ABSTRACT

of the thesis for degree of Doctor of Philosophy (PhD)
on specialty 6D060600 – Chemistry

Aitbekova Darzhan Ergalievna

Destructive hydrogenation of primary coal tar in the presence of nanocatalysts

General description of work. The dissertation work is devoted to the study of the catalytic properties of nanocatalysts based on microspheres and chrysotile supported by hydrogenating agents (nickel and cobalt) in the processes of thermal destruction and hydrogenation of primary coal tar and model organic objects (anthracene, phenanthrene, benzothiophene, benzofuran).

The relevance of the work. The study of nanocatalysts based on transition metals with high activity for processing heavy hydrocarbon raw materials is relevant today. The advantages of the nanocatalysts studied in this work are the use as carriers of industrial waste (microspheres of coal ash and chrysotile mineral), low consumption of the catalyst (1%) and the nature of one-time use, hydrogenation of primary coal tar under mild conditions.

Since there are differences in the physicochemical properties of coal tar and primary coal tar, it is important to consider separately the catalytic hydrogenation of primary coal tar. Primary coal tar consists of paraffin, naphthenic, aromatic and condensed aromatic hydrocarbons, common phenols. However, high-temperature coke-chemical resin abroad finds application in hydrogenation processes, and low-temperature resin is not processed by industrial hydrogenation method.

The continuous increase in demand for light petroleum products and high-quality chemical products requires the development of deep processing processes of high-molecular hydrocarbon raw materials. Increasing the requirements for the quality of the products obtained leads to the search for catalysts for the processing of these types of raw materials.

The purpose of the thesis – development of active and selective catalysts based on microspheres and chrysotile with supported hydrogenating agents (nickel and cobalt) for the process of hydrogenation of primary coal tar.

Research objectives. The following tasks were set in the work:

1. To study the physicochemical characteristics of catalysts prepared on the basis of microspheres and chrysotile;
2. To study the reduction of nickel and cobalt oxides on the surface of chrysotile;
3. Determine the optimal conditions for the adsorption of nickel and cobalt salts on the surface of chrysotile;
4. Establish the kinetic patterns of thermal destruction of primary coal tar in the presence of catalysts;

5. To study the effect of catalysts on the process of hydrogenation of model compounds (anthracene, phenanthrene, benzothiophene, benzofuran);

6. Determine the size of metal nanoparticles deposited on chrysotile and establish their effect on the activity and selectivity of the catalyst;

7. To study the kinetics of catalytic hydrogenation of phenanthrene;

8. To study the effect of microspheres with applied metals (nickel and cobalt) on the hydrogenation of primary coal tar;

9. Select the optimal conditions for the hydrogenation of primary coal tar with the selected catalyst and calculate the activation energy and thermodynamic parameter (enthalpy) of the hydrogenation of the tar.

Object and subject of research. The objects of study are primary coal tar, model objects (phenanthrene, anthracene, benzothiophene, benzofuran) and catalysts based on microspheres and chrysotile supported by hydrogenating agents (nickel and cobalt). The subjects of research are the processes of thermal destruction and hydrogenation of primary coal tar and model objects in the presence of prepared catalysts.

Research methods – proton magnetic resonance spectroscopy, infrared spectroscopy, gas-liquid chromatography, 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, Brunauer-Emmett-Teller method, temperature-programmable reduction, methods for calculating kinetic and thermodynamic parameters, probabilistic-deterministic planning of the experiment, statistical processing of results.

The scientific novelty of the results obtained consists in establishing the general patterns of thermal degradation and hydrogenation of primary coal tar in the presence of prepared catalysts based on microspheres and chrysotile with applied hydrogenating agents (nickel and cobalt), on the basis of which for the first time:

1. The physicochemical characteristics of the prepared catalysts have been established;
2. The reduction temperatures of nickel and cobalt oxides were determined and the activation energies were calculated;
3. Optimal conditions for the adsorption of nickel and cobalt salts on the surface of chrysotile have been established;
4. Kinetic parameters of thermal degradation of primary coal tar in the presence of catalysts were calculated using differential thermal analysis;
5. Possible schemes for the hydrogenation reaction of anthracene, phenanthrene, benzothiophene and benzofuran in the presence of a chrysotile-based binary catalyst are proposed;
6. It is shown that the high activity of the binary (nickel and cobalt) catalytic system in the process of hydrogenation of phenanthrene is characterized by the distribution of nanosized metal particles on the surface of chrysotile;

7. The rate constants of phenanthrene hydrogenation reactions in the presence of a binary (nickel and cobalt) catalyst based on chrysotile were calculated and a scheme for phenanthrene hydrogenation was proposed;

8. The effect of catalysts based on microspheres supported by metals (nickel, cobalt) on the yield of light and medium fractions of primary coal tar has been established;

9. Optimal parameters and a mathematical model for the catalytic hydrogenation of primary coal tar have been established. The rate and activation energy of the hydrogenation process have been determined using a mathematical model. The enthalpy of the process was calculated using the express method.

