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АО «ИНСТИТУТ ТОПЛИВА, КАТАЛИЗА И
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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DEVELOPMENT OF COMPOSITE MATERIALS BY COMBUSTION SYNTHESIS METHOD FOR CATALYTIC REFORMING OF METHANE TO SYNTHESIS GAS

Abstract. In the modern world, natural gas is the main source for obtaining synthesis-gas from methane. Production of synthesis-gas is constantly improved, as the demand for this raw material in the petrochemical industry is growing every year. Also, synthesis gas is used as an environmentally friendly source of heat and energy. Therefore, finding ways to activate CH_4 for synthesis of products is an important task of petrochemical industry. La – Mg – Mn – Ni - Al catalysts were prepared by the self-propagating high-temperature synthesis method, namely its modern modification - the solution combustion synthesis. The optimum content of metals in the catalyst was determined by varying the ratio of elements in samples. The conditions for conversion of methane to synthesis-gas were determined. It was found that the highest results on oxidative conversion to synthesis-gas can be obtained at 900°C and a space velocity of 2500 h^{-1} over 5% La + 10% Mg + 5% Mn + 20% Ni + 10% Al + 50% glycine catalyst. The catalysts were examined by a complex of physical and chemical methods, as a result of which it was established that a number of changes occur in the catalyst structure during the testing in a flowing catalytic installation. It has been shown that simple and mixed oxides, metal aluminates and spinel-type structures, the presence of which promotes the active work of catalysts for the oxidative conversion of methane, are present in the catalyst. In addition, elastic carbon nanotubes wrapped in a spiral with diameters of 40 - 50 - 70 nm were detected on the surface.

Key words: methane, hydrogen, synthesis gas, self-propagating high-temperature synthesis, solution combustion.

Introduction

Continuous increase in fuel consumption in the energy sector, in various branches of the chemical, petrochemical industry and transport leads to an increase in the volume of harmful substances entering the atmosphere. This is becoming more urgent due to the toughening of the requirements to the quality of the produced base and raw intermediate products of the petrochemical industry [1-4]. Therefore, studies aimed at developing of various catalysts for the complex treatment of gas emissions of industry, as well as catalysts that work effectively in the field of synthesis-gas production under more favorable conditions, are strategically important [5-9].

It is known that the activity of multicomponent catalysts is a complex function of the chemical composition and parameters of the micro- and macrostructure. Nature of the active centers, dispersion of the active components, morphology of the surface, presence of microstrains and defects in the structure are determined by the conditions of synthesis and subsequent heat treatment of the samples. Therefore, an intensive search of new methods for the preparation of catalysts for production of synthesis-gas has been carried out recently [10-14].

Solution combustion synthesis (SCS), self-propagating high-temperature synthesis (SHS) and other methods of preparation, in which the energy of exothermic reactions is used to prepare the active components of catalysts, relate to such promising methods [15-19]. The main advantages of these methods are: low energy costs, short synthesis times, no need for expensive equipment, the possibility of a one-stage conversion of inorganic materials to final products using chemical reaction energy, an increase in non-stoichiometric phases of products due to high thermal gradient and rapid cooling rate [20-22].

Experimental

Catalyst preparation

Nitric acid salts of various metals, in particular: lanthanum (III) nitrate, manganese (II) nitrate, magnesium nitrate, nickel nitrate, aluminum nitrate, and glycine were used to synthesize the desired catalysts. Preliminary calcination and treatment of salts were not performed. All used salts were weighed and thoroughly mixed in an agate mortar. Then the mixture of salts was placed in a quartz glass, into which 10 ml of distilled water, preheated to 80°C, was poured. The glass with the solution was transferred to the muffle furnace, preheated to 500°C, after complete dissolution of all salts. After 5-8 minutes, enough heat is generated to ensure the propagation of the combustion front, advancing with high speed and self-generation of heat. This leads to a sharp increase in temperature. The temperature inside the reaction front is so high that impurities with a low boiling point is evaporated, facilitating the production of more pure products. As a result, structures with a high concentration of defects of intermediate and non-stoichiometric compounds, which are one of the reasons for the high activity of SCS catalysts, are formed. After cooling, the catalysts were placed in a glass weighing bottles for storage.

Characterization techniques

Studies of the developed catalysts were carried out by various methods: elemental analysis, X-ray phase analysis (XRD), transmission electron microscopy on an EM-125K device. These analyzes were performed both before and after the tests of the synthesized catalysts in reactor of the flowing catalytic unit (FCU-1). Composition of the initial reaction mixture and reaction products was studied on the "Chromos GC-1000" chromatograph with "Chromos" computer software. XRD analysis was carried out on a DRON-4-0.7 diffractometer with CoKα radiation in the range of angles $2\theta = 6 - 100°$. Conditions for conducting of the XRD analysis: initial angle = 6.00; end angle = 100.00; step = 0.020; exposure dose = 0.6; speed = 2 g/min; the maximum number of pulses is 821. Samples were studied by the method of shooting to lumen in the form of dry suspensions using microdiffraction on the EM-125K transmission electron microscope.

