ABSTRACT

of the thesis for the degree of philosophy doctor (PhD)
by the specialty 6D072100 – Chemical technology of organic substances

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Catalytic synthesis based on carbon oxides

Synthesized compounds based on carbon oxides are an extensive and promising area of organic synthesis and petrochemistry. This important area is of increasing practical importance.

The dissertation work is devoted to the study of ecological pure "green" technology for the synthesis of practical valuable organic compounds based on carbon oxides (CO, CO_2) and available raw materials from petrochemical industries (α-olefins, alcohols, hydroxyarenes and their derivatives).

All studies were carried out for the first time, the results are presented in the form of four article in a journal with a non-zero impact factor according to the Scopus and Thomson Reuters information databases, two articles in journals recommended by CCFES (Committee of the Control in Field of Education and Science), and also one innovation patent RK and three of the RK patent for a utility model.

Relevance of the research topic. Based on carbon oxides (CO, CO_2), it is possible to synthesize almost all oxygen-containing organic compounds, which are valuable raw materials for the production of plastics, synthetic fibers, drugs, pesticides, etc.

The use of carbon oxides (CO, CO_2) in industrial organic synthesis makes it possible to properly expend natural resources and satisfy the demands for national economies noted above. It should also be noted that the use of carbon oxides, which are large-tonnage emissions of many industrial enterprises of our Republic (yellow phosphorus, calcium carbide, etc.), is also of great environmental importance. This is due to the high relevance of developing effective ways to produce useful organic compounds based on carbon oxides.

The development of homogeneous metal complex catalysis makes promising another way for the synthesis of esters - hydroesterification (hydroethoxycarbonylation) of alkenes with carbon monoxide and alcohols in the presence of metal complex catalysts. The advantage of this method of synthesis of esters is the relative availability of the initial reagents: olefins, alcohols and carbon monoxide, and the single-stage process. α-Olefins are a large-tonnage product of the refining industry; they are separated from the process gases of large industrial refining processes (cracking gases, coking gases, etc.).

Hydroxybenzoic acids and their derivatives find wide practical application. Salicylic acid and its derivatives (acetyl salicylic acid, p-aminosalicylic acid, etc.) have biological activity and are used in the manufacture of pharmaceutical preparations. p-Hydroxybenzoic acid and its derivatives possess a wide spectrum of biological activity and is a valuable monomer in the production of polymeric

materials. The novelty and competitiveness of the proposed research is the development of a more efficient method for the synthesis of hydroxybenzoic acids and their derivatives by carboxylation of phenol and their derivatives with readily available derivatives of carbon dioxide - alkaline salts of alkyl-acid acids, which excludes the stage of preparation of intermediate alkali metal phenoxides.

prof. X.A. Suerbaev and colleagues (Department of Physical Chemistry, Catalysis and Petrochemistry of Al-Farabi Kazakh National University) were investigated hydroalkoxycarbonylation of olefins in the presence of palladium complexes with phosphorus-containing ligands, and carboxylation hydroxyarens with alkali salts of alkylcarbonic acids. This dissertation is a continuation of this research.

The use of monoxide and carbon dioxide as a raw material base of industrial organic synthesis is of great importance in resource-saving technology and is of great environmental value. Homogeneous metal-complex catalysts are now of great interest and they have high hopes for solving important problems concerning the saving of raw materials and energy in the implementation of many industrial processes of basic organic and petrochemical synthesis. The results of the investigations in this directive of scientific research have important theoretical implications and are relevant to our Republic.

The aim of the thesis. Creating environmentally friendly "green" technology for the synthesis of practically valuable organic compounds (drugs, fragrances, monomers of polymeric materials, etc.) based on carbon oxides (large-tonnage emissions from many industrial production) and affordable petrochemical products (α-olefins, alcohols, hydroxyarenes and their derivatives).

The following tasks were set to achieve this goal:

- Development of highly efficient catalytic systems based on transition metal complexes with organophosphorus ligands and various stabilizers and promoters for the reaction of hydroalkoxycarbonylation of α-olefins without using solvents under mild process conditions (CO pressure not higher than 2.0 MPa, temperature not higher than 100 °C).

- Determination of the effect on the course of the reaction of carboxylation of phenols and their derivatives with alkaline salts of alkyl carboxylic acids of the nature of the initial substrates, carboxylate reactants and process conditions.

- Determination of the optimal parameters of the reaction of hydroalkoxycarbonylation of α-olefins at low pressures of carbon monoxide (≤ 2.0 MPa) in the presence of developed effective catalytic systems based on transition metal complexes with organophosphorus ligands and various stabilizers and promoters. Study of the kinetics and mechanism of the reaction under study.

- Search for catalysts based on Lewis acids for the electrophilic reaction of carboxylation of phenols and their derivatives with alkali salts of alkyl carboxylic acids. Investigation of the kinetics and mechanism of the reaction of carboxylation of phenols and their derivatives with alkaline salts of alkylcarbonic acids.

