**ABSTRACT**
**of PhD thesis by specialty 6D073900 - Petrochemistry**

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# Catalytic processing of the methane of natural gas into synthesis-gas on composite materials formed by solution combustion synthesis

## The relevance of research

Humanity is faced with a global problem in the XXI century. This is a change in the Earth's climate as a result of an increase in the concentration of greenhouse gases in the atmosphere. Humanity is already experiencing the greenhouse effect. To date, the problem of rational utilization of natural and associated petroleum gases and the termination of their flaring is one of the acute and unresolved environmental problems.

Natural gas is typically 90-98% methane and is cleaner and more energy efficient than oil or coal. 25 billion tons of carbon dioxide, which is the main cause of the greenhouse effect that causes global warming, is released into the atmosphere every year when all types of fuel are disposed of. This means that the search for real alternatives to hydrocarbon fuels is an extremely urgent problem.

Currently, many experts in the field of energy, activists of social movements in defense of the environment prefer hydrogen fuel. Research is ongoing to more widely implement the use of hydrogen fuel as a replacement for gasoline. The use of hydrogen in transport and energy in foreign countries is a promising direction, on which great hopes are pinned. Therefore, one of the urgent and most important tasks in the field of organic catalysis is the activation of methane, natural and associated petroleum gas (which contain from 65 to 98% methane) for the purposeful one-stage production of organic synthesis intermediates and fuel compositions using new-generation nanosized catalysts. An in-depth study of selective methane oxidation corresponds to the development priorities of Kazakhstan in the field of using its own hydrocarbon feedstock.

## Research goals and objectives

The aim of the work is to develop effective modern composite catalysts by solution combustion method for environmentally friendly production of synthesis gas, solving the problems of decarbonization and achieving carbon neutrality.

To achieve this goal, the following tasks have been set:

- Synthesis of massive, supported and block catalysts by the traditional impregnation method, the modern method of self-propagating high-temperature synthesis (SHS) and its modern modification - the method of solution combustion for the production of synthesis gas and hydrogen-containing fuel mixtures;
- Study of textural characteristics, elemental and phase composition, microstructure, morphology, and adsorption properties of catalysts by TEM, SEM, XRD, BET, TPD methods, etc. to identify factors that determine the activity and

stability of catalytic systems during long-term operation. Determination of the relationship between catalytic and physicochemical properties of catalysts;

- Testing of the developed catalysts in the methane reforming process. Determination of the dependence of catalytic activity on the composition and properties of the synthesized catalysts;

- Identification of the optimal conditions for the process by varying the technological parameters (temperature, space velocity, ratio of the components of the reaction mixture, the content of the active phase on the carrier, etc.);

- Determination of optimal methane reforming catalysts. Carrying out tests on an enlarged automated installation.

**Research methods**

Tests of the developed catalysts were carried out on a laboratory automated flow catalytic installation in a reactor with a fixed catalyst bed, as well as in an enlarged automated installation. The properties of the developed catalysts were studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray phase analysis (XRD), temperature-programmed desorption (TPD), and the Brunauer-Emmett-Teller (BET) method. The reaction products were analyzed by gas chromatography (GC).

**The main provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for defense:**

- method for preparation of active and selective Co-Al/urea, Co-Mg(+B)/urea, Co-Al-Mg-Mn/urea, Ni-Al-Mg/urea, Ni-Al-Mg-Mn/urea catalysts by solution combustion synthesis for partial oxidation of methane (POM) and carbon dioxide conversion of methane (CCM);

- optimal compositions of catalysts for oxidative conversion of methane: 30% Co - 70% Al / 60% urea, 60% Co - 40% Mg / 22% urea - 37% $H_3BO_3$, 20% Co - 20% Al - 5% Mg - 5 % Mn / 50% urea, 10% Ni - 35% Al - 5% Mg / 50% urea, 20% Ni - 20% Al - 5% Mg - 5% Mn / 50% urea;

- optimal conditions for carrying out POM and CCM in the presence of composite catalysts: for 60% Co - 40% Al: $CH_4$ conversion - 98%, $CO_2$ conversion - 86%, yield of $H_2$ - 99% and CO - 85% at 900°C; for 60% Co - 40% Mg: $CH_4$ conversion - 90%, selectivity by $H_2$ - 92% and CO - 95% at 900°C и W = 2500 $h^{-1}$; for 20% Al - 20% Co - 5% Mn - 5% Mg: $CH_4$ conversion - 98%, yield of $H_2$ - 98% and CO - 43% at 900°C and W = 2500 $h^{-1}$; for 10% Ni - 35% Al - 5% Mg: at oxidative conversion of $CH_4$: 98% conversion of $CH_4$, yield of $H_2$ - 98%, yield of CO - 40% at 900°C и W = 2500 $h^{-1}$; for carbon dioxide conversion of $CH_4$: $CH_4$ conversion - 99%, $CO_2$ conversion - 98%, yield of $H_2$ - 51%, yield of CO - 36% at 900°C и W = 2000 $h^{-1}$; for 20% Ni - 20% Al - 5% Mg - 5% Mn: yield of $H_2$ - 98%, CO - 43%, selectivity by $H_2$ - 99% and by CO - 98% at 900°C and W = 6500 $h^{-1}$;

- the role of substitution of $B^{3+}$ and $Mg^{2+}$ ions by $Co^{2+}$ ions in the Co-Mg catalyst with the addition of $H_3BO_3$, leading to an increase in the crystal lattice parameters of the resulting spinel;

- the role of water, which consists in the fact that the formation of dendrites increases and their combustion occurs much more intensively when the amount of added water is reduced to 15 ml during the preparation of catalysts. An insignificant amount of unreacted nickel oxides was found in the products and, accordingly, a larger amount of formed spinel, which, as expected, contributes to the activation of the synthesized catalysts.

