ABSTRACT
of PhD thesis by specialty 6D073900 - Petrochemistry

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Catalytic conversion of biogas to synthesis-gas

Relevance of the research topic. Vast reserves of gaseous hydrocarbons and gas mixtures containing them, primarily natural gas and its main component, methane, make them a promising resource capable of meeting humanity's needs for energy and hydrocarbon raw materials. Gas chemistry is becoming one of the fastest growing branches of the modern fuel and energy complex due to the growing interest in the use of available and relatively cheap natural gas resources as chemical raw materials. In the coming years, its development will largely determine the general development trends and structure of the world energy and chemical industry, in particular. This is especially true for Kazakhstan, which has significant reserves of gas condensate and natural gas. The main part of the extracted hydrocarbon raw materials is exported to the CIS countries and far abroad without preliminary processing or used as household gas. Gas processing plants (Zhanaozen, Karachaganak) are currently mainly engaged in cleaning gases from water, carbon dioxide and hydrogen sulfide impurities for the use of C_1-C_4 alkanes for domestic needs. This situation is due to the lack or absence of new catalytic technologies for the directed processing of light hydrocarbons. One of the serious problems of modern gas chemistry remains high costs for the conversion of hydrocarbons into synthesis gas, which is the main intermediate product of their conversion into final chemical products and liquid fuel. The search for more efficient and economical (in comparison with steam and autothermal reforming of natural gas) technologies for producing synthesis-gas is becoming one of the main scientific and technical directions in energy and gas chemistry. This also makes it possible to obtain cheap and affordable hydrogen for environmentally friendly transport and hydrogen energy. **The aim of the dissertation** is the development of active and thermostable supported monometallic Ni- and Co-, as well as bimetallic Ni-Co catalysts, which selectively conduct the process of converting biogas into synthesis-gas.

Research objectives:

- synthesis of catalysts by the traditional method of incipient wetness impregnation in air, as well as by the modern SHS method and study of their properties;
- determination of the optimal reaction parameters by varying the process conditions (temperature, space velocity, ratio of gases in the reaction mixture, content of the active phase) to obtain the maximum yield of products with rational consumption of raw materials and energy;
- investigation of the properties of catalysts by various physicochemical methods in order to establish the factors that determine the activity and stability of the developed catalysts in a continuous mode;

- study of the activity and stability of the developed catalysts in the process of catalytic conversion of biogas into synthesis-gas;

- determination of the relationship between catalytic and physicochemical properties of catalysts.

Research methods: The results of testing samples under flow conditions in a reactor with a fixed catalyst bed are given in the work. The properties of the developed catalysts were investigated by a complex of physicochemical methods: transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray phase analysis (XRD), Brunauer-Emmet-Teller (BET) method, temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), CO_2 desorption with temperature programming (TPD), elemental analysis (CHNS). The reaction products were analyzed by gas chromatography (GC).

The main provisions to be defended:

- method for preparing active and stable catalysts by impregnation and SHS for catalytic conversion of biogas into synthesis-gas;

- optimal catalyst compositions for the catalytic conversion of biogas into synthesis-gas;

- phase transition of a spinel-type metal oxide to the structure of a Co-Ni mixed metal of the face-centered cubic type;

- optimal conditions for carbon dioxide conversion of methane with the participation of supported oxide catalysts.

The main results of the study:

1. It has developed a series of 10% Ni/θ-Al_2O_3, 9% Ni-1% Co/θ-Al_2O_3, 7% Ni-3% Co/θ-Al_2O_3, 5% Ni-5% Co/θ-Al_2O_3, 3% Ni-7% Co/θ-Al_2O_3, 1% Ni-9% Co/θ-Al_2O_3, 10% Co/θ-Al_2O_3 catalysts, prepared by the traditional method of impregnation in terms of moisture capacity and a series 100% Ni, 90% Ni-10% Co, 70% Ni-30% Co, 50% Ni-50% Co, 30% Ni-70% Co, 10% Ni-90% Co, 100% Co catalysts, prepared by the modern SHS method for the catalytic conversion of biogas into synthesis gas.

2. The synthesized catalysts were characterized by physicochemical methods and tested in dry reforming of methane at 700°C. The TEM results showed that the smallest sizes of metal oxide crystallites were found for monometallic 10% Co/θ-Al_2O_3 and 10% Ni/θ-Al_2O_3 samples. The formation of Co-Ni spinel and oxide alloy was detected in bimetallic catalysts by XRD.

3. It was found that a bimetallic 5% Ni-5% Co/θ-Al_2O_3 catalyst has a high initial activity with a CH_4 and CO_2 conversion of 75% and 82%, respectively, at 700°C. However, activity declined rapidly over time. In this case, according to XRD data, there is a phase transition of the spinel-type metal oxide into the structure of the Co-Ni mixed metal of the face-centered cubic type.

4. It was determined that the monometallic 10% Ni/θ-Al_2O_3 catalyst is the most stable. The hydrogen yield on it decreased from 56% to 45% within 100 h with the

simultaneous transformation of the mixed Co-Ni oxide into a metal alloy of the face-centered cubic type.

5. It was found that the most optimal conditions are: T = 900°C, CH_4 : CO_2 : Ar = 1 : 1 : 1 and the gas space velocity of 6000 h^{-1} for the catalytic conversion of biogas into synthesis-gas on the developed catalysts.

6. The stability of a 10% Ni-90% Co catalyst prepared by the SHS method in the conversion of biogas to synthesis-gas for 100 h was first established.

Scientific novelty. New oxide catalysts prepared by the traditional incipient wetness impregnation method and the modern SHS method, exhibiting high activity and stability in the catalytic conversion of biogas into synthesis-gas, have been developed.

