

Physical and chemical characteristics and activity of nickel-modified cobalt-iron-containing catalysts in the reaction of dry reforming of methane

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ABSTRACT

In the process of dry reforming of methane (DRM), the activity of low-percentage catalysts based on cobalt and iron oxides and their modification with nickel oxide was studied. It has been established that the addition of nickel oxide into the $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst increases the degree of methane conversion from 14 to 89%, and also increases the yield of target reaction products H_2 to 43.0 vol.%, CO to 46.1 vol.% at 850 °C. On a $\text{Co}_3\text{O}_4\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst at 850 °C, methane conversion reaches to 88.1%, the yield of H_2 and CO is 44.8%. TPR- H_2 analyzes showed that the introduction of nickel oxide into $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ composition, in contrast to the $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst, the temperature peaks of $\text{Fe}_2\text{O}_3\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$, reduction shift towards lower temperatures and weaken the interaction of metals with the support - $\gamma\text{-Al}_2\text{O}_3$, and thereby the amount of active reduced particles of iron and nickel oxides increases, which ensures good catalytic activity of $\text{Fe}_2\text{O}_3\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$. According to the XRD results, spinel-like form - NiFe_2O_4 , NiAl_2O_4 and CoAl_2O_4 , also phase as Fe_2O_3 were obtained on the $\text{Fe}_2\text{O}_3\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst. This indicates that the developed catalysts form new phases that are active at high temperatures to produce synthesis gas in reduction-oxidation processes during the DRM reaction.

Keywords: greenhouse gas, methane, carbon dioxide, oxide catalysts, dry reforming of methane

1. Introduction

The global demand for energy in the world is gradually growing and at the moment exerting such strong pressure on the attrition of traditional types of fossil combustibles, from here the desire to explore/exploit new sources of energy aimed at ensuring a low-carbon economics [1]. CO_2 - major greenhouse gas (GHG) and a widespread waste gas in the chemicals and power sectors, its immediate application is a surefire way to reduce emission of carbon [2]. In addition, many studies are being conducted on the new use of CO_2 because of the increased threat posed by climate change [3]. One of these innovative approach is the dry reforming of methane (reaction of CH_4 and CO_2) to obtain synthesis gas. Dry reforming of methane (DRM) suggests appropriate solution to these main problems faced by modern society [4]. As a result of the efficient utilization of methane, along with low-carbon recirculation in the framework of

carbon trapping, utilization and warehousing, as well as the process of dry reforming of methane to obtain syngas has grown more lovable [5].

For the DRM reaction the best famous active catalysts are transition and noble metals such as Rh, Ru, Ni, Co, Ir, Pt, Pd and Fe are often considered [6-10]. Noble metals such as Pt, Ru or Rh are expensive and not economically profitable [11]. Thus, transition metals, Co, Ni and Fe are the most advisable catalysts for process of DRM from an economic point of view, since they combine high activity in the dry reforming of methane reaction with a comparatively low cost [12-14]. However, the iron-containing catalyst is less active [15] compared to cobalt. The cobalt-based catalyst is not resistant to coking in the reaction of DRM into synthesis gas. To increase the activity of catalysts, in particular, modified nickel-containing catalysts are used [16, 17]. Nickel catalysts are the most extensively investigated for this process, their primary benefit is their lower price [18, 19]. The addition of Ni to iron-cobalt containing catalysts led to a significant decrease in carbon precipitation in the DRM process and an increase in the activity of the catalysts [20-23].

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The authors of [24] studied the activity of 15Ni-5Fe-30Al catalyst during the process of DRM into syngas; at 600 °C, the methane conversion was 39%. The authors reported that according to XRD data, phases of spinel NiAl_2O_4 and metallic Ni are observed. During the reaction, the spinel phase decomposed and a Ni_3Fe alloy was obtained. Catalysts with a higher Fe/Ni ratio showed less conversion of initial gas and contained inactive spinel form FeAl_2O_4 .

Therefore, the goal of this work is to develop low-percentage, nickel-modified iron- and cobalt-containing catalysts for the reaction of DRM.

