

UDC 54-386, 54.057, 54-44

DOI: 10.15372/CSD2019177

## Bimetallic Ni–Co-Containing Catalyst for Dry Reforming of Methane into Synthesis Gas

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### Abstract

The activity of monometallic (Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and bimetallic (Ni–Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalysts deposited on  $\gamma$ -aluminium oxide was studied for the dry reforming of methane into synthesis gas. It was determined that the bimetallic catalyst is more active than the monometallic one. It was established with the help of a set of methods (X-ray phase analysis and temperature-programmed reduction with hydrogen) that the surface bimetallic Ni–Co alloy is formed in the presence of the bimetallic catalyst Ni–Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This alloy plays an essential part in the suppression of the formation of carbonaceous deposits on the catalyst surface and in the enhancement of the catalyst activity.

**Keywords:** catalyst, nickel oxide, cobalt oxide, dry reforming of methane, synthesis gas

### INTRODUCTION

Methane reforming is the main process of natural gas conversion into synthesis gas (a mixture of CO and H<sub>2</sub>) [1–4]. The latter is a valuable raw material to obtain various kinds of fuel and chemicals. Dry (carbon dioxide based) reforming of methane as an efficient method to utilize greenhouse gases (CH<sub>4</sub> and CO<sub>2</sub>), it may bring substantial economic, social and ecological profits in the case of its use in the industry [5]. Methane reforming by carbon dioxide attracts much attention of researchers all over the world. Catalysts based on precious metals (Pt, Ru, Rh, etc.) exhibit high activity and stability to the formation of carbonaceous sediments in the course of this reaction, however, they cannot be used on an in-

dustrial scale because of their high cost and limited resources [6]. The efficiency of the catalysts in the dry reforming of methane is affected by a number of factors including the composition of the active phase and support, the conditions of preliminary treatment of the catalyst etc. Efforts are focused at the development of an active, stable and available catalyst based on transition metals. As a rule, active components in them are Ni or Co [7, 8]. The studies are carried out both with monometallic Ni- and Co-containing catalysts and with bimetallic Ni–Co systems [9]. It was demonstrated in a number of works that monometallic Ni- or Co-containing catalysts are more active than bimetallic ones (Ni–Co), while other authors discovered the higher efficiency of bimetallic samples [8, 10]. Inconsistency of litera-

ture data stresses the necessity to carry out further investigation of the dry reforming of methane in the presence of bimetallic catalysts.

The goal of the work is comparative investigation of the efficiency of monometallic Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and bimetallic Ni-Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in the dry reforming of methane into synthesis gas; investigation of the effect of physicochemical characteristics on the catalytic properties of the synthesized catalysts.

## EXPERIMENTAL

Catalysts  $x$ Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $y$ Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $x$ Ni- $y$ Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (where  $x$  and  $y$  stand for metal content in the catalyst, mass %) were obtained by means of impregnation over the water-absorbing capacity of the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) with the aqueous solutions of metal salt Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (GOST 4055-70) or Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (GOST 4528-78), as well as their mixture, respectively. The thermal treatment of the samples was carried out in the air at 300 °C for 2 h, then at 500 °C for 3 h. The content of Ni and Co in monometallic catalysts was varied from 1 to 5 mass %, in the bimetallic catalyst it was 3 mass % Ni and 4 mass % Co.

Before the start of the catalytic investigation, the catalyst in the reactor was reduced for 2 h with a gas mixture containing 2 vol. % H<sub>2</sub> in Ar, at 700 °C, then it was cooled in the flow of reducing mixture down to the temperature of the experiment. The activity of the synthesized catalysts was tested in the dry reforming of methane in an automated laboratory set-up of the flow type [11]. Process conditions were: pressure 0.1 MPa, reaction temperature  $T_r = 600$ –850 °C, the volume flow rate  $W = 500$ –4000 h<sup>-1</sup>, the ratio CH<sub>4</sub>/CO<sub>2</sub> = 1 : 1, volume of the catalyst in the reactor 2 mL. The composition of initial reagents and reaction products was analyzed by means of gas chromatography using a Khromos GK-1000 chromatograph (Russia). The separation of H<sub>2</sub> and O<sub>2</sub> was carried out in a steel packed column with the CaA molecular sieve, while CH<sub>4</sub>, CO<sub>2</sub> and CO were separated using a porous layer of the HP/Plot Q sorbent.

