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Effect of Cobalt Oxide Content on the Activity of NiO-Co_2O_3/γ-Al_2O_3 Catalyst in the Reaction of Dry Reforming of Methane to Synthesis Gas

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Abstract

The effect of cobalt oxide content on the activity of NiO-Co_2O_3/γ-Al_2O_3 catalyst was investigated in process of dry reforming of methane (DRM) to synthesis gas. It was found that among the studied catalysts the highest activity is shown by the NiO-Co_2O_3/γ-Al_2O_3, where methane conversion is 89%. It was determined by the scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD) there are oxides of Ni and Co in the form of nanosized particles on active NiO-Co_2O_3/γ-Al_2O_3 catalyst and Co-Ni alloys, formed after the reaction of DRM, the size of 17–23 nm. Thermogravimetric Analysis (TGA)/ Differential Thermal Analysis (DTA)/ Differential Scanning Calorimetry (DSC) of catalyst showed that the highest weight loss (2.7%) is observed at a degree from 30 to 260 °C after DRM. After heating above 300 °C there is a slight increase in weight, accompanied by an exothermic effect on the DSC curve due to the gas adsorption used to purge the unit. The data indicate the absence of coke formation on NiO-Co_2O_3/γ-Al_2O_3 surface. According to TPR-H_2 there are peaks at relatively low temperatures of T^1_{max} = 205 °C and T^2_{max} = 497 °C on thermally programmed reduction (TPR) TPR-H_2 spectrum of NiO-Co_2O_3/γ-Al_2O_3, which are associated with the formation of easily reducible cobalt and nickel oxides, indicating the presence of active and mobile oxygen in the catalyst. These results confirm that the activity of NiO-Co_2O_3/γ-Al_2O_3 is due to the formation of nanophases, the presence of active oxygen, and the absence of coke on the catalyst surface.

1. Introduction

Global climate change associated with the release of greenhouse gases from the use of fossil fuels for domestic and industrial needs invariably has a destructive severe impact on the environment, of course, cause international concern [1–3]. With limited fuel reserves and an increase in the concentration of greenhouse gases (CO_2, CH_4, NO, etc.) in the atmosphere, the conversion of carbon dioxide and methane, especially into valuable products, is an urgent problem. The large reserves of natural gas containing more than 80% methane and renewable biogas, consisting mainly of CO_2 and CH_4, made it possible for many countries to produce valuable chemicals by dry reforming of methane (DRM) to synthesis gas [4–9]. Among the various methods of converting methane into valuable products, such as methane dehydroaromatization [10], autothermal reforming [11], or oxidative condensation [12] of methane, carbon dioxide conversion of methane is of particular interest because it uses two main greenhouse gases (CO_2 and CH_4) as feedstock; the ratio of H_2/CO in the reaction products is close to unity and this ratio of the synthesis gas more suited to Fischer-Tropsch synthesis [13–21]. Besides, the synthesis gas is used as a reducing agent in metallurgical processes.

The study of the development of the catalyst for the DRM process was focused on the search for a new catalyst, to achieve higher activity and better resistance to sintering and coke formation [22–26].

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Numerous scientific papers [23–31] report that transition metals of the VIII group, except for osmium, especially Ni, Co, Pd, Ir, and Pt, are active in the DRM reaction. Because of the high cost of noble metals and its deficit, to prepare the catalysts is mainly used nickel and cobalt. Nickel catalysts are the most widely studied for the DRM process; their main advantage is low cost and the addition of cobalt to the composition of the catalyst makes it possible to increase the activity of the catalysts [32–36].

We have previously investigated [37] in the reaction of carbon dioxide reforming of methane catalysts containing oxides of variable valence metals (NiO, La_2O_3, CuO, MoO_3, MgO, V_2O_5, WO_3, CoO, Cr_2O_3, ZnO, ZrO_2, CeO_2, Fe_2O_3) supported on the effective carrier – γ-Al_2O_3. Among the studied catalysts, the highest activity was shown by 3%NiO/γ-Al_2O_3. The yield of hydrogen and carbon monoxide reaches 45.4 and 42.4 vol.%, respectively, when methane conversion is 89%.