Compliance with the directions of scientific development or state programs. The dissertation work was carried out at the Department of Chemical Technology and Petrochemistry of the academician E.A. Buketov Karaganda University within the framework of the research topic “Integrated processing of hydrocarbon raw materials”.

Laboratory analyzes were carried out at Tsentrgeolanalit LLP (Karaganda), the chemical-analytical laboratory of Azimut Geology LLP (Karaganda), JSC Institute of Fuel, Catalysis and Electrochemistry named after. D.V. Sokolsky (Almaty), in the office of collective use of Nazarbayev University (Nur-Sultan), JSC “Eastern Research Coal Chemical Institute” (VUHIN) (Russian Federation, Yekaterinburg) and the Research Institute of Chemical Problems, Laboratory of Engineering Profile “Methods of Physical and Chemical Research”, Institute of Molecular Nanophotonics, Scientific Center of Nanotechnologies and Functional Nanomaterials at academician E.A. Buketov Karaganda University.

Theoretical and practical significance. The results of the study of catalytic hydrogenation of primary coal tar contribute to the field of hydrogenation processing of heavy hydrocarbon raw materials and to the field of development of nanocatalysts. The light fraction obtained in the process of hydrogenation of primary coal tar can be used as an additive in motor fuel to increase octane and cetane numbers, phenol and naphthalene derivatives, as raw materials for petrochemistry. The results of the study of the catalytic hydrogenation of primary coal tar (mathematical modeling, thermodynamic and kinetic parameters) can be presented as a basis for carrying out technical and economic calculations of a heavy hydrocarbon processing plant.

The main provisions for defense:

- Hydrogenation of a mixture of anthracene and phenanthrene with a ratio of 1:1 in the presence of a catalyst based on a microsphere with cobalt deposited provides the yield of hydrogenation products of 40.9%, destruction of 51.6% at a temperature of 420°C, initial hydrogen pressure of 3.0 MPa, the amount of catalyst 1.0%, duration of 60 min.

- Hydrogenation of anthracene and phenanthrene in the presence of a binary chrysotile-based catalyst with nickel and cobalt deposited provides the yield of hydrogenation products equal to 61.9% and 26.1%, respectively, and the yield of destruction products equal to 15.1% and 2.5%, respectively, at a duration of 60

minutes, an initial hydrogen pressure of 3.0 MPa, a temperature of 400°C and a catalyst amount of 1.0%.

- The optimal concentration of solutions of nickel (II) and cobalt (II) nitrates deposited on chrysotile is 5.0% that ensures the distribution of nickel and cobalt oxides on the surface of chrysotile with dimensions of 40-90 nm.

- Optimal conditions for hydrogenation of low-temperature resin are as follows: temperature is 430°C, initial hydrogen pressure is 2.0 MPa, duration is 80 min, catalyst consumption is 1.0% and water consumption is 0.5%. The yield of the fraction up to 300°C during hydrogenation of low-temperature resin under optimal conditions is 45±0.7%.

The author's personal contribution is the setting of the goal and objectives of the study, participation in the planning and conduct of the experiments, discussion of the patterns obtained and processing of the results, formulation of conclusions and preparation of manuscripts for publications.

Publications and approbation of the work. The main results of the dissertation research were published in 14 publications, including 3 articles in peer-reviewed scientific journals indexed in the Web of Science and Scopus databases, 3 articles in the journal approved by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science RK, 8 abstracts of reports at international conferences.

The results of the work were reported at international conferences: The IV International Scientific-Practical Conference “Integration of the Scientific Community to the Global Challenges of Our Time” (Sapporo, 2019); International scientific and practical conference “Innovations in the field of natural sciences as the basis of export-oriented industrialization of Kazakhstan” (Almaty, 2019); The 7th International Conference on Nanomaterials and Advanced Energy Storage Systems (Almaty, 2019); The VIII International Symposium on Specialty Polymers (Karaganda, 2019); XXII International Scientific and Practical Conference of Students and Young Scientists named after outstanding chemists L.P. Kulev and N.M. Kizhner, dedicated to the 110th anniversary of the birth of Professor A.G. Stromberg “Chemistry and chemical technology in the XXI century” (Tomsk, 2020); International Scientific and Practical Conference dedicated to the 1150th anniversary of Abu Nasr al-Farabi “Al-Farabi in the modern Kazakhstan context” (Karaganda, 2020); XXII International Scientific and Practical Conference of Students and Young Scientists named after outstanding chemists L.P. Kulev and N.M. Kizhner, dedicated to the 125th anniversary of the founding of Tomsk Polytechnic University “Chemistry and chemical technology in the XXI century” (Tomsk, 2021); All-Russian scientific and practical conference with international participation “Resource-saving and environmentally friendly processes in chemistry and chemical technology” (Perm, 2021).

The structure and scope of the thesis. The dissertation work is presented in the amount of 141 pages and includes standard sections: normative references, definitions, designations and abbreviations, introduction, literature review, experimental part, experimental results and their discussion, including 46 figures and 39 tables, conclusion, list of 223 used sources and an appendix.