ABSTRACT
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Development of composite materials by combustion synthesis for catalytic methane reforming into hydrocarbons and synthesis-gas

The dissertation is devoted to the development of composite materials by synthesis during combustion for the catalytic reforming of methane into hydrocarbons and synthesis gas.

Relevance of the research topic. World oil reserves are declining every day due to the continuous production and refining using the most modern technologies. Scientists around the world are looking for different types of raw materials and ways to use the huge resources of natural gas as a substitute for oil. In this regard, considerable attention is paid to natural and associated gases as an alternative source of raw materials for the petrochemical industry.

In recent years, the problem of finding renewable fuels has become very urgent in connection with a shortage of oil reserves. In the twenty-first century, humanity is faced with a global problem, such as Earth's climate change, which is a result of an increase in the concentration of greenhouse gases in the atmosphere. At present, humanity is feeling the greenhouse effect. The problem of greenhouse gases and their reduction is closely related to energy security, the stability of global energy markets and the sustainable development of each state and the world community as a whole. It is generally accepted that full restoration and mitigation of the effects of climate change is currently impossible, but measures must be taken to reduce the emissions of anthropogenic greenhouse gases. The study of the selective oxidative conversion of methane is consistent with Kazakhstan's development priorities in the use of its own hydrocarbons. According to forecasts, saturated hydrocarbons will not only maintain, but also strengthen their position as a raw material for producing valuable organic compounds and fuel compositions, which will contribute to the revival of the national petrochemical industry. The activation of natural and associated petroleum gas (containing from 65 to 98% methane) for the targeted single-stage synthesis using nanoscale catalysts is one of the most relevant and important tasks in the field of organic catalysis.

The gas processing factories of Kazakhstan are currently mainly engaged in the purification of gases from water, impurities of carbon dioxide and hydrogen sulfide for their use in domestic purposes. Therefore, there is a great economic incentive to develop effective catalysts for converting natural gas into valuable products. Natural gas is distributed all over the world (there is more of it than oil reserves) and this avoids dependence on oil producing countries. However, the main disadvantage of using methane as a source of chemicals and fuel is the relatively low cost of oil combined with the high cost of storing and transporting natural gas from remote tanks. So far, the only

economically affordable way to convert methane to more valuable chemicals is to produce synthesis gas. The production of synthesis gas from methane using active and stable catalysts plays an important role in the chemical and petrochemical industries.

Methane is the simplest hydrocarbon that exists in large quantities on our planet. It is the main component of natural gas with a concentration of up to 90-95% by volume. According to World Energy 2018, an annual statistical survey published by British Petroleum (BP) at the end of 2017, the world's proven natural gas reserves are estimated at 193.5 trillion. cubic meters. And in 2019, natural gas reserves rose to 196.9 trillion. cubic meters. Kazakhstan ranks 15th in the world and 4th place in the CIS in terms of natural gas reserves. When burned for energy, natural gas produces about half as much carbon dioxide (CO_2) as coal, so expanding its use around the world is critical to reducing CO_2 emissions. Combustion gas emits fewer pollutants. Gas is an ideal, cost-effective partner for renewable energy sources such as wind, solar and hydropower, providing a permanent backup source of energy.

Prospects for the development of the global gas processing industry are associated with the creation and implementation of new catalytic environmentally friendly technologies for producing synthesis gas and hydrocarbons based on the production of fuel mixtures. In recent years, natural gas has received increased attention as a raw material for the chemical industry. The first step in converting natural gas is often the targeted production of synthesis gas ($CO + H_2$) as an environmentally friendly modern fuel, as well as costly olefins. The synthesis gas can then be further used in various petrochemical syntheses (for example, Fischer-Tropsch) for the production of valuable chemical products.

The problem of rational utilization of natural and associated petroleum gases and the cessation of their burning in flares is today one of the acute and unresolved environmental problems. Especially in a crisis and a sharp decline in prices for natural resources, both natural and associated petroleum gases can be considered as an alternative source of valuable and very expensive petrochemicals and organic synthesis products on the world market.

The aim of the thesis is the development of effective and thermo stable catalysts by the combustion of solutions for the catalytic reforming of methane into hydrocarbons and synthesis gas.

