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NICKEL-CONTAINING COMPOUNDS FOR THE CATALYTIC CONVERSION OF METHANE TO GAS SYNTHESIS

Abstract. In recent decades, many experiments have studied the catalytic materials synthesis' that are active, selective and stable in the conversion of gaseous hydrocarbons to organic liquids. The resulting nickel-based catalysts are discussed in terms of their preparation, physicochemical characteristics, and internal properties that the conversion of methane to synthesis gas.

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

Introduction

Methane is considered the most significant source of hydrocarbons in the process of catalytic partial oxidation, since it is the main component of natural gas, which exists on Earth in abundance. One of the most common methods for producing catalysts today is self-propagating high-temperature synthesis (SHS). This is an exothermic reaction, which is carried out in the modes of layer-by-layer combustion or thermal explosion, based on the use of the internal chemical energy of the starting reagents. The advantages of this method are - low power consumption, simplicity and a one-step synthesis cycle, high productivity, cheap equipment, high purity of the product [1].

The use of natural gas, synthesis gas allows to obtain a wide range of chemical products [2]. For such processes, the most common are catalysts based on nickel and noble metals. Nickel is the cheapest raw material for the manufacture of the catalyst, but the main disadvantage of this metal is its high coke formation, which contributes to the rapid "aging" of the catalyst.

Methane steam reforming (SR) is a well-established process for converting hydrocarbons to synthesis gas in industry.

$$CH_4+H_2O \rightarrow CO+3H_2 \qquad \Delta H_{298}=+206\ kJ/mol$$

Recently there has been great renewal interest in the SR process because of its potential application in fuel cells [3]. However, this process has many disadvantages: firstly, in the process, an amusing amount of CO2 is generated along the way, which is difficult to separate; secondly high energy demand because SRM is a highly endothermic process.

The dry-reforming process (DR), on the other hand, produces the least amount of hydrogen per mole of methane consumed.

$$CH_4+CO_2 \rightarrow 2CO+2H_2 \qquad \Delta H_{298} = +247\ kJ/mol$$

Although this process has two major disadvantages: extremely high energy cost and rapid catalysts deactivation through carbon deposition [4].

The search for numerous experiments over several decades to develop alternative processes led to the process of catalytic partial oxidation of methane (POM) [5].

$CH4 + 0.5O2 \rightarrow CO + 2H2$ $\Delta H_{1173K} = -23.1$ kJ/mol

This process is described as slightly exothermic [6] and occurs 10–100 times faster than steam reforming, which allows the use of small reactors.

The aim of this work was synthesis of catalysts based on Ni-Al-Pt compounds, organic part were glycine [7] or urea [8-10]. The synthesis of nanostructure materials was do method self-propagating high temperature synthesis (SHS) or «burning solution». That process is based on a self-sustaining exothermic reaction of the interaction of dissolved components based on systems containing an oxidizing agent (metal nitrate) and a reducing agent [11]. It allows one to obtain inexpensive oxide catalysts in the form of nanosized powders (particle size less than 100 nm), which have very high catalytic activity at ambient temperature.

Experimental

Catalyst preparation

A preliminary calculated amount of metal salts of Ni and Al crushed to a jelly-like state was injected with a few drops of a solution containing a salt of Pt and mixed. Then placed in a quart glass and sent to a preheated muffle furnace (600-900°C). After 5-7 minutes, spontaneous combustion occurred. Catalyst samples were tested on an FCU-1 unit with a gradual increase in temperature from 600 to 900°C at space velocities of 2500, 4500, 6500 h-1. Studies of the developed catalysts were carried out using various methods: elemental analysis, X-ray diffraction analysis (XRD), transmission electron microscopy on an EM-125K device using the "shooting in the lumen" method in the form of dry suspensions using microdiffraction. These analyzes were performed both before and after testing the synthesized catalysts in a flow reactor with a catalytic unit (FCU-1).

Results and discussion

It has always been believed that there are two sources of raw materials for organic chemistry, which are a source of huge reserves - coal and gas. The possibility of obtaining hydrocarbon raw materials from coal has long been developed, but the imperfection of the technology, economic factors and the stringency of the conditions do not allow to introduce these processes into the industry. Whereas the processing of, for example, acetylene from natural gas has long been put into production on an industrial scale. Although the process is also with very low selectivity and yield at high temperatures and pressure. Moreover, the existence in nature of enzymes that convert methane to methanol is well known. Therefore, the constant desire to create new highly efficient and selective processes for processing natural gas into useful alkane compounds is justified.