2. Experimental procedures

2.1. Preparation

Low percentage mono 2 wt.% $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, 2 wt.% $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ and bimetallic 5 wt.% $\text{Co}_3\text{O}_4\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$, 5 wt.% $\text{Fe}_2\text{O}_3\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared by capillary impregnation of a granule ($d=2\text{mm}$) of a support ($\gamma\text{-Al}_2\text{O}_3$, S-180 m^2/g , $d\sim 3\text{mm}$; Changhai Jiuzhou Chemicals Co) according to moisture capacity with aqueous solutions, $\text{Fe}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, followed by drying them at 300 °C for 2 h and calcining at 500 °C (3 h).

2.2. Catalytic test

The activity of synthesized catalysts in the process of dry reforming of methane was tested in an automated flow-through catalytic device (Fig. 1). Mixed gas ($\text{CH}_4+\text{CO}_2 = 1:1$) was fed at a rate of 33.3 cm^3/min into the catalytic reactor from above, and after passing through the catalyst layer in the reactor, the mixture with reaction products was sent to the

chromatograph for analysis. The reactor temperature was set by a thermostat and controlled using a CA thermocouple, sheathed in quartz and located inside the catalyst layer. The initial gases and reaction products were analyzed on-line on CHROMOS GC-1000 chromatograph with a flame ionization detector and a thermal conductivity detector. On packed columns with an internal diameter of 3 mm, 2 m long, filled with CaA sorbents, the gases H_2 , N_2 , O_2 were determined, as well as for the determination of CO and CO_2 , the AG-3 composition phase was used, the gas of CH_4 was determined on an XSEP column. Air, hydrogen, and Ar were used as carrier gases. To process the chromatograms, absolute calibration with pure gases was used: methane, hydrogen, carbon dioxide and carbon monoxide, followed by plotting. Monitoring of the process of dry reforming of methane (supplied gas flow rate of the starting mixture and chromatographic analysis data) was monitored software.

Process conditions: pressure 0.1 MPa, $T_r = 500\text{-}850\text{ }^\circ\text{C}$, ratio $\text{CH}_4 + \text{CO}_2 = 1:1$, catalyst volume in the reactor 1.04 g.

2.3. Catalyst characterization

Temperature-programmed catalyst reduction of H_2

Temperature-programmed reduction (TPR- H_2) was carried out on the laboratory installation Universal Sorption Gas Analyzer (USGA-101), which includes a gas treatment system, a reactor (inner diameter 4 mm) with a tubular oven and a thermal conductivity detector. The sample (106 mg, fraction 0.125 mm) was pre-blown with Ar at 480 °C for 40 min, following cooling to 50 °C, then heated at a rate of 100 °C/min from 50 to 950 °C in a mixture



Fig.1. Automated flow catalytic device.

flow of 15 vol.% H₂ in Ar at feed rate 30 cm³/min. The variation of the hydrogen concentration in the flow was controlled using a thermal conductivity detector. Quantitative determination of absorbed hydrogen was carried out using a calibration based on the recovery of precise amounts of metal oxide.

XRD analysis

XRD patterns of the catalyst were carried out on MiniFlex 600 with CuK α radiation diffractometers, K-beta(x2) filter. Filming conditions of sample: U=40 kV; I=15 mA; shooting θ -2 θ ; detector 10 °C/min. XRD patterns on a semi-quantitative basis was performed using diffractograms of powder samples using the technique of equal portions and synthetic mixtures. The numerical ratios of the crystal phases are established. The interpretations of the phase were carried out using data from the PDXL 2 card file: PDF 2 powder phase database (Powder Phase File).

3. Result and discussion

The catalytic activity of oxide catalysts in redox reactions depended on the energy of the oxygen-metal bond, the qualitative characteristics of that energy being the temperature at the beginning of the hydrogen reduction process, as well as the temperature of the maximum on the curves of TPR-H₂ [25].

