Abstract

Abstract of the dissertation of Evgenia Abdulmutalipovna Skichko on the topic: "Carbon nanotube synthesis: research, modeling, optimization, scaling, application."

Relevance of the research topic. The extensive scientific interest in carbon nanotubes (CNTs) and carbon nanofibers (CNFs) is based on a number of their unique physical properties, which are orders of magnitude greater than the properties of similar materials used. The physical properties of CNTs and CNFs have been studied in detail in recent years, and potential areas of CNT application are currently being actively explored. One of the promising areas of application is the use of CNTs as a reinforcing additive in the manufacture of composite materials (composites). Due to their outstanding mechanical properties (elasticity, tensile strength), CNTs can increase the bending strength and crack resistance of ceramics. Another promising area of application is the manufacture of platinum cathode catalysts for hydrogen-air fuel cells (FCs) on CNTs as a carrier. To date, platinum catalysts on carbon blacks are the only catalytic system available on the market, but carbon blacks are highly susceptible to corrosion, which reduces the service life of the catalyst. For this reason, CNTs are considered as an alternative to carbon blacks.

These and many other areas of use determine the demand for large-scale industrial production of CNTs. Most authors agree that the most cost-effective method of producing CNTs is catalytic pyrolysis of carbon-containing gases. It is characterized by low cost, since it is carried out at atmospheric pressure and relatively low temperatures, as well as simple hardware design. Catalytic pyrolysis allows obtaining hydrogen in industrial quantities in addition to CNTs and CNFs, in addition, it is the most environmentally friendly, since there are no carbon dioxide emissions into the atmosphere during pyrolysis. Industrial production of CNTs, regardless of the method of their production, should be preceded by laboratory kinetic studies aimed at clarifying the kinetic features of the process under the selected synthesis conditions (catalyst, initial gas - carbon precursor, temperature, etc.) in order to determine the optimal synthesis conditions and the expected yield of CNTs. The type of carbon material obtained during pyrolysis (CNTs, CNFs, soot), its crystalline structure, external internal diameter, defectiveness are almost completely determined by the type of catalyst used, therefore, the study and selection of the catalyst is one of the important stages of the work, along with the study of the kinetic scheme, the development of mathematical models and the optimization of the process.

The aim of the study is mathematical modeling of kinetic regularities of CNT synthesis by catalytic pyrolysis of methane-hydrogen mixtures; mathematical modeling and optimization of a screw reactor for CNT synthesis, development of a software package for solving equations of the

created mathematical models.

To achieve the set goal, it is necessary to solve the following tasks:

1. Conducting experimental studies to select a pyrolysis catalyst that provides the highest yield of CNTs.

2. Experimental study of the kinetic patterns of CNT synthesis by catalytic pyrolysis of methane-hydrogen mixtures of various compositions, studying the effect of temperature and composition of the initial gas mixture, microscopic and statistical analysis of the results.

3. Building a kinetic scheme for the pyrolysis of methane-hydrogen mixtures, mathematical modeling of the kinetic patterns of CNT synthesis.

4. Mathematical modeling of CNT synthesis in a continuous screw reactor and optimization of its operating mode.

5. Building a process flow chart for hydrocarbon pyrolysis to produce two target products: CNTs and hydrogen.

6. Using the obtained CNTs as a carrier of a platinum catalyst in a hydrogen-air fuel cell.

7. Using the obtained CNTs as a reinforcing additive in ceramic composites based on aluminum and zirconium oxides.

Scientific novelty. In the process of completing the dissertation, new scientific results were obtained for the first time:

1. The dependences of the growth rate, CNT yield, catalyst deactivation time during catalytic pyrolysis on the hydrogen concentration in the initial methane-hydrogen mixture and the process temperature were revealed.

2. A mechanism for CNT synthesis was developed that takes into account the revealed effect of hydrogen concentration in the initial gas mixture. Taking this mechanism into account, mathematical modeling of the kinetic patterns of CNT synthesis by catalytic pyrolysis was carried out.

3. A mathematical model of a semi-industrial continuous screw reactor was developed, and its operating mode was optimized.

4. A model of the process flow chart of catalytic pyrolysis of methane-hydrogen mixtures to obtain CNTs and hydrogen was developed, including a pyrolysis unit, a unit for the extraction of product hydrogen, and a unit for the utilization of pyrolysis heat.

The theoretical and practical significance. Based on experimental studies, the ratio of metals in the active phase of the catalyst Fe:Co = 3:1 was selected to ensure the highest yield of CNTs. The results obtained confirm the effect of hydrogen concentration in the initial gas mixture on the growth rate, CNT yield, and catalyst deactivation time. Based on the developed mathematical model of pyrolysis, the optimal operating mode of a continuous screw reactor was determined, providing a CNT productivity of 106 g/h during pyrolysis of a methane-hydrogen mixture of the following composition: 70% vol. CH_4, 30% vol. H_2, pyrolysis temperature of 770°C and catalyst consumption of 140 mg/min. A software package for calculating mathematical models in the Java programming language has been developed.

The provisions submitted for defense:

- Results of experimental studies of kinetic regularities of CNT synthesis by catalytic pyrolysis of methane-hydrogen mixtures of variable composition, confirming the possibility of a significant increase in the yield of CNTs by varying the concentration of hydrogen in the initial gas mixture.

- Kinetic scheme of catalytic pyrolysis of methane, including the stages of removing amorphous carbon from the front surface of the active centers of the catalyst with hydrogen. Theoretical substantiation of the role of hydrogen in the process of catalytic pyrolysis of methane, explaining the extreme nature of the dependence of the yield of CNTs on the concentration of hydrogen in the initial gas mixture.

- Mathematical model of kinetic regularities of CNT synthesis by catalytic pyrolysis of methane-hydrogen mixtures. Mathematical model of a continuous screw reactor. Optimum operating mode of a screw reactor to achieve the highest productivity for CNTs. Software modules for calculating mathematical models. Results of using CNTs.