Catalytic reaction

A series of samples with various components in the La – Mg – Mn – Ni - Al catalyst was prepared by solution combustion synthesis method. The activity of the developed catalysts in the reaction of oxidative conversion of methane by oxygen was determined in a flowing catalytic unit FCU-1 at atmospheric pressure in a quartz reactor at the temperature range from 600 to 900°C. For the studies, a mixture of gases $CH_4 : O_2 : Ar = 2 : 1 : 2.8$, $CH_4 : O_2 : Ar = 34\ \% : 17\ \% : 49\ \%$ was used.

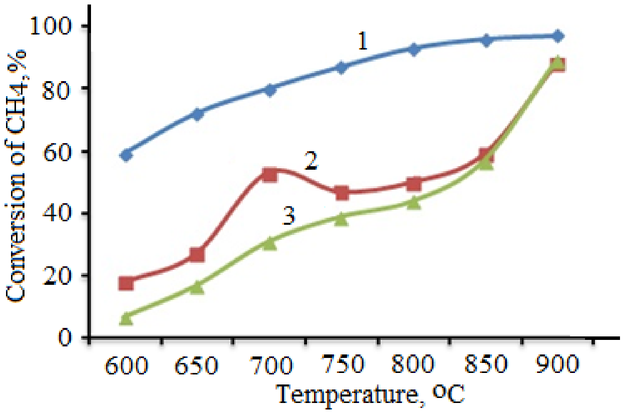
Results and discussion

The following optimal conditions: a space velocity (GHSV) 2500 h^{-1} in the 600 - 900°C temperature range were selected to determine the activity of La – Mg – Mn – Ni - Al catalysts after careful study of the literature data. In the process of repeatability tests, it was established that the maximum yield of methane to synthesis-gas is reached at 900°C. Table 1 shows the results of CO and H_2 yields for each catalyst with a specific set of metals. It is seen from the Table 1 that 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst is the most active with CO and H_2 yield up to 21 % and 65 %, respectively.

Table 1 - Catalysts prepared by SCS method for the oxidation of methane to synthesis gas

No	Chemical composition of catalysts, % wt.	Yield, %	
		CO	H_2
1	5 % La + 20 % Mg + 10 % Mn + 5 % Ni + 10 % Al + 50 % glycine	3	7
2	5 % La + 10 % Mg + 20 % Mn + 5 % Ni + 10 % Al + 50 % glycine	11	44
3	5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine	21	65
4	5 % La + 10 % Mg + 10 % Mn + 5 % Ni + 20 % Al + 50 % glycine	10	42

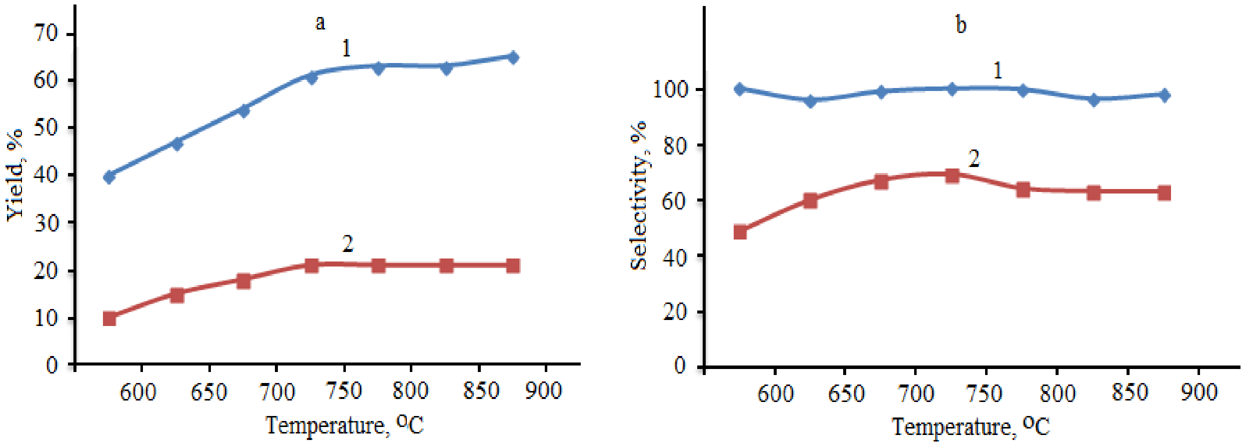
Effect of the variation of space velocity on the process indicators was investigated on the most active 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst. The results of the experiments are shown in Figure 1. As can be seen from Figure 1, the increase in space velocity does not promote the growth of conversion of methane to synthesis gas. This may be due to the fact that the gas does not have time to come into contact with catalyst to convert organic molecule to the target products in the process of increasing the space velocity.



GHSV, h^{-1}: 1 – 2500, 2 – 4500, 3 – 6500.

Figure 1 - Conversion of methane over the 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst at different space velocities

The following graphs in Figure 2 show that the highest yields of H_2 (65 %), CO (21 %) with selectivity for H_2 (98 %) and CO (63 %) are achieved at a space velocity of 2500 h^{-1}. Optimal yields and selectivities were recorded in the temperature range 800 - 900°C and pressure 0.39 MPa.



a – yield: 1 – H_2, 2 – CO; b – selectivity: 1 – H_2, 2 – CO.