The purpose of this work is to investigate the effect of cobalt oxide content in the composition of 3% NiO-Co_2O_3/γ-Al_2O_3 catalyst on its activity during the dry reforming of methane to synthesis gas; study of the influence of physical and chemical characteristics on the catalytic properties of the synthesized catalysts.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by capillary simultaneous impregnation of granules (d = 2 mm) of the carrier (γ-Al_2O_3) on moisture capacity by solutions of nitric acid salts of nickel and cobalt, and subsequent drying at 300 °C (2 h), and calcining at 500 °C for 3 h and obtained polyoxide nickel-cobalt-containing catalyst xNiO-yCo_2O_3/γ-Al_2O_3 (where x and y are the content of metal oxide in the catalyst, wt%).

The method of capillary impregnation of the carrier on moisture capacity by solutions salts of variable valency metals should increase the efficiency of the catalyst due to the distribution of the impregnated active components as a form of "crust" on the outer surface of the carrier granules. Such a method of catalyst preparation leads to an easier interaction of the starting reagents (CH_4, CO_2) with active phases concentrated on the surface of the carrier.

2.2. Catalytic tests

Before starting the catalytic studies catalyst in the reactor was reduced for 2 h with a gas mixture containing 2 vol.% H_2 in Ar, at 700 °C, and then cooled in the flow of reducing mixture to a temperature of the experiment. The activity of the synthesized catalysts in the dry methane reforming reaction was tested on an automated laboratory flow-through unit. Process conditions: pressure – P = 0.1 MPa, reaction temperature – Tr = 600–850 °C, volumetric flow rate – W = 500–4000 h^{-1}, CH_4/CO_2 ratio = 1:1, catalyst volume in the reactor 2 ml.

The volume rate of reaction was calculated by the formula:

$$W = \frac{60\,sec * V\,ml/min}{V_{cat}},$$

where V_{cat} = 2 ml.

The mixed gas (CH_4 + CO_2 = 1:1) was fed at a rate of 50 cm^3/min to the catalytic reactor from above, and after passing through the catalyst bed in the reactor, it was sent to the chromatograph to analyze the reaction products. The temperature of the reactor was set by a thermoregulator and monitored with an chromel-alumel thermocouple (ChA) thermocouple, enclosed in quartz and located inside the catalyst bedControl of the composition and flow rate of the initial reactive mixtures, regulation of the reactor and evaporator temperature, the start of the analyzes were carried out via software. The initial gases and reaction products were analyzed on-line on a chromatograph of the brand "Chromos GC-1000" (Novosibirsk, Russia) with a thermal conductivity detector. H_2, N_2, O_2 were determined using phases of the composition zeolite sorbent (CaA); column length – 3 m, d = 2 mm; T = 350 °C; carrier gas velocity (Ar) – 20 ml/min. Also, to determine of CO, CO_2, CH_4 gases phase of the coal sorbent – AG-3 composition was used, carrier gas velocity (H_2) – 20 ml/min, T = 250 °C [38]. Conversion of initial gases (CO_2, CH_4) and ratio H_2/CO was calculated according to the equations:

$$X_{CH_4} = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{out}}$$

$$X_{CO_2} = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{out}}$$

$$\frac{H_2}{CO} = \frac{[H_2]_{out}}{[CO]_{out}}$$

2.3. *Catalyst characterization*

The physical-chemical properties of nickel catalysts (that is, the distribution of the active phase on the surface of the catalyst and the presence of nanoscale particles) were studied at the Collective Use Center of the Institute of Coal Chemistry and Material Science SB RAS (Kemerovo, Russia) using the following methods and equipment: SEM on a JEOL JSM-6390 LA (Japan) with a JED 2300 (Germany) energy dispersive X-ray detector, TGA/DTA/DSC using the STA 449 Jupiter (NETZSCH, Germany) device, and XRD on a Bruker D8 ADVANCE A25 X-ray powder diffractometer (Germany) (CuKα radiation (λ = 1.5406 Å)), and Ni-filter in the secondary radiation by the method polycrystal [39]). Besides, the thermally programmed reduction of the catalyst was determined by the thermally programmed reduction – TPR-H_2 method on a universal sorption gas analysis – USGA-101 set-up in the laboratory of oxidative catalysis in the Institute of Combustion Problems (Almaty, Kazakhstan).

