

## Production of Hydrogen-Containing Clean Fuel from Biogas

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The article summarizes the results of research on the development of new effective catalysts for the carbon dioxide conversion of methane (model biogas mixture) in order to obtain synthesis gas - clean H<sub>2</sub>-containing fuel, as a result of combustion of which harmful impurities are practically not formed. The method of solution combustion synthesis was used to prepare the catalyst. It is known that the conversion of methane in production is carried out in the presence of various catalysts. In the course of the experiment, several samples of Ni - Al - Mg/urea catalysts were prepared with different water contents in the initial catalyst mixture. The tests were carried out on an automated unit in quartz reactor with a gradual increase in temperature from 600 to 900 °C. The content of the gas mixture before and after the reaction was analyzed by the chromatographic method on a Chromos-1000 device. According to the research, it was found that the most optimal catalyst is 10 % Ni – 35 % Al – 5 % Mg/50 % urea with the addition of 15 mL of water before solution combustion synthesis. The optimum product yields and selectivity were recorded at 900 °C: conversions of CH<sub>4</sub> and CO<sub>2</sub> were 99.4 % and 98.5 %, respectively, while the H<sub>2</sub> selectivity was 78.3 % on the developed catalysts, which exceeds many known data. The obtained results correlate with the data of physical and chemical methods. It has been shown that the catalysts contain simple and mixed oxides, metal aluminates and spinel-type structures, the presence of which contributes to the active operation of catalysts for the carbon dioxide conversion of methane.

### 1. Introduction

The global petrochemical and energy industries are paying significant attention to the production of natural gas, shale gas, methane in chemicals and value-added fuels to reduce the high dependence on oil. Natural gas, the bulk of which is methane, remains the cheapest raw material for chemicals and energy. It is possible to obtain ethylene from methane by the reaction of oxidative coupling on H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> heteropoly acid (Kassymkan et al., 2020), formaldehyde on sol-gel V/SiO<sub>2</sub> catalysts (Loricera et al., 2017), methanol on over La-Co-O and ZrO<sub>2</sub> supported molybdenum oxide catalysts (Zhang et al., 2005) and synthesis gas. There are several ways to obtain synthesis gas by steam reforming on MgAl<sub>2</sub>O<sub>4</sub>-supported Rh and Ir catalysts (Mei et al., 2014), partial oxidation of methane on composite SmCeO/γ-Al<sub>2</sub>O<sub>3</sub> supported Ni catalyst in membrane reactor (Elbadawi et al., 2020) and dry reforming on Ni-Co-rare earth oxide catalysts (Jiang et al., 2021).

Currently, an intensive study of processes has begun using biogas as an alternative source of both energy and feedstock for petrochemicals due to the continuous depletion of non-renewable energy sources and feedstock for petrochemical production. Biogas is an almost inexhaustible renewable resource for obtaining valuable products. Raw material for carbon dioxide reforming of methane may be considered as a model of biogas. Biogas is produced in various ways from the anaerobic fermentation of biomass and from any organic waste, for example, food waste (Ab Muis et al., 2021) and food waste with crude glycerol (Nizam et al., 2021). Currently, biogas is mainly used as a fuel. The development of processes for its use as a raw material for the production of motor fuels and other products is an urgent task. The most suitable for solving this problem is

the production of synthesis gas from biogas, or from a model mixture of methane with carbon dioxide to determine the process parameters in laboratory conditions.