Figure 2 illustrated TPR-H₂ profiles of mono-Co₃O₄/ γ -Al₂O₃ and bimetallic-Co₃O₄-NiO/ γ -Al₂O₃ catalysts. According to literature data [26], on mono and bimetallic catalysts at 250-301 °C, cobalt oxide (Co₂O₃) begins to be reduced to Co₃O₄ (Co₂O₃ → Co₃O₄). From 424 to 808 °C, both catalysts have 4 identical peaks of different intensities. At 424 °C, Co₃O₄ is reduced to cobalt (II) oxide (Co₃O₄ → CoO)

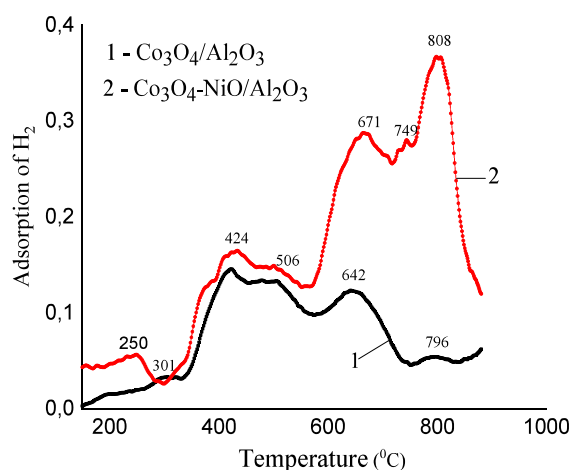


Fig. 2. TPR profiles of mono- Co₃O₄/ γ -Al₂O₃ and bimetallic- Co₃O₄-NiO/ γ -Al₂O₃ catalysts.

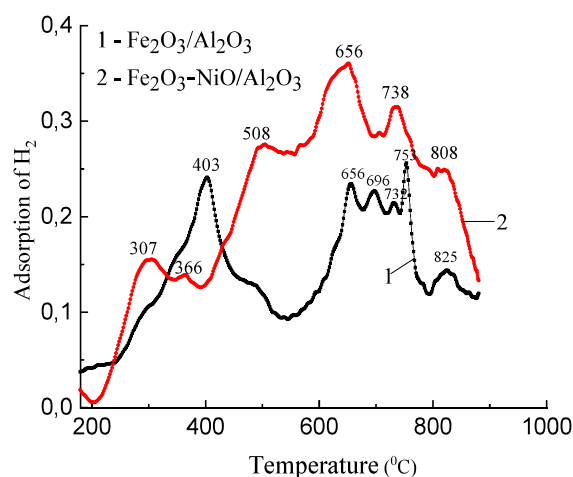


Fig. 3. TPR profiles of mono- Fe₂O₃/ γ -Al₂O₃ and bimetallic - Fe₂O₃-NiO/ γ -Al₂O₃ catalysts.

[27], T_{max} = 506 °C possibly refers to the reduction of cobalt (II) oxide to metallic Co⁰ [28]. The peaks at T_{max} = 642 and 671 °C can be related to the reduction of cobalt oxide, which is strongly bound to the carrier [29].

An additional small peak in the TPR-H₂ profile of Co₃O₄-NiO/ γ -Al₂O₃ at 749 °C can be referred to the reduction of NiO particles strongly bound to the support [30]. At the temperatures T_{max} = 796 and T_{max} = 808 °C, spinel-like forms of cobalt and nickel (CoAl₂O₄ and NiAl₂O₄) are formed, respectively on all catalysts [31]. The addition of nickel to cobalt offsets the reduction peak to higher temperatures such as 671 and 808 °C compared to Co₃O₄/ γ -Al₂O₃.

Figure 3 shows TPR profiles of mono-Fe₂O₃/ γ -Al₂O₃ and bimetallic - Fe₂O₃-NiO/ γ -Al₂O₃ catalysts.

