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# COMPARATIVE STUDY the ACTIVITY in DRY REFORMING of METHANE of BIOXIDE NiO-Co<sub>3</sub>O<sub>4</sub> and NiO-Fe<sub>2</sub>O<sub>3</sub> SYSTEMS SUPPORTED on the GRANULATED NATURAL DIATOMITE

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#### ABSTRACT

In this work, catalytic systems NiO-Co<sub>3</sub>O<sub>4</sub> and NiO-Fe<sub>2</sub>O<sub>3</sub> bioxide supported on the granulated natural diatomite from Georgia deposit were investigated as catalysts for the dry reforming of methane. The results showed that the NiO-Co<sub>3</sub>O<sub>4</sub>/D catalyst is more active and stable than NiO-Fe<sub>2</sub>O<sub>3</sub>/D. At the reaction temperature 850 °C the conversion of methane on the NiO-Co<sub>3</sub>O<sub>4</sub>/D catalyst was 77%, whereas on the NiO-Fe<sub>2</sub>O<sub>3</sub>/D – 42%. The activity of the NiO-Co<sub>3</sub>O<sub>4</sub>/D catalyst in the reaction is probably due to the high dispersity of the catalyst particles. The results of SEM-EDX, XRD, AES showed that cobalt oxide in the composition of NiO-Co<sub>3</sub>O<sub>4</sub>/D is in the form of nanoparticles with sizes much smaller than the sensitivity threshold of X-ray diffraction analysis (<100Å).

Keywords: methane, carbon dioxide, reforming, synthesis gas, oxide catalyst, support, natural diatomite

# **1. Introduction**

With the intensification of global climate change,  $CO_2$  utilization is becoming increasingly important. Dry reforming of methane (DRM) has attracted a lot of attention due to the conversion of two greenhouse gases,  $CO_2$  and  $CH_4$ , into synthetic gas (H<sub>2</sub> and CO), which is an important chemical feedstock for the production of high value-added products [1-9]. Despite the importance of DRM for industry and the environment, its successful commercialization remains a challenge due to the high operating temperature due to its endothermic nature and the tendency to deposit carbon caused by side reactions. All these features emphasize the need to develop catalyst systems with high activity, stability, and carbon/coke resistance.

To date, nickel-based materials have been proven to have excellent DRM performance when assessed from an industrial point of view due to their remarkable performance, availability, and low cost [10-12]. However, carbon deposition and metal sintering increase the tendency of nickel-based catalysts to deactivate. It has been established that deactivation mainly occurs due to the formation of inert carbon structures on the catalyst surface during DRM [13]. In the reaction network, the corresponding carbon formation reactions are methane dissociation and carbon monoxide disproportionation.

The nature of the modifying additive, the support, has a significant effect on the characteristics, selectivity and stabilization of supported nickel catalysts in DRM reactions. Various oxides such as  $Fe_2O_3$ ,  $Co_3O_4$ , MgO,  $La_2O_3$ ,  $CeO_2$  were added to Ni-based catalysts to improve catalytic performance by controlling the dispersion of active metal nanoparticles on the support surface or affecting the alkalinity and reducibility of catalysts [14-20].

Nickel and cobalt have similar electronic distributions, and they easily form bimetallic alloy nanoparticles, the unique properties of which promote the dissociation of intermediates on the catalyst surface. Studies show that cobalt-modified nickel catalyst has stronger carbon dioxide adsorption and activation ability and can release more \*O. A larger amount of \*O promotes the formation of \*CHO and enhances coking stability of the catalyst by inhibiting the formation of \*C [21]. Iron is an ideal promoter for nickel catalysts due to its low cost. The promoting effect of iron on nickel catalysts is explained by the improved reduction ability of nickel, the formation of an alloy with an enriched iron surface.