3. Results and discussion

At the initial stage, blank experiments (without catalyst) were carried out in the temperature range 650–850 °C, at a space velocity 1500 h^{-1}. The results of blank experiments showed that methane and carbon dioxide do not convert under these conditions. Further studies of the DRM reaction were carried out in the presence of catalysts: 3%NiO/γ-Al_2O_3, 3%Ni-5%Co/γ-Al_2O_3, 3%Ni-7%Co/γ-Al_2O_3 and 3%Ni-9%Co/γ-Al_2O_3. The catalysts were investigated in the reaction of DRM in the temperature range 600–850 °C, at a reaction volume rate of 1500 h^{-1}, the ratio of methane to carbon dioxide of $CH_4 : CO_2 = 1:1$.

In this work, we studied the effect of cobalt content on the activity of 3%NiO/γ-Al_2O_3 catalyst in the dry reforming reaction of methane to synthesis gas.

As can be seen from Fig. 1, the addition of cobalt oxide in an amount of 5 wt.% to the Ni/Al_2O_3 catalyst slightly increases the methane conversion. A further increasing concentration of cobalt oxide to 7 wt.% in the composition of Ni-Co/Al_2O_3 catalyst leads to an increase in methane conversion to 89% and the ratio of H_2/CO = 1. Activation of methane is the rate-determining step in the reaction DRM [40], therefore CH_4 conversion can be equated to the catalytic activity. It follows from the results that the addition of 7 wt.% cobalt oxide to the composition of the nickel catalyst leads to an increase in its catalytic activity in the DRM reaction.

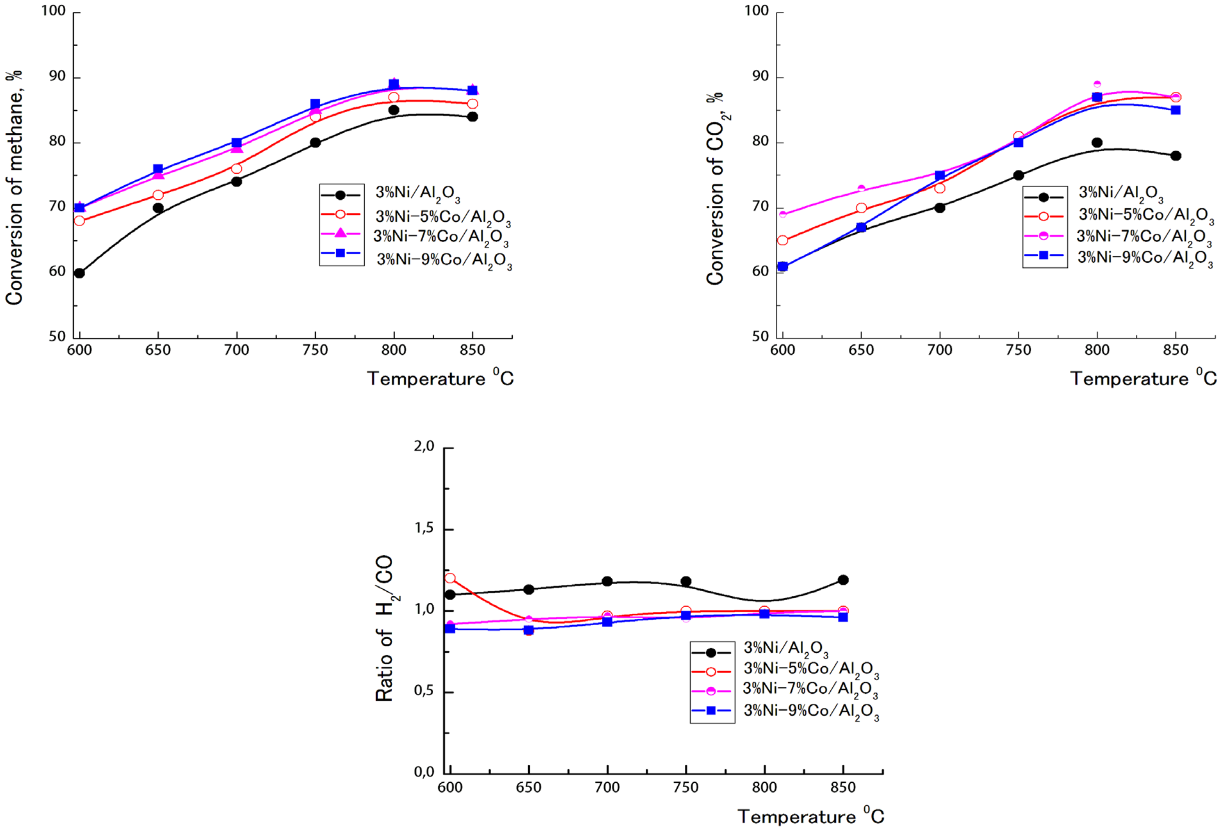


Fig. 1. The effect of cobalt content on the activity of 3%NiO/γ-Al_2O_3 catalyst.

