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## CARBON DIOXIDE CONVERSION OF METHANE ON $\text{LaNiO}_3$ AND $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$ PEROVSKITE CATALYSTS



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*Perovskite type catalysts are becoming more and more relevant due to their stability to high temperature and sintering in the process of obtaining synthesis gas. Modification of perovskite catalysts with cerium can improve oxygen mobility and intensity of interaction with active metal particles. The purpose of this work is to study the activity of perovskite type catalysts  $\text{LaNiO}_3$  and  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  in the process of carbon dioxide conversion from methane to synthesis gas. Methodology. The catalyst was synthesized by the Pechini method, studied using the X-ray phase method and chromatographic analysis. Results of work. Catalyst  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  prepared by Pechini method can provide almost complete conversion of methane and carbon dioxide gas at the reaction temperature of 850°C ( $X_{\text{CH}_4}$  98%,  $X_{\text{CO}_2}$  93.6%). X-ray phase analysis shows that the synthesized  $\text{LaNiO}_3$  and  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  are oxide catalysts of the perovskite type, and have a typical structure of perovskites, forming phases  $\text{LaNiO}_3$  and  $\text{CeO}_2$ . Conclusion. Studies have shown that varying the temperature of the reaction makes it possible to purposefully control the reaction in the direction of obtaining synthesis gas with a given ratio, to obtain valuable products such as acetic acid, acetic anhydride and ethylene glycol.*

**KEY WORDS:** perovskites, catalysts, conversion, methane, carbon dioxide, synthesis gas, greenhouse gases, ratio

## LaNiO<sub>3</sub> ЖӘНЕ La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> ПЕРОВСКИТТИ КАТАЛИЗАТОРЛАРЫНДА КӨМІРҚЫШҚЫЛ ГАЗЫНЫҢ МЕТАНҒА АЙНАЛУЫ

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*МКК процесінде синтез газын алу үшін перовскит типті катализаторлар жоғары температура мен агрегацияға тұрақтылығына байланысты өзекті бола түсуде. Перовскитті катализаторларды цериймен модификациялау оттегінің қозғалғыштығын және белсенді металл бөлшектерімен әрекеттесу қарқындылығын жақсартуға мүмкіндік береді. Жұмыстың мақсаты: метанның синтез газға көмірқышқылдық конверсиясы процесіндегі перовскитті LaNiO<sub>3</sub> және La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> катализаторларының белсенділігін зерттеу болып табылады. Әдістеме. Катализаторлар Печини әдісімен синтезделді, рентгендік фазалық және хроматографиялық талдау арқылы зерттелді. Жұмыстың нәтижелері. Печини әдісімен дайындалған La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> катализаторы 850°C реакция температурасында (X<sub>CH<sub>4</sub></sub> 98%, X<sub>CO<sub>2</sub></sub> 93,6%) метан мен көмірқышқыл газының толық дерлік түрленуін қамтамасыз ете алады. Рентгендік фазалық талдау синтезделген LaNiO<sub>3</sub> және La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> перовскит типті оксидті катализаторы болып табылатынын және LaNiO<sub>3</sub> және CeO<sub>2</sub> фазаларын құрайтын типтік перовскиттік құрылымға ие екенін көрсетеді. Қорытынды. Зерттеулер көрсеткендей, реакция температурасын өзгерту сірке қышқылы, сірке ангидридi және этиленгликоль сияқты құнды өнімдерді алу үшін берілген қатынаста синтез газын өндіру реакциясын арнайы бақылауға мүмкіндік береді.*

**ТҮЙІН СӨЗДЕР:** перовскиттер, катализаторлар, конверсия, метан, көмірқышқыл газы, синтез газ, парниктік газдар, қатынаста

## УГЛЕКИСЛОТНАЯ КОНВЕРСИЯ МЕТАНА НА ПЕРОВСКИТНЫХ КАТАЛИЗАТОРАХ LaNiO<sub>3</sub> И La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub>

