ABSTRACT

For the thesis «Development of a technology for the production of butyl alcohols by hydrogenation of carbonyl compounds» by Yegemberdiyeva Saltanat Zhumabekovna, submitted for the degree of Doctor of Philosophy (PhD) in specialty 6D072100 - «Chemical technology of organic substances»

Relevance of the research topic. It is economically feasible to develop highly efficient catalysts and new technologies for the production of butyl alcohol based on local secondary resources.

Saturated acyclic aldehydes are obtained by hydroformylation of unsaturated hydrocarbons, and oxo products of its processing (alcohols, hemiacetals, acetals, etc.) have long attracted the attention of researchers, for example, by the initial form of synthesis of new organic compounds containing an hydroxy group, using fatty aldehydes as raw materials. In the petrochemical industry, aldehydes are obtained by oxosynthesis technology by hydroformylation of unsaturated ethylene hydrocarbons. The main raw material of butyl alcohols is butyric aldehyde, which is formed during the hydroformylation of propylene.

The largest producers of butyl alcohols are the USA, China, Germany, Japan, Malaysia, Russia and many others. Currently, there is no production of butyl alcohols from organic oxo compounds in Kazakhstan. The steady upward trend in the consumption of butyl alcohols is explained by the growth in the number of chemical industries in Kazakhstan.

The processes of heterogeneous catalytic hydrogenation of organic carbonyl-containing compounds into corresponding alcohols often occur under harsh conditions (high T, P), therefore, the implementation of new hydrogenation routes under mild conditions (low T, P) and the use of highly critical liquid H_2O as a solvent is one of the main directions of «green chemistry».

In accordance with the Decree of the President of the Republic of Kazakhstan dated May 30, 2013 No. 577 «on the concept for the transition of the Republic of Kazakhstan to a «green economy». In accordance with the Law of the Republic of Kazakhstan dated April 28, 2016 No. 506-V ZRK «On amendments and Additions to Some Legislative Acts of the Republic of Kazakhstan on the transition of the Republic of Kazakhstan to a «green economy». Measures for the transition to a «green economy» in the areas of reducing air pollution and effective ecosystem management will be carried out in accordance with the concept.

Currently, two-component skeleton-nickel catalysts are widely used in the chemical-pharmaceutical, petrochemical and paint and varnish industries due to their high activity and technological convenience. They exhibit high activity and selectivity in hydrogenation reactions of oxygen- and nitrogen-containing organic compounds in the liquid phase.

For the hydrogenation of carbonyl-containing organic compounds with an open purpose, work is being carried out on the synthesis of modified casting nickel catalysts and the selection of optimal technological parameters for the production of saturated alcohols of the aliphatic series based on their highly active catalytic

systems.

In general, the review of literature sources and the results of the analysis of the levels of technology in the industry indicate the high relevance of the chosen topic for the dissertation research aimed at the development of butyl alcohol production technology.

The aim of the work is to study the effect of modifying additives Ru and Rh on the catalytic properties of skeletal Ni-Al in the process of selective hydrogenation of oil aldehyde to butyl alcohol.

To achieve the goal, the following **tasks** were solved:

-synthesis of modified nickel alloy catalysts and investigation of their physico-chemical and adsorption properties;

-determination of the dependence of the physico-chemical characteristics of catalysts on activity and selectivity by hydrogenation reaction of oil aldehyde into butyl alcohol.

-determination of technological parameters of the process of hydrogenation of oil aldehyde into butyl alcohol and finding the activity and selectivity of the catalyst for a certain period of time.

Research methods. To achieve the objectives of the study, the following physicochemical and analytical research methods were chosen: X-ray analysis (DRONE-50UM) and X-ray spectral analysis (Camebax SX50), study of the specific surface and porous structure of catalysts (BET), microscopic study of the granulometric composition of catalysts (MNM-7), electron microscopic examination of the catalyst (TECLA 242E), thermosorption analysis, IR Fourier spectroscopy (Shimadzu JR Prestige-21), chromatographic analysis (Chromium-4). Methods of mathematical modeling and statistical data processing were used in processing the results of experimental studies.

Objects of research work and area of interest.

The objects of research of the dissertation work are the initial compounds h-oil aldehydes, the final products - butyl alcohol, and alloy catalysts were obtained.

The subject of the study is the technology of producing butyl alcohol based on oil aldehyde using Ni-Ru and Ni-Rh alloy catalysts. Indicators of the activity and selectivity of the catalyst, at certain values of pressure and temperature, as well as composition and structure, from the surface of the catalyst.

The main provisions submitted for protection:

- hydrogenation of oil aldehyde into primary butyl alcohol and synthesis of heterogeneous catalysts;

- the effect of the composition of Ni-Ru and Ni-Rh catalysts on the activity and selectivity during the hydrogenation of oil aldehyde to butyl alcohol at room temperature and atmospheric pressure of hydrogen;

- experimental proof of the main causes of the influence of the nature and composition of the solvent on the adsorption and catalytic properties of nickel in the hydrogenation reactions of oil aldehyde into butyl alcohol;

- technology for the production of catalysts, as well as hydrogenation of oil aldehydes and their recommendations for use in the alcohol industry.