As can be seen from Fig. 3, with the addition of NiO to the Fe₂O₃/ γ -Al₂O₃ catalyst, the iron oxide phases are reduced at lower temperatures (from 307 to 808 °C) compared to the monometallic catalyst - Fe₂O₃/ γ -Al₂O₃ (from 403 to 825 °C). The advent of a low-temperature peak with a peak at T_{max} = 307 °C may be related to the recovery of iron oxide Fe₂O₃ → Fe₃O₄, which weakly interacts with the carrier [32]. The introduction of nickel oxide to Fe₂O₃/ γ -Al₂O₃ also resulted to the appearance of peak at relatively low temperature - T_{max} = 366 °C, which indicates further reduction of Fe₃O₄ to iron oxide FeO (II). Whereas on the Fe₂O₃/ γ -Al₂O₃ catalyst (Fig. 3), the appearance of iron (II) oxide as a result, of the reduction of Fe₃O₄ is observed at T_{max} = 403 °C [33]. An additional peak on the Fe₂O₃-NiO/ γ -Al₂O₃ catalyst at 508 °C possibly belongs to the recovery of nickel oxide to Ni, which corresponds to a weak interaction with the support [34]. Peaks at T_{max} = 656 °C (A = 60 μ mol/gKt) and T_{max} = 652 °C (A = 154 μ mol/gKt) on

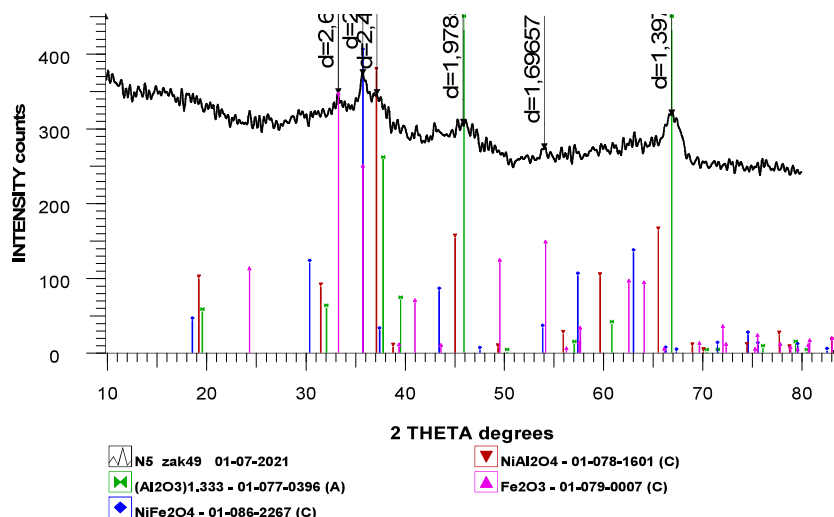


Fig. 4. XRD patterns of the Fe₂O₃-NiO/ γ -Al₂O₃ catalyst.

mono- and bimetallic catalysts, respectively, relate to the reduction of FeO \rightarrow Fe [35]. In addition, two additional peaks are observed on the monometallic profile at $T_{\text{max}} = 696$ and $T_{\text{max}} = 732$ °C, which relate to the obtain of the Fe_xNi_y/Al₂O₃ phase [36].

High temperature peaks in the range $T_{\text{max}} = 753$ °C ($A = 22$ $\mu\text{mol/gKt}$) and $T_{\text{max}} = 738$ °C ($A = 87$ $\mu\text{mol/gKt}$) possibly correspond to reduce of Fe₃O₄ to Fe and NiFe₂O₄ to Fe and Ni [37, 38]. The peak at $T_{\text{max}} = 825$ °C can be related to the recovery of aluminates, possibly FeAl₂O₄, since the reduction of NiAl₂O₄ is observed at a lower temperature ($T_{\text{max}} = 808$ °C) [39, 40].

After the addition of nickel, the reduction peaks of Fe₂O₃-NiO/ γ -Al₂O₃ shifted towards lower temperatures, and the amount of hydrogen adsorption increases. It is considered, that the introduction of nickel weakens the interaction of Fe and Ni with the

support- γ -Al₂O₃ and thereby increases the number of reduced particles [41].

Nickel-modified iron- and cobalt-containing (Fe₂O₃-NiO/ γ -Al₂O₃, Co₃O₄-NiO/ γ -Al₂O₃) catalysts were investigated by XRD analysis. XRD analysis data for modified catalysts are shown in Figs. 4 and 5.

