ABSTRACT
of the thesis for the degree of philosophy doctor (PhD)
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Catalytic transformations of olefins

The thesis is dedicated to the synthesis of new catalysts based on polymer-metal complexes (further PMC) of palladium(II) chloride, copper(II), iron (III) chloride and polyvinypyrrolydone (further PVP) for the two-phase oxidation of octene-1 in water-organic media with inorganic oxidizers and oxygen. Synthesized PMCs were used as catalysts in the liquid phase oxidation of octene-1 to octanone-2 with inorganic oxidizers (KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$) and oxygen under mild conditions. The influence of the nature of co-catalysts, the temperature, the nature of solvents (dimethylsulfoxide, dimethylformamide), the concentration of components and the stability of catalytic systems were studied. All studies were carried out for the first time, the results are presented in the form of one article in a journal with a non-zero impact factor according to the Scopus and Thomson Reuters information databases, three articles in journals recommended by CCFES (Committee of the Control in Field of Education and Science), and also in the form of the RK patent for a utility model.

Relevance of the research topic. Currently, heterogeneous catalysts are mainly used in petrochemistry, their activity and selectivity are often low, and the reaction conditions require considerable energy consumption. High activity and selectivity and mild reaction conditions are the main advantages of homogeneous metal complex catalytic systems.

They have been used in large-scale processes such as the production of acetic acid, carbonylation of methanol and acetaldehyde from ethylene or propylene oxide by epoxidation, butanal and higher aldehydes by hydroformylation of alkenes. The discovery of catalytic systems based on palladium complexes and the oxidation of olefins to aldehydes and ketones (Wacker process) and to acetals, ketals and enol ethers in $PdCl_2$ and $CuCl_2$ solutions stimulate research aimed at modifying catalytic systems, optimizing oxidation conditions to increase the rate and selectivity of reactions for the synthesis of ketones from higher α-olefins and cycloolefins. The disadvantages of the processes known in the literature are their high energy intensity and the use of expensive reagents.

The widespread use of homogeneous metal-complex catalysts in industry is limited primarily by the existing expensive procedures for the separation of catalysts from reaction products, which makes it difficult to reuse them. The use of two-phase catalysis makes possible to solve this problem. The idea was proposed back in the early 70s of the last century for water-soluble catalysts and metal complex catalysis in molten salts. Two-phase catalysis involves minimizing the use of auxiliary substances and it is focused primarily on environmentally suitable solvents.

Kazakhstan is the largest raw material supplier of hydrocarbons. But there are no domestic technologies for the deep processing of hydrocarbons in the Republic. The development of research in the field of two-phase homogeneous catalysis is initiated by the need to search for and develop new catalysts for organic and fine organic synthesis processes, to study the kinetic patterns and mechanisms for the formation and functioning of unsaturated compounds active in oxidation with the participation of palladium-polymer complexes as catalysts and co-catalysts.

A systematic study of the kinetics and mechanism, revealing the nature of catalytically active intermediates in the catalytic oxidation of unsaturated compounds in order to obtain valuable oxygen-containing compounds in solutions of dimethyl sulfoxide (DMSO) – water and dimethylformamide (DMF) – water in an oxygen medium in the presence of polymer-metal complexes has not previously been conducted.

The aim of the thesis is the development of efficient mixed catalytic systems based on polymer-metal complexes of $PdCl_2$-PVP, inorganic oxidizing agents (KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$) and co-catalysts ($CuCl_2$-PVP, $FeCl_3$-PVP) in biphasic water-organic media, in an inert and oxygen atmosphere for oxidation of octene-1 under mild conditions; the study of kinetics and the establishment of key stages, optimal conditions and calculation of the kinetic and activation parameters of the process.

The following tasks were set to achieve this goal:

1) to develop polymer-metal catalysts based on palladium(II), copper(II), iron(III) chlorides and a number of inorganic oxidizing agents and to study their composition and structure;

2) to study the oxidation reaction of octene-1 with inorganic oxidizing agents and oxygen in the presence of mixed catalysts in aqueous-organic solutions of DMSO-H_2O and DMF-H_2O and identify the main reaction products;

3) to study the kinetics of the oxidation reaction of octene-1 with oxygen in the presence of mixed catalysts in DMSO-H_2O and DMF-H_2O solutions;

4) to study the effect of temperature and concentration of components (catalyst, co-catalyst, octene-1, oxygen);

5) to investigate the stability of the developed catalytic systems.

Objects of study: polymer-metal complexes of palladium(II), copper(II) and iron(III), octene-1, inorganic oxidizers, oxygen.

The subject of scientific research: the reaction of oxidation of octene-1 with inorganic oxidizing agents and oxygen in the presence of mixed catalytic systems based on polymer-metal complexes of palladium (II), copper (II) and iron (III).

Research methods. The following methods of synthesis and research were used during the research on the topic of the thesisto solve the problems posed: conductometry, potentiometry, infrared spectroscopy, electron spectroscopy, gas chromatography, mass spectrometry, chemical modeling, chemical kinetics. The experiments were carried out on a thermostated unit with a vigorously shaken, non-flowing glass gradient-free thermostated reactor of the “catalytic duck” type, equipped with a potentiometric device and connected to a gasometric burette.

