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«Жанармай, катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

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 Socia1 Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество в 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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Ni-Al-Mg-Mn COMPOSITE CATALYSTS FOR PARTIAL OXIDATION OF NATURAL GAS

Abstract: the problem of rational utilization of natural and associated petroleum gases and the cessation of their flaring is one of the acute and unresolved environmental problems. The aim of this work is to develop effective thermally stable catalysts of a new generation for the processes of oxidative conversion of light alkanes of natural and associated gas into synthesis gas. The results of partial oxidation of the methane of natural gas on the catalysts prepared by solution combustion synthesis are presented. Investigation of the activity of catalysts produced from initial mixture of $Ni(NO_3)_2$ - $Al(NO_3)_3$ - $Mg(NO_3)_2$ - $Mn(NO_3)_2$ + urea of different composition was carried out for the production of synthesis-gas. It was found that the optimal conditions for producing of synthesis-gas are: CH_4 conversion higher than 95%, yield of target products: H_2 - 97 - 99% and CO - 40 - 43%, T = 900°C, space velocity – 2500 and 6500 h^{-1}. The catalysts were studied by X-ray diffraction, transmission electron microscopy, specific surface area, pore volume and average pore diameter. The presence in the catalysts of simple and mixed oxides, metal aluminates and spinel-type structures, the presence of which contributes to the active work of catalysts for oxidative conversion of CH_4, has been established.

Key words: catalytic oxidation, methane, synthesis-gas, nickel, magnesium.

Introduction. The problem of rational utilization of natural and associated petroleum gases and the termination of their combustion in flares is today one of the most acute and unsolved environmental problems. Both natural and associated petroleum gas can be considered as an alternative source of obtaining valuable and very expensive petrochemical and organic synthesis products on the world market, especially in times of crisis.

New catalytic technologies for the processing of hydrocarbon raw materials, which will make it possible to produce goods that meet international standards and are able to compete in the market, are becoming relevant and promising in connection with the entry of the Republic of Kazakhstan into the World Trade Organization. During the last two decades the catalytic reforming of methane has increasing interest as an alternative route for syngas production. The International Energy Agency (IEA) world energy outlook clearly states that “natural gas is certainly set to play a central role in meeting the world’s energy needs for at least the next two-and-a-half decades”. This means that technologies based on methane will have priority. Since 1750, methane has doubled, and could double again by 2050. Each year we add 350-500 million tons of methane to the air by raising livestock, coal mining, drilling for oil and natural gas, rice cultivation, and garbage sitting in landfills. Methane is greenhouse gas more than 25 times as effective in trapping heat in atmosphere as carbon dioxide. Reducing of sources of CH_4 and non-CO_2 greenhouse gases could lead to a decline in the rate of the global warming, reducing the danger of dramatic climate change. The production of synthesis-gas from methane using active and stable catalysts plays an important role in the chemical and petrochemical industries.

For the above processes, oxide catalysts [1], their mixtures, and composites based on them [2] have been recently used instead of the noble metals [3,4] that were used previously. The method of selfpropagating high-temperature synthesis has become widespread in recent years [5], especially its modification - the solution combustion synthesis (SCS) [6-8], as a result of which finely dispersed oxides and spinels are synthesized [9,10].

Previously, we investigated the process of oxidative conversion of light alkanes into synthesis-gasin the presence of oxygen on different types of catalysts: noble metals [11-13], oxides [14,15] and catalysts prepared by solution combustion synthesis [16]. **Materials.**

Many researchers reported that Mg, Mn and Ni-based catalysts possessed high activity, but one of the major problems encountered in the application of this process is catalyst deactivation mainly by carbon deposition. During the past decades nickel catalysts have been extensively studied [17], but few studies were made on Mg catalysts, Ni-Mg [18,19] and Mn catalysts [20].

The paper presents the data of the activity of the developed SCS catalyst based on Ni - Al - Mg - Mn, capable of carrying out the process of oxidative conversion of methane into synthesis-gas.