The solution combustion synthesis (SCS) is a modern effective method for the production of composite materials with controllable properties for a wide range of catalysts with universal properties, for example, the TiO<sub>2</sub>-doped Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst reduce the temperature of oxidative coupling of methane by 100 °C and maintain high thermal stability in comparison with similar catalysts prepared by traditional methods (Wang et al., 2017). SCS catalysts are successfully used in processes methane and other hydrocarbon conversion reactions to fuel and chemicals, for example, in water gas shift reaction (Jeong et al., 2016), steam reforming (Postole et al., 2015), biogas reforming (Zhumabek et al., 2021), biogas oxidative steam reforming (Vita et al., 2015), dry reforming (Xanthopoulou et al., 2019) as soon as in steam reforming of biomethanol for hydrogen production (Baneshi et al., 2014), and catalytic phenol degradation (Sun et al., 2013). SCS is a modification of the self-propagating high-temperature synthesis process. Solution combustion synthesis is used for the production of nano-sized bulk catalysts and supported catalysts. Structures with a high concentration of defects in intermediate and nonstoichiometric compounds are formed under conditions of fast rates of combustion and cooling reactions. They are one of the reasons for the high activity of SHS catalysts.

Biogas in the coming years may become the most important solution to the problems of energy supply to agricultural enterprises. The novelty of this work lies in the fact that a previously poorly covered direction of the use of biogas for production of motor fuel components over the new SCS catalysts is investigated.

Aim of the work is to develop catalysts for the conversion of model biogas (a mixture of methane with carbon dioxide) into hydrogen-containing clear fuel, which in the future will contribute to the organization of a new environmentally friendly energy-saving production.

## 2. Experimental

### 2.1 Preparation of catalysts

Nickel, magnesium, and aluminum nitrates, as well as urea, were used to synthesize catalysts. All initial salts were weighed and thoroughly mixed in an agate mortar. Then the mixture of salts was placed in a quartz beaker, which contained different volumes (0.015 – 0.1·10<sup>-3</sup> L) of distilled water, preheated to 80 °C. After complete dissolution of all salts, the glass with the solution was transferred to a muffle furnace preheated to 500 °C. Three thermocouples were installed on top. All thermocouples were in a glass inside a muffle furnace. The thermocouples were in contact with the bottom, middle, and surface layers of the solution. After about 5-8 min, in the presence of an organic combustion initiator - urea, enough heat is generated to ensure the propagation of the combustion front at a high speed and self-release of heat. This leads to a sharp rise in temperature. The temperature inside the reaction front is so high that the low boiling point impurities evaporate, resulting in cleaner products. Structures with a high concentration of defects in intermediate and nonstoichiometric compounds are formed, which are one of the reasons for the high activity of SCS catalysts.

### 2.2 Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD) using CuKα<sub>1</sub> radiation with wavelength λ = 1.5406 Å on a Siemens Spellman DF3 spectrometer. Scanning electron microscopy (SEM) of the catalysts was investigated using energy dispersive X-ray spectroscopy (EDX). The Brunauer-Emmett-Teller (BET) specific surface area and pore distribution were measured on a GAPP V-Sorb 2800 analyzer using a nitrogen-helium mixture as carrier gas.

### 2.3 Catalytic activity studies

The tests of the synthesized catalysts were carried out in an automated flowing catalytic unit in a tubular quartz reactor with a fixed catalyst bed. The studies were conducted using the reaction mixture containing CH<sub>4</sub>, CO<sub>2</sub>, and Ar at 600 - 900 °C, space velocity (GHSV) 2,000 h<sup>-1</sup> and atmospheric pressure. The composition of the initial reaction mixture (CH<sub>4</sub> : CO<sub>2</sub> : Ar = 33 % : 33 % : 34 %) and the products were studied by the chromatographic method using a chromatograph "Chromos GK-1,000" with software "Chromos".

## 3. Results and Discussion

### 3.1 Synthesis and characterization of catalysts

Two combustion modes, namely a volumetric explosion and a self-propagating mode, were observed in the synthesis of catalysts by solution combustion synthesis. The solution was heated and the water evaporated in the volumetric explosion mode. The gel is formed after the evaporation of water. The temperature in the glass gradually rose to a critical value. As soon as the temperature reached the critical one, an exothermic reaction began throughout the entire volume of the catalyst. Figure 1 shows the temperature-time profile of the

volumetric combustion regime of the system 10 % Ni(NO<sub>3</sub>)<sub>2</sub> + 35 % Al(NO<sub>3</sub>)<sub>3</sub> + 5 % Mg(NO<sub>3</sub>)<sub>2</sub> + 50 % urea with different volumes of added water as a solvent during the synthesis of samples.