The main results of the study:

- a method of hydrogenation of oil aldehyde under mild conditions has been developed, which helps to reduce energy consumption (a patent for a utility model has been obtained);

- new efficient catalytic systems based on an alloy nickel catalyst containing ruthenium or rhodium additives have been developed, allowing to increase the speed of the hydrogenation process by 1.7-1.9 times compared with a skeletal nickel catalyst without an additive;

hydrogenation of oil aldehyde under mild conditions is accompanied by high selectivity and stability, ensures the quality of the target product and is of practical interest for improving the technology for producing butyl alcohol;

- according to the developed technology, production tests were carried out at the HILL Corporation LLP enterprise.

Substantiation of the novelty and importance of the results obtained:

- it is shown that for the selective hydrogenation of oil aldehyde into butyl alcohol, a nickel metal forming atomic and molecular adsorbed forms of hydrogen is used as the active component of the catalyst;

- it has been established that modifying additives (Ru and Rh) are electron acceptors with respect to Al and γ-Al_2O_3, which strengthen the connection of the C=O group with the surface and form additional hydrogen activation centers;

- it is shown that the reaction of selective hydrogenation of oil aldehyde is a process that depends on the amount of modifying additives. For the synthesized nickel-ruthenium catalysts, the effect of the solvent nature on the conversion of oil aldehyde, which is 100% and the selectivity for butyl alcohol is 96%, was studied for the first time.

- the possibilities for the formation of the scientific basis for the synthesis of new catalysts with specified properties for the selective hydrogenation of oil aldehyde into butyl alcohol have been determined.

Theoretical significance. This work is crucial for understanding the complex mechanisms of hydrogenation of carbonyl compounds, a class of organic molecules characterized by a carbon-oxygen double bond, with the formation of butyl alcohols. The significance lies not only in the efficiency and selectivity of this transformation, but also in its environmental and economic consequences. By exploring new catalysts, reaction conditions, and process optimization, this dissertation contributes to a fundamental understanding of hydrogenation reactions, potentially revealing new catalyst designs and reaction pathways that are more efficient, less energy-intensive, and generate fewer by-products. In addition, this study can provide insight into reaction kinetics and thermodynamics, which is necessary to scale the process from laboratory to industrial scale. The developed methodologies can be applied to other hydrogenation processes, extending the impact of this work beyond butyl alcohols.

Its practical significance lies in its direct applicability to industrial processes and the possibility of a significant impact on chemical production. The new hydrogenation process described in detail in this paper solves several key industrial problems: it offers a method that potentially reduces energy consumption and operating costs, as well as increases the yield and purity of the resulting butyl

alcohols. This directly leads to an increase in the profitability and competitiveness of chemical manufacturers. By increasing the efficiency and sustainability of butyl alcohol production, this dissertation makes a significant contribution to the field of chemical technology and catalysis, and also has economic and environmental significance for chemical industry enterprises.

Based on the results of scientific and technical research, a method of hydrogenation of oil aldehyde under mild conditions has been developed, which helps to reduce energy consumption (utility model patent "Method for producing n-butyl alcohol" No. 6406, 09/10/2021, byul. №36).

Connection of the research with the plan of the scientific programs. The dissertation work was performed at the M. Auezov South Kazakhstan University at the Department of Oil Refining and Petrochemistry, on the topic: B-16-02-03 "Study of the composition and properties of oil from promising fields of the Republic of Kazakhstan, development of optimal technologies for their processing" (2015-2020), and GB-21-05-04 "Creation of new optimal catalytic systems for selective hydrogenation of saturated and unsaturated oxo compounds" (2021-2025).

The principle of reliability is justified by empirical data obtained as a result of extensive experimental work and thorough physico-chemical analyses using modern computer technologies. equipment and tools for complex research. This approach provides a high degree of reliability and reproducibility of the results, creating a solid scientific basis for the proposed technology. This evidence base, supported by modern analytical methods, enhances the reliability and applicability of the dissertation's contribution to the field of chemical technology.

Publications. The main provisions, results, conclusions and conclusions of the dissertation are presented in 12 printed works, of which: 3 articles in publications recommended by the National Research Council of the Republic of Kazakhstan, 1 article in the scientific journal "Research Journal of Chemical and Environmental Sciences", India, 2020, 1 article in the scientific journal "Catalyst Communications" Netherlands, 2021 G., in the scientific journal included in the database "Scopus", 7 articles in the collections of international scientific conferences, including 1 article published in the materials of foreign conferences, also received a patent of the Republic of Kazakhstan for a utility model.

The doctoral student's personal contribution to the preparation of each publication:

1. The article "Liquid-phase hydrogenation of butyl aldehyde promoted on skeletal nickel catalysts" in the journal "Catalysis Communications" - conceptualization of the study, in particular, hypothesizing the effectiveness of skeletal nickel catalysts in the hydrogenation of butyl aldehyde, data collection, analysis and interpretation.

2. The article "Molecules of kanykpagan baylanystardy sutegimen hydrleu" in the journal "KazUTZU Khabarshysy" - development and careful planning of the experiment, preparation of the manuscript.

3. The article "Catalyst atomdary men stuegi molecules alaryn himiyalyk baylanystarynyn zhylu activation" in the journal "KazUTZU Khabarshysy" - writing a manuscript, conceptualization and planning of the experiment.

4. Article "A comprehensive review on butyl alcohols synthesis through different methods" in the journal "Reports of the National Academy of Sciences of the Republic of Kazakhstan" - preparation of a comprehensive review of data on the research topic, preparation and writing of the manuscript.

The structure and volume of the thesis. The dissertation consists of an introduction, three chapters, a conclusion, a list of references and appendices. The work is presented on 105 pages, contains 25 tables, 41 figures and 3 appendices. The list of sources used includes 162 names.