ABSTRACT

dissertation for the degree of Doctor of Philosophy (PhD) in specialties 8D05301 - Chemistry

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The nanocatalyst based on microsilicate for hydroconversion of primary coal tar and oil sludge.

General characteristics of the work. The work is devoted to the study of hydroconversion of primary coal tar and oil sludge in the presence of nanocatalysts deposited on nickel, cobalt and iron microsilicate.

Relevance of the work. Currently, one of the pressing problems is the efficient use of natural resources, most of which are lost in the form of industrial waste, such as oil sludge generated during the transportation of oil through pipelines and containing valuable hydrocarbons. The global oil industry produces more than one billion tons of oil sludge every year. This poses a serious threat to the environment and human health, as oil sludge contains a variety of organic and inorganic compounds, including bacteria, parasites, heavy metals and inert solids. The choice of oil waste treatment method depends to a large extent on its composition and the amount of petroleum products.

In the Republic of Kazakhstan, the practice of handling oil waste is diverse, and there is no single integrated approach to their management, in particular due to the technological obsolescence of enterprises engaged in the production or use of oil sludge. Nevertheless, government programs for the disposal of oil sludge are increasingly being introduced, including innovative installations for the processing of hazardous waste.

The main goals of these programs are to improve the environmental situation, ensure economic benefits for oil refineries, as well as ensure the safety and rational use of natural resources. Experts believe that in order to achieve maximum results in this area, it is necessary to use modern technologies, effective catalysts that can contribute to the creation of highly efficient methods for processing oil sludge and low-temperature coal tar.

The difficulties of introducing hydrogenation processing of low-temperature coal tar are hindered by the high content of low-pyrolysis resins and total phenols, in addition, the processing of low-temperature coal tar and oil sludge by hydrogenation technologies requires the development of new efficient and selective nanocatalysts.

One way to solve the current problem of deep processing of oil sludge and low-temperature coal tar into light and medium fractions is to find promising resources for creating effective nanocatalysts. New catalysts for the treatment of heavy hydrocarbons should be simple and affordable, and their methods of production should comply with the principles of "green chemistry."

Microsilicate is an ecologically and economically affordable product from the "*Tau-Ken.temir"* Karaganda silicon plant. Currently, nanotechnology makes it possible to obtain metal nanoparticles with high reactivity, which can be used as catalysts. Application of group VIII metals (nickel, cobalt and iron) to the microsilicate leads to the formation of metal nanoparticles responsible for the activity and selectivity of the catalysts.

In this regard, the development of microsilicate-based catalysts showing high activity and selectivity is an urgent task of this dissertation study.

The purpose of the dissertation work is thermocatalytic transformations of heavy hydrocarbon raw materials (oil sludge and low-temperature coal tar) in the presence of nanocatalysts based on nickel, cobalt and iron applied to the microsilicate for the hydrogenation process of low-temperature coal tar and oil sludge and establishing the influence of these catalysts on the yield of light fractions.

Research objectives.

- establish the individual and chemical composition of microsilicate, oil sludge and microsilicate with deposited metals (nickel, cobalt and iron);
- determine specific surface, surface morphology, size of nanoparticles of deposited metals, acid number, adsorption isotherms, thermo-programmed reduction method, thermo-programmed desorption method of prepared nanocatalysts;
- study the kinetics of thermal destruction of oil sludge (Atasu-Alashankou) in the presence of a catalyst with metals (nickel, cobalt and iron) deposited on the microsilicate using the Ozawa-Flynn-Wall method;
- determine the kinetic parameters of thermal destruction of low-temperature coal tar in the presence of catalysts with nickel, cobalt and iron metal oxides applied to the microsilicate using the Ozawa-Flynn-Wall methods, the integral method and the method for determining the thermokinetic parameters by the inflection point on the thermogravimetric curve;
- determination of optimal conditions for the process of catalytic hydrogenation of oil sludge (Atasu-Alashankou), for comparison of catalytic activity of catalysts (deposited on nickel and cobalt microsilicate), process parameters: temperature, initial hydrogen pressure, process duration, catalyst consumption;
- establish the individual and chemical composition of the oil sludge fraction with a boiling point of up to 200℃ and 200-350℃;
- develop a cluster-associative model of the viscosity of a wide fraction of oil sludge with a boiling point of up to 350℃.