The source study base and research materials comprise 101 sources of references by the methods of synthesizing catalysts, the influence of the nature of catalysts, solvents and oxidizers on the oxidation process of various unsaturated compounds to oxygen-containing compounds (ketones, aldehydes), as well as by the other areas of natural science relating to the topic of this study.

Scientific novelty:

- polymer metal catalysts based on palladium(II), copper(II), iron(III) chlorides and a number of inorganic oxidizers were developed and their composition and structure were studied for the first time;
- oxidation reactions of octene-1 with inorganic oxidizers and oxygen in the presence of mixed catalysts in aqueous-organic solutions of DMSO-H_2O and DMF-H_2O were studied and the main reaction products were identified for the first time;
- the kinetics of the reaction of oxidation of octene-1 with oxygen in the presence of mixed catalysts in aqueous-organic solutions of DMSO-H_2O and DMF-H_2O was studied for the first time;
- the effect of temperature and concentration of components (catalyst, co-catalyst, octene-1, oxygen) was studied for the first time;
- the stability of the developed catalytic systems was studied for the first time.

The theoretical significance of the study. The composition and structure of complexes based on palladium(II), copper(II), iron(III) chlorides and PVP were synthesized and studied for the first time, and thermodynamic characteristics (Gibbs energy, enthalpy changes, entropy changes) were calculated. The resulting complexes were tested in the oxidation of octene-1 with inorganic oxidizing agents and oxygen in water-organic solutions under mild conditions. The kinetic and activation parameters of the reaction were determined, and the optimal conditions for the oxidation of octene-1 by oxygen were found.

Practical value.The value of the results obtained in the course of the thesis in the field of homogeneous catalysis, shown by the example of oxidation of octene-1 with oxygen and inorganic oxidizers (KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$) in the presence of developed mixed catalytic systems $PdCl_2$-PVP – co-catalysts (as a co-catalyst $CuCl_2$-PVP and $FeCl_3$-PVP were used) is in the possibility to use the data obtained for the synthesis of valuable oxygen-containing compounds under mild conditions. These compounds are used as non-toxic solvents for the synthesis of pharmaceuticals, paints and varnishes. Also they may serve as an important intermediate product in the industrial synthesis of alcohol, organic acids and a variety of other products.There are several advantages of polymer-metal complexes based on palladium(II), copper(II), iron(III) chloride salts and polymeric ligand - PVP, used as catalysts should be noted:

- the use of the developed polymer-metal catalysts to carry out reactions in environmentally acceptable solvents (PMC is highly soluble in water and organic solvents). Also, unsaturated compounds are oxidized in an acidic medium due to the use of poorly soluble water in the catalyst in the industry. To dissolve it completely, hydrochloric acid is added to the reaction mixture, which leads to equipment corrosion, and the use of chloride-containing compounds leads to the

formation of environmentally unsafe, harmful substances and, moreover, chloride ions inhibit the oxidation of olefins;
- synthesized catalysts are stable, and as shown by stability tests, they can be used at least five times;
- when using modified with PVP palladium(II) as a catalyst, the selectivity of reactions does not change even after five cycles; octanone-2 is the only product of the biphasic oxidation of octane-1 with oxygen in the temperature range 60-80 °C and at the atmospheric pressure. This fact is due to the formation of a rigid framework (matrix) by bulky polymer ligands, which limit the direction of coordination, thereby providing a stabilizing effect;
- for the complete oxidation of palladium(0) to the divalent state, the stoichiometric amount of copper (II) chloride is often lacking, as a result of which an inactive palladium metal is formed from the transition atom Pd^0 in the reaction medium; on the other hand, copper ions are very toxic for the life of living organisms in the water, since all industrial waste merges into water sources, it should be noted, that in this case, the harm is not determined by the quantity, but by the nature of the substance. It is known that high-molecular compounds have the ability to extract metal ions from contaminated sources in the form of polymer-metal complexes;
- modification of palladium(II) chloride with a polymeric ligand of PVP significantly reduces the cost of the catalyst;
- easy of separation of the product from the reaction mixture (the reaction product was separated from the catalyst by the extraction method, as a result of which the reaction product remained in the organic medium, and the catalyst in the aqueous phase).

Consequently, the layout of the octene–1 oxidation process in water–organic media with oxygen and inorganic oxidizing agents (KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$) under mild conditions proposed in this thesis meets the requirements of “green chemistry”.

The main provisions for the defense:

1. Development of polymer-metal catalysts based on palladium(II), copper(II) and iron(III) chlorides and PVP, a number of inorganic oxidizers, studying their composition and structure, calculation of thermodynamic characteristics (Gibbs energy, enthalpy change, entropy change).

2. Study of the oxidation reaction of octene-1 with inorganic oxidizers and oxygen in the presence of mixed catalysts in water-organic solutions of DMSO-H_2O and DMF-H_2O, identifying the main reaction products.