To achieve the goal, the following tasks were set:

- synthesis of catalysts by the traditional method of impregnation in air, as well as by the modern method of combustion in solution and the study of their properties;

- determination of the optimal process conditions by changing the process parameters (temperature, volume velocity, ratio of the components of the reaction mixture, active phase content), which allows to obtain the maximum yield of the product under conditions of raw materials and energy rational use;

- study of the properties of catalysts by various physicochemical methods in order to identify factors that determine the activity and stability of catalytic systems in a continuous mode;

- study of the activity, selectivity, stability of catalysts in the process of catalytic reforming of methane into synthesis gas and hydrocarbons;

- identification of the relationship of the catalytic and physico-chemical properties of the catalysts.

Objects of research: methane, composite materials, catalysts based on synthesis through combustion in solution.

Subject of research: the process of catalytic reforming of methane into synthesis gas and hydrocarbons.

Research methods. In this work, we used methods for testing samples under flowing conditions in a reactor with a fixed catalyst bed. The properties of the developed catalysts were studied by a set of physicochemical methods: transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray phase analysis (XRD) and the Brunauer-Emmett-Teller (BET) method. The reaction products were analyzed by gas chromatography (GC).

Scientific novelty. New composite materials have been developed to obtain active, efficient and thermo stable catalysts prepared by the modern solution combustion method for producing synthesis gas from methane.

- For the first time, the stability of Ni-Cr-Mg-Al systems synthesized by combustion in solution was established. It was found that the catalyst does not decrease its activity within 72 hours

- For the first time, the optimal ratios of Ni and Cr, Co and Mg were found to be 5:1 and 3:2, which, under certain technological conditions, provide 98% conversion of methane to synthesis gas with a selectivity of 92% for H_2 and 99% for CO.

- It is shown that in the case of adding urea to the composition of the catalysts, the concentration of cobalt cations in the spinel lattice is higher. In this case, Co_3MgO_4 is formed, and in the case of glycine, $CoMg_3O_4$ is formed to a greater extent.

- CoB_2O_4 formation has been established, which occurs when B^{3+} (ionic radius 0.23 Å) is replaced by Co^{2+} ions (ionic radius 0.72 Å), which leads to an increase in the spinel crystal lattice parameters.

- It was found that the preparation of the catalyst by impregnation is inferior to the method of synthesis of combustion of solutions, in which higher values of the conversion of raw materials and yield of H_2 are obtained.

The main provisions to be defended:

- a method for the preparation of active and selective catalysts by the method of burning solutions for partial oxidation of methane (POM), carbon dioxide conversion of methane (CCM) and oxidative condensation of methane (OCM);

- determined the optimal composition of the catalysts for the oxidative conversion of methane;

- the state of Ni and Co in the composition of the centers that determine the activity of the catalysts;

- optimal conditions for POM, CCM and OCM in the presence of composite catalysts.

Theoretical and practical significance of the research. Reducing the burning and utilization of natural gas in the process of partial oxidation of methane and in particular two greenhouse gases, which represent an alternative source of valuable chemical products, in the process of carbon dioxide conversion is one of the most important economic and environmental problems. As a result of research, new thermally stable high-performance new-generation catalysts have been developed for the selective production of synthesis gas and hydrocarbons from CH_4.

The development of new nanoscale catalysts and optimal technological conditions for the production of synthesis gas and hydrocarbons in the process of incomplete oxidative conversion of alkanes, as well as carbon dioxide conversion of methane, is a contribution to fundamental and applied catalysis.

The high scientific level of the study is confirmed by scientific publications both in Kazakhstan and in foreign journals, as well as testing results at international conferences and symposia.

Publications. The main results of the dissertation were co-authored in 17 publications, including 2 articles in international scientific journals included in the Scopus and Thomson Reuters database; in 4 articles in magazines 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 11 materials of international and national scientific conferences. According to the results of the work in co-authorship, 2 positive decisions on applications were also obtained (Patents for a utility model).

The structure and scope of the dissertation. The dissertation consists of an introduction, 3 chapters, general conclusions and a list of sources used. The dissertation is presented on 117 pages, contains 13 tables, 77 figures. The list of references contains 126 sources.

Based on the analysis of literature and experimental data, the following conclusions are made:

1. New composite materials have been developed for the preparation of active, effective and thermo stable catalysts prepared by the modern method of solution combustion to produce synthesis gas and ethylene from methane.