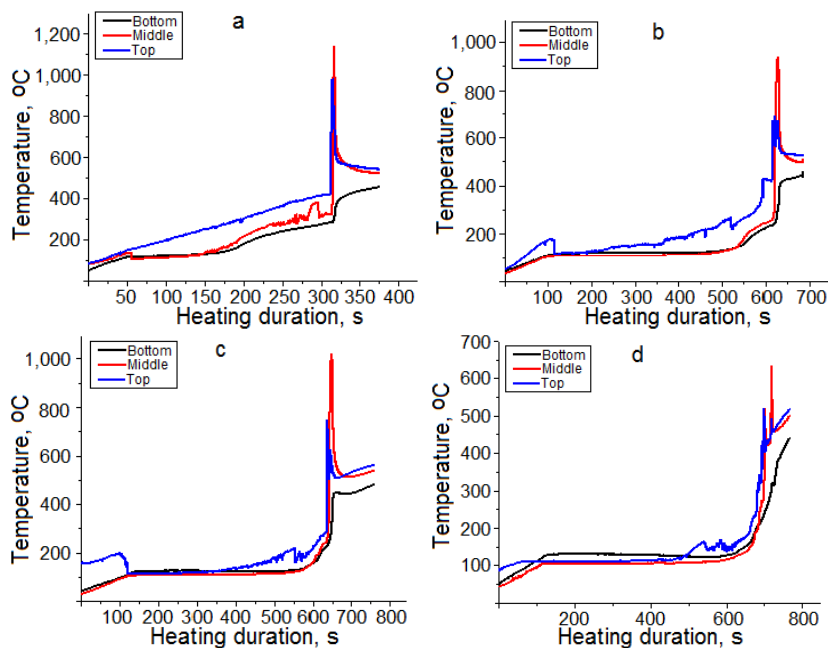


Figure 1: Temperature-time profile of the volumetric combustion mode of the 10 % Ni – 35 % Al – 5 % Mg/50 % urea catalyst. (a) – 15 mL H<sub>2</sub>O, (b) – 50 mL H<sub>2</sub>O, (c) – 75 mL H<sub>2</sub>O, (d) – 100 mL H<sub>2</sub>O

Water evaporates at 100 °C during synthesis (Figure 1). Starting from a temperature of 220 °C, a gel was formed, after heating to a temperature of 275 °C, an exothermic reaction took place, and the temperature increased sharply (Figure 1a). The maximum temperature in the lower part reached 514 °C, in the middle part - up to 1,100 °C, and in the upper part it reached 700 °C. The combustion temperature varied during the preparation of the catalysts at 500 °C and at different volumes of water. The presented results show that:

- An increase in the volume of H<sub>2</sub>O in the initial mixture leads to a decrease in the combustion temperature of the catalysts. As can be seen from Figure 2, the higher the concentration of water in the initial solution, the less dendrites were formed. The intensive formation of dendrites took place with a small amount of water. The formation of dendrites largely depends on the concentration of the substance in the water: if there is too much water, then the formation of dendrites is difficult.

