



New Composite Materials Prepared by Solution Combustion Synthesis for Catalytic Reforming of Methane

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Processing of natural gas into motor fuel has become one of the major problems of chemistry. Partial oxidation and CO₂ reforming of CH₄ attract a great attention in recent years. Resistant to temperature extremes and thermal shocks is one of the most important requirements for catalysts. Works on research of intermetallic compounds as a contact mass for conversion of methane were carried out. Method of self-propagating high temperature synthesis was used for synthesis of catalysts. Investigation of the activity of catalysts based on the initial mixture of metal oxides produced in the solution combustion synthesis process was carried out in the reaction of carbon dioxide conversion and partial oxidation of methane. 100 % methane conversion at 750 °C was carried out on the catalyst, whereas the conversion of CO₂ reached 81.7 % at 900 °C. H₂ yield reached 99.2 %, yield of CO - 99.1 % in the ratio of H₂/CO = 1.2. Effective catalysts for the production of synthesis gas from methane have been developed.

1. Introduction

Self-propagating high-temperature synthesis (SHS) method is used worldwide (Shuck et al., 2016) for the low-cost production of engineering and functional materials such as advanced ceramics, intermetallics, catalysts and magnetic materials. The method exploits self-sustaining solid-flame combustion reactions for the internal development of very high temperatures over very short periods. It therefore offers many advantages over traditional methods such as much lower energy costs, ease of manufacture and capability for producing materials with unique properties and characteristics. The interest to SHS catalysts is growing every year and now many countries intensively working with SHS and combustion synthesis catalysts: Russian Federation, USA, Kazakhstan, Japan, Armenia, Greece, Brazil, China, Spain, Korea, India, etc. (Varma et al., 2016). Very high interest to SHS catalyst can be explained by high activity of catalysts prepared by this methods and advantages of SHS method in comparison with traditional methods of preparation of catalysts. Method is attractive for industrial production: much lower energy consumption than traditional production methods, much lower energy costs, possibility for "just-in-time" manufacturing, high productivity, cheap catalysts, relatively simple process - easily adaptable to industrial scale, controlled physico-chemical properties of the products, large range of new materials which can be used in catalysis, it has wide diapason of structural forms of products - from granules of different size to blocks of honeycomb structure and different geometric forms. In addition, the environmental impact of SHS is very much lower than that of the traditional method, a fact which decreases even further the indirect cost of production (Marinou et al., 2015). For over the last few years, conversion of CO₂, in particular by its reaction with methane to form CO and hydrogen (commonly known as dry reforming of methane), has gained a lot of attention. During the past decades, nickel catalysts for dry reforming of methane have been extensively studied (Siang et al., 2017). It is known that nanosized metallic and polyoxide catalysts are developed for catalytic partial oxidation (CPO) of CH₄ into synthesis-gas during last decade (Ricca et al., 2016). It was demonstrated that the 0.5 % Pt - 0.5 % Ru/2 % Ce/(θ+α)-Al₂O₃ catalyst is highly active and selective in the above process as well (Tungatarova et al., 2010). The aim of our work was investigation the reaction of CH₄ with CO₂ (dry reforming) and O₂ (partial oxidation) catalyzed by NiO - Al - α-

Al_2O_3 , which were prepared by SHS method and traditional incipient wetness impregnation to demonstrate the benefits of SHS method.

2. Experimental

The SHS catalysts on the base of $\text{NiO} - \text{Al} - \alpha\text{-Al}_2\text{O}_3$ were prepared from powder mixtures consisting of nitrates, metals, and oxides. The specimens were preheated in an electric furnace at 700 – 900 °C for several minutes. The second series of catalysts was prepared by traditional method: samples were prepared by the incipient wetness impregnation of dispersed $\alpha\text{-Al}_2\text{O}_3$ (granule size 100 – 200 μm , S – 57.7 m^2/g) by water solutions of metal nitrates with subsequent heating on air at 250 °C within 5 h, at 600 °C within 2 h, and at 900 °C within 1 h. The tests were carried out in a fixed bed free flow quartz reactor without any pre-reduction. All of the tests were conducted at atmospheric pressure in a flow of $\text{CO}_2 - \text{CH}_4 - \text{N}_2$ mixture (1 : 1 : 1). Experiments on the partial oxidation of methane to synthesis gas were carried out on flow type installation at atmospheric pressure in a tubular quartz reactor with a fixed catalyst bed. Catalyst was placed in the central part of reactor and quartz wool placed above and below the catalyst bed. The initial reaction mixture 34 % $\text{CH}_4 + 17\% \text{ O}_2 + 50\% \text{ Ar}$ was used for the partial oxidation of methane to synthesis gas at 900 °C and flow rate of reactants 2,500 h^{-1} . An Agilent 6890N (Agilent Technologies, United States) gas chromatograph with computer software equipped with flame ionization and thermal conductivity detectors was employed for on-line analysis of initial substances and reaction products.

3. Results and discussion

The composition and structure of the catalyst was studied by XRD, SEM with a chemical analysis, the specific surface area was determined by BET. During the SHS experiments the combustion velocity and specific surface SHS catalysts data were measured, which varied from 7.4×10^{-3} to 12.4×10^{-3} m/s and from 0.3 to 2.1 m^2/g , respectively. The specific surface area is low. This is due to the high temperatures of combustion during SHS. SHS catalysts on the base of initial batch $\text{Al} - \text{NiO} - \text{Al}_2\text{O}_3$ with different ratio have similar qualitative composition, but there are differences in the phase ratio (Figure 1). The proportion between the phases determined from the relative intensities of the X-ray diffraction peaks are shown in Figure 1 and Figure 2. At 52 – 53 % Al and 26 – 27 % NiO observed maximum yield of the reaction products: NiAl , NiAl_2O_4 .