Currently, there is no industrial technology for producing synthesis gas by the method of carbon dioxide conversion of methane. Available developments are most often based on nickel catalysts used in the steam reforming process, they do not have sufficient selectivity and are quickly deactivated due to the formation of carbon, which covers active metal centers during catalysis, and accumulate in the pores of the catalyst, causing destructive changes and ultimately – decontamination [12].

According to the literature, it is known that the C-H bond energy in methane is approximately equal to the H-H bond energy in acetylene, benzene, and ethylene molecules. The ionization potential of methane is higher than that of benzene, ethylene and acetylene, but lower than the ionization potential of hydrogen. Methane has a lower proton affinity than a benzene and ethylene molecule, but more than hydrogen. From which it turns out that methane occupies an intermediate position between hydrogen and ethylene. Therefore, the activation of methane and its chemical reactions can be carried out in the presence of catalysts with 3d metals. In the periodic system, nickel is in a subgroup of elements such as palladium and platinum, which explains the similarity of the electronic configuration, especially the outer shells, as a result of which the elements of this group exhibit similar physical properties and chemical behavior [13]. Perhaps this explains the attempt to replace the expensive metals of the platinum subgroup with nickel.

The following are test results for the catalyst composition 50% Ni - 50% Al - (0.05%) Pt - glycine or urea catalyst. And also given elemental composition with different variation in quantity was considered.

Various elements in the catalysts form chemical bonds of varying degrees of strength. It is likely that someday it will be possible to explain the chemical properties of metal catalysts based on the ideas of quantum mechanics, but now it is necessary to establish essentially empirical correlations. As elements used in catalysts, transition metals are of the greatest importance. In the synthesis of catalysts, glycine was used as organic fillers, which made it possible to obtain a huge amount of particles in the form of spinels and various frame structures.

Figure 1 - TEM images of the 50 % Ni - 50 % Al – (0.05%)Pt- glycine catalyst before tests

On the other hand, the study of literary sources of aluminum oxide indicates a huge variety of the final compounds obtained, which is explained by the influence of everything: temperature, synthesis method, initial structure, pH of the solution used, and even the rate of solution merging and mixing. The influence of temperature in the range from 500 to 800°C on the structural composition of the catalyst was considered.

According to the analysis results, it was shown that at 500°C translucent films with seal sizes from 10-30 nm to 100 nm were shown. The microdiffraction pattern is represented by reflections and can be assigned to a mixture of phases: NiO (JSPDS, 4-835), χ-Al_2O_3 Alumina in the modification (JSPDS, 34-493), ϕ-$NiAl_{32}O_{49}$ (JSPDS, 20-777), PtO (JSPDS , 27-1331), Al_4C_3 (JSPDS, 38-799), AlN (JSPDS, 25-1133), Ni_3N (JSPDS, 10-280), NiO (JSPDS, 4-835).

In the samples obtained at 600°C, translucent films were shown with compaction sizes from 10-15 nm to 50 nm. The microdiffraction pattern is represented by reflections and can be attributed to a mixture of phases: $Al(OH)_3$ (JSPDS, 26-28), AlN (JSPDS, 25-1133), Pt_3O_4 (JSPDS, 21-1284), NiO (JSPDS, 4-835), ϕ-$NiAl_{32}O_{49}$ (JSPDS, 20-777), Ni_3N (JSPDS, 10-280), NiO (JSPDS, 4-835).

In the samples obtained at 700°C, translucent films were shown with compaction sizes from 10-15 nm to 50 nm. The microdiffraction pattern is represented by reflections and can be assigned to a mixture of phases: PtO (JSPDS, 27 -1331), $Al_{22}O_{39}N$ (JSPDS, 26-33), $NiAl_{26}O_{40}$ (JSPDS, 20-776), χ-Al_2O_3 Alumina in the modification (JSPDS, 4-880), $Al_9N_7O_3$ (JSPDS, 35-830), $NiAl_{32}O_{40}$ (JSPDS, 35-830) Pt (JSPDS, 27 -1331), Al_2Pt (JSPDS, 3-1006), NiO (JSPDS, 4-835)

Samples obtained at 800°C are translucent films with small particles on them ranging in size from 4-15 nm to 20 nm. The microdiffraction pattern is represented by reflections and can be assigned to a mixture of phases: NiO (JSPDS, 4-835), Al (JSPDS, 4-716), Al_3Ni_2 (JSPDS, 14-648), $NiAl_{26}O_{40}$ (JSPDS, 20-776), $Pt_{21}Al_6$ (JSPDS, 38-1179), $Al_{10}N_8O_3$ (JSPDS, 32-22), $NiAl_{32}O_{49}$ (JSPDS, 20-776), Pt (JSPDS, 4-802), $AlPt_2$ (JSPDS, 29-69). The most common types of particles formed are shown above as they decrease.

