**ABSTRACT**
**of the thesis for the degree of doctor of philosophy (PhD)**
**on specialty "6D073900 – Petrochemistry"**
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**"Oxidative reactions catalyzed by metal-polymer complexes"**

**General characterization of the work.** The thesis work is devoted to the catalytic oxidation of octene-1 and aliphatic alcohols in the presence of palladium(II)-polymer catalysts and immobilized catalase in an amphoteric cryogel matrix [APTAC]-[AMPS].

**Relevance of the research topic.** Catalysts based on metal complexes deposited on polymer substrates are widely used in various processes for converting hydrocarbon raw materials to produce a variety of reagents in order to solve economic problems by expanding the range of products. The relevance of the research also lies in the creation of a new generation of catalytic reactors capable of carrying out one-stage catalytic reactions of the oxidation of organic substrates with high speed, activity and selectivity under mild conditions.

**Purpose of work:** development of scientific bases of processes of catalytic oxidation of organic compounds (octene-1 and alcohols) in the presence of metal-polymer complexes under mild conditions in order to obtain practically important oxygen-containing compounds.

**In order to achieve the objective, the following tasks were carried out:**

- synthesis of metal-polymer catalysts based on palladium(II) chlorides with PVP and PEG polymers as catalysts and co-catalysts ($NaNO_2$, $CuCl_2$, $FeCl_3$);
- synthesis of biocatalysts based on immobilized catalase in the matrix of amphoteric cryogel [APTAC]-[AMPS];
- study of physicochemical characteristics of synthesized metal-polymer catalysts of two types;
- study of the oxidation reaction of octene-1 and aliphatic alcohols (ethanol, iso-propanol, n-butanol) with a number of oxidants ($NaBrO_3$, $K_2S_2O_8$, $H_2O_2$, воздухом, 100% $O_2$) in the presence of metal-polymer catalysts in aqueous-organic solutions in flow-through and traditional type catalytic reactors in the laboratory under mild conditions, identification of reaction products;
- determination of optimal conditions for oxidation of aliphatic alcohols, calculation of kinetic and thermodynamic parameters of reactions;
- development of hypothetical mechanisms of oxidation processes.

**Objects of study:** octene-1, ethanol, iso-propanol, n-butanol, palladium(II), copper(II), iron(III) complexes, polyvinylpyrrolidone, polyethylene glycol, catalase, co-oxidants, oxidants.

**Subject of study:** metal-polymer complexes (metal – Pd(II), Cu(II), Fe(III); polymer – polyvinylpyrrolidone, polyethylene glycol); catalase immobilized in the matrix of amphoteric cryogel; reactions of oxidation of octene-1 and alcohols by hydrogen peroxide, oxygen and air.

**Research methods.** Physicochemical properties of the developed polymers, cryogels, metal-polymer complexes, substrates and reaction products were

investigated by the following methods: conductometry, potentiometry, IR spectroscopy, scanning electron spectroscopy, permanganatometry. The composition and physicochemical characteristics before and after the experiments were analyzed by gas chromatography-mass spectrometry and gas-liquid chromatography, porosimetry. Oxidation of octene-1 and alcohols with inorganic oxidants, hydrogen peroxide, oxygen and air was carried out under mild conditions in flow-through and conventional type reactors in the laboratory.

**Scientific novelty and main results of the study:**

1. Polymer-metal catalysts based on d-metal chlorides (Me = Pd(II), Cu(II), Fe(III)) and polyethylene glycol for octene-1 oxidation were synthesized, their composition and structure were studied;

2. Catalysts based on immobilized catalase in the matrix of amphoteric cryogel [APTAC]-[AMPS] for the oxidation of alcohols (ethanol, iso-propanol, butanol) in aqueous-organic media were synthesized for the first time;

3. The compositions of PEG complexes with palladium(II), copper(II) and iron(III) chlorides were determined by potentiometric and conductometric titration methods. Their morphology and surface features were studied by IR spectroscopy and scanning electron microscopy, and the thermodynamic parameters of the complexes were calculated.

4. The oxidation of octene-1 by inorganic oxidants ($NaBrO_3$, $K_2S_2O_8$) under anaerobic conditions in dimethyl sulfoxide under mild conditions in the presence of a palladium-based complex and polyethylene glycol under laboratory conditions in a non-flow conventional-type reactor in aqueous-organic solutions under mild conditions was studied for the first time. The reaction product is octanone-2 obtained in yield (62-81%) and characterized by gas chromatography and mass spectrometry. A redox mechanism of the reaction has been proposed.

