ABSTRACT

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

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Hydrorefining of coal tar in the presence of nanocatalytic additives and polymeric materials

General description of work. The dissertation work is devoted to the study of the catalytic properties of a nanocatalyst based on chrysotile with a deposited active agent of nickel oxide, the influence of the size effect of particles of deposited nickel on the hydrogenation and cavitation of PCT, the establishment of kinetic parameters and thermodynamic functions of the hydrogenation and cavitation of coal tar. As physicochemical research methods and computational methods, the following methods were used: chromatography-mass spectrometry, X-ray phase analysis, X-ray fluorescence analysis, X-ray spectral fluorescence analysis, gravimetric analysis, the Brunauer-Emmett-Teller method, scanning electron microscopy, transmission electron microscopy and atomic emission spectral analysis, as well as methods for determining kinetic parameters and thermodynamic functions.

The relevance of the work. The complexity of organic matter, which is coal tar, as an object of study, necessitates the complex use of instrumental and destructive methods, which provide the possibility of comparing and systematizing data on the obtained fractions. The greatest difficulty in the study of high-temperature transformations of CT in the process of destructive hydrogenation is the analysis of the initial stages of destruction of CT in the presence of catalysts and polymeric materials. It should be noted that the nickel oxide catalyst deposited on the surface and inside of chrysotile in the presence of a polymer material has high activity and selectivity in the hydrogenation process and allows the process to be carried out under mild conditions. Chrysotile, which is the basis for the nanocatalyst, plays the role of a carrier and is an environmentally friendly waste of asbestos production, as well as the use of polymers such as PE, PS and PEG as a hydrogen donor for the process of thermal destruction and hydrogenation of CT allows to solve the problem of waste disposal containing polyolefin materials. Investigation of the composition of nanocatalysts and understanding the dependence of the catalytic properties of nanocatalysts on the size factor of particles deposited on chrysotile and the nature of polymer materials leads to an increase in the activity and selectivity of the selected nanocatalysts in the processes of thermal destruction, hydrogenation, and cavitation of coal tar. In this regard, the development of nanocatalysts based on chrysotile with high activity and selectivity for the processes of thermal destruction and hydrogenation of HHR is relevant today.

The degree of elaboration of the problem. Due to its specific and catalytic properties, chrysotile has found wide application in oil refining, chemical production and has taken a high position in catalysis, optoelectronics (in the works of K.K.Dzhamanbalin, Qidan Liu, V.I.Belotitsky, etc.). Chrysotile also found wide use in the catalysis of nitrophenol hydrogenation, in the demetalization of high-viscosity oil. However, there are no data in the literature on thermal destruction, hydrogenation, and cavitation of PCT and coal tar in the presence of a nanocatalyst with an active nickel deposited on the surface and inside chrysotile nanotubes.

The purpose of the thesis is to study the kinetics of thermal decomposition, hydrogenation of coal tar in the presence of a developed nanocatalyst based on chrysotile with a deposited active agent of nickel oxide, to determine the thermodynamic functions of the average fraction of coal tar and the enthalpy of hydrogenation reactions of polyaromatic hydrocarbons.

Research objectives. The work set the following tasks:

1. Investigate the surface morphology and particle size using a scanning electron microscope and transmission electron microscope and the crystal structure of fibers using X-ray phase analysis of chrysotile nanocatalyst with a deposited active agent nickel, textural characteristics of the initial chrysotile and nanocatalyst.

2. To study the effect of the size factor on the activity of the nanocatalyst (chrysotile with supported nickel) in the reaction of phenanthrene hydrogenation and PCT cavitation.

3. Determine the optimal conditions for the process of PCT hydrogenation in the presence of a nanocatalyst and a polymer material.

4. Determine the kinetic and thermodynamic parameters of thermal destruction, hydrogenation and cavitation of coal tar and primary coal tar.

5. Determine the individual and group composition of the primary coal tar and hydrogenated fraction.

6. Investigate the effect of water on the individual chemical composition of a wide fraction with t. 200-350 ^{o}C PCT in the process of cavitation.

Object and subject of research. The object of research is a nanocatalyst based on chrysotile with a deposited active agent of nickel oxide.

The subject of the research is the process of thermal destruction, catalytic hydrogenation, ultrasonic cavitation of PCT and HCT in a hydrogen atmosphere.

Scientific novelty of the results obtained. In the dissertation work for the first time:

- the crystal structure of the fibers in the composition of the investigated nanocatalyst of chrysotile with the applied active agent of nickel oxide and the presence of highly dispersed particles of nickel oxide and nanoparticles with sizes in the range of 12-18 nm, which are uniformly distributed on the surface of nanotubes of the nanocatalyst, have been established.