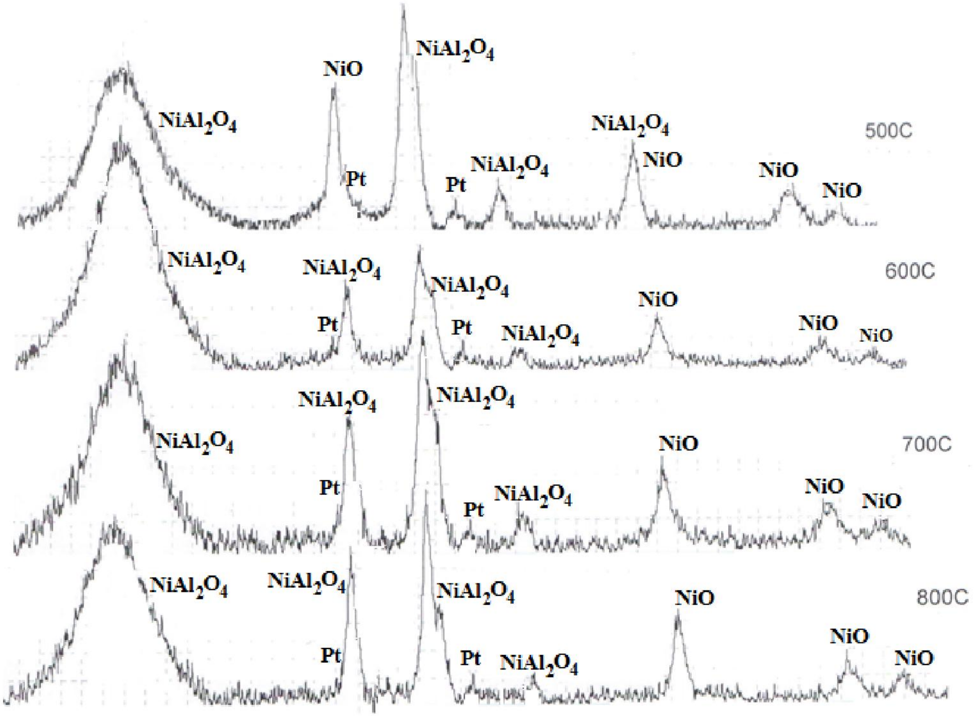

Figure 2 – XRD spectrum of the 50 % Ni - 50 % Al – (0.05%)Pt- glycine catalyst before tests

As can be seen from the experimental results, the temperature significantly affects the composition of the catalyst. At higher temperatures, metal atoms have time to recover, and also form more complex structures in the form of various spinels. It has been proven that reduced Ni can interact at high temperatures with the formation of $NiAl_2O_4$ spinels [14-16]. In fact, $NiAl_2O_4$ is not active in the reaction. But its reduced form tends to inhibit the formation of carbon deposits. This shows good stability, since reduced Ni from spinel tends to disperse, making sintering difficult. In addition, a synergistic effect exists between the carbon fraction and the metal-based fraction, which means that the experimental CO_2 and CH_4 conversions obtained in mixtures of carbon materials and metals are higher than the conversions calculated according to the law of mixtures (i.e., the addition of weighted individual transformations) [14,17].

X-ray diffraction analysis did not show significant differences between the samples. Figure 2 shows the spectra of the catalyst for 50% Ni - 50% Al - (0.05%) Pt-glycine. As a result of the data obtained, it is seen that the following phases are present in the catalysts: NiO (reflexes, Å: 2.41; 2.08; 1.48; 1.25; 1.21 - ASTM, 4-850); NiAl2O4 (reflexes, Å: 4.6220; 2.8420; 2.42100; 2.0065; 1.648; 1.5430; 1.4260 - ASTM, 10-339) and Pt (low-intensity reflexes, Å: 2, 26 ; 1.96 - ASTM, 4-802).