From Fig. 4 shown, that in the formulation of the Fe₂O₃-NiO/ γ -Al₂O₃ catalyst, iron located as phase Fe₂O₃, reflections of nickel aluminate NiAl₂O₄ and the NiFe₂O₄ phase are observed.

The XDR pattern of the Co₃O₄-NiO/ γ -Al₂O₃ catalyst (Fig. 5) shows reflections of the CoAl₂O₄ compound, which have a spinel structure. Nickel compounds are not separately identified. Reflections corresponding to nickel phases did not observed, probably because of its dispersion (less than 4 nm) [42]. In addition, it is possible, that nickel is contained in the solid solution based on CoAl₂O₄, since in the

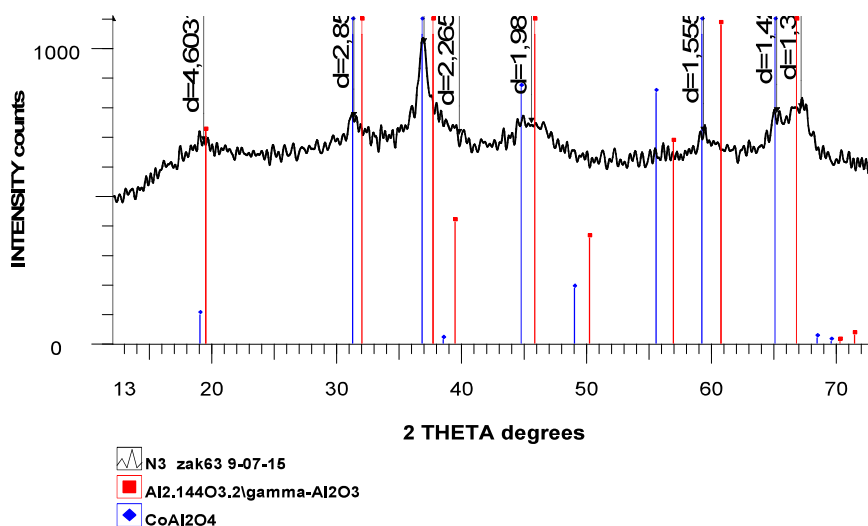


Fig. 5. XRD patterns of the Co₃O₄-NiO/ γ -Al₂O₃ catalyst.

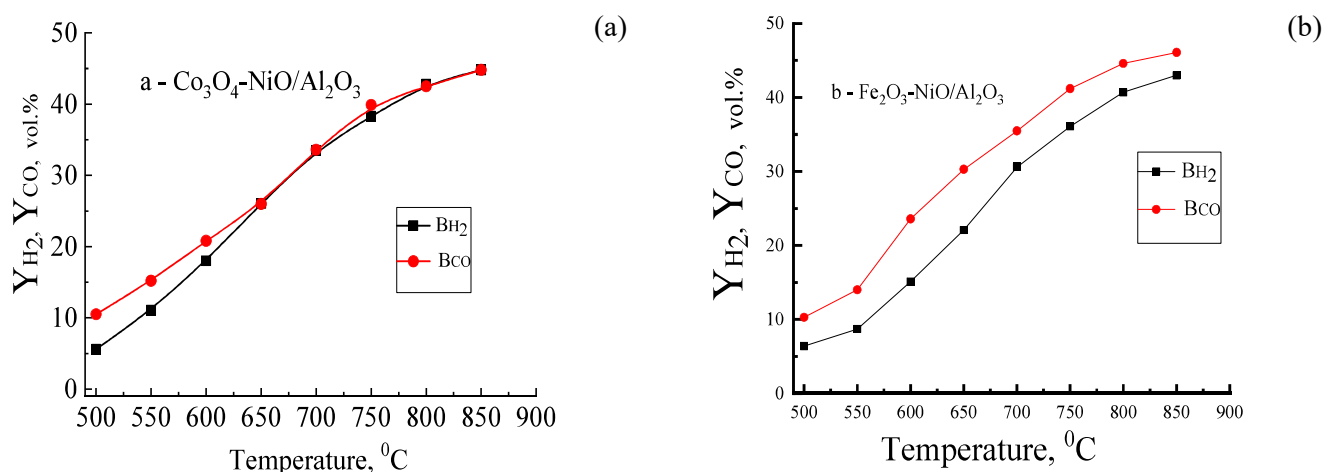


Fig. 6. The influence of the DRM reaction temperature on the catalyst activity: a- $\text{Co}_3\text{O}_4\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$; b- $\text{Fe}_2\text{O}_3\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$.

spinel form of the NiAl_2O_4 compound its lattice parameters are slightly lower than those of CoAl_2O_4 .