Methods. *Catalyst preparation*

A series of catalysts on the base of (50% $Ni(NO_3)_2$/50% urea, 41% $Ni(NO_3)_2$ + 3% $Al(NO_3)_3$ + 3% $Mg(NO_3)_2$ + 3% $Mn(NO_3)_2$/50% urea, 30% $Ni(NO_3)_2$ + 10% $Al(NO_3)_3$ + 5% $Mg(NO_3)_2$ + 5% $Mn(NO_3)_2$/50% urea, 20% $Ni(NO_3)_2$ + 20% $Al(NO_3)_3$ + 5% $Mg(NO_3)_2$ + 5% $Mn(NO_3)_2$/50% urea, 10% $Ni(NO_3)_2$ + 30% $Al(NO_3)_3$ + 5% $Mg(NO_3)_2$ + 5% $Mn(NO_3)_2$/50% urea, 5% $Ni(NO_3)_2$ + 35% $Al(NO_3)_3$ + 5% $Mg(NO_3)_2$ + 5% $Mn(NO_3)_2$/50% urea, 10% $Ni(NO_3)_2$ + 40% $Al(NO_3)_3$/50% urea) was prepared by solution combustion synthesis method. A mixture of salts and distilled water was placed in a quartz glass. The content of the glass was heated to 80 - 100°C. Then the beaker with the solution was placed in a preheated muffle furnace, where the catalysts were prepared at various temperatures. At the beginning of the reaction, a large amount of heat is generated, which ensures a rapid spread of the combustion front and a sharp increase in temperature. After several minutes, structural catalysts are formed, the formation of which is one of the reasons for the high activity of the prepared samples. The final form of the catalyst is shown in Figure 1.

Figure 1 - General view of the catalyst prepared by the SCS method

Characterization techniques

The catalysts were studied by XRD on a Siemens Spellman DF3 spectrometer with Cu-Kα (λ = 1.5406Å) radiation in steps of 0.03°/1" in the 2θ range from 5° to 100°. For semi-quantitative X-ray analysis, 5% KCl was added to the analyzed samples as an internal standard. Transmission electron microscopy (TEM) was used to determine the morphology of the developed catalysts. The electron-microscopic characteristics of the catalysts were obtained on an EMK-125 K microscope (Sumy, Ukraine) at an accelerating voltage of 75 kV. The SEM observations were carried out in a Quanta Inspect FEI scanning electron microscope and the EDS patterns were carried out by an EDX analyser on samples sputter-coated with gold with a coating thickness of 5-10 nm. Compressive strength was measured in a 100 kN strain-controlled universal tester at a displacement rate of 100 μm/min on cylindrical specimens of diameter 1 cm and height 2 cm. The initial mixture and reaction products were analyzed using a Chromos GC-1000 chromatograph with the Chromos software. Chromatographic peaks were calculated using calibration curves constructed for the corresponding products using the Chromos software for pure substances. The specific surface area was determined and the pore distribution in the catalysts was measured by the BET method (Brunauer–Emmett–Teller) using a GAPPV-Sorb 2800 analyzer. Nitrogen (99%) with helium (99%) was used as the carrier gas. Pore volume and average pore diameter were calculated by the BJH method using desorption isotherm curves.

Catalytic activity studies

SCS catalysts were placed in a fixed bed flow reactor of the automated flow laboratory installation with on-line analysis of initial materials and reaction products. The gas mixture $CH_4 : O_2 : Ar$ (2 : 1:3), (34% / 17% / 49%) was used to study the oxidative conversion of methane into synthesis gas under atmospheric pressure in the temperature range 700 - 900°C at the space velocity 500-8500 h^1. Obtained data were checked for reproducibility of the results. For this, the data obtained for one specific temperature were repeated at least 3 times until the results were completely reproducible.

Results and Discussion. Catalysts of the Ni - Al - Mg - Mn + urea series were prepared in a muffle furnace heated to 500°C. The composition of the initial mixture, combustion conditions and the final catalyst compositions are shown in Table 1.

