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METHANE CONVERSION ON CATALYSTS, OBTAINED BY THE METHOD SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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Abstract: The possibility of using the internal energy resources of thermosetting powder systems testifies to the high advantages of SHS with technical support. It serves as a basis for the creation of new advanced technologies that provide solutions to the problems of organizing highly efficient and dynamic production of various materials.

Keywords. composite material, Al₂O₃, ZrO₂, MgO, NiO, Ni, Influence of the CH₄ : CO₂ molar ratio.

Introduction

The method of self-propagating high-temperature synthesis (SHS) makes it possible to obtain granular and block catalysts for the generation of synthesis gas [1]. Among the latter, we can distinguish block metal-ceramic catalysts for the selective catalytic oxidation of methane, which are compact and have high productivity [2]. The development of efficient block catalysts can be the first step towards the creation of small mobile plants for chemical processing of associated gas in wells located in remote areas. Ni₃Al intermetallic powders with free nickel inclusions obtained by SHS are promising catalysts for methane carbon dioxide conversion [3, 4]. Today, group VIII metals of the periodic table deposited on various carriers, as well as oxides of elements with variable valence, sulfides and carbides, have been mainly studied as CCM catalysts [5-13]. As a rule, the most active catalysts are based on platinoids, and nickel systems are comparable to them. The obvious disadvantage of noble metals is their high cost, and the advantage of more high activity compared to Ni, Co and Fe and less susceptibility to poisoning [4, 5]. Nickel is the most promising metal due to its low cost, however, it undergoes deactivation

caused by sintering, oxide- equipment and strong zaplanowanie [5, 6]. The problem of decontamination of catalysts following carbon deposition, especially in the reaction of methane with carbon dioxide, encourages the search for new catalytic systems and unconventional methods of their synthesis. The specificity of the UCM catalyst presented in this paper is that the intermetallic compound is a carrier that provides high thermal conductivity along the catalyst layer and the presence of highly dispersed nickel particles as an active component for UCM [4]. Thus in the reaction of methane with carbon dioxide is formed synthesis gas with a low ratio of H₂/CO = 1 : 1, the optimal for the implementation of the oxo-synthesis and preparation dimethyl ether, which is environmentally clean fuel [5], providing no- smoky burning and cold starting engines [6], as well as having higher cetane number (50-55) compared to conventional diesel fuel (40-45) and a high efficiency comparable to that of hydrogen fuel [9]. Low energy consumption, high productivity, and ease of synthesis make this method promising for the production of heterogeneous catalysts. The possibility of using the internal energy resources of thermosetting powder systems

testifies to the high advantages of SHS with technical support. It serves as a basis for the creation of new advanced technologies that provide solutions to the problems of organizing highly efficient and dynamic production of various materials. The purpose of this work is to obtain catalysts by the SHS

method (SHS-catalysts) and to study their properties in the processes of UCM and selective oxidation of methane. Selective catalytic oxidation of methane on block catalysts prepared by the SHS method Block catalysts based on porous ceramica is a promising material for the chemical processing of natural carbohydrates. Compared to granular catalysts, they are characterized by higher values of heat and mass transfer, strength, and thermal resistance, which makes it possible to significantly intensify methane conversion reactions. For the production of porous ceramics, the method of burning out additives and foaming is most widely used [14]. These methods are multi-stage, time-consuming, and high-cost. Additional possibilities for the production of porous ceramics are provided by the use of the SHS method [15], which does not require expensive furnace equipment. This method allows you to obtain materials without the cost of electrical energy, to achieve special structural states (high degree of anisotropy, inclusion of non-uniform phases) and improved functional properties of materials (increased gas permeability, thermal conductivity, etc.). This is due to a high temperature (up to 3000 K), a large temperature gradient (up to 107 K/m) and a short time formation of ceramics (10⁻¹-10⁻³ s) in the wave of synthesis. The structure of the target product depends on the thermal conditions of combustion. Gorenje. For example, in the case of ordered spin combustion, gradient materials are formed in the form of alternating layers of different porosity and chemical composition (Fig. 1, a). Gorenje et al. In Gorenje gorenje, chaotic spin combustion produces anisotropic materials with slotted pores (Fig. 1, b), and in scintillating combustion — an isotropic material in the form of a bound system of droplets with a size of