- Development of laboratory and technological regulations for obtaining the target products.

Objects of study: carbon monoxide, carbon dioxide, metal complex catalysts ($PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$, $PdCl_2(PPh_3)_2$-PPh_3-p-TsOH), Lewis acids ($AlCl_3$, K_2CO_3), α-olefins (hexene-1, octene-1) alcohols and phenol.

The subject of scientific research: hydroesterification reactions (hydroalkoxycarbonylation) of terminal alkenes with carbon monoxide and alcohols in the presence of metal complex catalysts, as well as carboxylation of phenols and their derivatives with alkali salts of alkyl carbonic acids in the presence of Lewis acid catalysts.

Research methods. The following methods of synthesis and research were used during the research on the topic of the thesisto solve the problems posed: nuclear magnetic resonance spectroscopy, infrared spectroscopy, electron spectroscopy, gas chromatography, mass spectrometry. The experiments were carried out in a laboratory installation of autoclave type from stainless steel.

The source study base and research materials comprise 163 sources of literature on catalytic syntheses based on carbon oxides (CO and CO_2), methods for synthesizing metal complex catalysts, possible mechanisms for the reaction of hydroalkoxycarbonylation of olefins with carbon monoxide and alcohols in the presence of metal complex catalysts, and carboxylation of hydroxyarenes with metal alkylcarbonates in the presence of catalysts, as well as others areas of science related to the topic of this study.

Scientific novelty:

- The use of Lewis and Bronsted acids ($AlCl_3$, p-TsOH) as promoters of catalytic systems in the reaction of hydroalkoxycarbonylation of α-olefins has been studied.
- For the first time, various catalysts (Pd complexes) in the reaction of hydroalkoxycarbonylation of octene-1 were investigated.
- A possible mechanism for the reaction of hydroalkoxycarbonylation of terminal olefins with carbon monoxide and alcohols in the presence of palladium phosphine complexes was developed.
- The reaction of carboxylation of hydroxyarenes with alkali salts of alkyl carbonic acids in the presence of catalysts ($AlCl_3$, K_2CO_3) was studied for the first time.
- A possible mechanism was developed for the reaction of carboxylation of phenol with sodium ethyl carbonate in the presence of catalysts.

The theoretical significance of the study. The reactions of hydroethoxycarbonylation of octene-1 in the presence of three-component catalytic systems (dichlorobis (triphenylphosphine) palladium, triphenylphosphine, aluminum trichloride) and carboxylation of phenol with sodium ethyl carbonate in the presence of catalysts (aluminum trichloride, potassium carbonate) were studied for the first time. The optimal parameters for conducting the reaction data were determined.

Practical value.

- The catalytic systems $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$, $PdCl_2(PPh_3)_2$-PPh_3-p-TsOH based on palladium phosphine complexes in hydroalkoxycarbonylation of α-olefins were investigated.

- For the first time, the conditions for the reaction of hydroalkoxycarbonylation of octene-1 with various catalytic systems of palladium complexes were studied.

- A possible mechanism for the reaction of hydroalkoxycarbonylation of terminal olefins with carbon monoxide and alcohols in the presence of palladium phosphine complexes was developed.

- For the first time, the conditions for the reaction of carboxylation of hydroxyarenes with alkali alkyl acid salts in the presence of catalysts ($AlCl_3$, K_2CO_3) were investigated.

- A possible mechanism was developed for the reaction of carboxylation of phenol with sodium ethyl carbonate in the presence of catalysts.

The main provisions for the defense:

1. For the first time, highly efficient catalytic systems based on transition metal complexes with organophosphorus ligands and various stabilizers and promoters for the reaction of hydroalkoxycarbonylation of α-olefins without using solvents under mild process conditions (CO pressure not higher than 2.0 MPa, temperature not higher than 100 °C) were developed.

2. For the first time, the effects on the course of the carboxylation of phenols and their derivatives with alkali salts of alkyl carbonic acids on the nature of the initial substrates, carboxylation agents and process conditions were determined.

3. The optimal parameters for the reaction of hydroalkoxycarbonylation of α-olefins at low pressures of carbon monoxide (≤ 2.0 MPa) were determined for the first time in the presence of developed effective catalytic systems based on transition metal complexes with organophosphorus ligands and various stabilizers and promoters. The kinetics and mechanism of the reaction under study are investigated.

4. Catalysts based on Lewis acids were found for the first time for the electrophilic carboxylation of phenols and their derivatives with alkaline salts of alkyl carbonic acids, and the kinetics and mechanism of the carboxylation of phenols and their derivatives with alkyl carbonic acids were investigated.

5. Were developed laboratory and technological procedures for obtaining the target products.

The main results of the dissertation research were published in 22 scientific papers, including:

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

- two 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;

- eleven thesis's of reports at foreign and republican international conferences and symposia;

- one innovation patent of RK and three patents 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 163 titles. The work is presented on 153 pages, contains 66 figures and 37 tables.