Table 1 - The initial compositions of salts and final catalyst composition at 500^{o}C preheating temperature of solution

Starting compounds	Catalysts composition
50% Ni + urea	NiO, NiC, C
10% Ni + 40% Al + urea	$NiAl_2O_4$, NiC, NiO, Ni_2O_3
3% Ni + 3% Al + 3% Mg + 41% Mn + urea	$MgAl_2O_4$, Mn_3O_4, $MgMn_2O_4$, $MnAl_2O_4$
20 % Ni + 20% Al + 5% Mg + 5% Mn + urea	$NiAl_2O_4$, $MgAl_2O_4$, NiO, NiC, $MgNiO_2$, AlNi, Al_2O_3, Mn_3O_4
30% Ni + 10% Al + 5% Mg + 5% Mn + urea	$NiAl_2O_4$, $MgAl_2O_4$, NiC, MgO, Ni_2O_3, $MgNiO_2$, NiO, Mn_3O_4
20% Ni + 20% Al + 5% Mg + 5% Mn + urea spent	$NiAl_2O_4$, $MgAl_2O_4$, NiC, Ni, C

The following reactions are possible in the process of solution combustion synthesis:

$$Mg(NO_3)_2\,6H_2O \rightarrow MgO + NO_2 + O_2 + H_2O \quad (1)$$
$$MgO + Al_2O_3 \rightarrow MgAl_2O_4 \quad (2)$$
$$Mg(NO_3)_2\,6H_2O + Al \rightarrow MgAl_2O_4 + NO + NO_2 \quad (3)$$
$$NiO + Al_2O_3 \rightarrow NiAl_2O_4 \quad (4)$$
$$MgO + NiO \rightarrow Mg_xNi_yO_z \quad (5)$$
$$KMnO_4 \rightarrow KMnO_2 + O_2 \quad (6)$$
$$KMnO_2 \rightarrow K_2O + Mn_2O_3 \quad (7)$$
$$Mn_2O_3 \rightarrow Mn_2O + MnO \quad (8)$$
$$MnO + Al_2O_3 \rightarrow MnAl_2O_4 \quad (9)$$
$$MgO + MnO \rightarrow Mg_xMn_yO_z \quad (10)$$

Presence of products were confirmed by EDX analysis on the SEM, for example as shown in Figure 2 of 3% Ni + 3% Al + 3% Mg + 41% Mn + urea catalysts, X-ray diffraction pattern of the samples as shown in Figure 3 and Table 1.

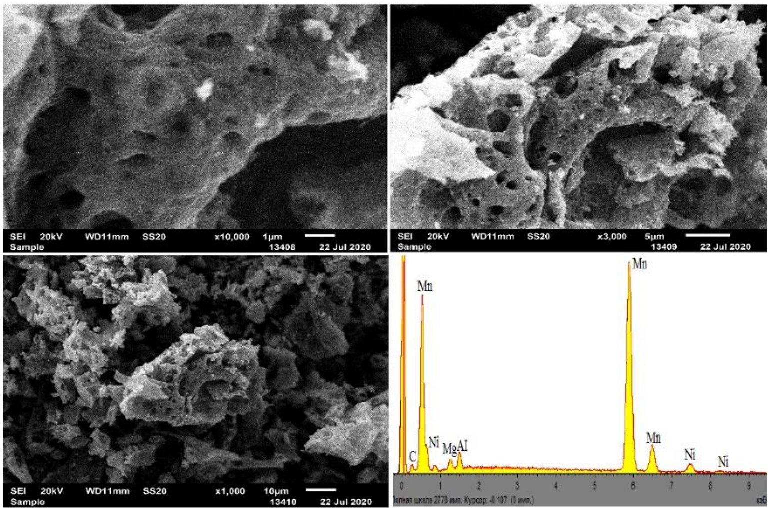

Figure 2 - SEM images of the 3% Ni + 3% Al + 3% Mg + 41% Mn + urea catalyst and its EDS

X-ray diffraction pattern of the samples are shown in Figure 3. It can be seen from the figure that the catalysts had a rather similar qualitative composition, but differed in the phase ratio. The phase ratio can be determined from the relative intensity of the X-ray diffraction peaks for each phase.