0.3—1.0 mm (Fig. 1, c). In this case, anisotropic materials are formed in the form of a bound system of droplets with a size of 0.3-1.0 mm (Fig. 1, c). The last two types of structures are optimal for block catalysts due to the highest open porosity (up to 75 %) and gas permeability. In the present work, powders of NiO, ZrO₂, MgO, Al, Ni, etc. were used as initial reagents for the preparation of block catalysts. After conducting SHS according to the method [16], the final product was a porous composite material consisting of Al₂O₃, ZrO₂, MgO, NiO, Ni, etc. The chemical composition of the finished catalysts is given in the table. The structure and composition of the material were regulated by changing the concentration, particle size of the initial reagents and the density of the charge. Based on the results of the experiments, an experimental SHS technology was developed for the production of porous catalytic blocks based on intermetallic and metal oxide compositions in the form of plates and hollow cylinders with dimensions up to 1200 mm (Fig. 2). The technological scheme of self-propagating high-temperature synthesis of block catalysts is similar to the traditional scheme for producing ceramics, except for the SHS stage, which replaces high-temperature sintering in the furnace, which reduces energy consumption in the production of materials.

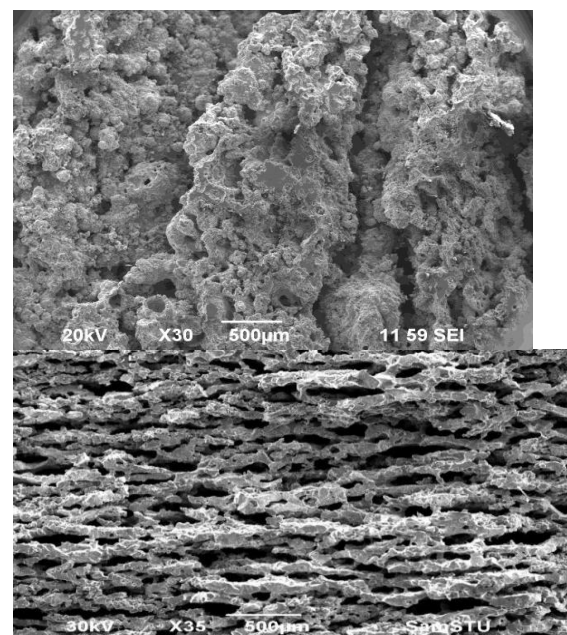


Fig. 1. Structure of porous cermet in the SHS

process: periodic gradient (a); with slotted pores (b)

Laboratory testing of the catalytic properties of materials in the reaction of selective oxidation was carried out by passing through a sample catalyst mixture of methane (29,6 %) — air at the the ture of 800 °C with a contact time of 0.5 s. the Porous samples of catalysts SVS and spongy Nickel pore sizes of 0.5—1.0 mm was inserted, and granule rovanie platinum and platinum-rhodium kata listory (courtesy of IK SB RAS) of size 0.25-0.5 mm were poured into a reactor with a length of 20 mm and a diameter of 12 mm. The results of comparative tests of SHS catalysts are presented in the table. It follows from them that the synthesis gas output (the total concentration of carbon monoxide and hydrogen) SHS catalysts reach the level of platinum and platinum-rhodium catalysts, and in the case of Ni_{52,9}ZrO_{29,5} they exceed them. Metal oxide SHS catalysts have a high catalytic activity when the process is carried out with short contact times with gas (less than 0.25 s). For Ni—Al₂O₃ granular catalysts used in industry, this time usually exceeds 1 s (for example, NIAP-22). Studies have shown that the H₂/CO ratio of methane conversion products on SHS catalysts is maintained at about two. The resulting synthesis gas is suitable for its subsequent conversion to liquid hydrocarbons by the Fischer-Tropsch process. Preliminary laboratory studies have shown the possibility of obtaining C₈—C₁₅ hydrocarbons suitable for use as motor fuel in this way. To ensure the catalytic conversion of natural hydrocarbons in the autothermal process (due to the heat of the selective oxidation reaction), a laboratory synthesis gas generator was created using a Ni_{52,9} ZrO_{29,5} catalyst in the form of a hollow cylinder. The schematic diagram of the reactor is shown in Fig. 3 Natural gas (methane, propane, butane) and air are fed into the mixing chamber, then the finished mixture with the addition of vapors water flows through the fire barrier to the catalytic unit, inside the walls of which the conversion process takes place. Presumably, the process involves the reactions of selective oxidation, vapor and