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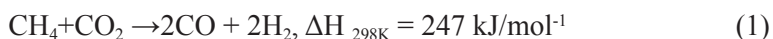
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*Для получения синтез-газа в процессе УКМ катализаторы перовскитного типа все больше приобретают актуальность за счет своей стабильности к высокой температуре и спеканию. Модификация перовскитных катализаторов церием может улучшить подвижность кислорода и интенсивность взаимодействия с частицами активного металла. Целью данной работы является исследование активности катализаторов перовскитного типа LaNiO<sub>3</sub> и La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> в процессе углекислотной конверсии метана до синтез газа. Методология. Катализаторы синтезированы по методу Печини, исследованы с помощью рентгенофазового метода и хроматографического анализа. Результаты работы. Катализатор La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> приготовленный методом Печини,*

может обеспечить почти полную конверсию метана и углекислого газа при температуре реакции 850 °С ( $X_{\text{CH}_4}$  98%,  $X_{\text{CO}_2}$  93,6%). Рентгенофазовый анализ свидетельствует о том, что синтезированные  $\text{LaNiO}_3$  и  $\text{La}_{0,9}\text{Ce}_{0,1}\text{NiO}_3$  являются оксидными катализаторами перовскитного типа, и имеет типичную структуру перовскитов образую фазы  $\text{LaNiO}_3$  и  $\text{CeO}_2$ . Заключение. Исследования показали, что варьирование температуры реакции дает возможность целенаправленного управления реакцией в сторону получения синтез-газа с заданным соотношением, для получения ценных продуктов, таких как уксусная кислота, уксусный ангидрид и этиленгликоль.

**КЛЮЧЕВЫЕ СЛОВА:** перовскиты, катализаторы, конверсия, метан, диоксид углерода, синтез – газ, парниковые газы, соотношение

**I**ntroduction. Excessive global emissions of greenhouse gases ( $\text{CO}_2$ ,  $\text{CH}_4$ , etc.), due to the burning of fossil fuels, especially the oil and gas industry, for the production of energy and electricity, is the main cause of air pollution and the greenhouse effect. Ultimately, this led to many problems, such as climate change and global warming of the earth's atmosphere, which will affect the normal life of people [1]. To reduce the impact of greenhouse gases on the environment, new forms of energy should be applied, such as hydrogen, which is more efficient, cleaner, with higher energy density and can be easily converted into electricity and heat as an environmentally friendly primary energy carrier. Light alkanes (i.e. methane, ethane, propane and butane) can be used to activate industrial plant  $\text{CO}_2$  emissions to produce synthesis gas, which is a key precursor for the production of higher hydrocarbon fuels through Fischer-Tropsch synthesis [2]. Synthesis gas from  $\text{CO}_2$  can be obtained by carbon dioxide conversion of methane (CCM) according to the reaction [3]:



The carbon dioxide conversion of methane leads to the production of  $\text{H}_2/\text{CO}$  close to unity and is of interest both for adjusting the synthesis gas composition and for reducing the carbon footprint of conversion by reducing emissions of the two most common greenhouse gases [4].

Many traditional metal/support catalyst systems, although highly active in the  $\text{CO}_2$  conversion process, deactivate within hours due to surface coke deposition or sintering of active metal clusters. To overcome these problems and withstand the extreme operating temperatures of CCM, active metals can be incorporated into crystalline oxides such as perovskites, pyrochlores, hydroxalicates and hexaaluminates. These metal-containing oxides, after reduction of the active metal, form a finely dispersed active catalyst [5]. Especially perovskites have high thermal stability, which makes them popular candidates for high temperature gas phase reactions. CCM can be catalyzed by metallic nickel, therefore, some perovskite oxides containing Ni cations can be precursors of this reaction [6]. Perovskite type oxide with the general formula  $\text{ABO}_3$  is considered a potential auto exhaust catalyst, where "A" represents an alkali metal or alkaline earth metal and "B" represents a transition metal [7]. Perovskite-type oxides with different physical properties can be synthesized by substituting different metals in positions "A" and "B" and varying the chemical composition [8]. Moradi et al. [9] reported that an A-situ substituted perovskite type oxide exhibits

significant electronic and ionic conductivity at elevated temperatures. In addition, partial "In-situ" substitution improves structural stability and catalytic behavior.