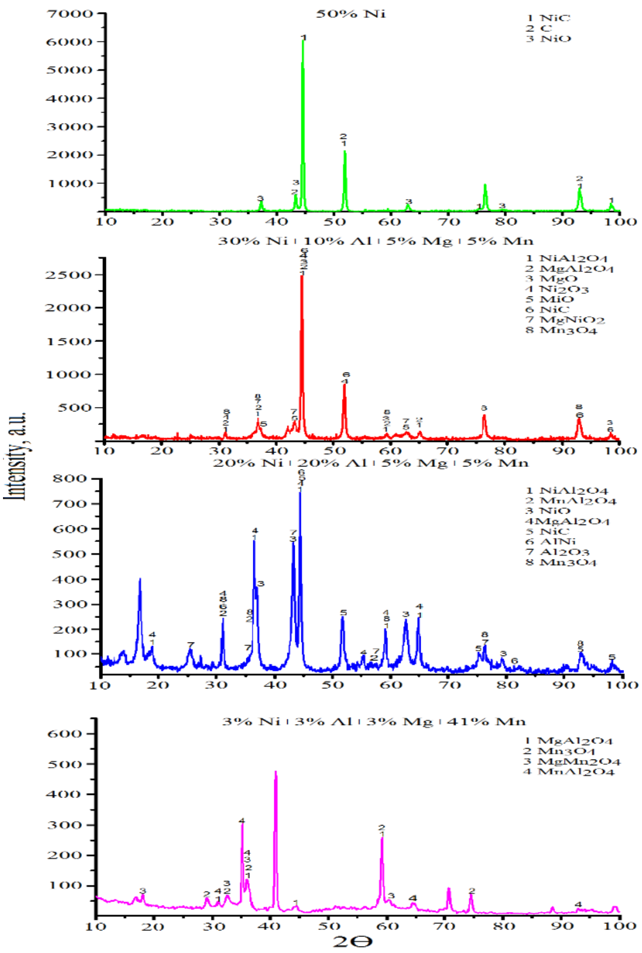

Figure 3 - X-ray spectra for the Ni - Al - Mg - Mn + urea catalysts

As a result of TEM studies at low magnification, a small frame-type aggregate of large dense particles with a size of 50-100 nm is shown on Figure 4.

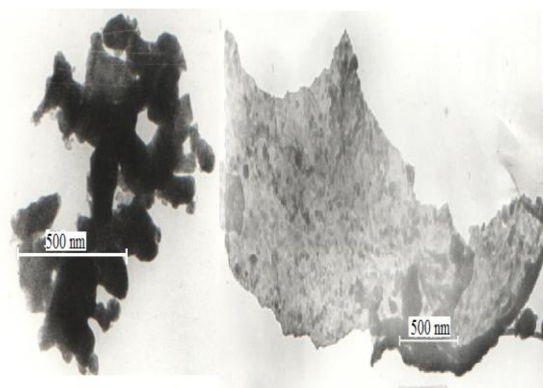

Figure 4 - TEM images of the 3% Ni + 3% Al + 3% Mg + 41% Mn + urea catalyst

The microdiffraction pattern is represented by reflections located along rings and individual reflections and can be attributed to a mixture of phases: MnO (JCPDS, 2-829), $MgAl_2O_4$ spinel (JCPDS, 21-1152), $NiAl_2O_4$ (JCPDS, 10-339), MgC_2 (JCPDS , 3-748), Ni_2O_3 (JCPDS, 14-481). Also, a semitransparent plate filled with particles with a size of 30-50 nm and more was shown. The microdiffraction pattern is represented by reflections that can be attributed to a mixture of phases: θ-Al_2O_3 (JCPDS, 35-121), $MnAl_2O_4$Galaxite (JCPDS, 29-880), β-MnO_2pyrolusite (JCPDS, 24-735).

The specific surface area of the catalysts is low. This is due to high combustion temperatures during preparation of catalysts. Despite this, the synthesized catalysts have a high specific activity, which allows them to compete even with catalysts of the Pt group.