Object and subject of the study. Oil sludge obtained in the process of oil transportation through the pipeline of Kazstransoil enterprises of the West Kazakhstan oils of the Republic of Kazakhstan was used as study objects. The product of the "*Tau-Ken.temir"* Karaganda silicon plant (microsilicate) was used as a carrier and catalyst for the conversion of oil sludge. To study the thermokinetic decomposition of low-temperature coal tar, raw materials obtained during the coking of coal at the coke-chemical production enterprise of Shubarkol Komir JSC were used. The subject of research is thermochemical and catalytic hydrogenation of the oil sludge and low-temperature coal tar.

Research Methods – chromato-mass spectrometry, differential thermal analysis, scanning electron microscopy, transmission electron microscopy, X-ray phase analysis, X-ray fluorescence analysis, scanning probe microscopy, atomic emission spectroscopy, multichannel emission spectra analyzer, The Brunauer-Emmett-Teller method, temperature-programmable reduction, thermo-programmed desorption method, Ozawa-Flynn-Wall method, probabilistic-deterministic experimental planning, cluster-associated viscosity model, statistical processing of results.

The scientific novelty of the results obtained is the establishment of general patterns of thermal destruction and hydrogenation of primary coal tar in the presence of prepared microsilicate-based catalysts with applied hydrogenating agents (nickel, cobalt and iron), on the basis of which for the first time:

- The individual and chemical composition of microsilicate, oil sludge and microsilicate with deposited metals (nickel, cobalt and iron) has been established.
- Specific surface, surface morphology, size of deposited metal nanoparticles, acid number, adsorption isotherms, temperature-programmable reduction, thermo-programmed desorption method of prepared nanocatalysts were determined.
- The kinetics of thermal destruction of oil sludge (Atasu-Alashankou) in the presence of the catalyst with metals (nickel, cobalt and iron) deposited on the microsilicate using the Ozawa-Flynn-Wall method was studied.
- The kinetic parameters of thermal destruction of low-temperature coal tar in the presence of the catalysts with nickel, cobalt and iron metal oxides applied to the microsilicate were determined using the Ozawa-Flynn-Wall methods, the integral method and the method for determining the thermokinetic parameters by the inflection point on the thermogravimetric curve.
- The optimal conditions for the process of catalytic hydrogenation of oil sludge (Atasu-Alashankou) were established and the catalytic activity of catalysts (deposited on nickel and cobalt microsilicate), process parameters: temperature, initial hydrogen pressure, process duration, catalyst consumption were compared.
- The individual and chemical composition of the oil sludge fraction with a boiling point of up to 200℃ and 200 - 350℃ has been established.
- The cluster-associative model of the viscosity of a wide fraction of oil sludge with the boiling point of up to 350℃ was developed.

Catalysts have been created that are characterized by the presence of active centers on the surface of the carrier (microsilicate), on which nickel and cobalt nanoparticles are located.

The results of the study can be used to develop effective technologies for processing oil sludge and improve environmental protection.

Compliance with the directions of development of science or government programs. The work was carried out within the framework of the fundamental research program on the project topic: "Nanocatalytic system for hydroprocessing of heavy hydrocarbon raw materials" (2022-2024, state registration No. IRN AR13268918) and under the applied research program on the project topic: "Hydrodemetallization of oil shale and low-temperature resin fraction of Shubarkol Komir JSC" (2023-2025, state registration No. IRN AR19679059**)**.