Figure 2 - Effect of the reaction temperature on the yield and selectivity of process over 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst

Figure 3 shows the XRD spectra of 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst. As a result of the obtained data, it was shown that the following phases are present in the catalysts: Ni (reflexes, Å: $2{,}03_{35}$; $1{,}89_{52}$; $1{,}76_{12}$; $1{,}26_{94}$; $1{,}24_{53}$ – ASTM, 4-850); MgO periclase (reflexes, Å: $2{,}51_{54}$; $2{,}41_{82}$; $1{,}48_{52}$; $1{,}36_{26}$; $1{,}33_{04}$; $1{,}21_{59}$ - ASTM, 4-829); La_2NiO_4 (reflexes, Å: $3{,}78_{75}$; $3{,}12_{40}$; $2{,}90_{15}$; $2{,}72_{66}$; $2{,}18_{71}$; $2{,}09_{67}$; $1{,}68_{77}$; $1{,}65_{20}$ – ASTM, 34-314); and Mn_3O_4 (low-intensity reflexes, Å: $5{,}04_{11}$; $2{,}53_{84}$; $3{,}33_{03}$ – ASTM, 4-732).

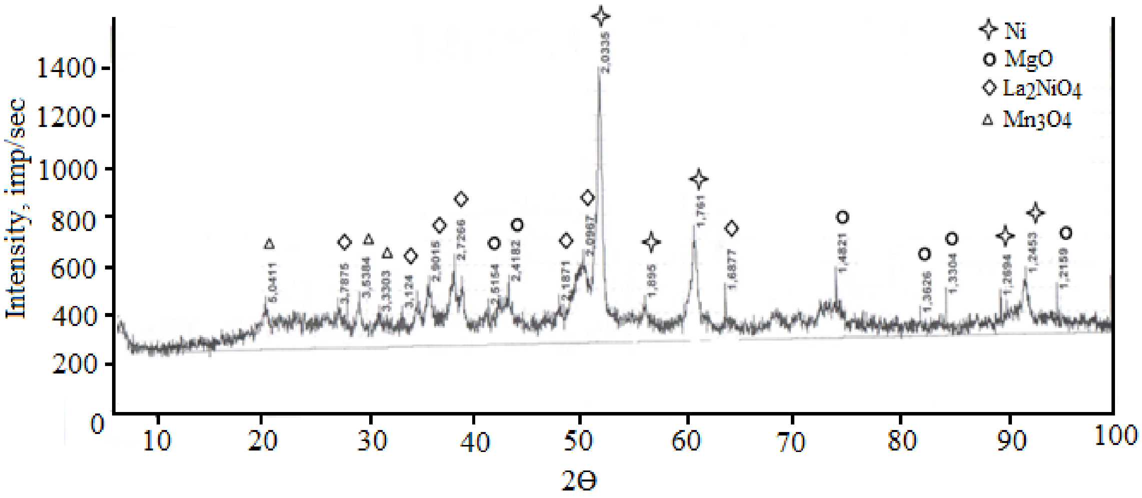


Figure 3 - XRD spectrum of the 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst

In the course of the study, the transmission electron microscope showed the results for the 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst before and after investigations on flow catalytic unit FCU-1. Figure 4a shows the accumulation of large particles isothermal shape with a size of 100 - 500 nm. The microdiffraction pattern is represented by a small set of reflexes, which can be attributed to $MgNiO_2$ (JSPDS, 24-712). Figure 4b shows an aggregate of large semitransparent particles with a size of 70 - 100 nm or more. However, small amorphous particles with a size of 10 - 15 nm are visible inside these particles on translucent edges. The microdiffraction pattern is represented by a small set of reflexes arranged in rings, which can be attributed equally to $Al_9N_7O_3$ (JSPDS, 35-830) or possibly to $LaAl_{11}O_{18}$ (JSPDS, 33-699).

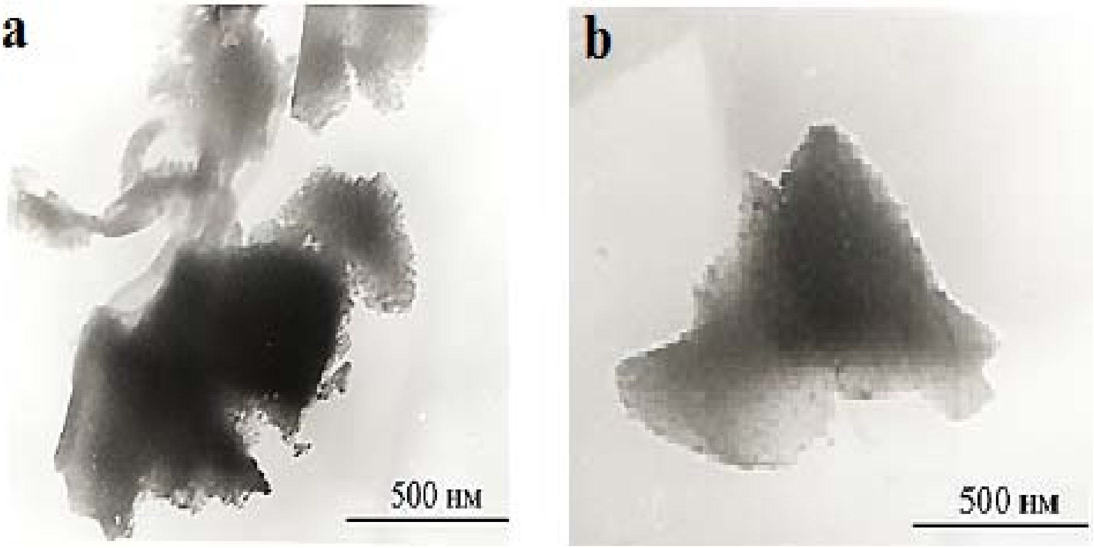


Figure 4 - TEM images of the 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst before the tests

Properties of catalysts after testing on the FCU-1 installation were studied repeatedly. The presence of carbon nanotubes was detected during the transmission electron microscope analysis. Nanotubes are elastic, often wrapped in a spiral, whose diameters reach 40 - 50 - 70 nm, Figure 5.