The physicochemical characteristics of the catalysts were studied by means of X-ray phase analysis (XPA) and temperature-programmed reduction with hydrogen (TPR-H<sub>2</sub>). X-ray phase analysis of catalyst samples was carried out at room temperature with the help of a powder X-ray diffractometer Bruker D8 ADVANCE A25

(Germany) with CuK<sub>α</sub> radiation ( $\lambda = 1.5406$  Å) and Ni-filter at the secondary radiation using the polycrystal method. To record representative X-ray patterns, the recording was carried out at long accumulation time (2 s), scanning step 0.02° over 2θ within the angle range 10–90°. The identification of phases present in the patterns was carried out using the powder database ASTM [12].

Experiments on TPR-H<sub>2</sub> were carried out using a USTA-101 set-up (Russia), which included the system of gas preparation, a flow reactor (inner diameter 4 mm) with a tubular furnace and a heat conductivity detector. The sample (100 mg, fraction 0.30–0.50 mm) was preliminarily blown with Ar at 480 °C for 40 min, then cooled to 50 °C, and heated at a rate of 10 °C/min from 50 to 950 °C in the flow of a mixture of 10 vol. % H<sub>2</sub> in Ar at the flow rate of 30 cm<sup>3</sup>/min. Analysis of the gas mixture was carried out with the help of the thermal conductivity detector.

## RESULTS AND DISCUSSION

Investigation of the activity of monometallic catalysts in the dry reforming of methane depending on the content of the active component showed (Table 1) that the most active catalysts among the studied ones are 3Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Important parameters of catalyst efficiency in the dry reforming of methane are the conversion of CH<sub>4</sub> and CO<sub>2</sub>, as well as the ratio of H<sub>2</sub>/CO. Results of the comparison of the efficiency of monometallic (3Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> и 4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and bimetallic (3Ni-4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalysts in methane reforming by carbon dioxide are shown in Fig. 1. One can see that in comparison with monometallic catalysts, the presence of bimetallic

TABLE 1

Effect of the content of active component on the efficiency of monometallic catalysts in the dry reforming of methane ( $T_p = 800$  °C,  $W = 1500$  h<sup>-1</sup>, the ratio CH<sub>4</sub>/CO<sub>2</sub> = 1 : 1)

Sample	CH <sub>4</sub> conversion, %	CO <sub>2</sub> conversion, %	H <sub>2</sub> /CO ratio
1Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	15	17	0.20
2Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	20	25	0.22
4Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	21	28	0.45
5Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	20	27	0.26
1Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	22	18	0.77
3Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	85	80	0.95
4Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	83	81	1.07