As a carrier of NiO-Co<sub>3</sub>O<sub>4</sub> and NiO-Fe<sub>2</sub>O<sub>3</sub> systems, gamma alumina is usually considered, but it can be destroyed at high temperatures and undergo a phase transition to alpha modification [22]. Zeolite and other mesoporous silica materials such as SBA-15, MCM-41 and KIT-6 have also been developed as supports for NiO-Co<sub>3</sub>O<sub>4</sub> and NiO-Fe<sub>2</sub>O<sub>3</sub> containing catalysts due to their large surface area and good thermal stability [23-25]. MCM-41 is a mesoporous material with a pore diameter of 2-4 nm, homogeneous 2-dimensional. Among various porous materials, diatomite is more attractive due to its highly porous structure and low density [26].

In this work, catalytic systems NiO-Co<sub>3</sub>O<sub>4</sub> and NiO-Fe<sub>2</sub>O<sub>3</sub> bioxide supported on the granulated natural diatomite from Georgia deposit were investigated as catalysts for the dry reforming of methane. Physicochemical characteristic of fresh and spent NiO-Co<sub>3</sub>O<sub>4</sub>/D and NiO-Fe<sub>2</sub>O<sub>3</sub>/D catalysts were investigated by modern Scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX), X ray diffractometry (XRD), Auger electron spectrometry (AES), etc. methods.

#### 2. Methods and materials

Catalysts containing NiO-Co<sub>3</sub>O<sub>4</sub> and NiO-Fe<sub>2</sub>O<sub>3</sub> were prepared by impregnating granulated natural diatomite (D) with a solution of nickel, cobalt, or iron nitrate salts according to the moisture capacity. The synthesized samples were dried at 300 °C for 2 h and at 500 °C for 3 h.

The ratio of oxides in the composition of the catalyst is 3 mas.% NiO-2 mas.%  $Co_3O_4$  and 3 mas.% NiO-3 mas.% Fe<sub>2</sub>O<sub>3</sub>.

The catalysts were tested in dry reforming of methane in the temperature range 500-850 °C, at volume rate 1000 h<sup>-1</sup>, at a ratio of  $CH_4:CO_2 = 1:1$ . The experiments were carried out on an automated flow-type installation, which we described in our earlier works [27, 28]. The physicochemical characteristics of catalysts were studied by SEM-EDX, XRD, AES, etc. methods.

# 3. Results and discussion

The important indicators of the catalyst efficiency in dry reforming of methane are the conversion of  $CH_4$  and  $CO_2$  [29]. Figure 1 shows the effect of the reaction temperature (from 500 to 850 °C) on the efficiency of catalysts in DRM. Considering the conversion of methane and carbon dioxide, it can be noted that NiO-Co<sub>3</sub>O<sub>4</sub> systems deposited on natural diatomite exhibit higher activity and stability in DRM than NiO-Fe<sub>2</sub>O<sub>3</sub>.

Since it is assumed that methane activation is the rate-determining step in the carbon dioxide conversion of methane [30], CH<sub>4</sub> conversion can be equated with catalytic activity. The catalyst NiO-Co<sub>3</sub>O<sub>4</sub>/D shows good activity and stability in the temperature range from 500 to 850 °C in the DRM. The conversion of methane increases from 26 to 77% with an increase in the reaction temperature. Whereas in the presence of the NiO-Fe<sub>2</sub>O<sub>3</sub>/D catalyst, with an increase in the reaction temperature, the methane conversion decreases to 41%, passing through a maximum at 750 °C (54%).



Fig. 1. Effect reaction temperature on the activity of NiO-Co<sub>3</sub>O<sub>4</sub>/D and NiO-Fe<sub>2</sub>O<sub>3</sub>/D in DRM: (a) conversion of methane; (b) conversion of carbon dioxide; (c) ratio of  $H_2$ /CO.



Fig. 2. SEM images and the respective EDX spectra of the NiO-Co<sub>3</sub>O<sub>4</sub>/D catalyst recorded before (a, b) and after (c, d) the DRM reaction.