Elements "A" or "B" can be partially replaced by other metallic elements to modify the structure or nature of the oxide in order to increase its catalytic activity. Perovskite-type oxide catalysts are active for the conversion of CO<sub>2</sub> with methane [9].

The most popular systems for carbon dioxide reforming of methane include LaNiO<sub>3</sub>; the formation of various crystalline phase states of LaNiO<sub>3</sub> on the surface makes the composition beneficial for accelerating the CCM reaction and reducing carbon deposits [10,11].

The authors of [12] report that 75% efficiency of CO<sub>2</sub> conversion to gaseous CH<sub>4</sub>/CO<sub>2</sub>/He = 10/10/80 at 700°C can be achieved on a 50 mg LaNiO<sub>3</sub> catalyst at a gas flow rate of 100 ml/min. Early studies have shown the possibility of adding base or noble metals to promote the substitution of La to form La<sub>1-x</sub>M<sub>x</sub>NiO<sub>3</sub> (eg M = Pt, Ce, Sr [8, 9]). The resulting compound has a high resistance to carbon deposition due to the presence of the optimal size of Ni crystallites and a large number of oxygen vacancies. Cerium-promoted catalysts have recently attracted increasing attention due to their high oxygen storage capacity and high oxygen mobility in the lattice. Structural defects in perovskite oxides can be formed by adding other metallic elements to increase its catalytic activity [13].

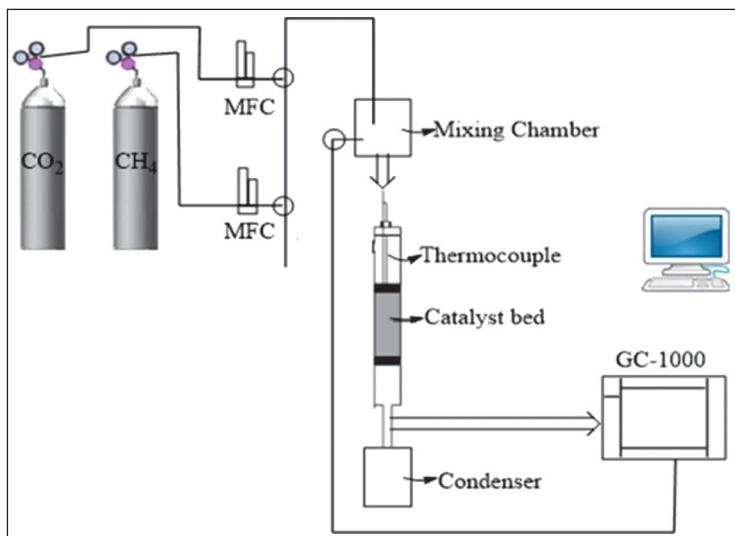
Therefore, the development of efficient and effective CCM catalysts remains an important task.

**Materials and research methods.** Ni(NO)<sub>2</sub> \* H<sub>2</sub>O (technical standard 4055-70); Ce(NO<sub>3</sub>)<sub>3</sub> \* H<sub>2</sub>O (technical standard 6-09-4081-75); La(NO<sub>3</sub>)<sub>3</sub> \* H<sub>2</sub>O; (technical standard 6-09-4676-863); H<sub>2</sub> - purity 99.9%; Ar - purity 99.9%; CH<sub>4</sub> - purity 99.9%, the gases were purchased from MTK "Cryogen", Russia, were used without additional purification.

