ANNOTATION

Dissertation for the degree of Doctor of Philosophy (PhD) in the specialty "8D07104- Chemical technology of inorganic substances"

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"Inorganic composite materials for hydrogen and nanocarbon production from methane"

Summary of work. This thesis work investigated the development of new inorganic composite materials with low metal oxide content (Fe, Ni, Ce) for catalytic decomposition of methane into hydrogen and nanocarbon. A comparative study of monometallic and bimetallic iron-based composites in the catalytic decomposition of methane was also carried out. The study also established the relationship between the characteristics of inorganic composite materials and their ability to actively participate in the studied process.

Relevance of the research topic. The demand for hydrogen is constantly increasing due to its use in chemical processing, electronics, food processing, metal and fuel cell production. The production of hydrogen, from water separation using sunlight or other renewable energy sources is not economically competitive. For this reason, hydrogen production will soon still involve the use of fossil fuels, mainly natural gas.

Catalytic methane decomposition (CMD) can be used to produce hydrogen without CO_x and has recently become a hot research topic. It produces pure hydrogen and carbon and there is no need to separate hydrogen from other gases such as CO_x in traditional processes. Kazakhstan has large reserves of natural gas, methane, but it is mainly used as a fuel. Therefore, the conversion of methane into valuable commodity products is of great economic and environmental importance for our country.

Hydrogen obtained during the methane decomposition reaction can be used as a reducing agent in metallurgical processes, as well as a feedstock for obtaining various chemical compounds (methanol, dimethyl ether, etc.); hydrogen is the most energy-intensive and environmentally friendly energy carrier. The obtained nanocarbon is used in production technologies, medicine, biotechnology and as tool materials. In addition, PFC is a promising alternative to existing methods of hydrogen production without carbon dioxide.

Studies of catalytic decomposition of methane using inorganic composite materials attract the world attention of scientists. Materials consisting of noble metals (Pt, Ru, Rh and others) show high efficiency and resistance to the formation of carbon deposits in the reaction process. However, their use at the industrial level is limited due to their high cost and limited resources. The efficiency of inorganic composite materials in catalytic decomposition of methane depends on various factors such as properties of the active phase and supporting material, material synthesis methods, pretreatment conditions, etc. Research efforts are focused on the

development of active, resistant and affordable transition metal based inorganic composites. Transition metal oxides such as Ni, Co, Fe often act as active components. The ability of catalysts containing nickel and iron to react during methane decomposition has been studied both on catalysts containing only iron and on systems with the simultaneous presence of iron and other metals [1,2]. The existing literature emphasizes the need for further systematic and more detailed studies on the reaction of catalytic decomposition of methane.

Aim of the work:

The aim of the work is to develop science-based active inorganic composite materials with defined directional catalytic properties for the decomposition of methane into hydrogen and nanocarbon.

To achieve the goal, the following objectives were set:

- Synthesis of new composites with low iron oxide content for H_2 production by methane decomposition. Testing the activity of synthesized composites in methane decomposition;
- Determination of the influence of the nature of carriers (Al_2O_3, SiO_2, etc.) and modifying additives (Cu, Ni, etc.) on the activity of iron composite in hydrogen production;
- Investigation of the influence of different methods of synthesis of modified iron composite on its activity in methane decomposition;
- Establishment of the relationship between physical and chemical characteristics and activity of the composite in the decomposition reaction.
- Development of technological regulations for obtaining 1 ton of optimal inorganic composite material, which is used for catalytic decomposition of methane into nanocarbon and hydrogen.

Objects of research: greenhouse gas-methane, inorganic composite materials based on metal oxides of variable valence.

Subject of the study: the process of methane decomposition to hydrogen and nanocarbon. Determination of the influence of the chemical composition of inorganic composite materials on their structure and catalytic activity in the process of methane decomposition; determination of factors influencing the activity and stability of the developed inorganic composite materials.

Research Methods. To study the efficiency of the developed inorganic composite materials, a specialized catalytic unit was used, where testing was carried out at changing temperatures in dynamic mode. The composition of starting materials and gas reaction products was analyzed using the method of gas chromatography on a calibrated chromatograph GC Chromos-1000. Physicochemical characteristics of composite materials were investigated by a complex of modern methods, such as SEM, XRD, PEM, DTA/TGA, TPR, BET and Raman spectroscopy.

Theoretical and practical significance of the study: In theoretical terms, the relationship between the activity of synthesized inorganic composite materials with

their texture and morphology in the process of catalytic decomposition of methane has been established. The practical significance lies in the fact that cheap, domestic raw material natural gas - methane - is used as a raw material for obtaining valuable products such as hydrogen and nanocarbon. As a result of the research new thermally stable high-performance inorganic composite materials of new generation for hydrogen and nanocarbon production from CH_4 have been developed.

Creation of new scientifically grounded nanophase inorganic composites as well as determination of optimal conditions for hydrogen and nanocarbon production during catalytic decomposition of methane represent a significant contribution to both fundamental and applied catalysis.

Scientific novelty of the work consists in the development of low-percentage inorganic composite materials for creation of waste-free one-stage catalytic processing of greenhouse gas - methane into valuable products - hydrogen and nanocarbon. A new composition and a special method of preparation of catalysts, which allows to control their physicochemical and catalytic properties, are proposed.

– New composites based on iron oxide synthesized by capillary impregnation and electrochemical deposition methods have been developed.

– It is shown that the activity of low Fe-Ni containing composites is influenced by the method of their synthesis. Fe-Ni catalyst prepared by electrochemical method is more active at high reaction temperatures (800-850 ^oC).