carbon dioxide conversion. Starting the process it is carried out by ignition of the fuel mixture at a ratio of air/natural gas equal to 6 : 1, with preheating the unit to 800 °C. In the stationary conditions of the mixture conversion (the volume ratio of air/natural gas is 2.5-3.0) , a temperature distribution from 1100 to 800 °C is established inside the wall of the catalytic unit. Studies have shown that the reactor provides a conversion rate of natural carbon- hydrogen up to 90-95 % to produce a product of the following composition,%: CO-17-19, H₂-33-35, remaining hydrocarbons-no more than 1-2, the rest N₂, H₂O, CO₂. The H₂/CO ratio is adjusted in the range of 1.7—2.2 by changing the composition of the natural gas and adding water vapor: the introduction of propane and butane into methane allows you to reach the lowest limit of the H₂/CO ratio, and the addition of water-the highest On the laboratory generator, I reached the synthesis gas capacity is 2 m³/h (hereafter m³ is a normal cubic meter of gas). A distinctive feature of the design is the absence of external energy consumption and compactness. The specific capacity of the reactor (the ratio of reactor capacity to volume) reaches 3 * 10³ h⁻¹, which exceeds the level of known synthesis gas generation systems based on granular catalysts (for example, NIAP-22). When you first start generator the value of the conversion of uglevodov Dov and concentration of the target Pro the product is monotonically increasing, reaching a stable level in 1-2 h. the Change of a couple meters due process activation of the catalyst, which include allocation catalyti centres (submicron of Nickel particles of 0.1—0.5 μm) on the free surface of the mother Ala phases of NiO-MgO (Fig. 4) the result of regenerative re actions involving H₂ and co. The stabilization of the catalytic properties is due to the achievement of a constant the total number of catalytic active centers. The deactivating effect of gas flows (processes of chemical corrosion and mechanical erosion on the free surface) is compensated by the formation of new centers due to the diffusion influx of nickel from the volume of the NiO-MgO phase. As studies have shown, with subsequent inclusions, the output

of the generator to the nominal characteristics occurs almost immediately after reaching the required temperature regime. The stability of the characteristics is confirmed by the test results of the generator for 20 hours. The mechanical integrity of the catalytic unit during operation is not significantly violated. However, there is only a change in the macrostructure of the material (see Figure 4). In the case of the ratio of air natural gas less than 2.5, the effect of carburization of the catalyst was observed. The elimination of free carbon from the material was achieved by adding excess air to the fuel mixture, which made it possible to completely restore the catalytic activity of the block. On the basis of the research carried out in the Department of Structural Macrokinetics of the TNC SB RAS, an experimental autothermal syngas generator with a capacity of up to 30 m³/h was created, and a project for the top of a catalytic unit obtained by the SHS method for an industrial autothermal syngas generator with a capacity of 400 m³/h was developed. Preliminary run-in of the unit as part of an industrial catalytic radiating burner in the mode of complete methane oxidation showed up. The relatively high operational life of the unit is more than 10,000 hours, which indicates its mechanical resistance to high temperature and corrosion. The resource of work on the catalytic activity in the partial oxidation mode requires additional research. Influence of the CH₄ : CO₂ molar ratio. The composition of the reaction mixture significantly affects the conversion values of CO₂ and CH₄. With an increase in the ratio of CO₂ : CH₄ from 1 to 3, the methane conversion increases from 64 to 78 % at a temperature of 800 °C; while how does the carbon dioxide conversion decrease from 73 up to 36 %. In this case, the carbon balance improves as the reaction mixture is enriched with carbon dioxide. The reason for the favorable effect of CO₂ on the CCM process is its ability to regenerate coked catalysts with the formation of CO and CH₄ by the mechanism of hydrogen disproportionation. From the results of the catalytic tests, it can be concluded that the modification of the Ni₃Al intermetallic compound with extremely small doses of