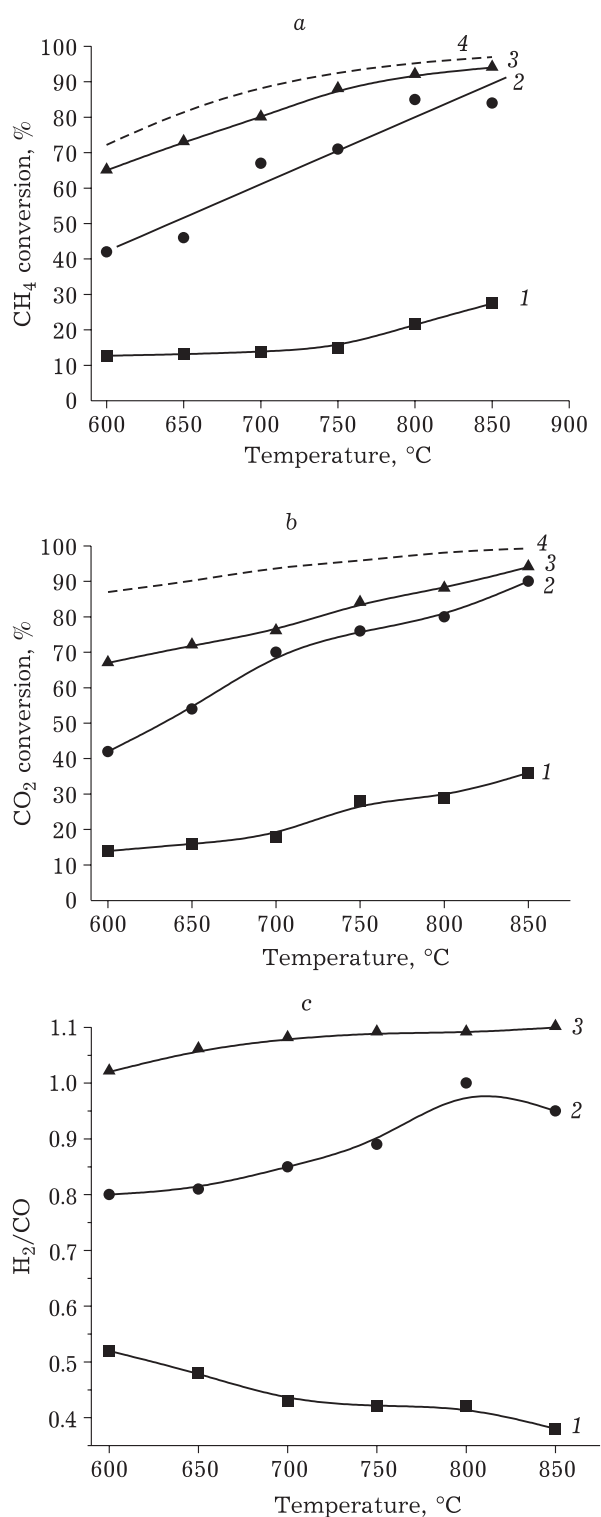


Fig. 1. Dependences of methane conversion (a), carbon dioxide conversion (b) and the H<sub>2</sub>/CO ratio (c) on the temperature of the dry reforming of methane in the presence of catalysts: 4Co/γ-Al<sub>2</sub>O<sub>3</sub> (1), 3Ni/γ-Al<sub>2</sub>O<sub>3</sub> (2), 3Ni-4Co/γ-Al<sub>2</sub>O<sub>3</sub> (3), values under the conditions of thermodynamic equilibrium (4).

ones helps to achieve a higher conversion of the reagents (CH<sub>4</sub> and CO<sub>2</sub>). As a result of the reaction in the presence of 3Ni-4Co/γ-Al<sub>2</sub>O<sub>3</sub>, synthe-

sis gas with a ratio of H<sub>2</sub>/CO ≈ 1.05 is formed, which is much higher than the H<sub>2</sub>/CO ratios observed when monometallic catalysts are used (see Fig. 1).

It was established by means of XPA that the reflections characteristic of the cubic lattice of the γ-Al<sub>2</sub>O<sub>3</sub> phase are recorded in all the samples under investigation (Fig. 2). The size of the coherent scattering region (CSR) of the initial γ-Al<sub>2</sub>O<sub>3</sub> is about 5 nm. Thermal treatment in the mode of the standard preparation of catalyst samples (at 300 °C for 2 h and subsequent heating at 500 °C for 3 h) does not cause any changes in the dispersion of the support, the CSR size remains about 5 nm. The CSR size of γ-Al<sub>2</sub>O<sub>3</sub> remains unchanged also after the deposition of nickel and cobalt salts on it by means of impregnation in the mode of the standard preparation of catalyst samples. The size of crystallites in the matrix increases insignificantly (to 6–7 nm) after the test of the catalysts in the carbon dioxide conversion of methane.

