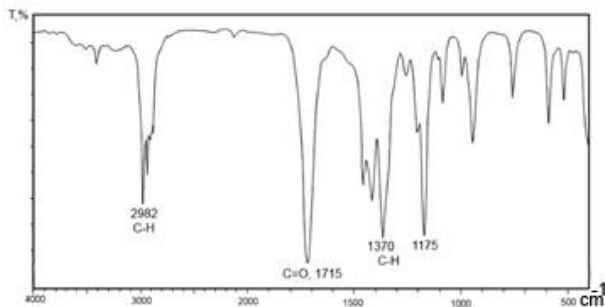


Fig.5. IR spectrum of methylethylketone

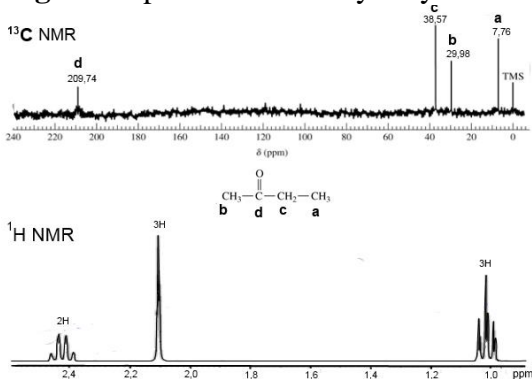


Fig. 6. NMR spectrum of methylethylketone

The results showed that high selectivity for methylethylketone (MEK) is observed in the entire temperature range of 50-100⁰C. From a practical point of view, a temperature range of 70-80⁰C, time 145 min., M (com.3): M (com.2) = 2: 1 ratio, solvent-hmfa is more suitable for the reaction. According to the MEK the conversion of B-1 was 99% and the selectivity was 98%. The coordination of the transition metal ion with the molecular oxygen is similar to the oxidation-reduction process that occurs as a result of the transition of electrons from metal to dioxygen ligand (O₂) (or vice versa), which causes changes in the IR spectra of complexes (Figure 7).

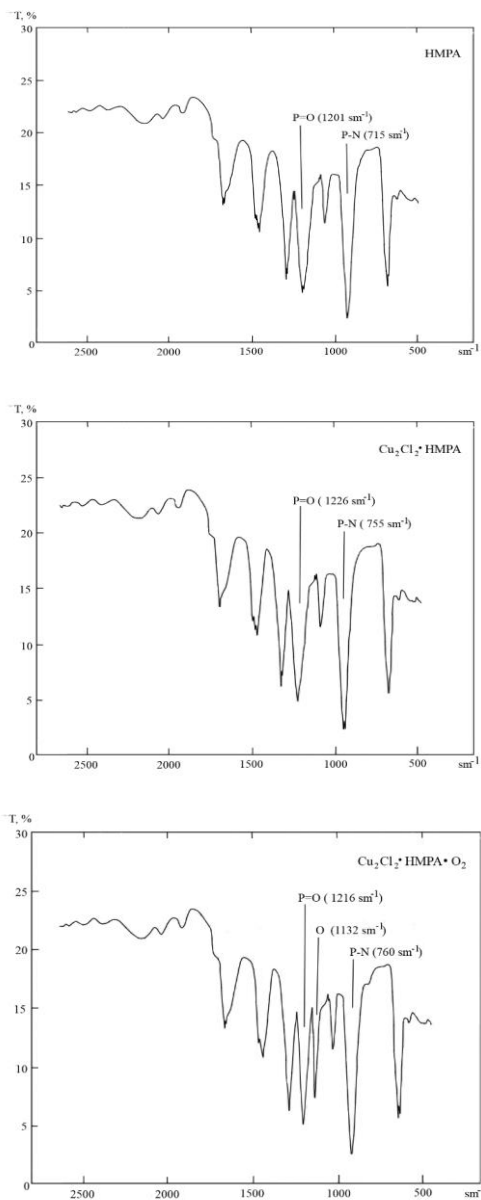
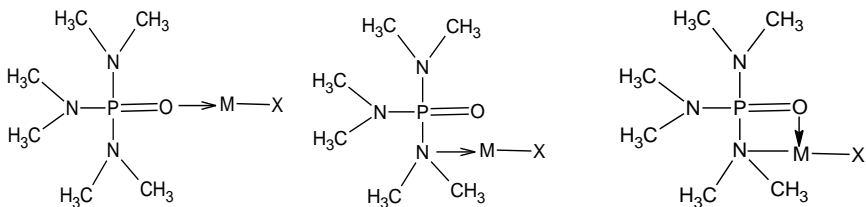