platinum leads to a significant increase in the activity of the samples during the conversion of methane with carbon dioxide. Stability testing. Check of rolling congestion on the stability of the work in the process of UKM osu They were produced at a temperature of 900 °C for 140 h with a molar ratio of CH₄: CO₂ = 1 : 1. The Pt / Ni₃Al catalyst worked stably for the first 65-70 hours, after which a slight decrease in activity was observed, while the CH₄ and CO₂ conversions decreased by only 2-4 % by the end of the test, whereas in the case of an unmodified matrix, the conversions decreased by 25-30 %. Despite the very low platinum content (dose 1·10¹⁷ ion Pt / cm²) the stability of the modified catalyst is significantly higher than that of the matrix. The reason for the increased resistance to carbon deposition is the extremely low solubility of carbon in noble metals, as well as the high dispersion of Pt over the entire surface of the sample. Comparison Pt-implanted catalysts with analogues available in the literature [14] showed an obvious advantage of the former in terms of stability: for example, a Pt-Ni catalyst deposited on a zeolite carrier was deactivated within 5-8 hours. Morphology. According raster electron Noah microscopy (SEM) and measurement results the specific surface adsorption method the initial sample of SVS-intermetallide Ni₃Al about lady macroporous structure (pore diameter 6-10-5 and 2-10-5 m) (Fig. 2, a) and a low specific surface of (0.5—1.0 m²/g). After the catalytic tests, there is a loosening of the surface as a result of catalytic erosion, the formation of nuclei of the nickel metal phase, as well as partial carburization of the contact, and at

different sites of the catalyst there are either frags mental globular accumulations of soot (see Fig. 2, b), or carbon fibers (see Fig. 2, c). The opposite results were obtained in the case of a platinum-modified Ni₃Al catalyst (Fig. 3, a). Surface of the original sample Pt/Ni₃Al (dose 1·10¹⁷ Pt ion/cm²) is a typical alloy chip, relatively smooth with minor roughness, having extended crevices with an average width of 0.1-0.5 microns. In the conditions of UKM the structure of this catalyst changes (see Figure 7,

b), but not as significantly as in the case of the unmodified Ni₃Al matrix.

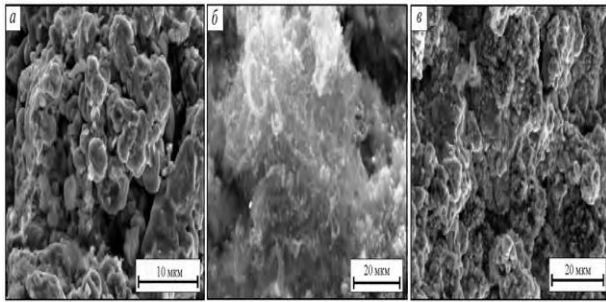


Fig. 2. SEM images of SHS-Ni₃Al intermetallic compound: initial (a) and with carbon deposition products on the surface

of the catalyst used in the UCM (b, c). Working conditions: 900 °C, CH₄: CO₂ = 1 : 1; time – 24 hours.

After catalytic tests, a certain part of the surface (about 20-30 %) remains without pronounced changes, the porosity is preserved, but faceted Ni crystallites (0.1—0.3 microns) are formed on the surface, which migrated to the surface from the volume of a multiphase heterogeneous system. In addition, the structure of this catalyst contains highly dispersed Pt particles ranging in size from ≈0.3-0.5 to 3-5 nm, which are stabilized mainly in the matrix of intermetallic and aluminum oxide. It is important to note that the highly dispersed platinum clusters formed during ion implantation are characterized by a sufficiently high stability during the heat treatment of the catalyst in the redox-stop medium of the UCM, i.e., the Pt particle size is preserved after testing in methane reforming for 24 hours at 600-800 °C. And most importantly, in this case, there is no carburization of contacts, i.e. neither soot nor carbon fibers (as in the case of an unmodified matrix) are not fixed. Thus, the modification of the catalytic system based on SHS-Ni₃Al intermetallic compound with platinum in very low concentrations by ion implantation significantly increases not only the catalytic activity, but also the stability of the catalysts over time. In addition, Pt increases the dispersion of nickel and slows down the diffusion of carbon formed during the

dissociative adsorption of methane and carbon dioxide, preventing the formation of nickel carbides and thus significantly slows down the processes carbon deposition.