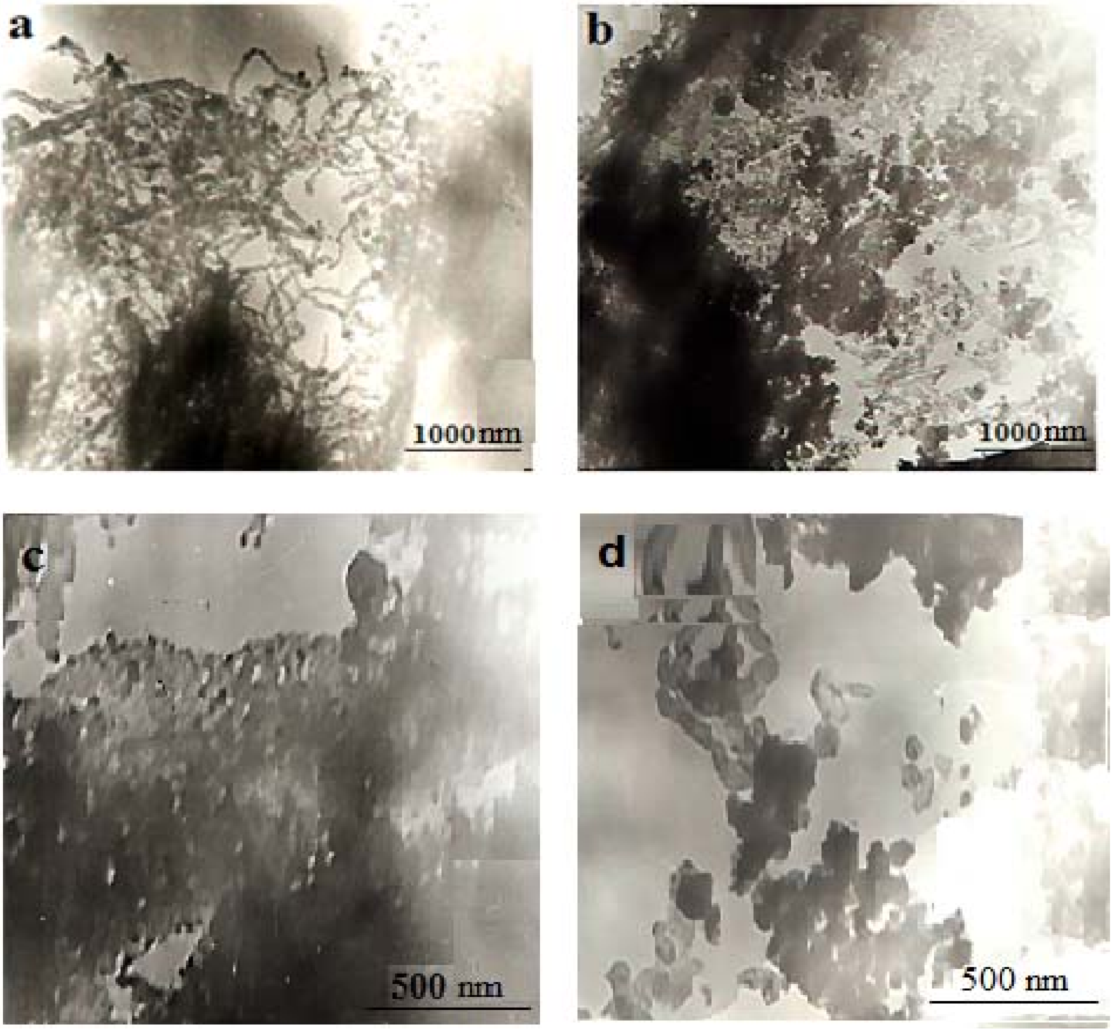


Figure 5 – TEM images of the 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst after tests

Figures 5a and 5b, presented at low magnification, show the accumulation of carbon nanotubes and dense round-shaped particles with a size of 50 - 70 - 100 nm. The microdiffraction pattern is represented by a large set of rings and reflexes corresponding to δ-$MgAl_{26}O_{40}$ (JSPDS, 20-660), it is possible presence of the La_2O_3 (JSPDS, 24-554) and LaN (JSPDS, 15-892) in mixture. Figure 5b shows a small aggregate of dense particles 60 - 100 nm in size (there are nanotubes), which can be attributed to $LaAl_{11}O_{18}$ (JSPDS, 33-699).

Figures 5c and 5d show aggregates of various shapes and densities with particle sizes from 10 - 20 to 50 - 100 nm. The diffraction pattern is represented by a large set of rings and reflexes and can be attributed to phase mixtures of Mg_2NiH_4 (JSPDS, 36-916), $NiLa_2O_4$ (JSPDS, 11-557), HNi_2 (JSPDS, 33-606), Mg_2C_3 (JSPDS, 1-1138), Al_2O_3 (JSPDS, 33-699), $La_2MnAl_{11}O_{19}$ (JSPDS, 36-1317) and MgO (periclase) (4-829).