Fig. 7. IR spectrum of Hmpa, $\text{Cu}_2\text{Cl}_2\cdot\text{Hmpa}$, $\text{Cu}_2\text{Cl}_2\cdot\text{Hmpa}\cdot\text{O}_2$ compounds

Hexamethylphosphoramide-hmpa is an ambident ligand. Thus, it binds to the metal ion at the expense of oxygen or nitrogen of the PO group. A comparison of the IR spectra of molecular Hmpa and chloride complexes of transition metals shows that the Hmpa coordination under the influence of Cu (I) and Fe (II) results in a mixing of the frequencies ν (P = O) - and δ (PN).

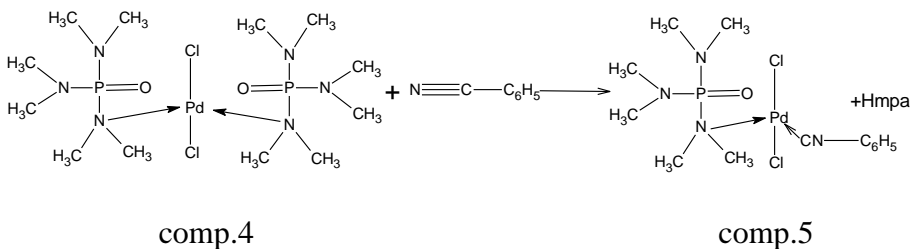


In this case (5 cm^{-1} difference) a strong displacement is observed. This indicates the formation of a dative bond between nitrogen and the metal ion. On the other hand, the frequency ν (P = O) is higher than that of the Hmpa molecule. This proves the presence of the O-M dative bond formed by the transferring of the π -orbital of oxygen with the free d-orbital of the metal.

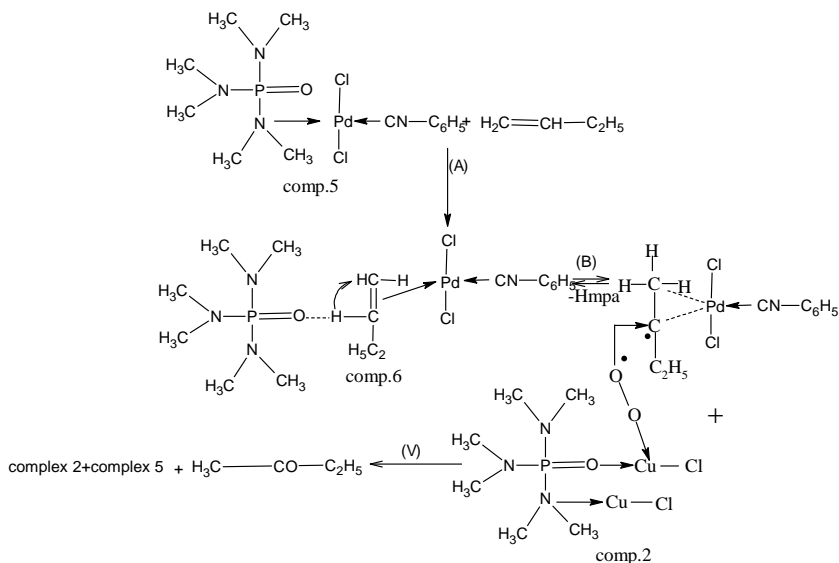
The IR spectra of the Cu (I) and Fe (II) dioxygen complexes, which show new lines with weak oscillation frequencies at 1132 and 1148 cm^{-1} , are very interesting. This is similar to the IR spectrum of a free superoxide ion ν (O_2) = 1145 cm^{-1} .