3. Study of the kinetics of the oxidation reaction of octene-1 with oxygen in the presence of mixed catalysts in aqueous-organic solutions of DMSO-H_2O and DMF-H_2O.

4. Study of the effect of temperature and concentration of components (catalyst, co-catalyst, octene-1, oxygen).

5. The study of the stability of the developed catalytic systems.

The main results of the dissertation research were published in 13 scientific papers, including:

- one article published in an international scientific journal, which has a non-zero impact factor according to the Scopus and Thomson Reuters information databases;

- three articles published in journals recommended by the Committee on the Control of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;

- eight theses of reports at foreign and republican international conferences and symposia;

- one patent of RK for a utility model.

The structure and scope of the thesis.

The thesis work includes an introduction, three sections, conclusion, and a list of references from 100 titles. The work is presented on 100 pages, contains 72 figures and 16 tables.

According to the results of the dissertation research, the following conclusions were made:

1. By the methods of potentiometry and conductometry, the formation,composition and stability of polymeric complexes palladium(II)–PVP, copper(II)–PVP, iron(III)–PVP were established. Furthermore, obtained thermodynamic characteristics of the studied reactions let reveal the optimal conditions for the synthesis of PMC. The coordination of the polymeric ligand of PVP in the complexes and the morphology of the synthesized complexes were studied using IR spectroscopy and scanning electron microscopy.

2. The kinetics, products and optimal reaction conditions in the oxygen atmosphere were studied by the methods of kinetics, volumetry, GC and mass spectrometry. The effect of temperature, nature of solvent, nature of catalyst and co-catalyst, concentration of catalyst and co-catalyst, octene-1, successive weights of octene-1 and oxygen on the stability of the catalytic system and the speed of the temperature process with the optimal composition of catalytic systems [Pd(II)(PVP)]:[Cu(II)PVP]/Fe(III)PVP)]: [C_8H_{16}] = 1: (5-10): 22 was investigated.

3. The conversion of octene-1 and the yield of octanone-2 depend on the process conditions, and the latter was 2-84%. The maximum rate of oxygen absorption in most experiments is observed at 80 °C. The highest conversion of octene-1 and octanone-2 yields were observed in the presence of a polar solvent DMSO. The main product of the reaction in most experiments is octanone-2 (50-84%). The maximum number of TON was 236 mol of acids/(mol of Cat), and the maximum number of TOF – 71 mol of acids/(mol of Cat·h) in the presence of DMSO.

4. Kinetic and activation parameters were calculated. It was established that the oxidation reaction of octene–1 in water-organic solutions proceeds via the coordination redox mechanism through the key stages:

- reduction of Pd(II)-PVP by octene-1 to Pd(0)-PVP with the formation of octanone-2;

- oxidation of Pd(0)-PVP to Pd(II)-PVP by the Cu(II)-PVP or Fe(III)-PVP complex.

The resulting Cu(0) or Fe(I) reacts with Cu(II) or Fe(III) with forming Cu(I) or Fe(II), which are easily oxidized to Cu(II) or Fe(III).

Evaluation of the tasks solutions completeness. All the tasks posed to solve the goal of this dissertation have been fully resolved. PMCs based on palladium(II), copper(II), iron(III) chlorides and PVP were developed, their composition and structure were studied. After determining the composition of PMCs, they were tested as catalysts for the oxidation of octene–1 by oxygen or inorganic oxidizing agents in water–organic solutions of DMSO–H_2O and DMF–H_2O. The reaction products were identified using a Shimadzu GC-17A gas chromatograph and Varian 3900 and mass-spectrometer Varian Saturn 2100T make. The kinetics of the oxidation reaction of octene–1 with oxygen in the presence of mixed catalysts in DMSO–H_2O and DMF–H_2O solutions was studied, and the effect of temperature and concentration of components (catalyst, co-catalyst, octene–1, oxygen) was considered. The stability of the developed catalytic systems was investigated.

Thus, the goals of the dissertation research have been achieved. Efficient mixed catalytic systems based on polymer-metal complexes $PdCl_2$-PVP, co-catalysts ($CuCl_2$-PVP, $FeCl_3$-PVP) and inorganic oxidizers (KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$) in biphase water-organic media in an inert and oxygen atmosphere for the oxidation of octene–1 under mild conditions have been developed; the kinetics was studied, key stages and optimal conditions were established, and the kinetic and activation parameters of the process were calculated, the stability of the catalyst based on a polymer-metal complex of palladium(II) and PVP was studied.

Evaluation of technical and economic efficiency proposed in the solution of the thesis. The solutions proposed within the framework of this dissertation work can form the basis for the production of practically important oxygen-containing compounds (optically active compounds, an intermediate product for the production of polymers, plasticizers, stabilizers and other auxiliary substances) and products of target use in various sectors of the national economy (synthetic surfactants and detergents, synthetic fuels, lubricants and additives to them). At the same time, for such production, oxidation processes take place under mild conditions, which make it possible to save material resources (available raw materials, direct methods of environmental synthesis, high selectivity, reducing losses of raw materials and products, combining processes), energy, as well as reducing or eliminating harmful emissions to environment.