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

1. For the first time, the reaction of hydroethoxycarbonylation of 1-hexene with carbon monoxide and ethanol (T = 120 ºC, τ = 5-6 h, Pco = 2-2.5 MPa) in the presence of three-component systems $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ and $PdCl_2(PPh_3)_2$-PPh_3-p-TsOH was studied, as a result of which the product yields were 80.4-84.6 %. Using chromatography-mass spectroscopic analysis, the yields of 77.8 % linear (enanthic acid of ethyl ester) and branched 22.2 % (2-methylcaproic acid of ethyl ester) products were determined.

2. For the first time, the reaction of hydroethoxycarbonylation of octene-1 with carbon monoxide and ethanol (T = 120 ºC, τ = 5-6 h, Pco = 2.5 MPa) was investigated in the presence of three-component $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ and $PdCl_2(PPh_3)_2$-PPh_3-p-TsOH, as a result of which the product yields amounted to 86.7-93.8 %. Using chromatography-mass spectroscopic analysis, the yields of 77.5 % linear (ethyl ester of pelargonic acid) and branched 22.5 % (ethyl ester of 2-methylcaprylic acid) products were determined.

3. For the first time, the reaction of hydroethoxycarbonylation of octene-1 with carbon monoxide and ethanol (T = 120 ºC, τ = 5 h, Pco = 5.0 MPa) was investigated in the presence of the three-component system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$, as a result of which octene-1 conversion was 88.5 %. Using chromatography-mass spectroscopic analysis, the yields of 70.1 % of linear (ethyl ester of pelargonic acid) and 29.9 % of branched (ethyl ester of 2-methylcaprylic acid) products were determined.

4. For the first time, the reaction of carboxylation of phenol with sodium ethyl carbonate in the presence of catalysts $AlCl_3$ and K_2CO_3 (T = 160 °C, P = 1.0 MPa, τ = 5-7 hours) was investigated, resulting in product yields of 36.0-80.0 %.

5. Possible mechanisms for the reactions of hydroethoxycarbonylation of olefins with carbon monoxide and ethanol in the presence of palladium phosphine complexes and carboxylation of phenol sodium ethyl carbonate in the presence of an $AlCl_3$ catalyst have been proposed.

6. Were developed laboratory and technological procedures for obtaining the target products.

Evaluation of the tasks solutions completeness. All the tasks posed to solve the goal of this dissertation have been fully resolved. Have been developed highly efficient catalytic systems based on transition metal complexes with organophosphorus ligands and various stabilizers and promoters for the reaction of hydroalkoxycarbonylation of α-olefins without using solvents under mild process conditions (CO pressure not higher than 2.5 MPa, temperature not higher than 120 °C). The effects on the course of the reaction of carboxylation of phenols and their derivatives by alkaline salts of alkyl carboxylic acids on the nature of the initial substrates, carboxylation agents and process conditions are determined. The

optimal parameters for the reaction of hydroalkoxycarbonylation of α-olefins at low pressures of carbon monoxide (≤ 2.0 MPa) were determined in the presence of developed efficient catalytic systems based on transition metal complexes with organophosphorus ligands and various stabilizers and promoters. The kinetics and mechanism of the reaction under study are investigated. Catalysts based on Lewis acids for the electrophilic carboxylation of phenols and their derivatives with alkaline salts of alkyl carbonic acids were found and the kinetics and mechanism of this reaction were studied. Developed laboratory and technological regulations for obtaining target products.

Thus, the goals of the dissertation research have been achieved. The scientific foundations of environmentally friendly "green" technologies for the synthesis of practically valuable organic compounds (drugs, fragrances, monomers of polymeric materials, etc.) based on carbon oxides (large-tonnage emissions from many industrial productions) and affordable petrochemical products (α-olefins, alcohols , hydroxyarenes and their derivatives).

Evaluation of technical and economic efficiency proposed in the solution of the thesis. The solutions proposed within the framework of this dissertation work may underlie the production of practically important oxygen-containing compounds synthesized on the basis of carbon oxides (CO, CO_2), which are valuable raw materials for the production of plastics, synthetic fibers, drugs, pesticides, etc. The advantage of this method of synthesis of esters is the relative availability of the initial reagents: olefins, alcohols and carbon monoxide, and the single-stage process. α-Olefins are a large-tonnage product of the refining industry; they are separated from the process gases of large industrial refining processes (cracking gases, coking gases, etc.). Hydroxybenzoic acids and their derivatives find wide practical application. Salicylic acid and its derivatives (acetyl salicylic acid, p-aminosalicylic acid, etc.) have biological activity and are used in the manufacture of pharmaceutical preparations. p-Hydroxybenzoic acid and its derivatives possess a wide spectrum of biological activity and is a valuable monomer in the production of polymeric materials.