5. The oxidation of octene-1 in aqueous-organic solutions in the presence of the catalytic system Pd(II)(PVP)-$NaNO_2$ at 70 $^oC$ under mild conditions was found to result in an octene-1 conversion of 3-26%. The influence of the nature of the solvent on the stability of the catalytic system and the rate of the temperature process was studied at the optimal composition of the catalytic system [Pd(II)(PVP)]:[$NaNO_2$]:[$C_8H_{16}$] = 1:(5-10):(22.3-44.5).

6. It was found that selective oxidation of ethanol to acetaldehyde (91.8% conversion), iso-propanol to acetone (87.6%), and n-butanol to butyraldehyde (80%) at 20 °C and atmospheric pressure under laboratory conditions in the presence of a biocatalytic system based on catalase enclosed in a cryogel was observed in a flow catalytic reactor. The following optimal conditions for the oxidation of ethanol and iso-propanol by hydrogen peroxide were found: T = 10-20 $^oC$, pH = 6.4-6.9, [alcohol]:[$H_2O_2$] = 50:50 vol.%. The kinetic ($K_m$ = 4.0 M, $\upsilon_{max}$ = $5\cdot10^{-2}$ mol/(l·min)) and activation parameters ($E_{act}$ = −7.31 kJ/mol, $\Delta S‡$ = −250.0−(−246.01) J/(mol·degree)) of the ethanol oxidation process were determined. A hypothetical radical mechanism for the oxidation of alcohols by cryogel-encapsulated catalase in the presence of hydrogen peroxide was proposed.

7. The oxidation of ethanol and iso-propanol by catalase enclosed in a cryogel matrix made of macroporous polyampholyte in a batch reactor with the participation

of hydrogen peroxide, molecular oxygen and air was studied for the first time. In the batch reactor, when ethanol was oxidized with hydrogen peroxide and molecular oxygen, the yield of acetaldehyde reached ~ 97-98%, and when iso-propanol was oxidized, the yield of acetone was ~ 95-96%. The TOF value for the flow catalytic reactor is 6 times higher than for the laboratory batch reactor. A mechanism of alcohol oxidation by catalase encapsulated in cryogel in the presence of oxygen and air has been proposed.

**The main points to be defended.**

1. The compositions of PLA PEG with palladium(II), copper(II) and iron(III) chlorides have been established. From the titration curves, the optimal molar ratio of the reagents was found (k = $[Me^{n+}]$:[PEG]). For the $Pd^{2+}$–PEG and $Fe^{3+}$–PEG systems, the $[Me^{n+}]$:[PEG] ratio was 1:4 and for Cu2+–PEG it was 1:2. The increase in electrical conductivity is due to the released H+ ions during the reaction between PEG with copper(II), palladium(II) and iron(III) ions. The calculated thermodynamic parameters (Gibbs energy, enthalpy and entropy) for the $Cu^{2+}$–PEG and $Cu^{2+}$–PVP systems indicate the occurrence of complexation between metal ions and the polymer ligand. As the temperature increases, the stability of the complexes decreases.

2. The oxidation of 1-octene in aqueous organic solutions was carried out in the presence of a catalytic system based on palladium and polyethylene glycol with inorganic oxidizing agents ($NaBrO_3$, $K_2S_2O_8$) under anaerobic conditions in dimethyl sulfoxide under mild conditions in a static reactor. The reaction product is octanone-2, obtained in 62–81% yield and characterized by gas chromatography and mass spectrometry. It has been found that the catalysts can undergo five successive cycles without significant loss of catalytic efficiency. The oxidation process of 1-octene occurs via a redox mechanism and consists of two key stages.

3. The oxidation of 1-octene was carried out in aqueous-organic solutions in the presence of the Pd(II)(PVP)–NaNO2 catalytic system at 70 °C under mild conditions in a static reactor. The conversion of octene-1 depends, as well as the yield of octanone-2, depending on the process conditions and amounted to 3–26%. The effect of the nature of the solvent on the stability of the catalytic system and the rate of the temperature process was studied at the optimal composition of the catalytic system [Pd(II)(PVP)]:$[NaNO_2]$:$[C_8H_{16}]$ = 1:(5–10):(22.3–44 ,5). It has been established that the same catalytic solution can oxidize 2-3 successive portions of 1-octene at almost the same rate.