The X-ray diffraction patterns of initial catalysts contain the reflections of cobalt oxide (Co<sub>3</sub>O<sub>4</sub>), while the phase of nickel oxide (NiO) cannot be recorded, maybe because of its fine state (less than 4 nm) (see Fig. 2, a). It should be stressed that according to XPA data the samples of initial catalysts prepared by the joint deposition of nickel and cobalt salts contain the phase of the mixed cobalt and nickel oxide, while individual Co<sub>3</sub>O<sub>4</sub> and NiO phases are not observed.

As a result of the action of the reaction medium, the phase composition of the catalyst changes (see Fig. 2, b). For instance, after the participation of the Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst in the dry reforming of methane, the X-ray diffraction patterns of the catalyst contain the phases face-centred cubic (fcc) metal nickel with increased lattice parameter (3.542 Å) in comparison with the known data from the PDF-2 database (3.524 Å). The size of CSR of Ni<sup>0</sup> formed after the reaction is about 17 nm. An inverse situation is observed with the phase composition of the Co/γ-Al<sub>2</sub>O<sub>3</sub> catalyst: after its participation in the reaction, Co<sup>0</sup> cannot be detected, which may be due to the high dispersion, as well as to the substantial background because of cobalt fluorescence. The diffraction patterns of the bimetal catalyst sample after the reaction contain reflections corresponding to the metal phase with the cubic hexagonal lattice; its parameter is 3.535–3.540 Å. It may be assumed that a Co-Ni alloy with fcc lattice is formed. The size of CSR of the metal phase is within the range 17–23 nm.