5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst was investigated on a scanning electron microscope; the elemental composition of sample was established during the analysis. Figure 6 illustrates the results of these analyzes.

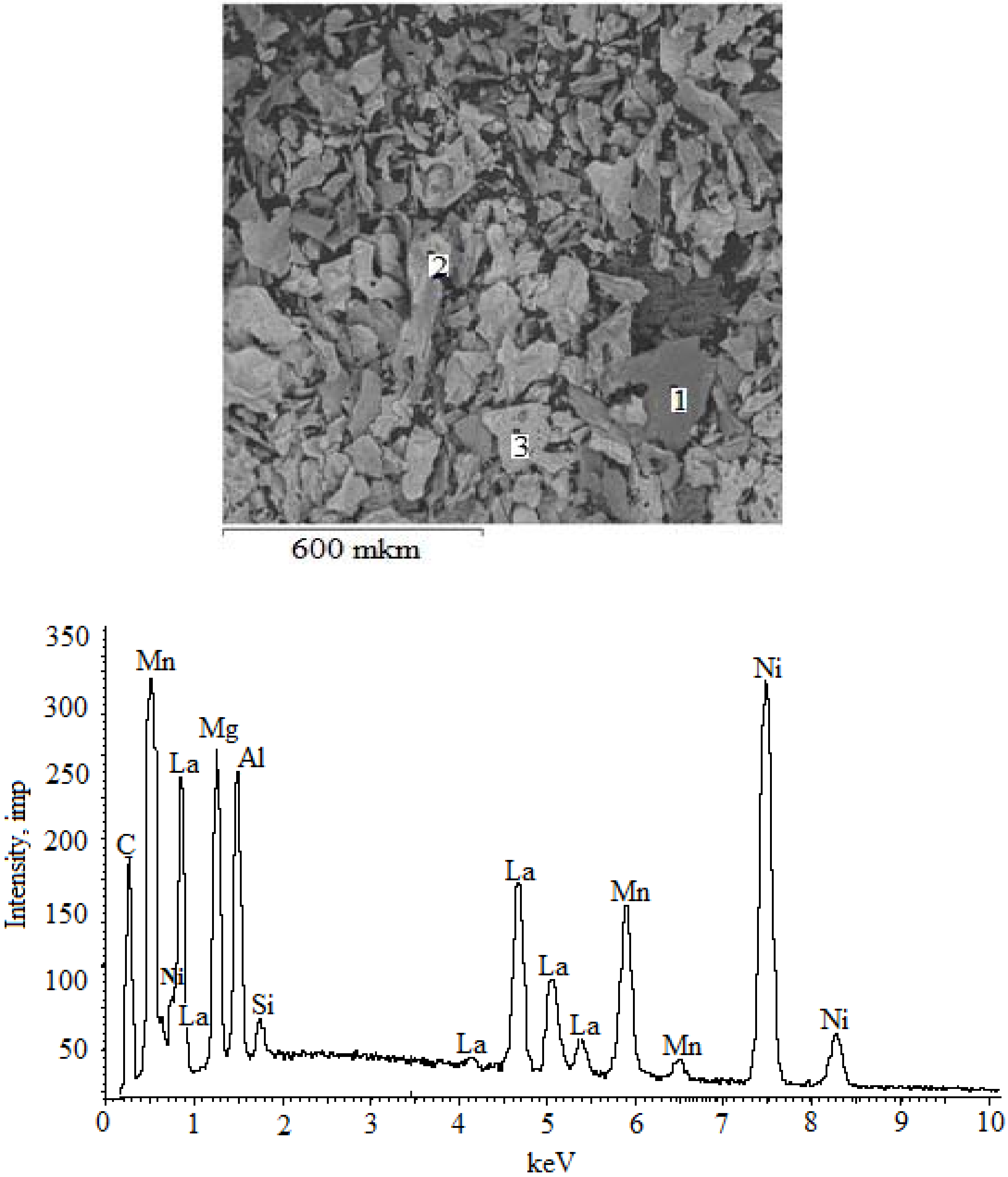


Figure 6 - SEM images of the 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst before the tests

The results of elemental analysis for catalyst at the points indicated in the images correspond to the experimental data. It was shown that the surface of catalyst is not homogeneous.

Figure 7 shows the results of the sample analysis on a scanning electron microscope after the tests. According to elemental analysis, only a decrease in oxygen was detected, as well as a lack of nitrogen in the sample. This is connected, apparently, with the fact that their volatilization from the catalyst occurs at high temperatures. The percentage of nickel and lanthanum increased, which indicates the compaction of these components in the mass of catalyst.