The minimal displacement of ν (P = O) peaks in the complexes of Pd (II) with Hmpa ($\Delta\text{PO} = + 3 \div 5 \text{ cm}^{-1}$) proves that there is no M-O bond. Thus, PdCl_2 and Hmpa compounds are binded by a nitrogen atom.

This proposal has been confirmed by repeated experimental testing of oxidation of butene-1 with Hmpa, complex 4 and 5 η^1 -dioxygen complex 2 at 75°C . Butene-1 absorbed in Hmpa is not oxygenated by the η^1 -dioxygen complex, but butene-1 conversion is observed in the presence of complexes 4 and 5. At the same time, butene-1 conversion was 35% in complex 4 and 98% in complex 5.



Thus, during the interaction of complex 5 with B-1, an intermediate complex 6 (direction A) is formed due to the reconstruction of π - bond electrons. The intermediate complex 6 then interacts with the oxygen-coordinating complex (direction B) 3 obtaining the MEK the main product and formation of chlorides of the transition metals (direction V).



A combined catalyst allowing the oxidation reaction of butene to methyl ethyl ketone under mild conditions (low temperature and atmospheric pressure), with high selectivity ($S = 98-99\%$) and yield (96-98%) has been developed. The proposed binary

system coordinates butene-1 and molecular oxygen, and thus the oxidation reaction takes place not directly between butene-1 and oxygen, but between their coordinated activated states in the presence of a specific complex catalyst. Due to the mild nature of the reaction, the amount of additional products and the stages of obtaining that require further cleaning are significantly simplified. In addition, the same effect is obtained when using air as a source of oxygen due to the selective absorption of oxygen. Since the absorption of oxygen is irreversible, the possibility of easy removal of excess oxygen from the environment after the formation of the oxygen complex is an advantage of the developed method from the point of view of safety.

Under mild conditions, according to MEK high selectivity, single-phase, low consumption of chlorides of transition metals, simplicity of obtaining of the main product and process safety are undoubtedly superior to existing processes and will provide a great opportunity for industrial application.

The fourth chapter provides information on the synthesis of cyclic ligand complex compounds of 3d-transition metals, the catalytic activity of unsaturated hydrocarbons in the oxidation reaction and the heterogeneity of these complexes.

Along with linear catalysts, cyclic biocatalysts that imitate the properties of natural enzymes - metalporphyrine compounds are of great interest. The application of porphyrin complexes of transition metals as a catalyst occupies a special place in the development of new high-selectivity oxidation methods of hydrocarbons under mild conditions.

Catalysis in the presence of metalporphyrine is of great interest in connection with some biochemical reactions, as well as organic synthesis. There is no doubt that the first stimulus that led to the study of porphyrins and their complexes with metals is due to their catalytic properties.

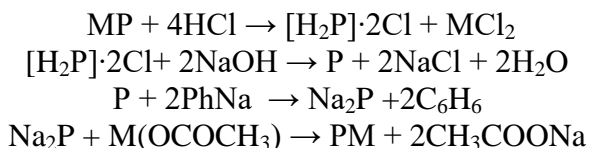
Unlike complexes of organic compounds, porphyrin complexes of transition metals can be considered as natural enzymes. However, artificial synthetic porphyrins are virtually insoluble in

hydrocarbons and require complex and expensive additional chemical reagents to homogenize the systems. In this regard, they are considered more promising natural porphyrins. They contain ether, ester fragments and alkyl radicals, which ensure good solubility in hydrocarbons. Among natural porphyrins oil porphyrin complexes are of particular interest.

Metal complexes and metal porphyrins are catalysts that imitate some important catalytic properties of natural enzymes. One of the properties of these compounds is that they absorb molecular oxygen and convert it into the supraoxide anion O_2^{2-} in their cavities. Due to its high activity, the latter oxidizes hydrocarbons to aldehydes, ketones and hydroxyl compounds at relatively low temperatures. In this regard, metal complex catalysis is one of the key determinants of scientific and technical progress, as it creates opportunities for the creation and application of selective and highly efficient catalysts to intensify production.