Laboratory analyses were carried out at Centergeolanalit LLP (Karaganda), the chemical and analytical laboratory of Azimut Geologiya LLP (Karaganda), on the basis of the organic synthesis laboratory of the national research Tomsk State University (Russian Federation, Tomsk), on the basis of the catalytic research laboratory of Tomsk State University (Russian Federation, Tomsk), Institute of Petroleum Chemistry (Tomsk, Russian Federation), where on the basis of the laboratory of hydrocarbons and high-molecular oil compounds: Sokolsky Institute of Fuel, Catalysis and Electrochemistry JSC (Almaty), at the Scientific Research Institute of Chemical Problems, Engineering Laboratory "Methods of Physical and Chemical Research," Institute of Molecular Nanophotonics, Scientific Center for Nanotechnology and Functional Nanomaterials at Karaganda University named after E.A. Buketov

Theoretical and practical relevance. The theoretical and practical significance of this study lies in the development and study of the microsilicate-based nanocatalyst with supported active metals for the hydroconversion process of low-temperature coal tar and oil sludge. The results obtained can make an important contribution to the understanding of the mechanisms of thermal destruction and hydrogenation of oil sludge and low-temperature coal tar, the creation of new methods for processing hydrocarbon materials, which is of great importance for the energy, oil refining and petrochemical industries of the Republic of Kazakhstan.

The main provisions put forward for defense:

1. The kinetics of thermal decomposition of oil sludge (Atasu-Alashankou) in the presence of a catalyst with metals (nickel, cobalt and iron) deposited on the microsilicate was studied using the Ozawa-Flynn-Wall method.

The content of the deposited metal on the microsilicate was (wt%): nickel - 1.5, cobalt - 1.5, iron - 1.5, respectively. The calculated activation energies of the original oil sludge and the mixture of oil sludge with catalysts ranged from 59 to 158 kJ/mol. The correlation coefficient value ($R^2 \geq 0.997$) provides good convergence with experimental results.

2. The kinetics of thermal decomposition of low-temperature coal tar was investigated in the presence of catalysts with nickel, cobalt and iron metal oxides applied to the microsilicate were studied using various methods, including the Ozawa-Flynn-Wall method, the integral method and the method for analyzing thermokinetic parameters based on the inflection point on the thermogravimetric curve.

The values of activation energy of thermal destruction of low-temperature coal tar in the absence of - 297.5 kJ/mol a were calculated, in the presence of a nanocatalyst the value was - 54.0 kJ/mol, respectively. The calculated values of activation energies and pre-exponential factor increase as a result of thermal destruction from the initial primary coal tar to mixtures containing catalyst and tar, from 39.4 kJ/mol to 54.42 kJ/mol and from $1.86 \cdot 10^3$ s^{-1} to $1.1 \cdot 10^5$ s^{-1}, respectively.

3. Optimal conditions for catalytic hydrogenation of oil sludge (Atasu-Alashankou) were determined, and catalytic activity of catalysts containing nickel 1.5% and cobalt 1.5% supported on microsilicate was compared. Using the Protodyakonov-Malyshev method, optimal conditions for catalytic hydrogenation of

oil sludge (Atasu-Alashankou) were established: the amount of added nanocatalyst containing nickel applied to the microsilicate was 1.2-1.5%; initial hydrogen pressure 2.5-3 MPa; temperature 400-410 °C; the duration of the process is 50-60 minutes. During the hydrogenation of oil sludge, the maximum total yield of light fractions of 62.1% and a decrease in the kinematic viscosity from 2.2 to 1.2 mm^2/s were achieved.

4. A cluster-associative model was developed for changing the viscosity of a wide fraction of oil sludge with a boiling point of up to 350°C. It was first established that the specific activation energy of the viscous current, E/ā, remained within the van der Waals attraction energy of 2-20 kJ/mol, respectively. Based on the Frenkel equation, values of flow activation energy (E/ā) for oil sludge of 2.499 kJ/mol and two fractions of 2.803 and 3.141 kJ/mol from the hydrogenate were obtained.