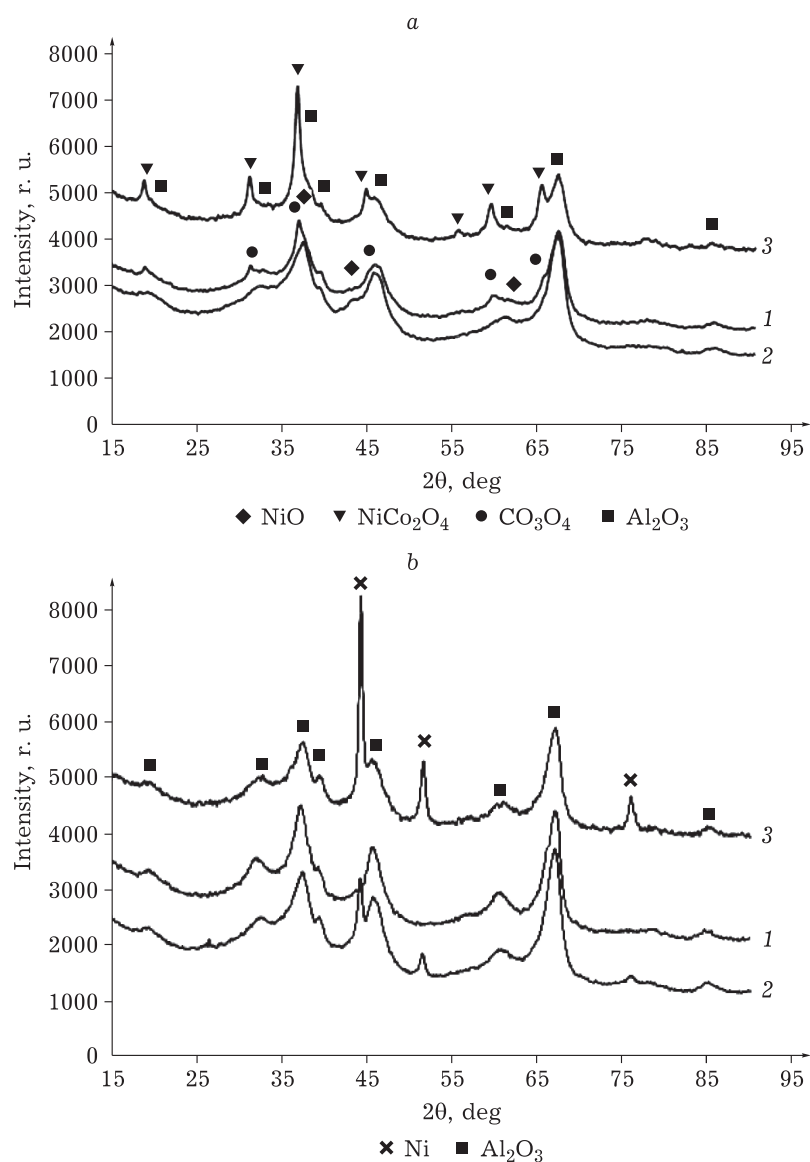


Fig. 2. Diffraction patterns of catalysts before (a) and after (b) reaction: 4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (1); 3Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (2); 3Ni-4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (3).

The catalytic activity of oxide catalysts in the oxidation-reduction reactions is usually explained by the energy of oxygen-metal bond, which is qualitatively characterized by the temperature of the start of reduction with hydrogen, as well as the temperatures of maxima on the curves of TPR-H<sub>2</sub>. The TPR-H<sub>2</sub> curves for catalysts 3Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3Ni-4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are presented in Fig. 3. Four peaks are observed on the TPR-H<sub>2</sub> curves for 3Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, with the maxima of hydrogen absorption temperatures  $T_{\max}^1$ ,  $T_{\max}^2$ ,  $T_{\max}^3$  and  $T_{\max}^4$  equal to 460, 530, 625, and 814 °C, respectively. A weak peak at  $T_{\max}^1$  relates to the reduction of nickel cations in NiO particles not connected with the support [13]. The

$T_{\max}^2$  and  $T_{\max}^3$  peaks relate to the reduction of NiO particles characterized by so-called weak and strong metal-support interaction, respectively [14, 15]. An intense peak at  $T_{\max}^4 = 814$  °C is due to the presence of dispersed spinel-like forms NiAl<sub>2</sub>O<sub>4</sub> in the sample [16]. The TPR-H<sub>2</sub> curves for catalyst 4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> contain four peaks with the maxima at  $T_{\max}^1$ ,  $T_{\max}^2$ ,  $T_{\max}^3$  and  $T_{\max}^4$ . The peaks at  $T_{\max}^1$  and  $T_{\max}^2$ , equal to 306 and 423 °C, respectively, relate to the reduction of cobalt oxide to Co<sup>0</sup> (Co<sub>3</sub>O<sub>4</sub> → CoO → Co<sup>0</sup>). The sample also contains hardly reducible cobalt-support compounds ( $T_{\max}^3 = 639$  °C,  $T_{\max}^4 = 796$  °C) [17]. For the 3Ni-4Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, TPR-H<sub>2</sub> curves contain four peaks with  $T_{\max}^1$ ,  $T_{\max}^2$ ,  $T_{\max}^3$  and  $T_{\max}^4$ ,