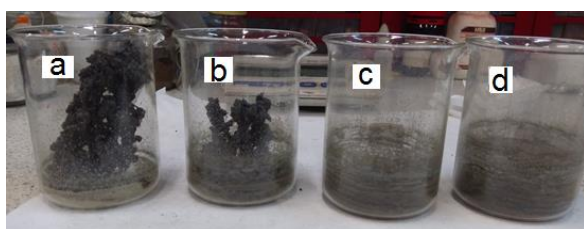


Figure 2: 10 % Ni – 35 % Al – 5 % Mg/50 % urea samples after solution combustion synthesis in the presence of: (a) - 15 mL H<sub>2</sub>O, (b) - 50 mL H<sub>2</sub>O, (c) - 75 mL H<sub>2</sub>O, (d) – 100 mL H<sub>2</sub>O

- Dendritic combustion was discovered. When burning in solutions, combustion occurs in dendrites, the concentration of reactants in which is higher than in the case when dendrites are not formed. This explains the higher combustion temperature in the first case.
- The number of exothermic peaks depends on the amount of water (Figure 1): one in the case of 15 mL (Figure 1a), three in the case of 50 mL (Figure 1b), two in the case of 100 mL and 75 mL (Figures 1c and 1d). The first peak corresponds to the reaction  $\text{Ni}(\text{NO}_3)_2 + 5\text{CH}_4\text{N}_2\text{O} \rightarrow \text{Ni}_x\text{O}_y + \text{CO}_2 + \text{N}_2 + \text{H}_2\text{O}$ . The presence of the second peak indicates the formation of hydrogen and the implementation of the reaction  $\text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O}$ . The third peak corresponds to the reaction  $\text{C} + \text{NiO} \rightarrow \text{Ni}$ .

- Combustion takes place both in the liquid phase and in the gas phase.

The phase composition of a series of Ni + Al + Mg catalysts was studied by XRD method. Figure 3 shows the XRD spectra of the catalysts.

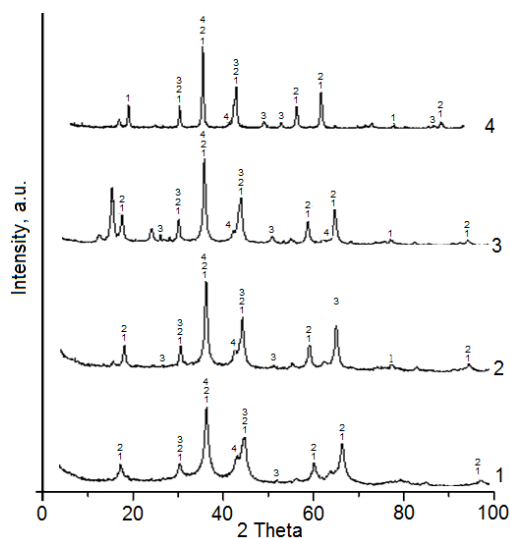


Figure 3: X-ray spectra of the Ni – Al – Mg/urea catalyst. 1-  $\text{NiAl}_2\text{O}_4$ , 2 -  $\text{MgAl}_2\text{O}_4$ , 3 -  $\text{Ni}_2\text{O}_3$ , 4 -  $\text{NiO}$

As a result of the X-ray phase study, it was found that the samples contain:  $\text{NiAl}_2\text{O}_4$  (JCPDS, 10-0339),  $2\theta = 19.07, 31.40, 37.00, 44.99, 55.97, 59.66, 65.53, 77.74, 94.66$ ;  $\text{MgAl}_2\text{O}_4$  (JCPDS, 21-1152),  $2\theta = 19.03, 31.27, 36.85, 44.83, 55.66, 59.37, 65.24$ ;  $\text{Ni}_2\text{O}_3$  (JCPDS, 14-0481),  $2\theta = 27.59, 31.94, 39.13, 44.83, 51.59, 56.78, 66.76, 87.88$ ;  $\text{NiO}$  (JCPDS, 44-1159),  $2\theta = 37.25, 43.28, 62.85, 75.40$ .

From the results of adsorption / desorption of  $\text{N}_2$ , it follows that with an increase in the amount of water (from 15 to 100 mL) added to dissolve the initial mixture, the average pore and surface size increases by 3 times. This is due to the intensity and time of water evaporation during the formation of the reaction product, as well as to the formation of complex compounds with water during the dissolution of nitrates and urea. The more water, the more porous the material is formed and the combustion temperature decreases. This has a positive effect on the surface area of the nanocatalyst. This conclusion is confirmed by the XRD data. The higher the amount of water added to the initial mixture, the lower the amount of nickel oxides (spinel formation depends on temperature).