4. Oxidation of ethanol, iso-propanol and n-butanol by a synthesized biocatalyst based on catalase encapsulated in a cryogel matrix of macroporous polyampholite in flow and non-flow reactors with the participation of hydrogen peroxide, molecular oxygen and air was carried out. The conversion of ethanol to acetaldehyde in the flow catalyzed reactor reaches 91.8%, iso-propanol to acetone 87.6%, and n-butanol to butyraldehyde 80% at 20 °C and atmospheric pressure. The effect of temperature, pH and volume ratio of substrate and oxidant on the degree of conversion of ethanol and iso-propanol was studied. Kinetic ($K_m$, $\upsilon_{max}$) and activation parameters ($E_{act}$, $\Delta S‡$) for ethanol oxidation were calculated. Mechanisms of alcohol oxidation processes are proposed.

**Theoretical and practical significance of the work:** The obtained results of research on the thesis topic, conducted at the interface of polymer chemistry, catalysis, nanomaterials and nanotechnology will serve as a basis for the oxidation of a variety of organic compounds with the production of a variety of reagents to solve economic problems by expanding the range of products, as well as reducing import substitution and a prerequisite for the formation of a scientific school and a new scientific direction "Development of polymer-protected and nanocatalysts". Developed cryogel-immobilized nanocatalysts in the work, due to their high activity and selectivity, can be used in the future to conduct large-scale laboratory tests, in addition to oxidation, hydrogenation and isomerization processes, and catalytic reactors of flow and traditional non-flow type can be in demand for technological processes of the petrochemical sector of the RK, such as selective oxidation of alcohols and a variety of hydrocarbon compounds.

**Relevance to the directions of science development or state programs:** The work was carried out within the framework of the project funded by the MES RK: "Development of new heat- and salt-resistant amphoteric terpolymers for increasing oil production" (Grant of MES RK for 2021-2023, IRN AR09260574).

**Publications.** Research results of the dissertation work have been published in 18 scientific papers, including:

- 4 articles in international peer-reviewed journals, including Polymers for Advanced Technologies (Q2, percentile 84, SJR = 0.59), Catalysts (Q2, percentile 86, SJR = 0.69), Materials today: Proceedings (Q2, SJR = 0.45), Chimica Techno Acta (Q4, SJR = 0.15);
- 3 articles included in the list of journals recommended by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan;
- 11 theses of reports at foreign and republican international conferences and symposia.

**Doctoral student's personal contribution to each publication:**

1. The article "Oxidation of iso-propanol and n-butanol by catalase encapsulated within macroporous polyampholyte cryogel matrix" in the journal "Polymers for Advanced Technologies": preparation and analysis of literature data, obtaining experimental data at the Private Institute "Institute of Polymeric Materials and Technologies", processing of results, calculations, data processing.

2. Article "In situ entrapment of catalase within macroporous cryogel matrix for ethanol oxidation: flow-through mode versus batch reactor" in the journal "Catalysts": obtaining experimental data at the Private Institute "Institute of Polymeric Materials and Technologies", processing the results, calculations, design of the data.

3. Article "Catalytic activity of bimetallic catalyst Pd(II)(PVP)-Cu(II)(PVP) in oxidation of octene-1" in the journal "Materials today: Proceedings": obtaining experimental data, analysis and data processing.

4. Article "Complexes of polyvinylpyrrolidone and polyethylene glycol with palladium(II) ions: characterization and catalytic activity" in the journal "Chimica

Techno Acta": acquisition and discussion of experimental data, data analysis and processing.

5. Article "Studying the composition of complexes on the basis of palladium(II), copper(II), iron(III) chlorides and polyvinylpyrrolidone" in the journal "News of the Academy of sciences of the Republic of Kazakhstan. Series chemistry and technology": review preparation, data analysis, obtaining, discussion and processing of results.

6. Article "Synthesis and study of the composition of a polymermetallic complex based on copper(II) chloride and polyethylene glycol" in the journal "Herald of the Kazakh-British technical university": review preparation, data analysis, obtaining, discussion and processing of results.

7. Article "Synthesis and characterization of copper(II) chloride complexes with non-ionic polymers PEG and PVP" in the journal "Chemical Journal of Kazakhstan": obtaining, discussion and processing of results.

8. Proceedings of reports of scientific conferences and symposiums: obtaining and description of experimental data, discussion and obtaining the results of analyses, preparation of materials.

**Structure and volume of the dissertation.** The thesis includes an introduction, three sections, conclusion, and a list of used sources of 209 titles. The work is outlined on 107 pages, contains 42 figures and 17 tables.