The activity of the investigated catalysts in the process of DRM in the $T_r = 500\text{-}850\text{ }^\circ\text{C}$ was studied. The table shows the results of catalyst activity at the reaction temperature of $800\text{ }^\circ\text{C}$, reaction volume rate of 1000 h^{-1} and $\text{CH}_4\text{:CO}_2$ ratio of 1:1.

It can be seen, that on both catalysts the conversion of the initial gases and the yield of H_2 and CO are not high.

To increase activity, the catalysts were modified with nickel oxide; the results of studying the catalysts in the DRM reaction are presented in Fig. 6.

On the $\text{Co}_3\text{O}_4\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst, the yield of H_2 and CO at $500\text{ }^\circ\text{C}$ is 5.6 and 10.5 vol.%, respectively. During the reaction temperature increases from 500 to $850\text{ }^\circ\text{C}$, the yields of hydrogen and monoxide increase. At $850\text{ }^\circ\text{C}$, the yield of hydrogen and carbon monoxide reaches to 44.8%, the ratio $\text{H}_2/\text{CO} = 1$. On $\text{Fe}_2\text{O}_3\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst at the reaction temperature

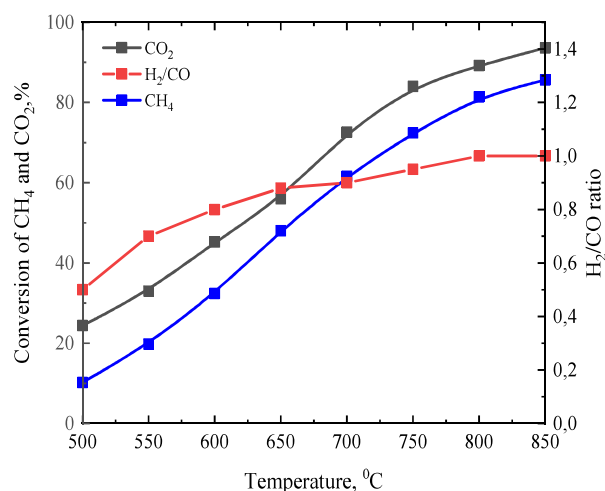


Fig. 7. The influence of the DRM reaction temperature on the $\text{Co}_3\text{O}_4\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst activity.

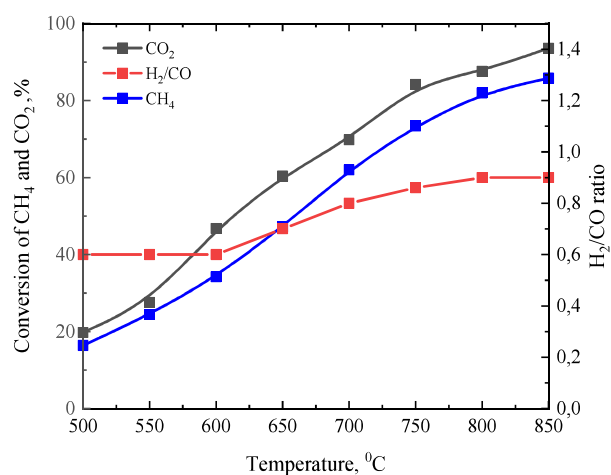


Fig. 8. The influence of the DRM reaction temperature on the $\text{Fe}_2\text{O}_3\text{-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst activity.

of $500\text{ }^\circ\text{C}$, formation of 6.4 vol.% hydrogen and 10.3 vol.% carbon monoxide is observed in the reaction products, with a further increase to 43 vol.% H_2 and CO to 46.1 vol.% at $850\text{ }^\circ\text{C}$.