After that, the physicochemical characteristic of NiO-Co<sub>3</sub>O<sub>4</sub>/D  $\mu$  NiO-Fe<sub>2</sub>O<sub>3</sub>/D were investigated. Figures 2-4 demonstrate the results obtained from SEM-EDX and XRD analyses respectively, conducted before and after the DRM reactions for the developed granulated diatomite-based catalyst systems with the bioxide (NiO-Co<sub>3</sub>O<sub>4</sub>) and (NiO-Fe<sub>2</sub>O<sub>3</sub>) catalysts.

Based on SEM images of both bioxide catalysts' samples (Figs. 2 and 3) recorded before the DRM reaction, they look practically similar. No details of the structure of the catalysts deposited on the surfaces of the primary diatomite particles, constituting the carrier's granules, were observed within the resolution of the scanning microscope (~60Å). Moreover, in addition to the EDX peaks of the catalysts (Ni and Co, Fig. 2b and Ni and Fe, Fig. 3b), the peaks corresponding to the components of the diatomite carrier (Si, Al, Mg, Ca, Fe) also simultaneously present. Taking into account the depth of penetration of the accelerated electrons at 20 KeV (~1 µ), generating secondary X-ray radiation, one may conclude that the thickness of the catalyst deposited on the surfaces of the diatomite particles in addition to the thickness of the sputtered conducting Au layer (~100Å) and the thickness of the adsorbed carbon (~50Å) does not totally exceed a few hundreds of angstroms (≤1000Å). Judging from the common character of the samples of both catalyst systems before the reaction, it may be added to the above that carbon content is practically the same (slightly high in the case of NiO-Fe<sub>2</sub>O<sub>3</sub> catalyst); the content of Ni is higher than that of Co that is in the correlation with the composition of (NiO-Co<sub>3</sub>O<sub>4</sub>), while for (NiO-Fe<sub>2</sub>O<sub>3</sub>) the content of Fe is higher than the content of Ni. Obviously, in the latter case, on the EDX peak of Fe contained in the catalyst, an additional intensity, caused by the admixture Fe of diatomite, is superimposed; the content of which may amount to  $\leq 1\%$ .

The SEM images of the surface of the (NiO- $Co_3O_4$ ) catalyst sample after the reaction (Fig. 3c) demonstrate the formation of spherical nanoparticles of the reduced Ni with sizes from 200 to 1000Å. These nanoparticles have a crystalline structure (111, 200, and 220 peaks corresponding to pure Ni crystal lattice are present, Fig. 4.a, pattern-2) formed during the sintering of the NiO catalyst's nanoclusters reduced by hydrogen. The latter is detected by a series of NiO peaks (111, 200, 220) on the XRD spectrum taken before the reaction (Fig. 4a, pattern-1). Taking into consideration the low intensity of these peaks, the sizes of NiO crystallites (X-ray coherent scattering regions) are slightly bigger than the X-ray diffraction sensitivity threshold ( $\approx 100$ Å). At the same time, the absence of the reflection peaks from the  $Co_3O_4$  (or  $Co_2O_3$ ) lattice in patterns 1 and 2, Fig. 4a, in addition to the series of peaks of NiO and the reduced Ni, confirms that cobalt oxide in the synthesized bioxide catalyst (NiO-Co<sub>3</sub>O<sub>4</sub>) is available in the form of nanoparticles with the sizes much less than the X-ray diffraction sensitivity threshold (<100Å). The presence of cobalt oxide in the catalyst



Fig. 3. SEM images and the respective EDX spectra of the NiO-Fe<sub>2</sub>O<sub>3</sub>/D catalyst recorded before (a, b) and after (c, d) the DRM reaction. SEM image of the local area with CNWs/MWCNTs precipitates on the surface of NiO-Fe<sub>2</sub>O<sub>3</sub>/D after the DRM reaction (e) and respective EDX spectrum (f) taken from the selected local area.

is unambiguously detected in the samples in both conditions (before and after the DRM reaction), using the respective EDX spectra (Fig. 2b and Fig. 2d). The joint consideration of XRD and SEM/EDX data shows that in the process of DRM reaction on the surface of the (NiO-Co<sub>3</sub>O<sub>4</sub>) catalyst synthesized on the granulated diatomite carrier, reduction of Ni and formation of spherical nanoparticles of pure Ni via sintering takes place. However, the highly dispersive oxide either is not reduced or if the reduction of Co takes place, it appears in the form of the initial nanoparticles of cobalt oxide without sintering.