- It was found that the smallest sizes of metal oxide crystallites were found for monometallic 10% Co/θ-Al_2O_3 and 10% Ni/θ-Al_2O_3 samples. The formation of Co-Ni spinel and oxide alloy was detected by XRD in bimetallic catalysts.

- It was determined that among the bimetallic compositions, high initial activity was found on a 5% Ni-5% Co/θ-Al_2O_3 catalyst with a CH_4 and CO_2 conversion of 75% and 82% at 700°C, respectively. However, the activity rapidly decreased with increasing time, according to XRD data, along with the phase transition of the spinel-type metal oxide to the structure of the Co-Ni mixed metal of the face-centered cubic type.

- It was revealed that the monometallic 10% Ni/θ-Al_2O_3 catalyst is the most stable, for which the hydrogen yield decreased from 56 to 45% within 100 h while changing the mixed Co-Ni oxide to a metal alloy of the face-centered cubic type.

- The stability of a 10% Ni-90% Co catalyst prepared by the SHS method in the conversion of biogas into synthesis-gas for 100 h has been determined for the first time.

- It was found that the preparation of the catalyst by the modern SHS method is inferior to the impregnation method in terms of moisture capacity, in which higher values of feed conversion and synthesis-gas yield were obtained.

Theoretical and practical significance of the research. Environmental problems are becoming more and more urgent in the modern world. Large amounts of CH_4 and CO_2 are emitted into the atmosphere due to the growing human production activity. Since the start of the industrial revolution, CO_2 concentrations have increased by more than 45%, from 280 ppm in the mid-18th century to 415 ppm in 2019. Biogas is mainly composed of 50-87% methane, 13-50% carbon dioxide and other gases. The conversion of biogas solves two important issues: the utilization of greenhouse gases and the possibility of obtaining synthesis-gas with an optimal ratio of 1 : 1, in which it is possible to carry out the Fischer-Tropsch synthesis reaction, the production of gasoline, aviation kerosene, ethanol and other oxygen-containing compounds. The development of new supported catalysts, as well as the optimal technological conditions for the production of synthesis-gas in the catalytic conversion of biogas is a contribution to the petrochemical sector, namely to gas processing. The high scientific level of the carried out research is confirmed by scientific publications both in Kazakhstan and in journals

from far abroad, as well as by the approbation of the results at international conferences and symposia.

Connection of the topic with the research plan and various State programs. The work was carried out within the framework of projects funded by the MES RK: AP05133881 «Catalytic processing of C_1-C_4 hydrocarbons into industrially important gas and petrochemical monomers» (No state registration 0118RK00275, 2018-2020); AP08052090 «Creation of catalytic systems with controlled properties for the synthesis of valuable commodity products» (No state registration 0120RK00141, 2020-2022).

Description doctoral contribution to the preparation of each publication.

The doctoral student was directly involved in the preparation of catalysts, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article Mono- and bimetallic Ni Co catalysts in dry reforming of methane in the magazine ChemistrySelect (2021, Vol. 6, P.3424-343. IF 1,811. Quartile Q2 https://doi.org/10.1002/slct.2021).

The doctoral student was directly involved in the preparation of catalysts, obtaining experimental data, processing and interpreting experimental results for the preparation of the article Catalytic reforming of methane into synthesis-gas in the magazine Materials Today: Proceedings (2020, Vol.31, P.595-597. https://doi:10.1016/j.matpr.2020.07.406).

The doctoral student was directly involved in the preparation of catalysts, obtaining experimental data, processing and interpreting experimental results for the preparation of the article Oxide Ni-Cu catalysts for the purification of exhaust gases in the magazine Chemical Engineering Transactions (2020.– Vol. 81, – P. 925-930. IF 0,68. Quartile Q3 https://doi.org/10.3303/CET2081155).

The doctoral student was directly involved in the preparation of catalysts, obtaining experimental data, processing and interpreting experimental results for the preparation of the article Catalytic processing of natural gas into olefins in the magazine Chemical Engineering Transactions (2020.– Vol. 81, – P. 1057-1062. IF 0,68. Quartile Q3 https://doi.org/10.3303/CET2081177).

The doctoral student was directly involved in the preparation of catalysts, obtaining experimental data, processing and interpreting experimental results for the preparation of the article Catalytic conversion of methane into syngas and ethylene in the magazine News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology (2019. - Vol. 3, No 435. - P. 6-12. IF 0,251. https://doi.org/10.32014/2019. 2518-1491.22).

The doctoral student was directly involved in the preparation of catalysts, obtaining experimental data, processing and interpreting experimental results for the preparation of the article Catalytic processing of propane into important petrochemical products in the magazine. News of the National Academy of Sciences of the Republic of

Kazakhstan. Series Chemistry and Technology (2020. – Vol. 3(441). – P. 110-119. IF 0,251. https://doi.org/10.32014/2020.2518-1491.51).

The doctoral student was directly involved in the preparation of catalysts, obtaining experimental data, processing and interpreting experimental results for the preparation of the article Selective catalytic oxidation and steam oxygen conversion of methane into synthesis gas in the magazine. News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology (2020. - Vol. 3(441). - P. 96-103. IF 0,251).

The doctoral student was directly involved in the preparation of catalysts, obtaining experimental data, processing and interpretation of experimental results for registration of a patent for a useful model No. 5701 (Publ. In bull. No. 52 of 12.25.2020) for a Method for preparing a catalyst for obtaining synthesis gas.

In addition, the doctoral student was directly involved in obtaining and discussing experimental data published in 10 abstracts of international conferences.