Author's personal contribution – the author was directly involved: in setting the tasks of the dissertation work; independently conducted experiments on the preparation of catalysts of metals supported on microsilicate and the study of the effect of supported catalysts on the thermocatalytic conversion of heavy hydrocarbon raw materials; participated in the processing and interpretation of data obtained using physicochemical methods for the study of catalysts and products formed in their presence; presented the results at various conferences; prepared material for publications in scientific journals:

1. «Determination of optimal conditions for processing oil bottom sediments using electrohydraulic effect» https://doi.org/10.15587/1729-4061.2021.241763

2. «A kinetic study of the thermal decomposition of primary coal tar in the presence of catalysts with nickel, cobalt, and iron oxides supported onto microcilicate» https://doi.org/10.3103/S0361521922010086

3. «Kinetic study of the thermolysis process of oil sludge (Atasu-Alashankou) with nickel, cobalt and iron deposited on microsilicate» https://doi.org/10.15587/1729-4061.2022.255666

4. «Kinetic of oil sludge thermolysis process in presence of nickel, cobalt and iron-supported microsilicate» https://doi.org/10.2478/pjct-2023-0030

5. «Viscosity model for the middle fraction of Atasu-Alashankou oil sludge»https://doi.org/10.1016/j.mencom.2024.04043

6. «Kinetics of Thermolysis of a Low-Temperature Tar in the Presence of a Catalyzer Agent with Deposited Metals» https://doi.org/10.31489/2022Ch4/4-22-19

7. «Determination of Optimal Conditions for Catalytic Hydrogenation of Oil Sludge (Atasu-Alashankou)» https://doi.org/10.31489/2959-0663/2-23-15 and participated in 6 international conferences.

Publications and testing of the dissertation work. The main results of the dissertation research are published in 13 publications, including 5 articles in peer-reviewed scientific publications, indexed in the database Web of Science and Scopus: Solid fuel chemistry (IF 0.937, quartile Q4); Eastern-European Journal of Enterprise Technologies (IF Q2, percentile 56%, 2021); Eastern-European Journal of Enterprise Technologies (percentile 53%, IF Q2, 2022); Polish Journal of Chemical Technology (IF Q3, percentile 41%), 2 articles in the publication approved by the Committee for Quality Assurance in Education and Science of the Ministry

of Education and Science of the Republic of Kazakhstan (Bulletin of the Karaganda University (IF 0.5, quartile Q4); Eurasian Journal of Chemistry (IF 0.5, quartile Q4), 6 abstracts published at international conferences**.**

The results of the work were reported at international conferences: "Microsilicum catalyst for the anthracene hydrogenation process" Chemistry and chemical technology in the 21st century: materials of the XXII International Scientific and Practical Conference of Students and Young Scientists named after outstanding chemists L.P. Kulev and N.M. Kizhner, (Tomsk, 2021); "Kinetics of thermal destruction of low-temperature resin with catalytic additive with deposited metals" of the VIII International Russian-Kazakhstan Scientific and Practical Conference "Chemical Technologies of Functional Materials," organized jointly by the Al-Farabi Kazakh National University (Faculty of Chemistry and Chemical Technology of KazNU) and Novosibirsk State Technical University (Novosibirsk, 2022); "Kinetics of thermal destruction of primary coal tar in the presence of microsilicate containing Ni, Co, Fe" Chemistry and chemical technology in the 21st century: materials of the XXIII International Scientific and Practical Conference of Students and Young Scientists named after outstanding chemists L.P. Kulev and N.M. Kizhner, (Tomsk, 2022); XI International Russian-Kazakh Symposium "Coal Chemistry and Ecology of Kuzbass" "Thermal destruction of oil sludge (Atasu-Alashankou) in the presence of a heterogeneous catalyst" (Kemerovo, 2022); XII International Conference "Chemistry of Oil and Gas," "Kinetics of Thermal Destruction of Primary Coal Tar Applied to Nickel, Cobalt and Iron Microsilicate" (Tomsk, 2022); XI International Russian-Kazakhstan Symposium "Coal Chemistry and Ecology of Kuzbass" "Influence of a binary catalyst (CoFe) on the kinetics of thermal destruction of oil sludge (Atasu-Alashankou)" (Kemerovo, 2023).

Structure and scope of the dissertation work. The dissertation is presented in the amount of 136 pages and includes standard sections: an introduction, three chapters, including 21 figures and 22 tables, an opinion, a list of 265 sources used and appendices.