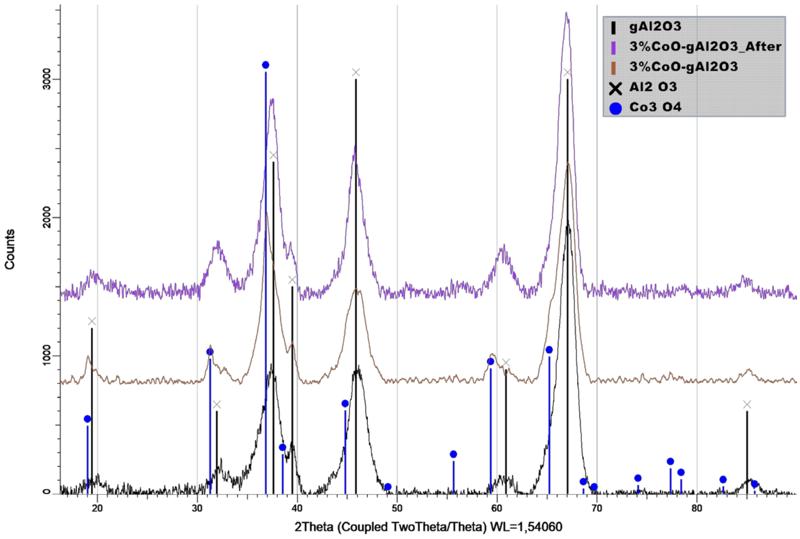


Fig. 2. X-ray diffraction pattern of 3% Co/γ-Al_2O_3 catalyst before and after DRM reaction.

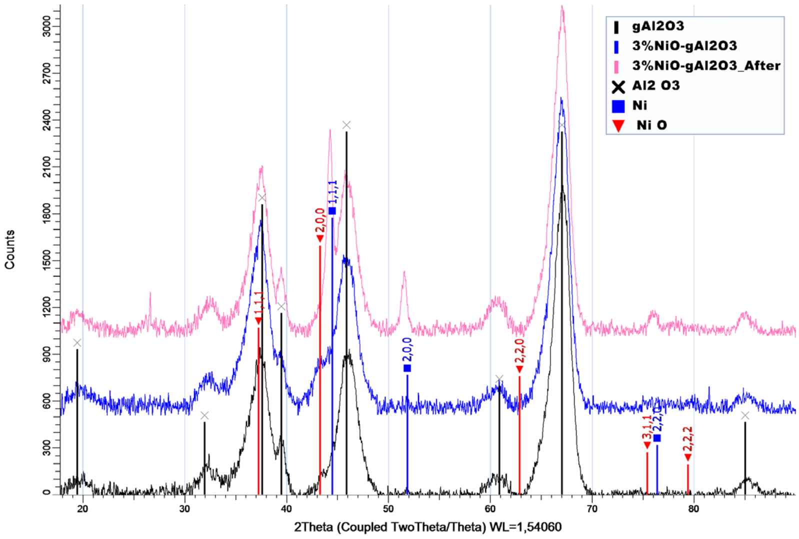


Fig. 3. X-ray diffraction pattern of 3%Ni/γ-Al_2O_3 catalyst before and after DRM reaction.

To clarify the dependence of the activity of the catalysts on their physical and chemical characteristics, the samples were studied by a set of methods (XRD, TGA, SEM).

Figures 2 and 3 show the XRD patterns of nickel and cobalt oxides supported on γ-Al_2O_3 before and after testing them in the DRM process.

According to XRD results, it follows that the size of the coherent scattering region (CSR) of the initial γ-Al_2O_3 is about 5 nm, moreover, the dispersion of the γ-Al_2O_3 carrier does not change after impregnation by oxides of nickel and cobalt (Figs. 2 and 3). The CSR size of γ-Al_2O_3 in the presence of NiO and Co_3O_4 is about 5 nm. The dispersion of the matrix changes slightly after the participation of catalysts of individual nickel and cobalt oxides in the reaction of carbon dioxide conversion of methane, the size of the CSR of γ-Al_2O_3 increases to 6 nm. Similarly, for catalysts containing co-existed nickel and cobalt oxides, the size of the CSR matrix increases to 7 nm after the reaction (Fig. 4).