The analysis of SEM images of the catalyst system (NiO-Co<sub>3</sub>O<sub>4</sub>)/D recorded after the DRM reaction (Fig. 2c) shows that during the DRM reaction the formation of free carbon in the solid form of Multi wall carbon nano tubes (MWCNTs) or Carbon nano wires (CNWs) does not take place on the given bioxide catalyst. Most likely, the formation of free carbon in a gaseous phase (reaction product) during the DRM reaction with the above catalyst is abandoned. The latter is witnessed by practically the same amount of surface carbon on the samples as before as well as after the reaction (compare Fig. 2). The same was witnessed from practically the same intensity of (002) peaks of carbon (marked by  $\mathbf{\nabla}$  at  $2\theta = 26.2^{\circ}$ ) available in the X-ray diffractogram shown in Fig.4.a, pattern-1, and pattern-2 respectively, recorded from the samples of the above catalyst system before and after the DRM reaction.

The SEM images of the (NiO-Fe<sub>2</sub>O<sub>3</sub>)/D catalyst system taken after the DRM reaction (Fig. 3c) show that during the reaction with this bioxide catalyst, the formation of free carbon in the form of MWCNTs or CNWs does not take place. However, an extremely rare case is demonstrated in Fig. 3e showing the local micro area containing the precipitates of MWCNTs (or CNWs). This case is taken as an exception for this particular granule since no such precipitates were detected in any other granules of the same sample. Here should be noted that, as a rule, for the examination, we randomly select two granules from each series of samples and analyze them in the SEM chamber. Apparently, the formation of MWCNTs in this particular area of this particular granule is caused by a local violation of the composition of the diatomite particles (or any other impurities) as well as of the catalyst that was detected in the EDX spectrum of this local area (see Fig. 3f). Namely, according to the respective EDX spectrum, the Si/Al ratio, in this case, is equal to  $\approx 12$  while for the initial diatomite taken from the deposit (Georgia) it varies from 18 to 25 (see any EDX spectrum in Figs. 2 and 3). Moreover, the concentration of Fe in this local area is 5 times higher than that for the given catalyst (3%). See the EDX spectrum in Fig. 3f. The anomaly detected in this individual sample of this catalyst system after the DRM reaction is that the increased concentration of Fe and Ni was revealed in the respective EDX spectra (Fig. 3d,f), which is almost

2 times higher than that for the given catalyst (3% + 3%) and the detected concentrations of Fe and Ni in the sample before the reaction (see Fig. 3b). Such a big content of Fe (or Fe<sub>3</sub>O<sub>4</sub>) was not detected in the respective diffractograms (see Fig. 4b pattern-2) that demonstrate the reduction of Ni while no signs of the reduced Fe (or the initial iron oxide) have been revealed in pattern-1 and pattern-2, Fig. 4b.

Moreover, the intensities of carbon (002) XRD peaks (marked by  $\mathbf{\nabla}$ ) recorded before and after the reaction remain unchanged as in the case of the catalyst with the 2%  $Co_3O_4$  (compare Fig. 4a and Fig. 4b). The same is witnessed by the EDX data that correlate with the XRD data (see Fig. 3). The distribution of the intensity in the diffractogram, shown in Fig. 4b, may be caused by the even increased amount of Fe (Fe<sub>3</sub> $O_4$ or  $Fe_2O_3$ ) in the sample, in the form of ultra dispersive ~1 nm size nanoparticles with the amorphous (X-ray amorphous) structure, which is the matter they are not detected in the diffractogram. The presence of diatomite in all the diffractograms (Fig. 4a,b) was detected by the same variation of the background intensity and the superimposed broad diffraction peak around  $2\theta = 22^{\circ}$ , which can be attributed to the amorphous SiO<sub>2</sub>, as the main component phase of diatomite. To explain the revealed phenomenon of total suppression of the free carbon formation in the forms of CNWs (or MWCNTs) in the process of the DRM reaction using the granulated diatomitebased catalyst systems with the bioxide catalysts,