*Preparation of catalysts.* Catalysts LaNiO<sub>3</sub> and La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> were synthesized by the Pechini method [14]; metal nitrates of the corresponding stoichiometry were used in the synthesis. In particular, 1.6 g La(NO<sub>3</sub>)<sub>3</sub>•6 H<sub>2</sub>O; 0.18 g of Ce(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O and 1.19 g of Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O together with 1.58 g of citric acid are dissolved in 100 ml of water at a ratio of metal cations and citric acid 1:1, designated as a solution A. 1.58 g of citric acid are dissolved in 2 ml of ethylene glycol and designated as solution B. Solution B was added dropwise to solution A. The resulting solution was stirred for 15 minutes at 400 rpm and then heated to 120°C to form a viscous gel and finally a solid precursor was obtained. This product was then transferred to an air calcination oven at 750 °C for 5 hours to obtain the corresponding catalyst samples.

*Studies of the activity and phase composition of catalysts.* The study of the activity of the synthesized catalysts in the process of carbon dioxide conversion of methane was carried out on an automated laboratory unit of the PKU-1 flow type (*Scheme 1*). The tests were carried out in a quartz tubular quartz reactor with an inner diameter of 10 mm and a length of 22-25 cm with a fixed catalyst bed. The catalyst volume was 2 ml. The reactor is vertically located in the furnace. The reactor temperature was set by a temperature controller and controlled by a XA thermocouple, sheathed in quartz and located inside the catalyst layer. The mixed initial gas mixture (CH<sub>4</sub>+CO<sub>2</sub>=1:1) was fed at a rate of 50 cm<sup>3</sup>/min into a quartz reactor with a catalyst on top. Further, the remainder of the initial reagent and the reaction products are sent online for analysis to the Chromos GC - 1000

chromatograph equipped with a thermal conductivity detector and a flame ionization detector for identification. Before starting the reaction, the catalysts were reduced at 500°C for 3 hours in a flow of H<sub>2</sub> and Ar at a total gas flow rate of 20 ml/min.



Scheme 1 - Flow catalytic plant

The catalysts were tested in the temperature range of 500-850°C with  $W=1000 \text{ h}^{-1}$ , the ratio of reagents (CH<sub>4</sub>:CO<sub>2</sub>) was maintained equal to 1:1 at a total gas mixture flow of 33.3 ml/min, at atmospheric pressure. The conversions of CH<sub>4</sub>, CO<sub>2</sub> and the yields of H<sub>2</sub>, CO were calculated as follows [9]:

$$\% \text{ conversion } CH_4 = \frac{[n(CH_4)_{in} - n(CH_4)_{out}]}{[n(CH_4)_{in}]} * 100 \quad (2)$$

$$\% \text{ conversion } CO_2 = \frac{[n(CO_2)_{in} - n(CO_2)_{out}]}{[n(CO_2)_{in}]} * 100 \quad (3)$$

$$Y_{H_2} \% = \frac{[n(H_2)_{out}]}{[2n(CH_4)_{in}]} * 100 \quad (4)$$

$$Y_{CO} \% = \frac{[n(CO)]}{[n(CO_2)_{\text{на входе}} + n(CH_4)_{\text{на входе}}]} * 100 \quad (5)$$

$$\frac{H_2}{CO} = \frac{n_{out}(H_2)}{n_{out}(CO)} \quad (6)$$

The phase composition of the catalysts was determined using X-ray diffraction analysis on a modernized DRON-3 automated diffractometer with CuK $\alpha$ -radiation,  $\beta$ -filter. Conditions for shooting diffraction patterns: U=35 kV; I=20 mA; shooting  $\theta$ -2 $\theta$ ; detector 2 deg/min.

**Results and discussion.** At the initial stage, the LaNiO<sub>3</sub> and La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> catalysts synthesized by the Pechini method were studied using the X-ray phase method (XRD). Figure 1 shows X-ray diffraction patterns of LaNiO<sub>3</sub> and La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> catalysts. Figure 1

shows that  $\text{LaNiO}_3$  gives diffraction lines characteristic of highly crystalline  $\text{LaNiO}_3$ . The  $\text{LaNi}_2$  and  $\text{La}_2(\text{NiO}_4)$  phases are also observed.