Thus, a decrease in the volume of water in solution leads to an increase in the concentration of  $\text{NiAl}_2\text{O}_4$  spinel.  $\text{NiO} + \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4$ ,  $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$ .

SEM studies have shown that an increase in the amount of added water in the initial solution leads to an increase in the number of pores, which is consistent with the BET analysis data.

### 3.2 Catalysts testing

The process of carbon dioxide reforming of methane was investigated on 10 % Ni – 35 % Al – 5 % Mg/50 % urea catalyst prepared by SCS method in a reaction mixture of 33.3 %  $\text{CH}_4$  + 33.3 %  $\text{CO}_2$  + 33.3 % Ar at space speed 2,000  $\text{h}^{-1}$ , Figure 4.

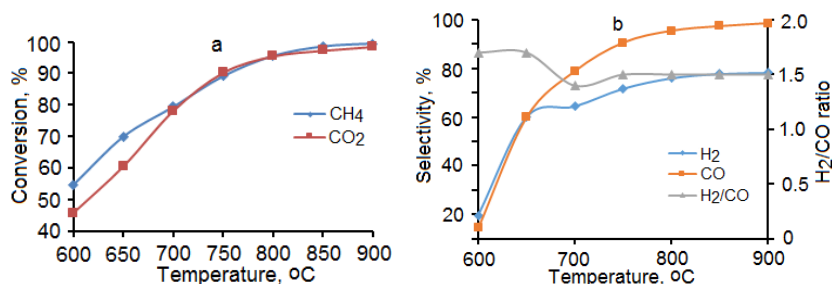


Figure 4: Influence of the reaction temperature on conversion, selectivity and  $\text{H}_2/\text{CO}$  ratio on the 10 % Ni – 35 % Al – 5 % Mg/50 % urea catalyst at 800 °C and addition of the 15 mL  $\text{H}_2\text{O}$

Figure 4 shows that high yields of H<sub>2</sub> (49.1 %) and CO (36.6 %) with selectivity for H<sub>2</sub> (76.1 %) and CO (95.5 %), have been achieved at 800 °C, addition of 15 mL H<sub>2</sub>O and space velocity 2,000 h<sup>-1</sup>. It was found that the process indicators at 800 °C are quite close to those at 900 °C. Thus, it was possible to significantly reduce the temperature of the maximum indicators of the process of carbon dioxide conversion of methane on the above catalysts.

The effect of various methods of preparation catalysts with different water content in the initial catalyst mixture on conversion, product yields, their selectivity, and H<sub>2</sub>/CO ratio was investigated, Table 1.

*Table 1: The effect of preparation methods of 10 % Ni – 35 % Al – 5 % Mg/50 % urea catalysts with different water content in the initial catalyst mixture on conversion of methane, product selectivity and H<sub>2</sub>/CO ratio*

H <sub>2</sub> O, mL	T, °C	C <sub>CH<sub>4</sub></sub> , %	S <sub>H<sub>2</sub></sub> , %	S <sub>CO</sub> , %	H <sub>2</sub> /CO
15	600	54.8	50.9	41.5	2.0
	700	79.4	64.5	78.9	1.4
	800	95.5	76.1	95.5	1.5
	900	99.4	78.3	98.6	1.5
50	600	50.0	45.7	52.1	1.3
	700	82.7	65.5	83.6	1.3
	800	95.8	73.3	95.6	1.2
	900	99.1	73.8	99.0	1.3
75	600	54.7	47.2	62.1	1.1
	700	82.5	67.2	87.0	1.2
	800	95.9	72.4	95.8	1.3
	900	98.7	77.3	97.2	1.4
100	600	50.6	41.4	54.3	1.2
	700	78.8	61.5	80.2	1.3
	800	94.5	71.8	94.8	1.3
	900	98.8	75.8	99.2	1.3