There is a cobalt oxide phase in the XRD-pattern of the sample of the initial 3%Co/γ-Al_2O_3 catalyst (Co_3O_4) (Fig. 2). Though there is no phase of metallic cobalt in the X-ray diffraction patterns of the catalyst after participating in the reaction of DRM this is probably due to its low dispersion and significant background because of its fluorescence.

There is also no NiO phase on the XRD-pattern of the sample of the initial 3%Ni/γ-Al_2O_3 catalyst with individual nickel oxide. However, there are reflections of the FCC nickel phase in the X-ray diffraction patterns of the catalyst after participation in the DRM reaction, it should be noted

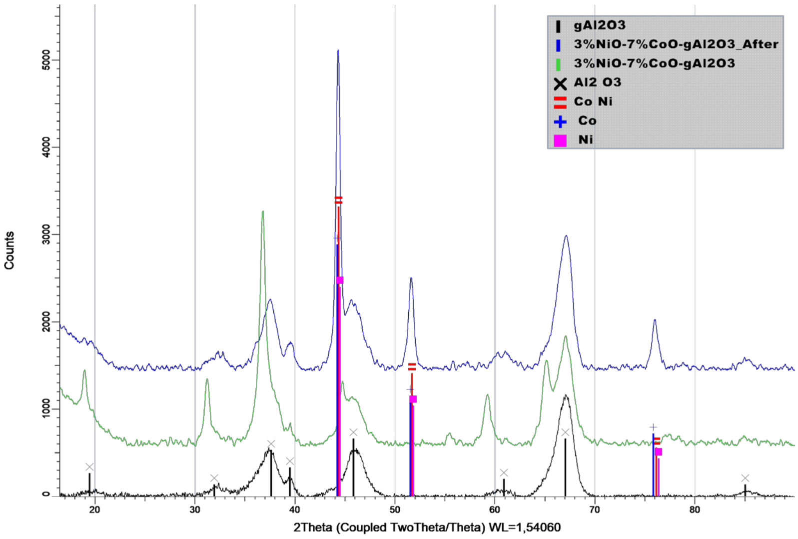


Fig. 4. X-ray diffraction pattern of 3%Ni-7%Co/γ-Al_2O_3 catalyst before and after DRM reaction.

that it has an increased parameter of the crystal lattice in comparison with the database of PDF-2, 3.542 Å instead of tabulated 3.524 Å. The CSR size of nickel formed after the reaction of DRM is about 17 nm.

In addition to the carrier phase (γ-Al_2O_3), there is an aluminium cobaltite phase in the sample of the initial catalyst 3%Ni-7%Co/γ-Al_2O_3. There in no cobalt oxide (Co_3O_4) and nickel oxide phases. After the participation of 3%Ni-7%Co/γ-Al_2O_3 catalyst in the reaction of DRM (Fig. 5), there is appeared a metal phase with a cubic hexagonal lattice. The parameter of this phase is 3.535–3.540 Å, the parameter follows that the Co-Ni solid solution is formed with an face-centered cubic (FCC) FCC-lattice.

A study of the catalysts by scanning electron microscopy showed that a sample of nickel-cobalt catalysts are more dispersed in comparison with a 3%Ni/γ-Al_2O_3 (Fig. 6).

Figure 6 also shows that on the surface of the 3%NiO/γ-Al_2O_3 and 3%NiO-9%Co_2O_3/γ-Al_2O_3 catalysts it is observed the formation of the coke of black shade (areas are marked by arrows), unlike of 3%NiO-7%Co_2O_3/γ-Al_2O_3 catalyst. On the surface of the active 3%NiO-7%Co_2O_3/γ-Al_2O_3 catalyst, there are Ni and Co oxides in the form of nanosized particles. These results confirm that the formation of nanophase and the absence of coke formation on the surface of the carrier have a significant role in the activity of the catalyst.