The results on the yield of hydrogen and CO, as well as the selectivity for catalysts are presented in Figure 5.

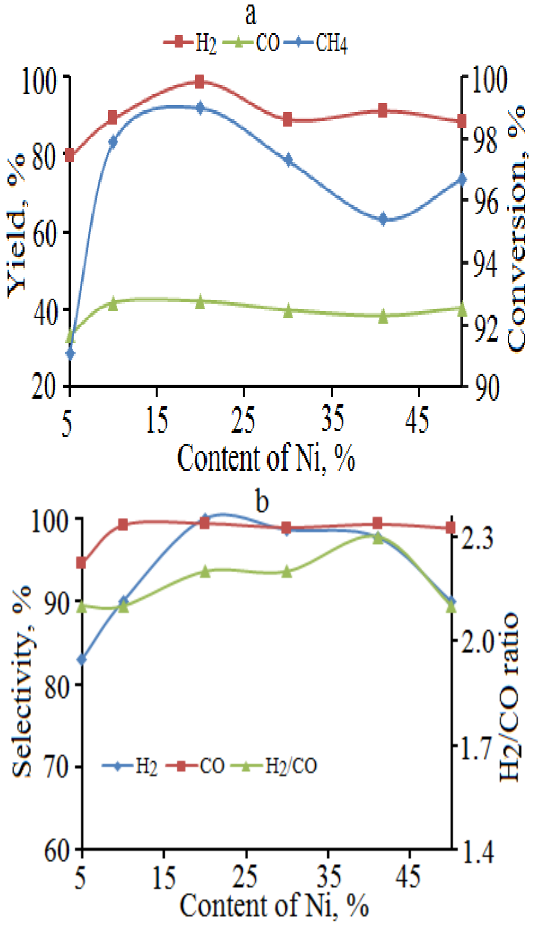

Figure 5 - Conversion of methane, yields, selectivities by H_2 and CO, as well as H_2/CO ratio on catalysts at different concentrations of Ni in the oxidation of methane to synthesis gas

Figure 5 shows that 20% Ni content is optimal for producing the highest syngas results from the entire series of catalysts prepared by the solution combustion method. High selectivities for H_2 and CO (100% and 99.4%, respectively) and yields for H_2 and CO (97.5% and 40.2%, respectively) were produced on the above catalyst composition. The H_2/CO ratio close to 2 was found under these conditions, which is suitable for the production of olefins and alcohols in the future.

Unlike Ni, the optimum Mg content is 5%, where optimum results are obtained. The yields of H_2 and CO corresponded to 97% and 43%, the selectivity for H_2 - 100% and for CO - 99%, Figure 6. The H_2/CO ratio reached 2.2.

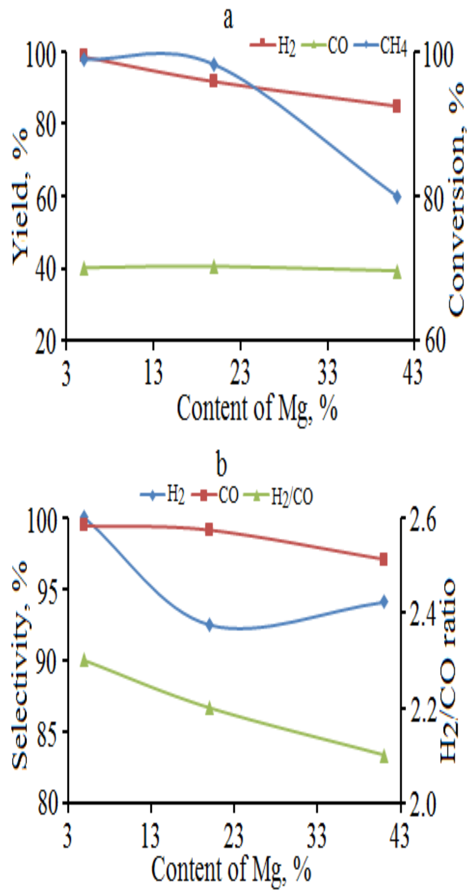

Figure 6 - Conversion of methane, yields, selectivities by H_2 and CO, as well as H_2/CO ratio on catalysts at different concentrations of Mg in the oxidation of methane to synthesis gas

The Mn content also affects the performance of the oxidative conversion of methane into synthesis gas. With an increase in the Mn content, starting from 5% in the composition of the catalyst, the yields of the target products, as well as their selectivity, begin to decrease continuously.