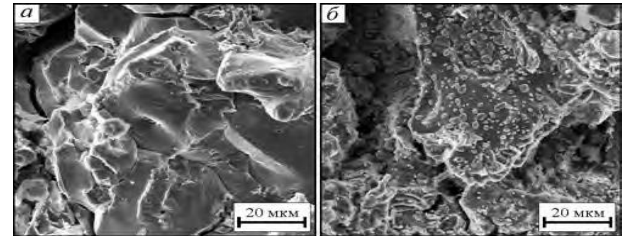


Fig. 3. SEM images of the initial (a) and spent (b) platinum - modified SHS intermetallic compound (Pt/Ni₃Al) in the UCM process. Working conditions: 800 °C, CH₄: CO₂ = 1 : 1, time – 24 h

Conclusions

1. Based on the method of self-propagating high -temperature synthesis (SHS), an energy- saving technology for compact production has been developed solid catalytic blocks in the form of cylinders and plates.
2. It is shown that the block catalysts produced by the SHS method have a high catalytic activity in the reaction of selective catalytic oxidation of methane, reaching the level of platinum catalysts in the synthesis gas yield
3. A laboratory autothermal synthesis gas generator with a capacity of 30 m³ / h on block SHS catalysts has been developed.
4. For the carbon dioxide conversion of methane to synthesis gas, an effective catalyst has been developed — a platinum-modified intermetallic compound (Pt/Ni₃Al) characterized by high activity, stability and increased resistance to coal deposition.

5. The results of the conducted research can be used to create highly active and stable catalysts for processing meta- na into synthesis gas.

Literature

1. Григорян Э.И., Мержанов А.Г. Катализаторы XXI ве- ка // Наука — производству. 1998. № 3(5). С. 30—41.
2. Maksimov Yu.M., Kirdyashkin A.I., Baev V.K., Gushin A.N. // *Advances in Science and Technology*. 2010. Vol. 63. P. 297.
3. Пат. 2349380 РФ. Катализатор и способ получения синтез-газа углекислотной конверсией метана / Ю.С. Найбороденко, Н.Г. Касацкий, В.Д. Китлер, Л.А. Аркатова и др. 2009.
4. Аркатова Л.А. // *Журнал физической химии*. 2010. Т. 84. № 4. С. 647.
5. Арутюнов В.С., Крылов О.В. Окислительные превра- щения метана. М.: Наука, 1998.
6. Ferreira-Aparicio P., Marquez-Alvarez C., Rodriguez-Ramos I., Schuurman Y., Guerrero-Ruiz A., Mirodatos C. // *J. Catal* 184 (1) (1999) 202.
7. Rostrub-Nielsen J.R., Bak-Hansen J.H. // *J. Catal*. 144(1993) 38.
8. Wang H.Y., Ruckenstein E. // *Appl. Catal. A* 204 (2000) 143.
9. Пористая конструкционная керамика / Под ред. Кра- сулина. М.: Metallurgy, 1980.
10. Пат. 255221 СССР. Способ получения тугоплав- ких неорганических соединений / А.Г. Мержанов, В.М. Шкиро, И.П. Боровинская. 1967.
11. Кирдяшкин А.И., Юсупов Р.А., Максимов Ю.М., Китлер В.Д. // *Физика горения и взрыва*. 2002. Т. 38. № 5. С. 85.
12. Arkatova L.A. // *Catalysis Today*. 2010. Vol. 157. P. 170.
13. Brown I.G. // *Review of Scientific Instruments*. 1994. Vol. 65. P. 3061.
14. Zhang J., Wang H., Dalai A.K. // *J. Catal*. 249 (2007) 300.
15. Semelsberger T.A., Borup R.L., Greene H.L. // *J. Power Sources*. 156 (2006). 497.

16. Bradford M., Vannice M. // *Catal. Rev. Sci. Eng.* 41 (1999) 1.
17. Wang J.C.B., Hsiao S.Z., Huang T.J. // *Appl. Catal. A* 246 (2) (2003) 197.
18. Sazonova N.N., Sadykov V.A., Bobin A.S., Pokrovskaya S.A., Gubanova E. // *React. Kinet. Catal. Lett.* 98 (1) (2009) 35.
19. Rostrub-Nielsen J.R., Bak-Hansen J.H. // *J. Catal.* 144 (1993) 38.
- Wang H.Y., Ruckenstein E. // *Appl. Catal. A* 204 (2000)