Taking into account the importance of metal-porphyrin compounds in the catalytic reactions of alkenes, catalytic properties of depths of individual metalporphyrin complexes obtained on the basis of metalporphyrin concentrates separated from Azerbaijan heavy oil by selective extraction way have been studied.

The catalytic properties of olefins are studied in the oxidation reaction of olefins with molecular oxygen. Obtaining of individual metal porphyrin complexes on the basis of oil concentrate has been carried out in four stages.



The formation of metal porphyrins has been confirmed by UV, IR and mass spectroscopy. Ultraviolet and visible absorption spectra of petroleum porphyrin concentrate and metalporphyrin in the visible region are given in Figure 8.

It should be noted that the intense Sore line ($\lambda_{\text{max}} \sim 400 \text{ nm}$) is characteristic for the UV/visible region of all petroleum porphyrins. In addition to this line in the electron absorption spectrum is observed in 4 lines of low intensity.

Comparison of the spectrum of iron porphyry with the spectrum of petroleum porphyry showed that lines 1 and 3 were more intense, and lines 2 had almost the same intensity as oil porphyrins. The insertion of an iron atom into the porphyrin ring leads to the shortening of the Sore line. In addition, instead of 4 lines, 2 lines of noticeable intensity (1 and 2) are observed.

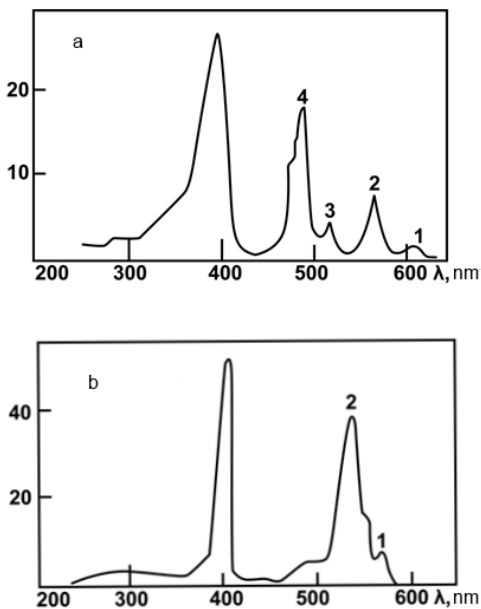


Fig. 8. Electron absorption spectra of oil porphyrin (a) and iron porphyrin (b) in parafine at 25°C.

The IR spectra of the synthesized metal (II) porphyrins are given in Figure 9.