Fig. 4. Series of wide-angle XRD patterns of granulated diatomite carrier-based catalyst samples with (a) – (NiO-Co<sub>3</sub>O<sub>4</sub>) and (b) – (NiO-Fe<sub>2</sub>O<sub>3</sub>) catalysts recorded before (patterns-1) and after (patterns-2) the DRM reaction.



Fig. 5. The series of peaks of carbon KLL differential Auger-electron spectra recorded from the samples of granulated diatomite carrier-based catalyst systems with (a) - (NiO-Co<sub>3</sub>O<sub>4</sub>) and (b) - (NiO-Fe<sub>2</sub>O<sub>3</sub>) catalysts, recorded before (curves-1) and after (curves-2) the DRM reaction.

and to determine the type of surface carbon species, the samples examined by the SEM-EDX techniques were additionally tested using the Auger-electron spectroscopy (AES).

In Fig. 5a,b the series of peaks of carbon KLL differential AES spectra are shown which were obtained from the surfaces of the samples of the above catalyst systems in the 200-300 eV energy range after removing ~200Å thickness anti-charging gold coating from the surfaces of the investigated samples via bombardment of the analyzed area with the argon ions of 2 KeV energy.

Consequently, the AES peaks (curves-1) represent the state of the physical surface of the fresh catalyst systems before the deposition of gold coating, while the AES peaks presented in the curves-2 characterize the state of the surface composition of the spent catalyst systems' samples after the DRM reaction. The latter (Fig. 5a,b) demonstrates the clearly expressed peculiarities of the fine structure (shape, energetic displacement of main and plasmon peaks, and their intensity ratio) of the first derivative of carbon atoms' KLL Auger-transition peaks, typical to the short-range order polyvariant configuration of carbon atoms' groups which can exist in sp<sup>3</sup>, sp<sup>2</sup>, and mixed (sp<sup>3</sup> + sp<sup>2</sup>) electronic hybridizations.

### 4. Conclusions

Thus, for the first time, natural diatomite from deposits in Georgia have been investigated as support

for NiO-Co<sub>3</sub>O<sub>4</sub> and NiO-Fe<sub>2</sub>O<sub>3</sub> systems. The catalysts NiO-Co<sub>3</sub>O<sub>4</sub>/D and NiO-Fe<sub>2</sub>O<sub>3</sub>/D were tested in dry reforming of methane in the temperature range 500-850 °C. The results showed that the NiO-Co<sub>3</sub>O<sub>4</sub>/D catalyst is more active and stable than NiO-Fe<sub>2</sub>O<sub>3</sub>/D. At the reaction temperature 850 °C the conversion of methane on the NiO-Co<sub>3</sub>O<sub>4</sub>/D catalyst was 77%, whereas on the NiO-Fe<sub>2</sub>O<sub>3</sub>/D – 42%.

The activity of the NiO-Co<sub>3</sub>O<sub>4</sub>/D catalyst in the reaction is probably due to the high dispersity of the catalyst particles. The results of SEM-EDX, XRD, AES showed that cobalt oxide in the composition of NiO-Co<sub>3</sub>O<sub>4</sub>/D is in the form of nanoparticles with sizes much smaller than the sensitivity threshold of X-ray diffraction analysis (<100Å).

It was shown that the developed granulated diatomite carrier-based NiO-Co<sub>3</sub>O<sub>4</sub>/D new catalyst system with the bioxide 3 mas.% NiO-based catalyst, with the determined optimal ratio of components, exhibits superior carbon/coke resistance, among others because of its ability of total suppression of the free carbon formation process in the form of MWCNTs (or CNWs) in the wide range of temperatures during the DRM reaction.