On optimal 20% Ni + 20% Al + 5% Mg + 5% Mn + 50% urea catalyst under conditions: 34% CH_4, 17% O_2 and 49% Ar, $CH_4 : O_2 = 2 : 1$, catalyst volume 2 ml in the temperature range 850 - 900°C, the effect of the space velocity from 500 to 8500 h^{-1} was investigated.

At a space velocity of 6500 h^{-1}, hydrogen yields were achieved up to 97.5 - 98.7%, CO - up to 43% with selectivity up to 100% for hydrogen and 99.4% for CO, H_2/CO ratio = 2.2 - 2.4. Similar results were obtained at a space velocity of 2500 h^{-1}. A further increase in the space velocity led to a decrease in the process parameters.

Comparison of catalyst preparation methods (solution combustion method and traditional impregnation method) for yield and selectivity for H_2 and CO at 900°C for 20% Ni + 20% Al + 5% Mg + 5% Mn + 50% urea catalyst was carried out. It has been shown that the solution combustion method has some advantages over the impregnation method. This is an important result, since the method of solution combustion is more economical, it is carried out within a few minutes compared to many hours of high-temperature impregnation process.

The stable operation of the catalyst was confirmed during continuous operation of the sample for 60 h, Figure 7. Product yields, methane conversion, and selectivity for CO and H_2 showed constant results throughout the entire test period.

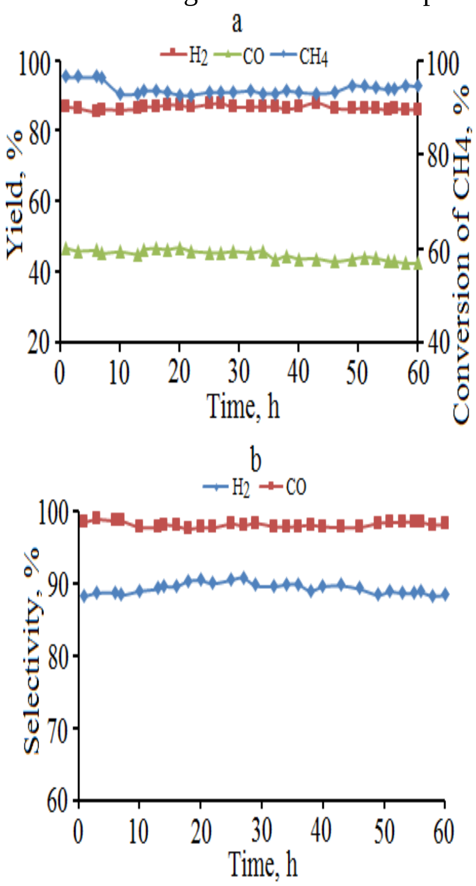

Figure 7 - Effect of the duration of experiment on the stability of 20% Ni + 20% Al + 5% Mg + 5% Mn + 50% urea catalyst

Conclusion. Thus, it was found that the synthesized 20% Ni + 20% Al + 5% Mg + 5% Mn + 50% urea catalysts are active in the reaction of partial conversion of methane into synthesis-gas. The optimal conditions for the maximum operation of this catalyst are: 34% CH_4, 17% O_2, 49% Ar, space velocity – 2500 and 6500 h^{-1} at the temperature of 900°C. The presence in the catalysts of simple and mixed oxides, metal aluminates and spinel-type structures, the presence of which contributes to the active work of the catalysts for the oxidative conversion of methane, has been established. 97.5 - 98.7% of H_2, 43% of CO with selectivity up to 100% for H_2 and 99.4% for CO, H_2/CO ratio = 2.2 - 2.4 were obtained as a result of the research. It has been shown that the solution combustion method has some advantages over the impregnation method for preparation of catalysts, which is an important practical achievement for further applications in catalysis, since. In addition to economic advantages, this method is also more environmentally friendly, since less exhaust gases are released into the atmosphere at significantly shorter preparation time.