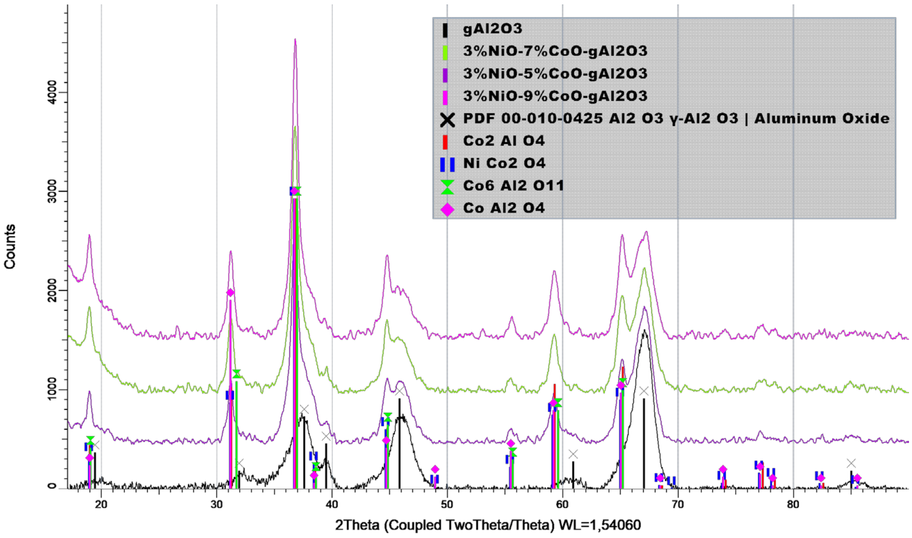
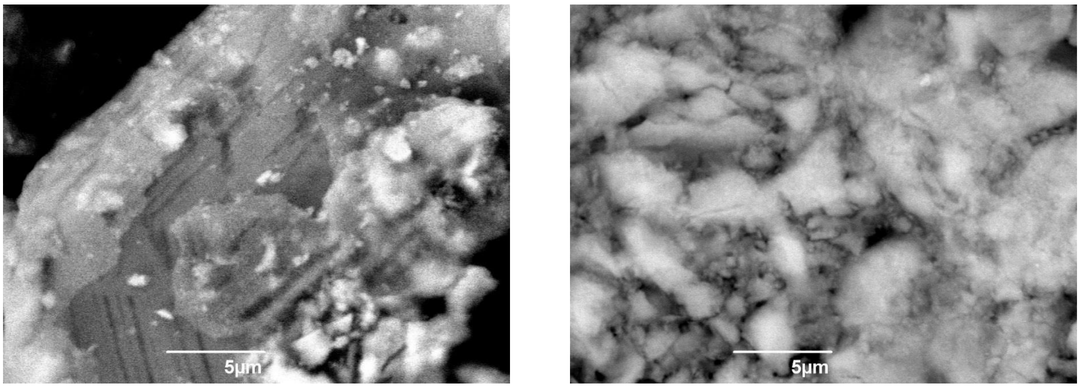
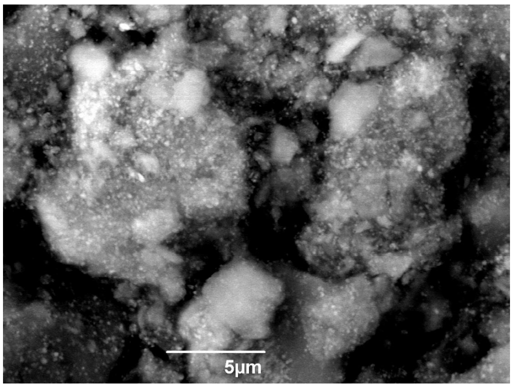


Fig. 5. XRD pattern of 3%Ni-5%Co/γ-Al_2O_3, 3%Ni-7%Co/γ-Al_2O_3, 3%Ni-9%Co/γ-Al_2O_3 catalysts after the reaction of DRM.



3%NiO/γ-Al_2O_3 3%NiO-7%Co_2O_3/γ-Al_2O_3



3%NiO-9%Co_2O_3/γ-Al_2O_3

Fig. 6. SEM micrographs: registration of back scattering electrons.

To determine the optimal pre-treatment conditions of the 3%NiO-7%Co_2O_3/γ-Al_2O_3 catalyst which showed the highest activity in reaction of DRM, and the appearance of coke on the catalyst surface after the DRM reaction, the sample was studied by the complex of thermal analysis methods, that is TGA/DTA/DSC method. The results are shown in Fig. 7.