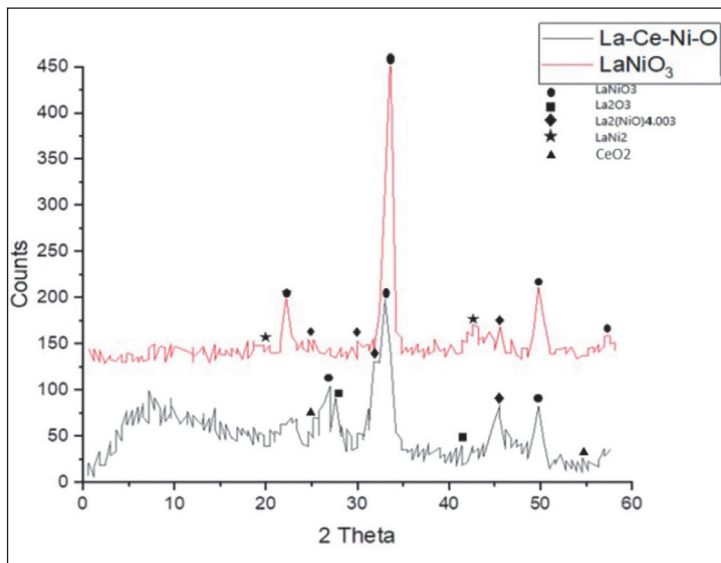


Figure 1 - X-ray patterns of  $\text{LaNiO}_3$  and  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  catalysts

The x-ray diffraction pattern of the  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  catalyst also shows reflections characteristic of the highly crystalline rhombohedral  $\text{LaNiO}_3$  phase, and the formation of diffraction reflections of crystalline  $\text{La}_2\text{O}_3$  phases (JCPDS 22-0369) with a degree of substitution of 0.1 is clearly detected, which is associated with the presence of  $\text{CeO}_2$  oxide, also revealed formation of  $\text{La}_2\text{NiO}_{4.003}$  (JCPDS 81-1962) [15]. The results obtained indicate that the synthesized  $\text{LaNiO}_3$  and  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  are oxide catalysts of the perovskite type. The catalytic activity of  $\text{LaNiO}_3$  and  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  perovskite samples was studied in the CCM process at a space velocity  $W=1000 \text{ h}^{-1}$  and a ratio of  $\text{CH}_4:\text{CO}_2=1:1$  in the temperature range of  $500\text{--}850^\circ\text{C}$ . The results of the influence of the reaction temperature on the conversion of methane and carbon dioxide are shown in Figure 2.

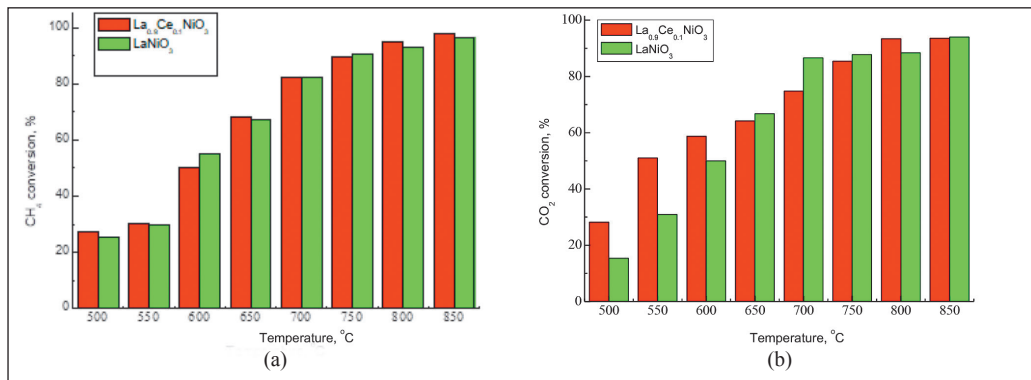


Figure 2 - Influence of reaction temperature on the activity of  $\text{LaNiO}_3$  and  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  catalysts in the CCM process