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ТАБИҒИ ГАЗДЫ КОМПОЗИТТІ Ni-Al-Mg-Mn КАТАЛИЗАТОРЛАРЫНДА ПАРЦИАЛДЫ ТОТЫҚТЫРУ

Аннотация: табиғи және ілеспе мұнай газдарын ұтымды пайдалану және олардың жануын тоқтату мәселесі өзекті және шешімі табылмаған экологиялық мәселелердің бірі болып табылады. Бұл жұмыстың мақсаты – табиғи және ілеспе газдың жеңіл алкандарының синтез-газға тотығу конверсиясы үрдістері үшін жаңа буынды тиімді термиялық тұрақты катализаторларын жасау. Ерітінді де жану әдісімен дайындалған катализаторлардағы табиғи газ метанының жартылай тотығу нәтижелері келтірілген. Синтез-газ алу үшін әр түрлі құрамдағы Ni $(NO_3)_2$ - Al $(NO_3)_3$ - Mg $(NO_3)_2$ - Mn $(NO_3)_2$ + мочевина қоспаларынан жасалған катализаторлар белсенділігіне зерттеулер жүргізілді. Синтез-газ алудың оңтайлы шарттары: CH_4-ның конверсиясы 95%, мақсатты өнімнің шығымы: H_2 - 97-99% және CO - 40-43%, T = 900°C, көлемдік жылдамдығы - 2500 және 6500 $сағ^{-1}$. Катализаторларға рентгендік фазалық талдау, сәулелі электронды микроскопиялық зерттеулер жүргізілді, сондай-ақ катализаторлардың меншікті беттік ауданы, кеуектер көлемі мен кеуектердің орташа диаметрі анықталды. CH_4-ның тотығу конверсиясы үшін катализаторлар құрамында негізгі және аралас оксидтер, металл алюминаттары және шпинель типті құрылымдардың бар екендігі анықталды, олар катализаторлардың белсенді жұмыс жасауына әсер етеді.

Түйін сөздер: катализдік тотығу, метан, синтез-газ, никель, магний.

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Ni-Al-Mg-Mn КОМПОЗИТНЫЕ КАТАЛИЗАТОРЫ ПАРЦИАЛЬНОГО ОКИСЛЕНИЯ ПРИРОДНОГО ГАЗА

Аннотация: проблема рационального использования природных и попутных нефтяных газов и прекращения их сжигания является одной из острых и нерешенных экологических проблем. Целью данной работы является разработка эффективных термически стабильных катализаторов нового поколения для процессов окислительной конверсии легких алканов природного и попутного газа в синтез-газ. Приведены результаты частичного окисления метана природного газа на катализаторах, приготовленных методом растворного горения. Проведено исследование активности катализаторов, полученных из исходной смеси $Ni(NO_3)_2$ - $Al(NO_3)_3$ - $Mg(NO_3)_2$ - $Mn(NO_3)_2$ + мочевина различного состава для получения синтез-газа. Было установлено, что оптимальными условиями получения синтез-газа являются: конверсия CH_4 более 95%, выход целевых продуктов: H_2 - 97 - 99% и CO - 40 - 43%, T = 900°C, объемная скорость - 2500 и 6500 $ч^{-1}$. Катализаторы были исследованы методами рентгенофазового анализа, просвечивающей электронной микроскопии, была определена удельная поверхность, объем пор и средний диаметр пор. Установлено наличие в катализаторах простых и смешанных оксидов, алюминатов металлов и структур типа шпинели, наличие которых способствует активной работе катализаторов окислительного превращения CH_4.

Ключевые слова: каталитическое окисление*, метан, синтез-газ, никель, магний.*

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