It can be seen on the TGA curve of the initial sample (Fig. 7a) that during heating the most intense weight loss is observed at 30 to 255 °C and this is associated with the release of H_2O (m/z=18), CO (m/z=28), O_2 (m/z=32), CO_2 (m/z=44) and the amount of weight loss is 1.85%. The maximum release rate occurs at temperature of 110–160 °C. Further extraction of H_2O (m/z=18), CO (m/z=28), O_2 (m/z=32), CO_2 (m/z=44) occurs evenly and ends at a temperature of 460 °C. The obtained results may be indicative of the effectiveness of the pre-activation of catalysts, carried out by us at 500 °C.

The greatest weight loss is observed after the reaction of DRM (Fig. 7b) from 30 to 260 °C and is 2.77%. By mass spectra seen release of H_2O (m/z=18), CO_2 (m/z=44) and lack of CO (m/z=28), O_2 (m/z=32). After heating above 300 °C, a slight increase in the weight of the sample is observed, accompanied by an exothermic effect on the DSC curve. This may be due to the adsorption of the gas used to purge the unit. This data can indicate the absence of the coke formation on the surface of 3%NiO-7%Co_2O_3/γ-Al_2O_3 catalyst after the reaction of DRM that is consistent with the results of the study by SEM.

The catalytic activity of the oxide catalyst in the oxidation-reduction reactions depends on the binding energy of the oxygen-to-metal that can be quality characterized by the onset temperature hydrogen reduction process as well as the temperature maxima on the curves TPR-H_2 [41, 42].

Figure 8 shows the spectra of TPR-H_2 analysis of 3%NiO-(5–9%)Co_2O_3/γ-Al_2O_3 catalysts with different content of cobalt and without one. The TPR-H_2 catalysts analysis spectrum shows four intense peaks.

Figure 8 shows that a change in the content of cobalt oxide in the composition of Ni-Co catalysts leads to a significant change in the profile of the TPR-H_2 curve.

As for nickel-cobalt catalysts compared to the catalyst of 3Ni/γ-Al_2O_3 [43], T^4_{max} is decreased from 814 to 747–807 °C, that related to nickel reduction in the composition of $NiAl_2O_4$. T^4_{max} for

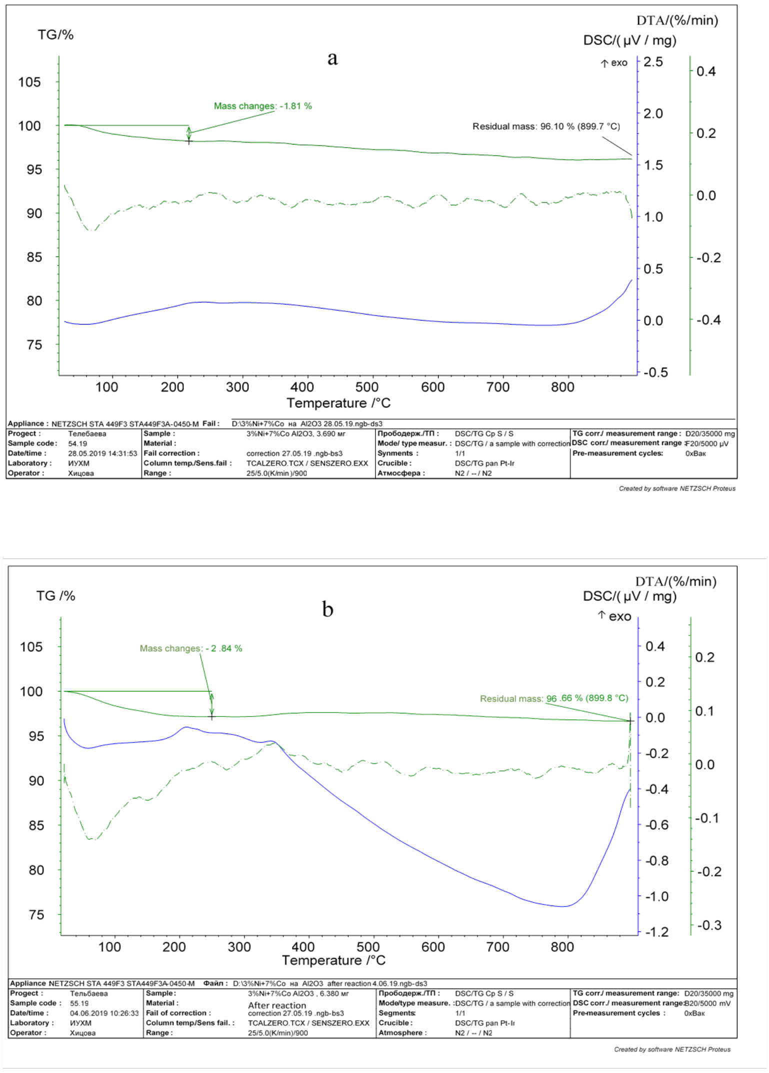


Fig. 7. TGA/DTA/DSC analysis of 3%Ni-7%Co/γ-Al_2O_3 catalyst before and after reaction of DRM.