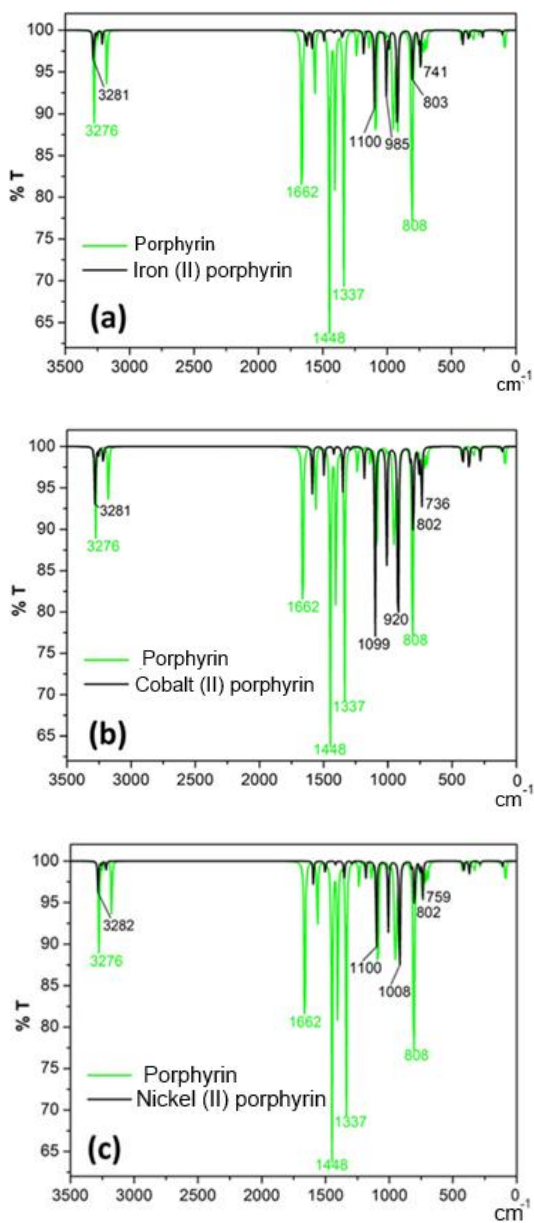


Fig. 9. IR spectra of synthesized metal (II) porphyrins

The values of the electron absorption bands and IR-spectral lines of the synthesized petroleum metal porphyrin complexes (CoP, FeP, MnP, NiP) are given in Table 2.

Table 2

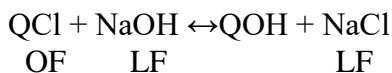
Physicochemical characteristics of synthesized petroleum metal porphyrin complexes (CoP, FeP, MnP, NiP)

Metalporphyrin complexes	Maximum characteristic absorption bands in electron spectra, nm	Maximum characteristic absorption bands in IR spectra, ν cm^{-1}
Co ^{II} P	417, 533, 551	108 (βNC_4), 279 (βCo), 736 (βNC_4), 802 (CH), 920 (CH), 1099 (HC=CH), 1350 (CNC), 1589 (C-CH-C), 3216 (CH), 3281 (HC=CH)
Fe ^{II} P	411, 534, 570	105 (βNC_4), 293 (FeN_4), 741 (N_4), 803 (CH), 985 (N_4), 1100 (HC=CH), 1183 (N_4), 1584 (C=C), 3213 (CH), 3281 (CH)
Mn ^{II} P	405, 520, 556	108 (βNC_4), 285 (MnN_4), 806 (CH), 986 (N_4), 1095 (HC=CH), 1183 (N_4), 1449 (C=C), 3213 (CH), 3281 (CH)
Ni ^{II} P	415, 528, 557	112 (βNC_4), 284 (βNi), 759 (C-CH-C), 802 (CH), 1008 (N-Ni-N), 1100 (HC=CH), 1353 (CNC), 1595 (C-CH-C), 3222 (CH), 3282 (HC=CH)

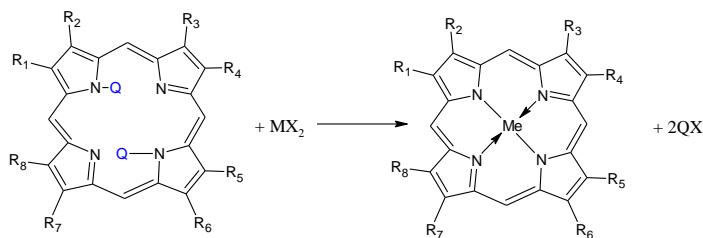
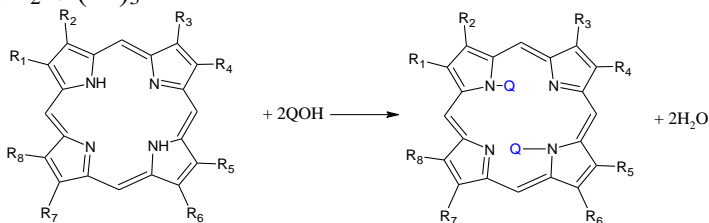
In order to reduce the cost of obtaining porphyrin complexes and to conduct these reactions safely, a new method of synthesis based on the technique of interfacial catalysis of porphyrin compounds has been developed. Using this method, the process of replacing hydrogen atoms attached to the nitrogen atom in the macrocyclic porphyrin ring is carried out in a two-phase system: an aqueous solution of alkali (50%) and a solution of porphyrin in benzene. Quaternary ammonium salts have been used as interfacial

catalysts. If to consider the high dependence of solid alkaline solutions on the proton of free hydroxyl ions, deprotonation processes of various organic compounds have been carried out in a 2-phase system. In our case, interfacial catalysts have been used in liquid-liquid and solid-liquid systems.