Comparative results of methane carbon dioxide conversion on catalysts with different water contents showed that the preparation method plays an important role. The conversion of both methane and CO<sub>2</sub> gradually increases with an increase in the amount of water from 15 to 75 mL. The conversion of CH<sub>4</sub> and CO<sub>2</sub> decreases upon further addition of water to 100 mL. However, the yields of H<sub>2</sub> and CO, as well as their selectivity, on the contrary, slightly decrease with increasing water content. The H<sub>2</sub>/CO ratio in products, like other indicators, falls from 1.5 to 1.3. Optimal yields and selectivity were recorded at addition of 15 mL of water during the preparation of catalysts at a temperature of 800 °C and a pressure of 0.39 MPa. Comparison of catalysts prepared by SCS method showed that the results obtained on Ni – Al - Mg catalysts exceed the data on Co - Mg samples (Xanthopoulou et al., 2019) for methane conversion by 10 %, for hydrogen selectivity - by 14 %, while similar data were obtained for Al - Co catalysts (Zhumabek et al., 2021).

#### 4. Conclusions

In the present work, 10 % Ni – 35 % Al – 5 % Mg/50 % urea catalysts with different water content in the catalyst mixture were prepared by solution combustion synthesis. The results obtained using XRD, SEM, and BET methods correlate with the quantitative results of carbon dioxide conversion of methane and provide useful information for understanding the catalytic activity of catalysts in the production of synthesis gas. Studies have shown that the higher the water content in the initial solution, the less dendrites are formed and their combustion is slower, and the more unreacted nickel oxides and, accordingly, the amount of spinel NiAl<sub>2</sub>O<sub>4</sub> decreases. With a methane conversion of 99.4 % and CO<sub>2</sub> conversion of 98.5 %, the selectivity for H<sub>2</sub> was 78.3 % and for CO - 98.6 % on the developed catalysts at 900 °C and a space velocity of 2,000 h<sup>-1</sup>. It was established that the catalysts contain simple and mixed oxides, metal aluminates and spinel-type structures, the presence of which contributes to the active operation of catalysts for the carbon dioxide conversion of methane. Thus, an inexpensive and fairly easy-to-prepare catalyst for biogas reforming was developed.