The following Figs. 7 and 8 show the degree of conversion of CH_4 and CO_2 and the H_2/CO ratio depending on the temperature of the DRM process.

As can be seen from Figs. 7 and 8, with the addition of NiO into the $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ compositions, the degree of methane conversion at $850\text{ }^\circ\text{C}$ increases to 89% and 88.1%, respectively, compared to monometallic catalysts. This change is related to the obtaining of easily recoverable new phases between nickel and iron oxides [43].

During the increase DRM reaction temperature, the ratio of reaction products (H_2/CO) changes from 0.7 to 1. These data are great significance, since it is known, that different syntheses require different compositions of synthesis gas with different amounts

of hydrogen: with a ratio of $H_2/CO = 2:1$ can be obtained methanol, ethanol and ethylene; for the synthesis of ethylene glycol required ratio synthesis gas = 1.5:1, synthesis gas at 1:1 ratio is converted into acetic acid.

4. Conclusion

Thus, ($Co_3O_4/\gamma-Al_2O_3$, $Fe_2O_3/\gamma-Al_2O_3$, $Fe_2O_3-NiO/\gamma-Al_2O_3$ and $Co_3O_4-NiO/\gamma-Al_2O_3$) catalysts were prepared, and their activity was studied in the process of DRM. It has been established that the addition of nickel oxide into the $Fe_2O_3/\gamma-Al_2O_3$ catalyst increases the degree of methane conversion to 89%, and also increases the yield of target reaction products achieved: H_2 to 43.0 vol.%, CO to 46.1 vol.%. On $Co_3O_4-NiO/\gamma-Al_2O_3$ catalyst at 850 °C reaction, the yield of H_2 and CO is achieved to 44.8%. It has been determined that by varying the reaction temperature, it is possible to producing syngas with a different ratio of hydrogen to carbon monoxide, for further use as an initial gas for the production of alcohols and carboxylic acids.

The results of XRD analysis of the catalysts showed that with the addition of Ni into the $Fe_2O_3/\gamma-Al_2O_3$ composition of the catalyst phases as Fe_2O_3 and $NiFe_2O_4$ are observed. This may indicate the formation of active phase of the modified catalyst in reduction-oxidation processes during the DRM reaction. It was determined that the XRD pattern of the $Co_3O_4-NiO/\gamma-Al_2O_3$ catalyst contains reflections of the $CoAl_2O_4$ compound, which have a spinel structure, reflections corresponding to nickel phases did not observed, probably because of its dispersion (less than 4 nm). Therefore, methane conversion (88.1%) on the $Co_3O_4-NiO/\gamma-Al_2O_3$ catalyst is lower than $Fe_2O_3-NiO/\gamma-Al_2O_3$.

Using TPR- H_2 methods, it was determined that spinel-like forms are formed on $Co_3O_4/\gamma-Al_2O_3$ catalyst at high temperatures. The addition of NiO to $Co_3O_4/\gamma-Al_2O_3$ catalysts has almost the same character, but shifts the high-temperature reduction peaks towards higher temperatures.

TPR- H_2 analyzes showed that when nickel is added to the $Fe_2O_3/\gamma-Al_2O_3$ composition, in contrast to the $Co_3O_4/\gamma-Al_2O_3$ catalyst, the temperature peaks of the reduction of $Fe_2O_3-NiO/\gamma-Al_2O_3$ shift towards lower temperatures and weaken the interaction of metals with the carrier - $\gamma-Al_2O_3$. Also thereby increases amount of reduced particles, which provides good catalytic activity of $Fe_2O_3-NiO/\gamma-Al_2O_3$ at high temperatures, and may also be resistant to coke formation.