- the specific surface area (109.9 m^2/g) and the volume of the sorption space (0.169 cm^3/g) of the nanocatalyst based on chrysotile with the deposited active agent of nickel oxide on the surface and inside the chrysotile were determined.

- the influence of the size factor on the activity of the nanocatalyst (chrysotile with supported nickel) in the reaction of phenanthrene hydrogenation and PCT cavitation is shown.

- a kinetic scheme has been developed, kinetic parameters and thermodynamic functions of destructive hydrogenation and cavitation have been determined, kinetic parameters of thermal destruction of primary coal tar have been established according to thermogravimetric analysis.

- the optimal conditions for the process of PCT hydrogenation in the presence of a nanocatalyst and a polymer material have been determined.

- the individual and group composition of the primary coal tar and the hydrogenated fraction was established.

- shows the effect of water on the individual chemical composition of a wide fraction with t. 200-350 ^{o}C PCT in the process of cavitation.

Connection of work with the plan of scientific-research work and State programs. The dissertation work was carried out within the framework of research work carried out at the Karaganda University named after E.A. Buketov in accordance with the fundamental research program of the Ministry of Education and Science of the Republic of Kazakhstan under the project "Thermochemical processing of heavy oil residues mixed with primary coal tar in an atmosphere of coke oven gas" (2015-2017, state registration No. 0115RK00935).

Theoretical and practical significance. The theoretical significance lies in the expansion of fundamental knowledge about the group and individual composition of the fraction up to 200 and 200-300 °C, obtained from the hydrogenate during the hydrogenation of PCT in the presence of a nanocatalyst containing an active agent of nickel and a polymer material. A kinetic model of catalytic hydrogenation and hydrodynamic cavitation of a wide fraction of HCT in the presence of a nanocatalyst for the transformation of a PAH mixture is proposed, which makes it possible to describe all the chemical transformations of the components in the reaction mixture. The calculated rate constants and thermodynamic functions of formation of intermediates can be included in the reference material.

The developed nanocatalyst allows under mild conditions at low pressure and temperature to carry out the process of PCT hydrogenation with a high yield of light and medium fractions (52-55 wt.%). The data obtained using ultrasonic cavitation treatment of the PCT fraction in the presence of a nanocatalyst can be used in scaling up for the commercialization of this development.

The main provisions for the defense:

- a decrease in the average particle size of nickel increases the yield of paraffin-naphthenic hydrocarbons in the process of hydrogenation and cavitation of PCT;

- the probable kinetic scheme of the kinetics of the process of hydrogenation and cavitation of the fraction 230-300 °C of coal tar;

- preliminary activation of chrysotile and application of an active element to the surface of chrysotile, determination of the optimal conditions for PCT

hydrogenation and the influence of factors on the yield of light and medium fractions, establishment of the individual and group composition;

- comparison of the results of calculating the thermodynamic functions of the fraction 230-300 °C of coal tar obtained by the unified additive method with reference data.

The author's personal contribution is that the author personally analyzed and systematized scientific and technical literature, planned and carried out experiments to obtain a nanocatalyst based on chrysotile with an applied active agent of group VIII of the periodic system D.I. Mendeleev and testing on a model organic object, generalization and interpretation of the results obtained and their theoretical justification.

Publications and approbation of work. Based on the results of the dissertation work, 12 publications were published, including 1 article in a rating journal included in the Web of Science and Scopus databases, 3 articles in publications recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, abstracts of 5 reports and 3 articles in collections of works conferences. Fragments of the work were reported at the XXII International Scientific and Practical Conference of Students and Young Scientists "Chemistry and Chemical Technology in the XXI century" named after outstanding chemists L.P. Kulev and N.M. Kizhner, dedicated to the 125th anniversary of the founding of Tomsk Polytechnic University (Tomsk, 2021); the 83rd International Scientific and Technical Conference of Faculty, Researchers and postgraduates "Chemical Technology and Engineering", (Minsk, 2019); the XIV international scientific-practical conference dedicated to the memory of the founders of the Kostanay branch of "ChelSU" T.Zh. Atzhanov and A.M. Rodnov, the 25th anniversary of the Constitution and the Assembly of the People of Kazakhstan "The paradigm of modern science through the eyes of the young" (Kostanay, 2020); the international scientific-practical online conference "The integration of science, education and production - the basis for the implementation of the Plan of the Nation (Saginov readings No. 12)" (Karaganda, 2020).

The structure and scope of the thesis. The dissertation work is presented in the volume of 160 pages and includes standard sections: an introduction, three chapters, including 32 tables, 38 figures, a conclusion, a list of 314 used sources and an appendix.