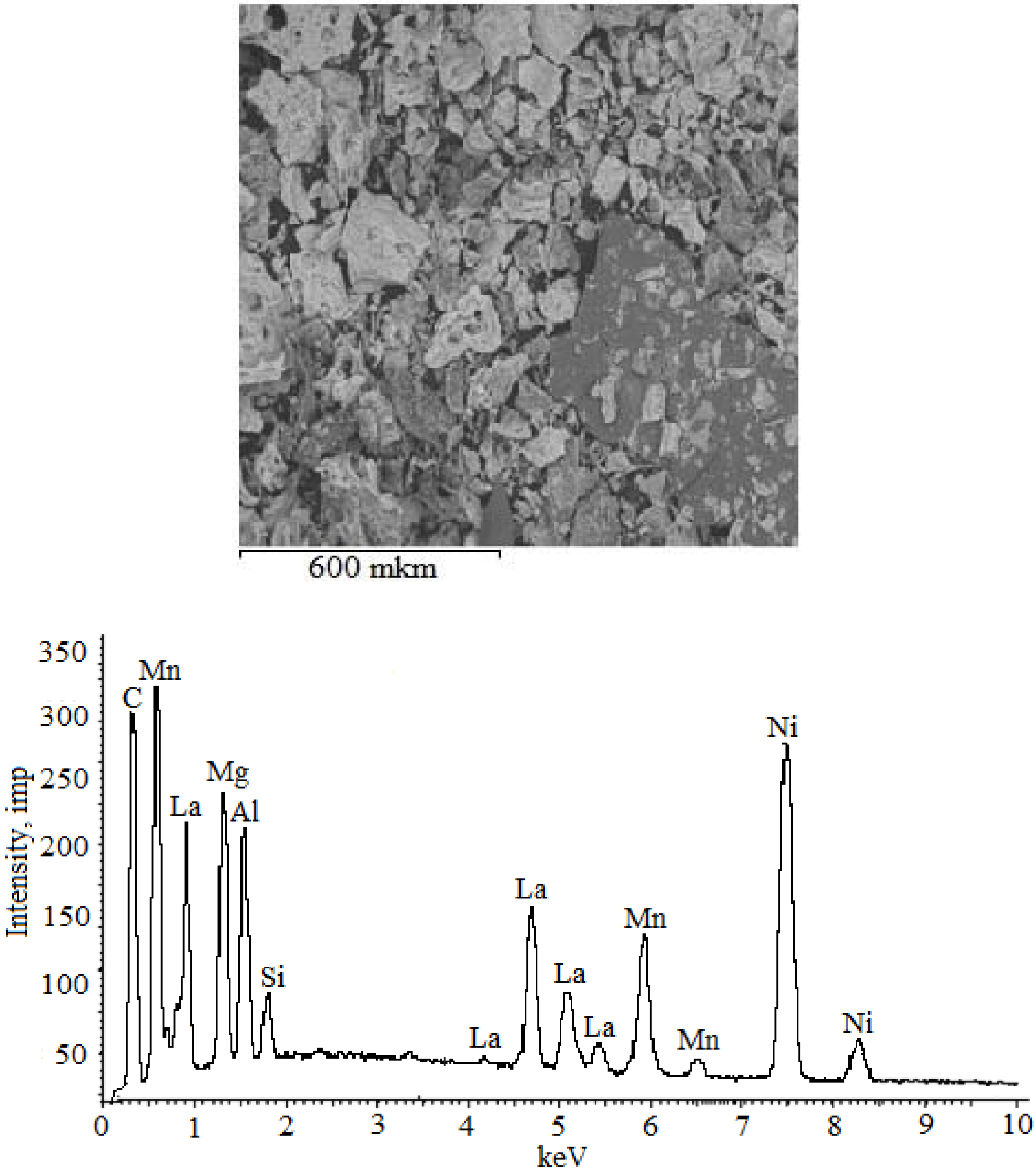


Figure 7 - SEM images of the 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al + 50 % glycine catalyst after the tests

Conclusion

Based on the results of the tests, the following conclusions can be drawn:

- 5 % La + 10 % Mg + 5 % Mn + 20 % Ni + 10 % Al catalyst was the most active for conversion of methane to synthesis gas from numerous combinations of catalysts with the following set of La – Mg – Mn – Ni - Al components prepared by solution combustion synthesis;
- space velocity of 2500 h^{-1} at temperature of 900°C are optimal conditions for the active operation of this catalyst;
- the presence of simple and mixed oxides, metal aluminates and spinel-type structures in the catalyst, the presence of which promotes their active work in the process of oxidative conversion of methane, was established by TEM and SEM research. The presence of carbon nanotubes was also established. Nanotubes are elastic, often wrapped in a spiral with diameters of 40 - 50 - 70 nm.

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REFERENCES

[1] Hiblot H, Ziegler-Devin I, Fournet R, Glaude PA (**2016**) Steam reforming of methane in a synthesis gas from biomass gasification, Int J Hydrogen Energ, 41:18329-18338. http://dx.doi.org/10.1016/j.ijhydene.2016.07.226 (in Eng).

[2] Angeli SD, Turchetti L, Monteleone G, Lemonidoua AA (**2016**) Catalyst development for steam reforming of methane and model biogas at low temperature, Appl Catal B: Environ, 181:34–46. https://doi.org/10.1016/j.apcatb.2015.07.039 (in Eng).

[3] Kho ET, Scott J, Amal R (**2016**) Ni/TiO_2 for low temperature steam reforming of methane, Chem Eng Sci, 140:161–170. https://doi.org/10.1016/j.ces.2015.10.021 (in Eng).

[4] Dedov AG, Loktev AS, Komissarenko DA, Parkhomenko KV, Roger A-C, Shlyakhtin OA, Mazo GN, Moiseev II (**2016**) High-selectivity partial oxidation of methane into synthesis gas: the role of the red-ox transformations of rare earth-alkali earth cobaltate-based catalyst components, Fuel Process Technol, 148:128–137. https://doi.org/10.1016/j.fuproc.2016.02.018 (in Eng).