**Scientific novelty**

New active, efficient and thermostable catalysts of a new generation were developed, which were prepared by a modern method of solution combustion for the production of synthesis gas and hydrogen from methane.

- The temperature-time profiles of the volumetric combustion regime of systems in the preparation of catalysts were established for the first time: 30% Co - 70% Al / 60% urea, 20% Co - 20% Al - 5% Mg - 5% Mn / 50% urea, 10% Ni - 35% Al - 5% Mg / 50% urea, 20% Ni - 20% Al - 5% Mg - 5% Mn/50% urea;

- The role of Al in solution, leading to an increase in the $CoAl_2O_4$ spinel concentration in the 30% Co - 70% Al / 60% urea catalyst, as well as to a change in the crystal lattice parameters without structural changes, on which the conversion of methane depends, was shown for the first time. Such non-stoichiometric spinels are formed as a result of self-propagating high-temperature synthesis with very high heating and cooling rates, which leads to a high concentration of defects in catalysts that are active sites of catalysis;

- Two oxygen adsorption centers have been identified for the first time, which may play an important role in the reactions of oxidative processes. The strongly bound form of oxygen is the most reactive and participates in partial oxidation reactions;

- For Ni-Al-Mg/urea catalysts, it was found for the first time that the physical properties and atomic structure of the catalysts created by solution combustion depend on the amount of water used in the initial solution in the preparation of the catalysts. A decrease in the volume of water added during the synthesis of catalysts leads to an increase in the concentration of $NiAl_2O_4$ spinel, which is formed by the reaction $NiO + Al_2O_3 \rightarrow NiAl_2O_4$, $Ni^{2+} \rightarrow Ni^{3+}$;

- It has been shown that catalysts with a high content of $NiAl_2O_4$ spinel, but with a smaller surface area, are the most active. This means that the chemical composition is the decisive factor for a given reaction; the reaction is not limited by methane adsorption, so the surface does not affect the results;

- The conditions for reforming methane into modern environmentally friendly hydrogen-containing fuel on the developed catalysts were first proposed;

- The developed catalyst compositions are protected by 2 utility model patents of the Republic of Kazakhstan.

**Connection of the topic with research work and State programs**

The work was carried out within the framework of grant projects funded by the Ministry of Education and Science of the Republic of Kazakhstan: AP05132348 «Development of modern modified fuels and hydrocarbons for various purposes

from gaseous material on new generation composite materials» (state registration number 0118RK00272, 2018-2020); AP08855562 « Development of fundamental aspects of catalytic reforming of renewable natural raw materials - biogas for the development of environmentally friendly high-performance fuels » (state registration number 0120RK00479, 2020-2022).

**Personal contribution of the author, publications and approbation of practical results of the work**

The personal contribution of the author lies in the analysis of literary studies, the implementation of the experimental part of the work, physical and chemical methods of analysis, generalization and interpretation of the obtained experimental data and conclusions.

The main results of the dissertation work were published in co-authorship in 16 publications, including 5 articles in international scientific journals included in the Scopus and Thomson Reuters database; in 1 article in a journal recommended by the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan; in 8 materials of international and republican scientific conferences. Based on the results of work in co-authorship, 2 patents for a utility model of the Republic of Kazakhstan were also obtained.

The main results and provisions of the dissertation were presented at the following scientific conferences:

- 12$^{th}$ Natural Gas Conversion Symposium NGCS, June 2-6, 2019, San Antonio, USA;
- 22$^{nd}$ Conference Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction PRES19, October 20-23, 2019, Crete, Greece;
- 26$^{th}$ North American Catalysis Society Meeting NAM26, June 23-28, 2019, Chicago, USA;
- The 8$^{th}$ Asia-Pasific Congress on Catalysis, August 4-7, 2019, Bangkok,Thailand;
- V International Conference Catalysis for Renewable Sources: Fuel, Energy, Chemicals CRS-5, September 2-6, 2019, Crete, Greece;
- 2$^{nd}$ Intern. Conf. on Reaction Kinetics, Mechanisms and Catalysis RKMC, May 20-22, 2021, Budapest, Hungary;
- 24$^{th}$ Intern. Congress of Chemical and Process Engineering CHISA, March 15-18, 2021, Prague, Czech Republic;
- XXIV International Conference on Chemical Reactors CHEMREACTOR-24, September 12-17, 2021, Milan, Italy.