Figure 2 a, b shows that the conversion of the initial reagents (CH<sub>4</sub> and CO<sub>2</sub>) on perovskite LaNiO<sub>3</sub> and La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> catalysts increases with an increase in the temperature of the CCM process. On the LaNiO<sub>3</sub> catalyst at an initial process temperature of 500°C, the conversion of CH<sub>4</sub> is X<sub>CH<sub>4</sub></sub> = 25.6% and CO<sub>2</sub> - X<sub>CO<sub>2</sub></sub> = 15.4%, the yield of H<sub>2</sub> is 8.8%, the yield of CO is 13.0% and increases, respectively, to 96.4 and 94.0% at 850°C. It should be noted that one of the advantages of using perovskite as a catalyst is that the strong interaction between Ni and La<sub>2</sub>O<sub>3</sub> can prevent metal sintering [16].

Partial substitution of La for Ce in LaNiO<sub>3</sub> increases the activity of the catalyst (La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub>) at relatively low temperatures (500–600°C) of the CCM process. On a Ce-containing catalyst, the conversion of CH<sub>4</sub> at 500°C is X<sub>CH<sub>4</sub></sub> = 27.6 and CO<sub>2</sub>-X<sub>CO<sub>2</sub></sub> = 28.2%, the yield of H<sub>2</sub> is 8.5%, the yield of CO is 11.2%. At 600°C, the conversion of methane and carbon dioxide is - X<sub>CH<sub>4</sub></sub> = 50.2 and X<sub>CO<sub>2</sub></sub>=58.8%, the yield of hydrogen and carbon monoxide YH<sub>2</sub> = 27.8 (600 °C) and Y<sub>CO</sub>=23.2%, respectively.

Figure 3 shows the results of the influence of the reaction temperature on the H<sub>2</sub>/CO ratio in the reaction products of CCM on LaNiO<sub>3</sub> and La<sub>0.9</sub>Ce<sub>0.1</sub>NiO<sub>3</sub> catalysts. It can be seen from the obtained data that when the reaction temperature is varied from 500 to 850°C, the H<sub>2</sub>:CO ratio in the reaction products changes from 0.6 to 1.5. The ratio of target products in the temperature ranges of 575-600 and 750-800°C is closer to 1.0 on both catalysts. The maximum ratio H<sub>2</sub>:CO=1.5 is achieved on the LaNiO<sub>3</sub> catalyst in the temperature range 600-650°C. Synthesis gas, consisting of a mixture of H<sub>2</sub> (47.5%) and CO (42.1%) in various proportions, is an alternative source of feedstock for the petrochemical industry.

As a result of the study, it was determined that varying the reaction temperature in the range from 500 to 850 °C makes it possible to control the reaction in the direction of obtaining synthesis gas with a given ratio, i.e. for the production of acetic acid and acetic anhydride, the ratio H<sub>2</sub>:CO = 1:1 and for the synthesis of ethylene glycol - 1.5:1.0.

Synthesis gas can be effectively used in the power industry for the production of heat and electricity at gas turbine and combined cycle plants and in metallurgy for the reduction of iron ores.

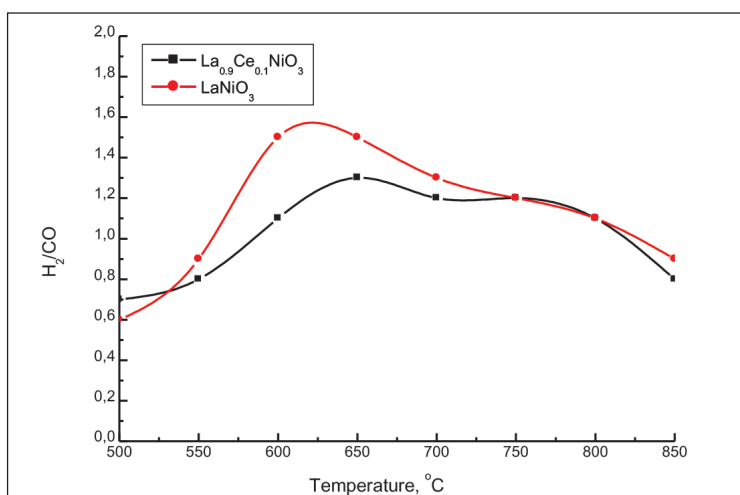



Figure 3 - Influence of the reaction temperature on the H<sub>2</sub>/CO ratio in the CCM process