[5] Palcheva R, Olsbyea U, Palcut M, Rauwel P, Tyuliev G, Velinov N, Fjellvag HH (**2015**) Rh promoted $La_{0.75}Sr_{0.25}(Fe_{0.8}Co_{0.2})_{1-x}Ga_xO_3$-perovskite catalysts: Characterization and catalytic performance for methane partial oxidation to synthesis gas, Appl Surf Sci, 357:45-54. http://dx.doi.org/10.1016/j.apsusc.2015.08.237 (in Eng).

[6] Rogatis LD, Mortini T, Cognigni A, Olivi L, Fornasiero P (**2009**) Methane partial oxidation on NiCu-based catalysts, Catal Today, 145:176-185. https://doi.org/10.1016/j.cattod.2008.04.019 (in Eng).

[7] Makarshin LL, Sadykov VA, Andreev DV, Gribovskii AG, Privezentsev VV, Parmon VN (**2015**) Syngas production by partial oxidation of methane in a microchannel reactor over a $Ni–Pt/La_{0.2}Zr_{0.4}Ce_{0.4}O_x$ catalyst, Fuel Process Technol, 131:21-28. https://doi.org/10.1016/j.fuproc.2014.10.031 (in Eng).

[8] Dedov AG, Loktev AS, Komissarenko DA, Mazo GN, Shlyakhtin OA, Parkhomenko KV, Kiennemann AA, Roger AC, Ishmurzin AV, Moiseev II (**2015**) Partial oxidation of methane to produce syngas over a neodymium–calcium cobaltate-based catalyst, Appl Catal A, 489:140–146. https://doi.org/10.1016/j.apcata.2014.10.027 (in Eng).

[9] Peymani M, Alavi SM, Rezaei M (**2016**) Preparation of highly active and stable nanostructured Ni/CeO_2 catalysts for syngas production by partial oxidation of methane, Int J Hydrogen Energ, 41:6316-6325. https://doi.org/10.1016/j.ijhydene.2016.03.033 (in Eng).

[10] Vella LD, Specchia S (**2011**) Alumina-supported nickel catalysts for catalytic partial oxidation of methane in short-contact time reactors, Catal Today, 176:340-346. doi:10.1016/j.cattod.2010.11.068 (in Eng).

[11] Kim HW, Kang KM, Kwak H-Y (**2009**) Preparation of supported Ni catalysts with a core/shell structure and their catalytic tests of partial oxidation of methane, Int J Hydrogen Energ, 34:3351–3359. doi:10.1016/j.ijhydene.2009.02.036 (in Eng).

[12] Zhang J, Jin L, Li Y, Hu H (**2013**) Ni doped carbons for hydrogen production by catalytic methane decomposition. Int. J. Hydrogen Energy. 38:3937-3947. https://doi.org/10.1016/j.ijhydene.2013.01.105 (in Eng).

[13] González-Cortés SL, Imbert FE (**2013**) Fundamentals, properties and applications of solid catalysts prepared by solution combustion synthesis (SCS), Appl Catal A, 452:117–131. http://dx.doi.org/10.1016/j.apcata.2012.11.024 (in Eng).

[14] Kirillov VA, Fedorova ZA, Danilova MM, Zaikovskii VI, Kuzin NA, Kuzmin VA, Krieger TA, Mescheryakov VD (**2011**) Porous nickel based catalysts for partial oxidation of methane to synthesis gas, Appl Catal A, 401:170-175. https://doi.org/10.1016/j.apcata.2011.05.018 (in Eng).

[15] Kaddeche D, Djaidja A, Barama A (**2017**) Partial oxidation of methane on co-precipitated Ni–Mg/Al catalysts modified with copper or iron, Int J Hydrogen Energ, 42:15002-15009. https://doi.org/10.1016/j.ijhydene.2017.04.281 (in Eng).

[16] Khan NA, Kennedy EM, Dlugogorski BZ, Adesina AA, Stockenhuber M (**2014**) Partial oxidation of methane with nitrous oxide forms synthesis gas over cobalt exchanged ZSM-5, Catal Commun, 53:42-46. https://doi.org/10.1016/j.catcom.2014.04.012 (in Eng).

[17] Larimi AS, Alavi SM (**2012**) Ceria-Zirconia supported Ni catalysts for partial oxidation of methane to synthesis gas, Fuel, 102:366-371. https://doi.org/10.1016/j.fuel.2012.06.050 (in Eng).

[18] Tungatarova SA, Dossumov K, Baizhumanova TS, Popova NM (**2010**) Nanostructured supported Pt-, Ru- and Pt-Ru catalysts for oxidation of methane into synthesis-gas, J Alloys Compd, 504: 349–352. doi:10.1016/j.jallcom.2010.04.223 (in Eng).

[19] Lim M-W, Yong S-T, Chai S-P (**2014**) Combustion-synthesized Nickel-based catalysts for the production of hydrogen from steam reforming of methane, Energy Procedia, 61:910-913. https://doi.org/10.1016/j.egypro.2014.11.993 (in Eng).