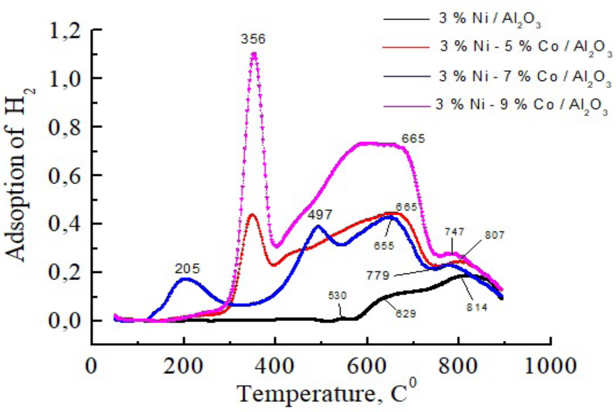


Fig. 8. TPR-H_2 spectra of catalysts.

nickel-cobalt catalysts depends on the content of cobalt oxide in the composition of the catalyst, during the increasing content of cobalt oxide from 5 to 9 wt.%, it decreases from 807 to 747 °C.

Compared to 3Ni/γ-Al_2O_3, the addition of 5 wt.% cobalt oxide (3%Ni-5%Co/γ-Al_2O_3) leads to the appearance of peaks T^1_{max} = 356 °C which indicates the reduction of cobalt oxide at lower temperatures. The increase in the content of cobalt oxide to 7 wt.% leads to a change in the TPR profile of the catalyst. There are four peaks in the curves TPR-H_2 for 3%Ni-7%Co/γ-Al_2O_3 catalyst with maxima hydrogen absorption temperature T^1_{max}, T^2_{max}, T^3_{max} and T^4_{max}, equal to 205, 497, 655, and 779 °C, respectively. The appearance of a low-temperature peak with a maximum at T^1_{max} = 205 °C may be due to the reduction of oxides on the surface of the carrier, most likely cobalt oxide [44]. The appearance of the T^2_{max} = 497 °C peak is associated with the formation of easily reduced nickel oxides. This indicates the activity and mobility of oxygen in a 3%NiO-7%Co_2O_3/γ-Al_2O_3 catalyst in comparison with other studied catalysts. These results suggest that the efficiency of 3%NiO-7%Co_2O_3/γ-Al_2O_3

catalyst is also due to the presence of active oxygen on the catalyst surface.

Increasing the cobalt oxide content to 9 wt.% leads to an increase in the peak intensity at T^1_{max} = 356 °C, also peak at T^2_{max} = 665 °C the last can be attributed to the hard reducible cobalt-carrier compounds.

4. Conclusion

Thus, the effect of cobalt oxide content on the activity of the 3%Ni /$\gamma-Al_2O_3$ catalyst in the DRM to synthesis gas was studied. Based on the study, the effective composition of the nickel-cobalt catalyst was determined, with the content of Ni-3 wt.% and Co-7 wt.% oxides supported on $\gamma-Al_2O_3$. On the 3%NiO-7%$Co_2O_3/\gamma-Al_2O_3$ catalyst under the conditions of the process W = 1500 h^{-1}, $CH_4:CO_2$ = 1:1, T = 800 °C, methane conversion is 89%, the ratio of H_2/CO = 1.

According to physical and chemical studies, the increased catalytic activity of a nickel-cobalt catalyst with the cobalt oxide content of 7 wt.% depends on the formation of dispersed easily reduced nanophases in the catalyst which leads to an increase in the activity and mobility of oxygen involved in the DRM reaction. These characteristics together positively affect the catalytic activity of 3%NiO-7%$Co_2O_3/\gamma-Al_2O_3$ catalyst in the process of dry reforming of methane to synthesis gas.

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