Benzene has been used as the liquid phase and benzyl triethylammonium chloride (BTEAX) – as the solid phase. The metallization process of porphyrins has been carried out in a 50% aqueous solution of benzene (or toluene) -NaOH using BTEAX (0.001 mol for 0.3% petroleum porphyrin) as an interfacial catalyst.



where, OF-organic phase, LF-liquid phase, $\text{Q}=\text{N}^+(\text{R})_4$;
 $\text{C}_6\text{H}_5\text{CH}_2\text{N}^+(\text{R}')_3$



- | | |
|-------------|--------------|
| Me=Fe (IV) | Me=Cd (VIII) |
| Me=Co (V) | Me=Cr (IX) |
| Me=Ni (VI) | Me=Zn (X) |
| Me=Mn (VII) | |

The catalytic properties of the synthesized petroleum metalporphyrins have been studied in the decomposition of hydrogen peroxide and oxidation reactions of unsaturated hydrocarbons.

The catalytic activity of porphyrin complexes for the decomposition reaction of hydrogen peroxide in the DMFA-KOH-H₂O₂ system has been studied and the results have been shown in Table 3.

The ability of metal cations in petroleum metalporphyrins to combine various ligands makes these compounds catalytically active in the decomposition reaction of hydrogen peroxide.

Table 3

Decomposition rate (W) of H₂O₂ at different concentrations of catalysts and catalytic activity (A) of metal porphyrins (Fe-P, Co-P, Mn-P and V-P). T = 335K, C_{H₂O₂} = 3,93 mol/l, C_{KOH} = 1,73 · 10⁻² mol/l

Catalyst	C _{cat} 10 ⁻⁵ , mol/l	W, ml O ₂ /min	A, C ⁻¹
Without catalysts		0,8 ± 0,2	
Fe-P	0,26	0,81 ± 0,01	17,86 ± 0,35
Fe-P	1,19	1,27 ± 0,56	5,92 ± 0,24
Fe-P	3,60	1,00 ± 0,05	1,57 ± 0,15
Fe-P	3,75	1,125 ± 0,008	1,78 ± 0,08
Fe-P	8,45	1,08 ± 0,038	0,75 ± 0,004
Co-P	0,120	1,54 ± 0,05	74 ± 25
Co-P	1,08	1,54 ± 0,053	8,5 ± 0,37
Co-P	3,68	1,87 ± 0,18	3,1 ± 0,26
Mn-P	0,26	1,27 ± 0,085	31,8 ± 0,28
Mn-P	2,41	1,19 ± 0,07	2,85 ± 0,16
Mn-P	7,14	1,38 ± 0,08	1,18 ± 0,1
Mn-P	16,55	1,28 ± 0,07	0,39 ± 0,025
V-P	0,26	1,28 ± 0,09	29,8 ± 2,8
V-P	0,56	1,51 ± 0,065	14,8 ± 0,68
V-P	1,39	1,95 ± 0,01	7,8 ± 0,37
V-P	10,48	5,34 ± 0,71	2,95 ± 0,38

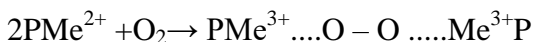
Oxidation of hydrocarbons with molecular oxygen is the base for many technological processes in modern petrochemistry. Oxygen-retaining compounds - peroxides, alcohols, ketones,

aldehydes, acids, oxides of olefins - are widely used as solvents, initial materials in chemical synthesis, monomers in the production of polymeric materials, raw materials for synthetic detergents.

From the scientific and practical point of view, metal porphyrins are important in the complexes. As a result of the use of these catalysts, it was possible to carry out the oxidation of hydrocarbons at low temperatures. In addition, the selectivity of the reaction increases significantly. In this regard, a method of selective oxidation of hydrocarbons has been developed, which leads to the production of suitable alcohols and carbonyl compounds.