In future studies of the dry methane reforming catalyst, the inevitable deposition of carbon on the surface is still a major problem. The use of low cost porous supports and proper catalyst activation/ calcination procedure, promoter to metal ratio is the ideal way to avoid deactivation and ensure stable performance of the DRM catalyst.

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# Сравнительное исследование активности в сухом риформинге метана биоксидных систем NiO-Co<sub>3</sub>O<sub>4</sub> и NiO-Fe<sub>2</sub>O<sub>3</sub>, нанесенных на гранулированный природный диатомит

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### АННОТАЦИЯ

В данной работе в качестве катализаторов сухого риформинга метана исследованы каталитические биоксидные системы NiO-Co<sub>3</sub>O<sub>4</sub> и NiO-Fe<sub>2</sub>O<sub>3</sub>, нанесенные на гранулированный природный диатомит месторождения Грузия. Результаты показали, что катализатор NiO-Co<sub>3</sub>O<sub>4</sub>/D более активен и стабилен, чем NiO-Fe<sub>2</sub>O<sub>3</sub>/D. При температуре реакции 850 °C конверсия метана на катализаторе NiO-Co<sub>3</sub>O<sub>4</sub>/D составила 77%, тогда как на NiO-Fe<sub>2</sub>O<sub>3</sub>/D - 42%. Активность катализатора NiO-Co<sub>3</sub>O<sub>4</sub>/D в реакции, вероятно, обусловлена высокой дисперсностью частиц катализатора. Результаты SEM-EDX, XRD, AES показали, что оксид кобальта в составе NiO-Co<sub>3</sub>O<sub>4</sub>/D находится в виде наночастиц с размерами, значитель-

но меньшими порога чувствительности рентгеноструктурного анализа (<100Å).

*Ключевые слова:* метан, диоксид углерода, риформинг, синтез-газ, оксидный катализатор, носитель, природный диатомит.

# Түйіршіктелген табиғи диатомиттерге отырғызылған NiO-Co<sub>3</sub>O<sub>4</sub> және NiO-Fe<sub>2</sub>O<sub>3</sub> биоксидтік жүйелерінің метанның құрғақ реформингінде белсенділігін салыстырмалы зерттеу

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#### АҢДАТПА

Бұл жұмыста метанның құрғақ риформингінің катализаторлары ретінде Грузия кен орнындарының түйіршіктелген табиғи диатомитіне отырғызылған NiO-Co<sub>3</sub>O<sub>4</sub> және NiO-Fe<sub>2</sub>O<sub>3</sub> каталитикалық биоксидті жүйелері зерттелді. Нәтижелер NiO-Co<sub>3</sub>O<sub>4</sub>/D катализаторының NiO-Fe<sub>2</sub>O<sub>3</sub>/D-ге қарағанда белсендірек және тұрақты екенін көрсетті. Реакция температурасы 850°С болғанда NiO-Co<sub>3</sub>O<sub>4</sub>/D катализаторында метанның конверсиясы 77% болса, NiO-Fe<sub>2</sub>O<sub>3</sub>/D - 42% - ды құрады. NiO-Co<sub>3</sub>O<sub>4</sub>/D катализаторының реакциядағы белсенділігі катализатордың бөлшектерінің жоғары дисперстілігіне байланысты болуы мүмкін. SEM-EDX, XRD, AES нәтижелері NiO-Co<sub>3</sub>O<sub>4</sub>/D құрамындағы кобальт оксиді рентгендік дифракциялық талдаудың сезімталдық шегінен (<100Å) элдекайда аз өлшемдері бар нанобөлшектер түрінде болатынын көрсетті.

*Түйінді сөздер:* метан, көмірқышқыл газы, риформинг, синтез-газ, оксидті катализатор, тасымалдағыш, табиғи диатомит.