#### Nomenclature

T – temperature, °C

C<sub>CH<sub>4</sub></sub>, – conversion of methane, %

S<sub>H<sub>2</sub></sub> – selectivity by hydrogen, %

S<sub>CO</sub> – selectivity by CO, %

λ - wavelength, Å

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## References

- Ab Muis Z., Sadikin A.N., Hashim H., Ho W.S., Yunus N.A., Jensani M.K.N., Bong C.P.C., Subramaniam T., 2021. Design and Development of Food Waste to Biogas Converter System. *Chemical Engineering Transactions*, 83, 535-540.
- Baneshi J., Haghghi M., Jodeiri N., Abdollahifar M., Ajamein H., 2014. Urea-Nitrate Combustion Synthesis of ZrO<sub>2</sub> and CeO<sub>2</sub> Doped CuO/Al<sub>2</sub>O<sub>3</sub> Nanocatalyst Used in Steam Reforming of Biomethanol for Hydrogen Production. *Ceramics International*, 40, 14177-14184.
- Elbadawi A.A.H., Ge L., Zhang J., Zhuang L., Liu S., Tan X., Wang S., Zhu Zh., 2020. Partial Oxidation of Methane to Syngas in Catalytic Membrane Reactor: Role of Catalyst Oxygen Vacancies. *Chemical Engineering Journal*, 392, 123739.
- Jeong D.W., Jang W.J., Shim J.O., Roh H.S., 2016. High Temperature Water-gas Shift without Pre-Reduction over Spinel Ferrite Catalysts Synthesized by Glycine Assisted Sol-gel Combustion Method. *International Journal of Hydrogen Energy*, 41, 3870-3876.
- Jiang C., Loisel E., Cullen D.A., Dorman J.A., Dooley K.M., 2021. On the Enhanced Sulfur and Coking Tolerance of Ni-Co-rare Earth Oxide Catalysts for the Dry Reforming of Methane. *Journal of Catalysis*, 393, 215-229.
- Kassymkan K., Zhang X., Sarsenova R.O., Zheksenbaeva Z.T., Tungatarova S.A., Baizhumanova T.S., 2020. Catalytic Processing of Natural Gas into Olefins. *Chemical Engineering Transactions*, 81, 1057-1062.
- Loricera C.V., Alvarez-Galvan M.C., Guil-Lopez R., Ismail A.A., Al-Sayari S.A., Fierro J.L.G., 2017. Structure and Reactivity of sol-gel V/SiO<sub>2</sub> Catalysts for the Direct Conversion of Methane to Formaldehyde. *Topics in Catalysis*, 60, 1129-1139.
- Mei D., Glezakou V.A., Lebarbier V., Kovarik L., Wan H., Albrecht K.O., Gerber M., Rousseau R., Dagle R.A., 2014. Highly active and stable MgAl<sub>2</sub>O<sub>4</sub>-supported Rh and Ir catalysts for methane steam reforming: A combined experimental and theoretical study. *Journal of Catalysis*, 316, 11-23.
- Nizam J.M.Kh., Niza S.A., Norzita N., Fakhrullah A.M., Zarina A.M., Aisah A.U., 2021. Anaerobic Co-Digestion of Food Waste with Crude Glycerol for Biogas Production. *Chemical Engineering Transactions*, 83, 577-583.
- Postole G., Nguyen T.S., Aouine M., G lin P., Cardenas L., Piccolo L., 2015. Efficient Hydrogen Production from Methane over Iridium-Doped Ceria Catalysts Synthesized by Solution Combustion. *Applied Catalysis B: Environmental*, 166-167, 580-591.
- Sun H., Liang H., Zhou G., Wang S., 2013. Supported Cobalt Catalysts by One-Pot Aqueous Combustion Synthesis for Catalytic Phenol Degradation. *Journal of Colloid and Interface Science*, 394, 394-400.
- Vita A., Italiano C., Fabiano C., Lagan  M., Pino L., 2015. Influence of Ce-Precursor and Fuel on Structure and Catalytic Activity of Combustion Synthesized Ni/CeO<sub>2</sub> Catalysts for Biogas Oxidative Steam Reforming. *Materials Chemistry and Physics*, 163, 337-347.
- Wang P., Zhao G., Liu Y., Lu Y., 2017. TiO<sub>2</sub>-doped Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst for oxidative coupling of methane: Solution combustion synthesis and MnTiO<sub>3</sub>-dependent low-temperature activity improvement. *Applied Catalysis A: General*, 544, 77-83.
- Xanthopoulou G., Karanasios K., Tungatarova S., Baizhumanova T., Zhumabek M., Kaumenova G., Massalimova B., Shorayeva K., 2019. Catalytic Methane Reforming into Synthesis-gas over Developed Composite Materials Prepared by Combustion Synthesis. *Reaction Kinetics, Mechanisms and Catalysis*, 126, 645-661.
- Zhang X., He D., Zhang Q., Xu B., Qiming Zhu Q., 2005. Comparative Studies on Direct Conversion of Methane to Methanol/Formaldehyde over La-Co-O and ZrO<sub>2</sub> Supported Molybdenum Oxide Catalysts. *Topics in Catalysis*, 32, 215-223.
- Zhumabek M., Xanthopoulou G., Tungatarova S.A., Baizhumanova T.S., Vekinis G., Murzin D., 2021. Biogas reforming over Al-Co catalyst prepared by solution combustion synthesis method. *Catalysts*, 11, 274.