Low-temperature catalytic oxidation of unsaturated ketones, alcohols and aldehydes of great interest in organic synthesis of unsaturated hydrocarbons: propylene, butene-1, butene-2 and isobutylene in the presence of metallocomplex catalysts of petroleum metal porphyrins has been studied. The oxidation reaction of C₃ and C₄ olefins has been carried out in the presence of Co, Fe, Mn-porphyrin complexes separated from oil (Table 4).

In the intermediate stage of oxygenation, a high-valent metal atom containing porphyrin complex is formed.



A perfect feature of these compounds is their ability to adsorb molecular oxygen that can pass to the supramolecular anion O₂²⁻ in the inner sphere. It has been found that the obtained metalporphyrine complexes absorb oxygen in the intermediate stage in the oxidation reaction of olefins at a ratio of 2:1 mol. In this case, the molecular oxygen absorbed in the complex cavity is strongly activated. Oxygenated complexes of metalporphyrins formed in the intermediate stage are reversible compounds.

As it can be seen from the IR spectra of oxygen complexes, the wavelength of 1127 cm⁻¹ confirms the presence of an oxygen fragment in the complex. In the IR spectra of oxygenated complexes available in the literature sources, the frequency ν (O-O) corresponds to the wavelength of 1104-1226 cm⁻¹. In this regard, it should be

noted that the absorption band 1127 cm^{-1} is formed during the interaction of molecular oxygen with metalporphyrins and it is a confirmation of the formation of dioxygenated adduct. Alcohol, ketones, etc. are suitable for hydrocarbons at low temperatures with high activity of dioxide oxygen. oxidizes to oxygen-retaining organic compounds.

Table 4

Yield of oxygen compounds depending on the amount of catalyst

Catalyst amount Oxygen compounds	Yield of oxygenated compounds %			
	0.005%	0.01%	0.05%	1.5%
$\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$	3,5	6,3	7,9	7,6
$\text{CH}_2=\text{CH}-\text{C}\begin{matrix} \text{O} \\ // \\ \text{H} \end{matrix}$	4,2	4,9	5,1	4,8
$\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}=\text{CH}_2$	6,1	7,4	7,6	7,3
$\text{CH}_3-\underset{\text{O}}{\text{C}}-\text{CH}=\text{CH}_2$	5,3	5,67	9,1	8,1
$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{C}\begin{matrix} \text{O} \\ // \\ \text{H} \end{matrix}$	2,4	3,1	3,7	3,5

The optimal parameters of the oxidation reaction have been determined: temperature, amount of catalyst, gas supply rate in the catalytic tube. The temperature for the oxidation process was $95\text{ }^\circ\text{C}$, the rate of delivery of propylene - 10 ml/min.

One of the possible ways to increase the efficiency of porphyrin catalysts is to "heterogeneize" them, i.e. to attach them to the active surface carriers with high dispersion.

It should be noted that in nature, metalporphyrins act in an "immobilized" state. Of course, the structure that exists in nature is very perfect, only modeling of the functions of biological objects can lead to positive results.

The porphyrin complexes of the transition metals have been also immobilized on the silica gel. There are a number of reasons for choosing silica gel as a carrier. Silica gel has an advantage over other carriers due to the following properties.

- first, a highly developed special surface (several hundred m^2/g) allows to create a significant density of the impregnated complex;
- second, the presence of silanol group silica gel on the surface allows to use a wide range of their functional properties for different options of fixing metal complexes;
- third, a sufficiently high thermal, chemical and mechanical resistance makes silica gel more suitable than other carriers;
- fourth, the continuously expanding range of silica gel offers a wide selection of carriers with the most diverse parameters and properties;
- fifth, silica gel is relatively affordable and inexpensive compared to other specific immobilizer enzyme-like structures.