Despite the fact that such catalysts have good enough activity, they all undergo coking. Over time, this leads to the deactivation of the catalysts, which requires their regeneration and leads to an increase in production costs. A disadvantage of the known catalysts and carriers is that they are oxidized at high temperatures in a redox environment, which significantly reduces the contact strength between the particles [18-20]. In the continuation of the study, analyzes were carried out for the catalyst composition 50 % Ni - 50 % Al – (0.05%)Pt- glycine (500°C) after the main multiple tests on the FCU-1 device.

Figure 3 (A, B) shows translucent films with seals 10-30 nm in size. And dense aggregates, on the edges of which there are particles with a size of 10-20 nm. The microdiffraction pattern is represented by a large set of reflections located along the rings and individual reflexes and can be assigned to a mixture of phases: δ-$NiAl_{26}O_4$ (JSPDS, 20-776), δ-Al_2O_3 (JSPDS, 4-877), Al_4C_3 (JSPDS, 38-799), ϕ-$NiAl_{32}O_{49}$ (JSPDS, 20-777), PtO (JSPDS, 27-1331), $Al_9N_7O_3$ (JSPDS, 35-83).

Figure 3 (C) shows a large and dense aggregate, along the edge of which both small particles with a size of 20-60 nm and large ones with signs of faceting of a size of 200-500 nm are observed. The microdiffraction pattern is represented by rows of reflections and a large set of individual reflexes and can be assigned to a mixture of phases: large $NiAl_{10}O_{16}$ (JSPDS, 37-1292) or equally $9Al_2O_3 \cdot 2NiO$ (JSPDS, 22-451), γ-Al_2O_3 (JSPDS, 29-63) and (JSPDS, 10-425), AlN (JSPDS, 34-679) and χ-Al_2O_3 Alimina in the modification (JSPDS, 34-493). Small: Pt (JSPDS, 4-802), AlNi (JSPDS, 20-19), Ni_3N (JSPDS, 20-19), Ni_3C (JSPDS, 6-497), δ-$NiAl_{26}O_{40}$ (JSPDS, 20-776), Al (JSPDS, 4-787). However, after catalytic studies on the known catalyst, carbon deposition is observed, accompanied by the formation of nickel carbide and graphite-like carbon, which leads to the fact that the activity of the catalyst decreases (the catalyst is deactivated).

Figure 4 shows the accumulation of aggregates of elastic carbon nanotubes reaching a cross section of 20-40 nm, as well as a dense aggregate, along the edge of which particles of 10-50 nm in size and dense large round particles of 100-200 nm or more are observed . The microdiffraction pattern is represented by rings and a small set of reflections that can be attributed to a mixture of phases: PtO_2 (JSPDS, 23-1306), AlH_3 (JSPDS, 23-761), C - Zonsdaleite (JSPDS, 19-268) - tubes, $AlPt_2$ (JSPDS, 29-692), AlC_3 (JSPDS, 35-749) Ni3C (JSPDS, 6-497), ϕ-$NiAl_{32}O_{49}$ (JSPDS, 20-777), Al_2OC (JSPDS, 36-148).

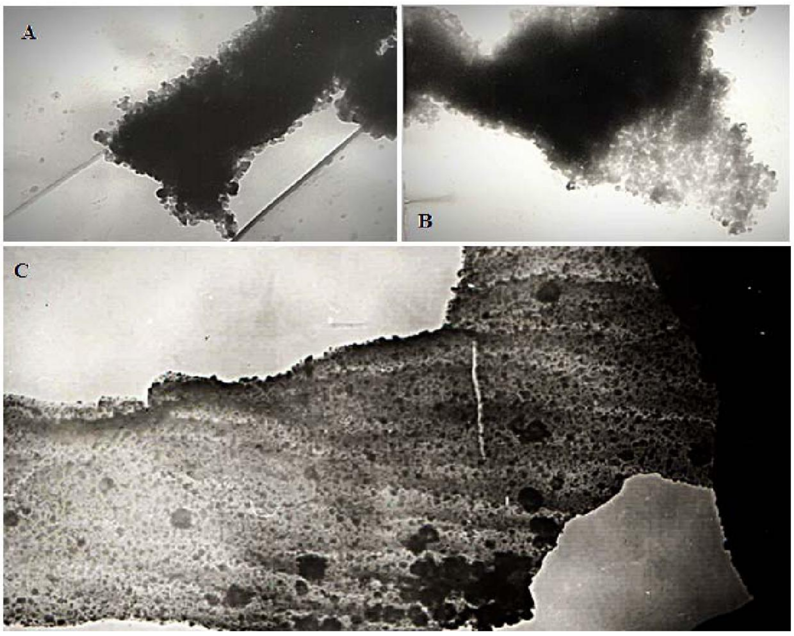

Figure 3 – TEM images of the 50 % Ni - 50 % Al – (0.05%)Pt- glycine catalyst after tests