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Физико-химические характеристики и активность модифицированных никелем кобальт-железосодержащих катализаторов в реакции углекислотной конверсии метана

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АННОТАЦИЯ

В процессе углекислотной конверсии метана исследована активность низкопроцентных катализаторов на основе оксидов кобальта и железа и их модификации оксидом никеля. Установлено, что введение оксида никеля в состав $Fe_2O_3/\gamma-Al_2O_3$ катализатора повышает степень конверсии метана от 14 до 89%, а также увеличивает выход целевых продуктов реакции H_2 – до 43,0 об.%, CO – до 46,1 об.% при 850 °С. На $Co_3O_4-NiO/\gamma-Al_2O_3$ катализаторе при 850 °С конверсия метана достигает 88,1%, выход водорода и монооксида углерода составляет 44,8%. ТПВ анализы показали, что при добавлении никеля в состав $Fe_2O_3/\gamma-Al_2O_3$, в отличие от $Co_3O_4/\gamma-Al_2O_3$ катализатора, температурные пики восстановления $Fe_2O_3-NiO/\gamma-Al_2O_3$ смещаются в сторону более низких температур и ослабляют взаимодействие металлов с носителем - $\gamma-Al_2O_3$ и, тем самым, увеличивая количество активных восстановленных частиц оксидов железа и никеля и обеспечивая хорошую каталитическую активность $Fe_2O_3-NiO/\gamma-Al_2O_3$. Согласно результатам РФА, на исследуемых катализаторах образуются фазы в виде Fe_2O_3 и шпинелеподобные формы $-NiFe_2O_4$, $NiAl_2O_4$ и $CoAl_2O_4$. Это свидетельствует о том, что на разработанных катализаторах образуются новые фазы, которые являются активными при высоких температурах для получения синтез-газа в окислительно-восстановительных процессах во время реакции УКМ.

Ключевые слова: парниковый газ, метан, диоксид углерода, оксидные катализаторы, углекислотная конверсия метана

Метанның көмірқышқылды конверсиясы реакциясына никельмен модифицирленген кобальт-темір катализаторларының физикалық-химиялық сипаттамасы және белсенділігі

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АНДАТПА

Метанның көмірқышқылды конверсиясы процесінде төмен пайыздық кобальт және темір оксидтері негізіндегі және олардың никель оксидімен модификациясы катализаторлардың белсенділігі зерттелді. $Fe_2O_3/\gamma-Al_2O_3$ катализаторына никель оксидін енгізгенде метанның конверсиясы 14-тен 89%-ға дейін арттыратыны, сонымен қатар, 850 °С температурада мақсатты реакция өнімдерінің шығымы H_2 – 43,0 көл.%-ға дейін, CO – 46,1 көлем.% -ға дейін жоғарылайтыны анықталды. $Co_3O_4-NiO/\gamma-Al_2O_3$ катализаторында 850 °С температурада метанның конверсиясы 88,1% жетті, сутегі мен көміртегі тотығының шығымы 44,8% құрады. ТТБ талдаулары көрсеткендей, никельді $Fe_2O_3/\gamma-Al_2O_3$ құрамына қосқанда, $Co_3O_4/\gamma-Al_2O_3$ катализаторынан айырмашылығы, $Fe_2O_3-NiO/\gamma-Al_2O_3$ тотықсыздануының температуралық шыңдары төменгі температураға ауысады және $\gamma-Al_2O_3$ тасымалдағышы мен металдардың өзара әрекеттесуін әлсіретеді сол арқылы темір және никель оксидтерінің белсенді тотықсызданған бөлшектерінің мөлшері артады, бұл $Fe_2O_3-NiO/\gamma-Al_2O_3$ жақсы каталитикалық белсенділігін қамтамасыз етеді. РФТ нәтижелері бойынша зерттелген катализаторларда Fe_2O_3 түріндегі фаза және шпинель тәрізді формалар - $NiFe_2O_4$, $NiAl_2O_4$ және $CoAl_2O_4$ түзілді. Бұл әзірленген катализаторлар МКК реакциясы кезінде тотығу-тотықсыздану процестерінде синтез газын алу үшін жоғары температурада белсенді жаңа фазалар түзетінін көрсетеді.

Түйінді сөздер: парниктік газ, метан, көмірқышқыл газы, оксидті катализаторлар, метанның көмірқышқылды конверсиясы