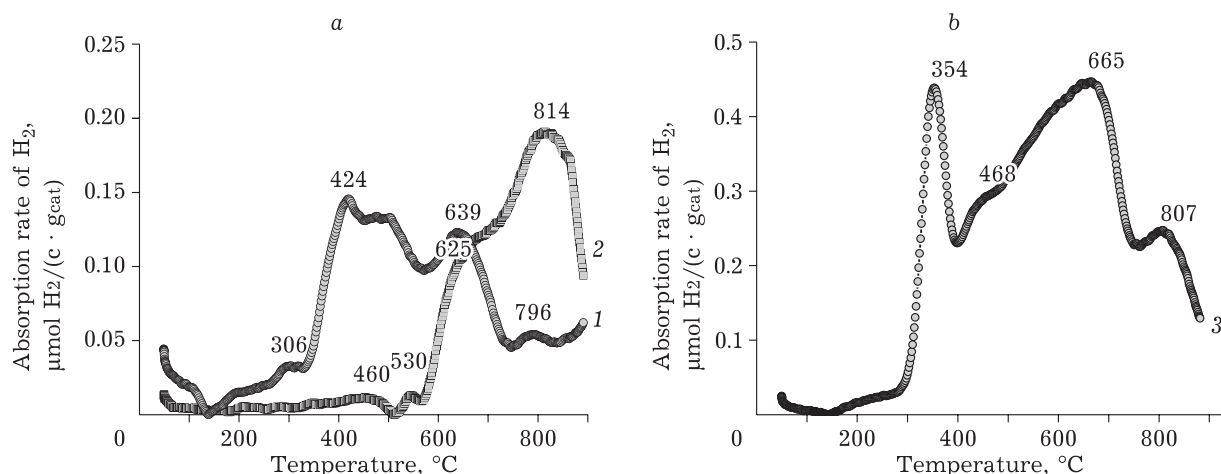


Fig. 3. TPR- $H_2$  profiles for catalysts  $4Co/\gamma-Al_2O_3$  (1),  $3Ni/\gamma-Al_2O_3$  (2),  $3Ni-4Co/\gamma Al_2O_3$  (3).

equal to 354, 468, 665 and 807 °C, respectively. In the bimetal catalyst, the intensity of  $T_{max}^4$  related to nickel reduction in  $NiAl_2O_4$  decreases. This is an evidence of the fact that the addition of cobalt may prevent the formation of  $NiAl_2O_4$ , thus increasing the fraction of  $Ni^{2+}$  in the deposited particles and promoting the formation of Ni-Co alloy during the reduction of the catalyst. The formed alloy is considered to provide an increase in stability against the carbonization of Ni-Co-containing catalysts in reforming processes [17, 18]. An intense peak at  $T_{max}^1 = 354$  °C may be related to the formation of Ni-Co alloy as a result of the reduction of the catalyst. The formation of this alloy promotes improvement of the mobility of active oxygen forms, which has a positive effect on catalyst activity in the reaction under investigation [19]. The formation of the Ni-Co alloy is also confirmed by XPA results (see Fig. 2).

## CONCLUSION

It is established that, in comparison with monometal catalysts  $4Co/\gamma-Al_2O_3$  and  $3Ni/\gamma-Al_2O_3$ , the bimetal sample  $3Ni-4Co/\gamma-Al_2O_3$  exhibits higher activity in the dry reforming of methane providing methane conversion close to that observed under the conditions of thermodynamic equilibrium even at the process temperature of 600 °C. In the presence of the bimetallic  $3Ni-4Co/\gamma-Al_2O_3$  catalyst, the synergic effect is observed, which is due to the formation of Ni-Co alloy. Facilitation of catalyst reducibility occurs, which provides an increase in the concentration of metal particles – active centres, which may be a reason for the improvement of catalytic proper-

ties. It is established that for the bimetal catalyst, the smaller fraction of nickel is in hardly reducible nickel-aluminium spinel. Under the conditions of the dry reforming of methane (the ratio  $CH_4/CO_2 = 1 : 1$ ,  $W = 1500$  h<sup>-1</sup>,  $T_p = 600$  °C) in the presence of  $3Ni-4Co/\gamma-Al_2O_3$  catalyst, the following reaction parameters were achieved:  $CH_4$  conversion 66 %,  $CO_2$  conversion 67 %, the ratio  $H_2/CO = 1.01$ .

## Acknowledgements

The work was carried out with support from MON RK Project No. AR05132114.

Physicochemical studies were carried out using the equipment of the Sharing Centre at the FRC CCC SB RAS within the Project No. AAAA-A17-117041910151-9.

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