– According to the results of BET, TPR-H_2 and XRD, the increase in the activity of Ni-Fe composites in methane decomposition compared to Ni-foam is due to the increase in the textural characteristics of the composites, as well as the formation of Ni-Fe alloy. The formation of Ni-Fe alloy contributes to the decrease in the recovery temperature of the composite. Raman studies of the composites worked in PFC showed that graphite with higher defectivity is formed on Ni-Fe 150 cycles, which showed the most enhanced activity and stability in the methane decomposition reaction, which favors the passage of methane decomposition on the Ni-Fe 150 cycles sections not covered by carbon.

– Fe-Ni composites prepared by capillary impregnation method according to the moisture capacity of the carrier (γ-Al_2O_3) are more active at relatively low temperatures (650-750 ^oC) of the PFC process, compared to composites prepared by electrochemical method.

– It is established that in comparison with bimetallic Fe-Ni/γ-Al_2O_3 composites polyoxide iron-nickel-cerium composites show higher activity in the reaction of catalytic decomposition of methane.

– According to XRD, SEM and Raman data, 1-2 layer graphene is formed on 15%Fe - 5%Ni/γ-Al_2O_3 composite at methane decomposition, the growth center of which can be aggregated particles of Fe or Ni oxides. On Fe-Ni-Ce/γ-Al_2O_3 composite, single-layer nanotubes are formed. The introduction of cerium oxide into the 15%Fe - 5%Ni/γ-Al_2O_3 composite promotes the dispersion of active phases,

thereby creating conditions for the nucleation and growth of free carbon in the form of nanotubes, which has a positive effect on the activity and stability of 15%Fe - 5%Ni- 2%Ce/γ-Al_2O_3 composite in methane decomposition.

– The high level of scientific research is confirmed by publications in both domestic and foreign journals, as well as presentation of results at international conferences.

Personal contribution of the author. The author has conducted a review and analysis of literature on the investigated topic, studied the methods of preparation of composite materials for the use of the CDM reaction, as well as the characterization of the isolated reaction products. In addition, the contribution of the doctoral student is the processing and interpretation of the obtained results, as well as approbation at conferences and formalization in the form of scientific articles.

1.Catalytic Decomposition of Methane over Al_2O_3 Supported Mono- and Bimetallic Catalysts // Bulletin of Chemical Reaction Engineering & Catalysis (literature data analysis, experimental data acquisition and results processing); 2. Effect of preparation method on the activity of Fe_2O_3-NiO/ γ-Al_2O_3 catalyst in decomposition of methane // Eurasian Chemico-Technological Journal (literature analysis, empirical data collection and analysis of results); 3. Electrochemical synthesis of Fe-containing composite for methane decomposition into hydrogen and nano-carbon \\ Chemical Papers (analyzing literature data, collecting data through experiments and analyzing the results obtained); 4. Effects of cerium oxide on the activity of Fe-Ni/Al_2O_3 catalyst in the decomposition of methane // Inorganic Chemistry Communications (literature review, empirical data collection and analysis of findings); 5. Влияние взаимодействия компонентов в никель-кобальтовых катализаторах на их активность в разложении метана // Горение и плазмохимия (literature review, empirical data collection and analysis of findings). 6. Effect of the interaction of components in a nickel molybdenum catalyst on its activity in decomposition of methane to hydrogen // Chemical Bulletin of Kazakh National University (literature review, empirical data collection and analysis of findings); 7. Utility model patent №6952. «Катализатор для получения водорода из метана» (analysis of literature data, comparison of obtained data with literature data). 8. Proceedings of scientific conferences and symposia (obtaining and describing experimental data, discussing and obtaining analytical results, preparing proceedings).

Relation to research works and state programs. The research was carried out in accordance with the plan of research work under the project AR08855564 "Obtaining hydrogen and nanocarbon from natural gas - methane", carried out under the budget program 217 "Development of Science", subprogram 102 "Grant financing of scientific research for 2020-2022", state registration number: 0120RK00398.

Main points to be defended

1. Promotion of 20%Fe/γ-Al_2O_3 composite by nickel oxide leads to an increase in the activity of the sample in the decomposition of methane to hydrogen

and nanocarbon (methane conversion 92%, hydrogen productivity 2,1 mmol/g^{-1}), at low temperatures (650-750 ^{o}C) due to the formation of the easily reducing phase $NiFe_2O_4$.

2. At methane decomposition on Fe-Ni/γ-Al_2O_3 composite one or two layer graphene is formed, the growth center of which is aggregated particles of Fe or Ni oxides. Introduction of cerium oxide into Fe-Ni/γ-Al_2O_3 composition promotes dispersion of active phases, thus creating conditions for nucleation and growth of free carbon in the form of nanotubes, which positively affects the activity and stability of Fe-Ni-Ce/γ-Al_2O_3 catalyst in methane decomposition.

3. Deposition of iron on porous nickel foam by electrochemical method allows to obtain a sample that is active at high reaction temperatures (800-850 ^{o}C) of methane decomposition (methane conversion 91%, hydrogen productivity 2,1 mmol/g^{-1}), due to the formation of Ni-Fe alloy. The number of layers of graphene formed on the composite depends on the increase of the iron deposition cycle on the composite.

Publications. The results of the performed works are reflected in 12 scientific papers, including:

- in 2 articles published in journals recommended by the Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- in 5 abstracts of reports at international and national conferences and symposia;
- in 4 articles published in peer-reviewed journals included in Scopus database;
- 1 patent for utility model of the Republic of Kazakhstan.