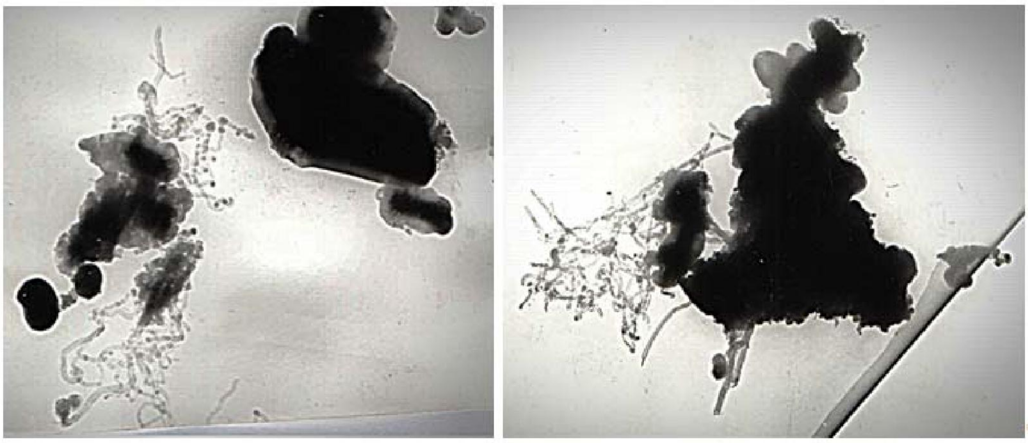

Figure 4 - TEM images of the 50 % Ni - 50 % Al – (0.05%)Pt- glycine catalyst after tests with carbon nanotubes

Conclusion

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

- organic fillers affect the composition and properties of the same catalysts;
- in catalysts prepared by the SHS method, temperature significantly affects the composition — moreover, if we study the most active centers of the catalyst for this system, we can synthesize a need composition;
- the catalyst was most active for conversion methane to synthesis gas from numerous combinations of catalysts with the following set of catalyst components from 50% Ni - 50% Al - (0.05%) Pt-glycine obtained by synthesis during combustion in solution at 800°C;
- the presence of carbon nanotubes in the spent catalyst samples was also revealed. The nanotubes are elastic, often wrapped in a spiral with a diameter of 50 - 70 nm.

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МЕТАННЫҢ СИНТЕЗ - ГАЗҒА КАТАЛИЗДІК КОНВЕРСИЯЛАУДА НИКЕЛЬҚҰРАМДЫ ҚОСЫЛЫСТАР

Аннотация. Соңғы онжылдықта көптеген тәжірибелерде газ тәрізді көмірсутектерді органикалық сұйықтықтарға тотықтыра айналдыру барысында белсенді, селективті және тұрақты болып табылатын каталитикалық материалдардың синтезі зерттелді. Метанның синтез-газға айналу конверсиясыда алынған никель негізіндегі катализаторларды дайындау және олардың физикалық-химиялық сипаттамаларына талдау жасау.

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

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НИКЕЛЬ-СОДЕРЖАЩИЕ СОЕДИНЕНИЯ ДЛЯ КАТАЛИТИЧЕСКОЙ КОНВЕРСИИ МЕТАНА В СИНТЕЗ ГАЗА

Аннотация. В последние десятилетия во многих экспериментах изучался синтез каталитических материалов, которые являются активными, селективными и стабильными при превращении газообразных углеводородов в органические жидкости. Полученные катализаторы на никелевой основе обсуждаются с точки зрения их приготовления, физико-химических характеристик и внутренних свойств, при которых происходит конверсия метана в синтез-газ.

Ключевые слова: метан, водород, синтез-газ, самораспространяющийся высокотемпературный синтез, сжигание раствора.

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