[20] Kostenko SS, Ivanova AN, Karnaukh AA, Polianczyk EV (**2017**) Conversion of methane to synthesis gas in a non-premixed reversed-flow porous bed reactor: A kinetic modeling, Chem Eng Process, 122:473-486. https://doi.org/10.1016/j.cep.2017.05.014 (in Eng).

[21] Pruksawan S, Kitiyanan B, Ziff RM (**2016**) Partial oxidation of methane on a nickel catalyst: Kinetic Monte-Carlo simulation study, Chem Eng Sci, 147:128-136. https://doi.org/10.1016/j.ces.2016.03.012 (in Eng).

[22] Velasco JA, Fernandez C, Lopez L, Cabrera S, Boutonnet M, Jaras S (**2015**) Catalytic partial oxidation of methane over nickel and ruthenium based catalysts under low O_2/CH_4 ratios and with addition of steam, Fuel, 153:192-201. https://doi.org/10.1016/j.fuel.2015.03.009 (in Eng).

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МЕТАНДЫ СИНТЕЗ ГАЗҒА КАТАЛИТИКАЛЫҚ РИФОРМИНГІЛЕУДЕ ЖАНУ ӘДІСІМЕН КОМПОЗИТТІ МАТЕРИАЛДАРДЫ ЖАСАУ

Аннотация. Қазіргі заманда метаннан синтез-газ алудың негізгі көзі табиғи газ болып табылады. Мұнай-химия өнеркәсібінде синтез-газды өндіру үнемі осы шикізатқа деген қажеттіліктің жыл сайын артуына әкелуде. Сонымен қатар, синтез-газ экологиялық таза жылу және энергия көзі ретінде пайдаланылады. Сондықтан мұнай-химия өнеркәсібінде органикалық синтездің жартылай өнімдерін алу мақсатына бағытталған және метанды белсендіру жолдарын табу маңызды міндет болып табылады. Осыған байланысты жоғарытемпературада өздігінен жану синтезі әдісі, әсіресе оның заманауи түрлендірілген ерітіндіде жану үрдісі бойынша La – Mg – Mn – Ni – Al катализаторлары дайындалды. Зерттеу метанның конверсиясының синтез-газға айналуының оңтайлы жағдайлары және элементтердің қатынасын түрлендіру нәтижесінде катализатордың құрамындағы металдардың мөлшері анықталды. Метанның синтез-газға тотыға айналу барысында 5% La + 10% Mg + 5% Mn + 20% Ni + 10% Al + 50% глицин катализаторында температура 900^{o}C болғанда және 2500 сағ$^{-1}$ көлемдік жылдамдықта анағұрлым жоғары нәтижелерді алуға болатыны анықталды. Катализаторларды ағымды каталитикалық қондырғада зерттегеннен соң, физика-химиялық әдістерімен зерттеу барысында катализаторлардың құрылымы өзгеріске ұшырайтыны кешенді анықталды. Зерттеу барысында катализаторлардың құрамында металл алюминаттары мен құрылымы шпинель түріндегі жәй және аралас оксидтерінің бар болуы анықталынып, олардың метанның тотыға айналуына белсенді әсер ететіндігі көрсетілген. Сонымен қатар, беткі қабатында диаметрі 40 - 50 - 70 нм-болатын спиральға жиі оралған иілімді көміртекті нанотүтікшелердің түзілгені анықталды.

Түйін сөздер: метан, сутек, синтез-газ, жоғарытемпературада өздігінен жану синтезі, ерітіндіде жану.

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РАЗРАБОТКА КОМПОЗИТНЫХ МАТЕРИАЛОВ МЕТОДОМ ГОРЕНИЯ ДЛЯ КАТАЛИТИЧЕСКОГО РИФОРМИНГА МЕТАНА В СИНТЕЗ-ГАЗ

Аннотация. В современном мире природный газ является основным источником получения синтез-газа из метана. Производство синтез-газа постоянно совершенствуется, так как спрос на это сырье в нефтехимической промышленности растет с каждым годом. Кроме того, синтез-газ используется в качестве экологически чистого источника тепла и энергии. Поэтому поиск путей активации CH_4 для синтеза продуктов является важной задачей нефтехимической промышленности. Методом самораспространяющегося высокотемпературного синтеза, а именно современной его модификацией - процессом горения в растворе были приготовлены La – Mg – Mn – Ni - Al катализаторы. В результате варьирования соотношения элементов в образцах было установлено оптимальное содержание металлов в катализаторе и определены условия конверсии метана в синтез-газ. Найдено, что при 900^{o}C и объемной скорости 2500 ч$^{-1}$ на катализаторе 5% La + 10% Mg + 5% Mn + 20% Ni + 10% Al + 50% глицин возможно получение наиболее высоких результатов по окислительному превращению в синтез-газ. Катализаторы были исследованы комплексом физико-химических методов, в результате чего установлено, что в процессе проведения испытаний на проточной каталитической установке в структуре катализатора происходит ряд изменений. Показано, что в катализаторе присутствуют простые и смешанные оксиды, алюминаты металлов и структуры шпинельного типа, присутствие которых способствует активной работе катализаторов окислительного превращения метана. Кроме того, на поверхности обнаружены эластичные, часто завернутые в спирали с диаметрами 40 - 50 - 70 нм углеродные нанотрубки.

Ключевые слова: метан, водород, синтез-газ, самораспространяющийся высокотемпературный синтез, горение в растворе.

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