2. As a result of the study of catalysts based on $Co(NO_3)_2$ - $Mg(NO_3)_2$ - H_3BO_3 - urea/glycine systems and a comprehensive study of their physicochemical properties, it was found that the formation of CoB_2O_4 probably occurs when B^{3+} is substituted (ionic radius 0.23 Å) with Co^{2+} ions (ionic radius 0.72 Å), which leads to an increase in the spinel crystal lattice parameters. $CoMg_3O_4$ spinel is formed by replacing magnesium cations with cobalt cations.

3. The presence in the catalysts of simple and mixed oxides, metal aluminates, and spinel-type structures, the presence of which contributes to the active operation of the catalysts for the oxidative conversion of methane, was established. In the case of adding urea to the composition of the catalysts, a higher concentration of cobalt cations in the

spinel lattice. In this case, Co_3MgO_4 is formed, and in the case of glycine, $CoMg_3O_4$ is formed to a greater extent.

4. It has been shown that at space velocities from 1500 to 2500 h^{-1} it is possible to obtain the highest yield and selectivity for the target products. The compositions with the highest Ni contents obtained the highest synthesis gas results. Nevertheless, at a 25% Ni content in the composition of the catalyst, the selectivity for the target products are quite high and the H_2/CO ratio is most optimal compared to the rest of the sample compositions.

5. For the first time, the optimal ratios of Ni and Cr, Co, and Mg were found to be 5:1 and 3:2. This ensures 98% conversion of methane into synthesis gas with a selectivity of 92% for H2 and 99% for CO under certain technological conditions.

6. For the first time, the stability of Ni-Cr-Mg-Al systems synthesized by burning in solution was established. It was found that the catalyst does not decrease its activity within 72 hours

7. It was established that the most active in the formation of the target products (olefins) among the studied compositions is 10% K - 30% Mn - 10% Nb / 50% glycine catalyst prepared by burning in solution. It was determined that during the oxidative conversion of a mixture of 41.8% CH_4 + 16.2% O_2 + 42% Ar and a ratio of CH_4:O_2 = 2.5:1.0 and a space velocity of 3500 h^{-1}, the optimum temperature for the formation of 3.3% C_2H_6 and 14.3% C_2H_4 is T = 8000 °C, at which the total yield of olefins is 17.6%.

8. It was found that the preparation of the catalyst by impregnation is inferior to the method of synthesis of combustion of solutions, in which higher values of the conversion of the feed and the yield of H_2 are obtained. An analysis of the results allows us to conclude that it is possible to optimize the process of oxidative conversion of methane by selecting the technological parameters of the reaction and improving the composition and method of preparation of the catalysts.

Assessment of the completeness of solutions to the tasks. All the tasks set for solving the purpose of this dissertation are solved completely.

As a result of the work, the tasks were successfully solved and new stable nanoscale catalysts of a given composition, dispersion, structure and optimal technological conditions for the processes of oxidative conversion of light alkanes to synthesis gas and olefins were developed, and the conditions for the formation of the most active properties of alkane processing catalysts were identified; the laws of selective production of synthesis gas and olefins from methane on catalysts prepared by the solution combustion method, as well as by the traditional method of impregnation by moisture capacity, the physicochemical characteristics of the developed catalysts by a set of methods, and their relationships with catalytic properties are established.

Thus, the goals of the dissertation research were achieved - composite materials were developed by the synthesis method in the combustion process to produce synthesis gas and hydrocarbons in the processes of partial oxidation and carbon dioxide methane conversion.

Assessment of technical and economic efficiency proposed in the dissertation. Developed highly selective catalysts and methods for producing olefins and synthesis gas from methane, used as the target product, as well as suitable for Fischer-Tropsch synthesis, can be proposed for degradation in small modular plants and mini-plants in oil production areas where associated gases are burned on the torches. This will be the first step to the future reorientation in the raw material basis to enable a smooth transition from the generally accepted technologies for producing fuels and organic substances from oil to new technologies for producing the same products from gaseous raw materials, which could significantly reduce the cost of the target products and reduce environmental pollution. Among the factors contributing to the implementation of this process, it should be noted that this technology is promising for the development of low-pressure fields with a residual pressure of 10-20 atm. Additional factors that can increase the efficiency of the process can be the parallel production of pure carbon dioxide (during oxidation) and its consumption (during carbon dioxide conversion) and the production of a significant amount of reaction water, which can be used to fuel the reaction cycles.