Immobilization of porphyrin complexes on silica gel has been carried out by four methods (impregnation, heat treatment, adsorption, precipitation). Taking into account all indicators the technique of the process, it should be noted that the most perfect method for this process is the sedimentation method. Spectroscopic properties of immobilized porphyrine complexes have been studied. It has been found that during immobilization there is no interaction between the carrier and the porphyrin complex impregnated on the carrier. Physicochemical and catalytic properties of porphyrin complexes immobilized on silica gel have been studied on the decomposition reaction of hydrogen peroxide (figure 10).

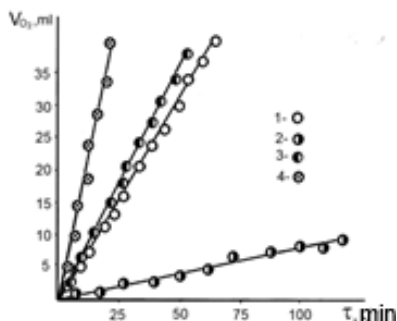


Fig.10. Decomposition of hydrogen peroxide at 298 K without catalyst (3) and in the presence of SiO₂ (2), CoP / SiO₂ (4) and FeCIP / SiO₂ (1). The density of the complex is 2% by weight.

The results show that the reaction is faster with porphyrin immobilized on silica gel than with carrier alone.

MAIN RESULTS

- 2 types of systems based on 3d-transition metals have been developed for selective liquid phase oxidation of unsaturated hydrocarbons with environmentally friendly oxidants under mild conditions. The I system type is based on linear metal complexes of transition metals and effective in the oxidation of alkenes from molecular oxygen to ketones. II type metalporphyrin is based on catalysts and designed for the oxidation of alkenes. New methods of obtaining oxygen-containing products based on the use of these systems have been developed.
- Complex compounds of 3d-transition metals with molecular oxygen were obtained by the proposed synthesis methods. A total of 19 linear metal complexes have been synthesized. The composition and structure of complexes have been determined by physicochemical methods (IR, UV, mass spectroscopy, electron spectroscopy, EPR). The results of these studies confirm the formation of oxygen complexes with 3d-transition metals. The

fact of activation of molecular oxygen during coordination in the external sphere has been identified. The complexing of oxygen with transition metal compounds causes changes in the spin state, electron density, and distance between atoms of oxygen, which corresponds to the freely activated form of the molecule. During absorption, oxygen is not used to oxidize the metal and the valence of the metal remains unchanged.

3. The catalytic properties of the synthesized oxygenated systems have been studied in the oxidation reactions of unsaturated hydrocarbons (ethylene, propylene, butene-1). A combined catalyst has been developed that allows the oxidation reaction of butene to methyl ethyl ketone under mild conditions (low temperature and atmospheric pressure), with high selectivity ($S = 98-100\%$) and yield (96-98%). The proposed binary system coordinates butene-1 and molecular oxygen, and thus the oxidation reaction takes place not directly between butene-1 and oxygen, but between their coordinated activated states in the presence of a specific complex catalyst. Due to the mild nature of the reaction, the amount of additional products and the stages of acquisition that require further cleaning are significantly simplified. In addition, the same effect is obtained when using air as a source of oxygen due to the selective absorption of oxygen. Since the absorption of oxygen is irreversible, the possibility of easy removal of excess oxygen from the environment after the formation of the oxygen complex is an advantage of the developed method from the point of view of safety.
4. Porphyrin complexes of 3d-transition metals have obtained by two methods - the reaction of hydrogen atom in the porphyrin ring with the metal atom and the method based on the technique of interfacial catalysis, and the catalytic activity of metalporphyrins in the oxidation reaction of olefins has been studied. The use of metalporphyrins as a catalyst in the oxidation reaction of olefins allows the oxidation reaction of hydrocarbons to the corresponding alcohol and ketone to take place at low temperatures.

5. Heterogeneous synthesis methods along with effective homogeneous catalytic systems based on linear and cyclic complexes of 3d-transition metals for the oxidation reaction of alkenes have been developed for the production of oxygen-containing organic compounds. Organic complexes of linear complexes (copolymer of styrene-divinylbenzene), cyclic complexes immobilized on inorganic carrier (silica gel) have been synthesized and their catalytic activities have been studied.

The main results of the dissertation are reflected in the following publications

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