The obtained results indicate that the cerium-modified  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  perovskite-type catalyst exhibits increased activity at relatively low temperatures (500–600 and 800°C) compared to the  $\text{LaNiO}_3$  perovskite catalyst. The activity of the  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  catalyst can be explained by the fact that it provides a larger number of oxygen atoms for the reaction with the adsorbed CH group to form CHO and further dissociation of CHO into CO and  $\text{H}_2$ , which agrees with the data of. According to the authors of, partial replacement of  $\text{La}^{3+}$  by  $\text{Ce}^{4+}$  leads to a higher conversion of  $\text{CH}_4$  and  $\text{CO}_2$  due to the redox properties of cerium, which contributes to the disproportion of  $\text{CO}_2$  on oxygen vacancies generated by cerium, providing a greater number of oxygen species that oxidize carbon on the surface. It is also noted in [17] that the partial replacement of the metal in positions “A” and “B” with some other metals (for example, Ca, Sr, Co, Ce, Pt, etc.) in a perovskite catalyst suppresses carbon deposition after by increasing the number of oxygen vacancies, and also increases the structural stability and catalytic activity of oxides due to the synergistic effect.

**Conclusions.** Thus, modern literature data on the influence of the nature of perovskite catalytic systems on the carbon dioxide conversion of methane were analyzed and possible ways of improving perovskite catalysts for the production of synthesis gas from two greenhouse gases ( $\text{CH}_4$  and  $\text{CO}_2$ ) were discussed.

Oxide catalysts  $\text{LaNiO}_3$  and  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  were prepared by the Pechini method and, according to XRD data, they are oxide catalysts of the perovskite type. The study of the activity of catalysts in the process of CCM to synthesis gas showed that the conversion on perovskite  $\text{LaNiO}_3$  and  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  catalysts of the initial reagents  $\text{CH}_4$  and  $\text{CO}_2$  increases with an increase in the reaction temperature from 500 to 850°C. It has been established that the addition of cerium to the composition of  $\text{LaNiO}_3$  leads to an increase in catalytic activity in the CCM process at low temperatures (500-650°C). At a reaction temperature of 500°C, the conversion of  $\text{CH}_4$  and  $\text{CO}_2$  on  $\text{La}_{0.9}\text{Ce}_{0.1}\text{NiO}_3$  is  $X_{\text{CH}_4} = 27.6$  and  $X_{\text{CO}_2} = 28.2\%$ , the yield of  $\text{H}_2$  is - 8.5%, the yield of CO is -11.2%.

It is shown that when the reaction temperature is varied from 500 to 850°C, the  $\text{H}_2/\text{CO}$  ratio in the reaction products of CCM changes from 0.6 to 1.5. As a result of the study, it was determined that varying the reaction temperature in the range from 500 to 850 °C makes it possible to control the reaction in the direction of obtaining synthesis gas with a ratio of  $\text{H}_2:\text{CO} = 1:1$  and 1.5:1.0. Synthesis - gas with a ratio of  $\text{H}_2/\text{CO}=1:1$  is used to produce acetic acid and acetic anhydride, and for the synthesis of ethylene glycol -  $\text{H}_2/\text{CO}=1.5:1$ .

Perovskite-type catalysts for utilizing greenhouse gases  $\text{CH}_4$  and  $\text{CO}_2$  with the production of valuable hydrogen products and/or synthesis gas with various  $\text{H}_2/\text{CO}$  ratios open up great prospects for application and are in demand. 

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