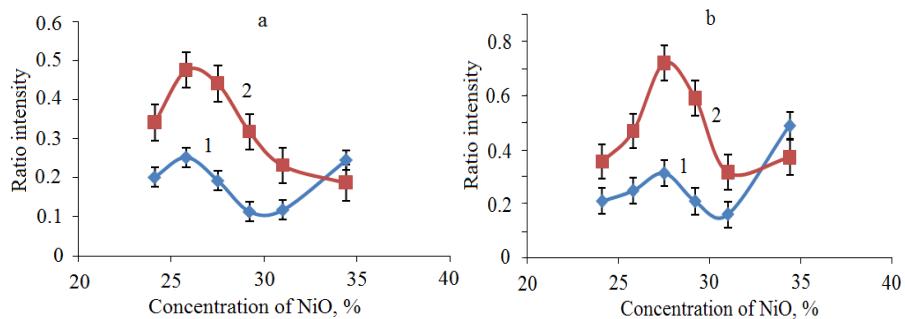


Figure 1: Dependence of concentrations ratio of different phases in SHS catalysts at change of NiO content in composition of initial batch $\text{NiO} - \text{Al} - \text{Al}_2\text{O}_3$. a: 1 – AlNi/Al , 2 – AlNi/NiO ; b: 1 – $\text{NiAl}_2\text{O}_4/\text{Al}$, 2 – $\text{NiAl}_2\text{O}_4/\text{NiO}$

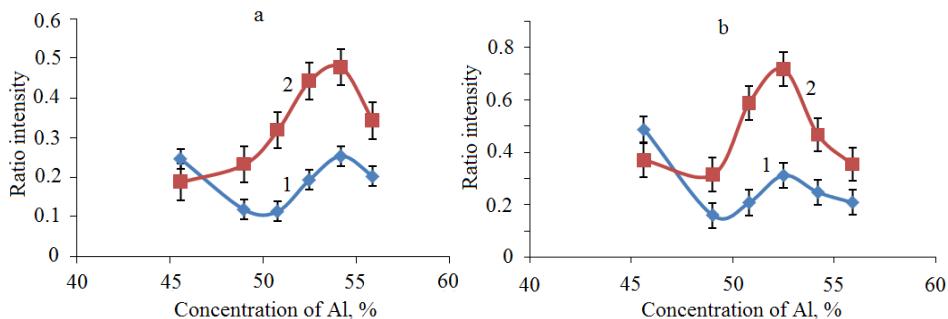


Figure 2: Dependence of concentrations ratio of different phases in SHS catalysts at change of Al content in composition of initial batch $\text{NiO} - \text{Al} - \text{Al}_2\text{O}_3$. a: 1 – AlNi/Al , 2 – AlNi/NiO ; b: 1 – $\text{NiAl}_2\text{O}_4/\text{Al}$, 2 – $\text{NiAl}_2\text{O}_4/\text{NiO}$

Thus, changes in the composition of the initial batch results in a change in the phase ratio in SHS reaction products (Figure 1 and Figure 2).

It was found that the increase of NiO concentration and decrease of the Al concentration in the initial charge increases combustion velocity. It is connected with approach the stoichiometric composition, and therefore a greater heat generation affects the increase in the reaction rate.

The study of SHS catalysts structure was carried out using a scanning electron microscope (catalysts with NiO: 24.1 and 34.4 wt% concentration in the initial batch). It was found that the phase analysis by method of chemical analysis is corresponding to the data of XRD analysis: Al, α -Al₂O₃, Al-Ni, Ni, NiO, NiAl₂O₄. Figure 3 demonstrates analysis data for catalyst with initial batch composition: 24.1 % NiO + 55.9 % Al + 20 % Al₂O₃.

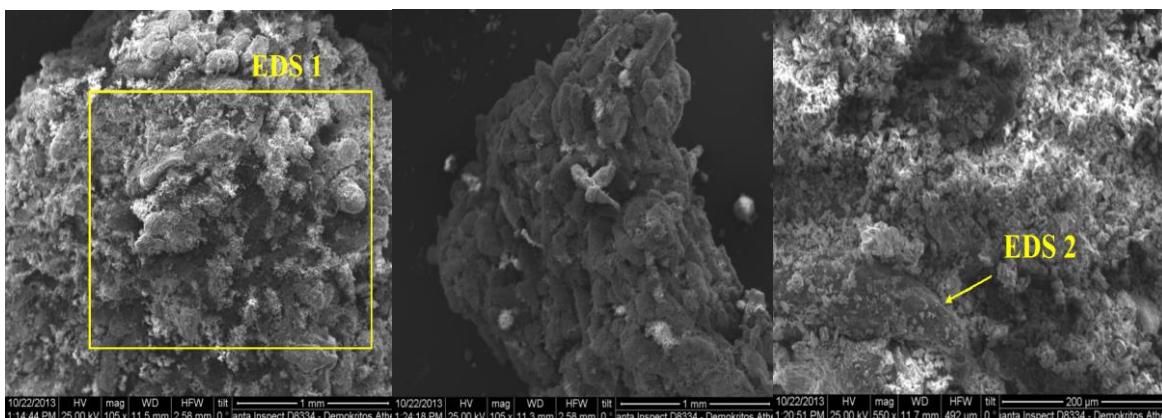


Figure 3: SEM catalyst photos on the base of initial batch: 24.1 % NiO + 55.9 % Al + 20 % Al₂O₃ (furnace temperature T = 900°C)

Chemical analysis show that the nickel, aluminum and oxygen ratio varies in different areas of catalyst. A high content of nickel, aluminum and oxygen corresponds to the spinel phase. The virtual absence of oxygen at a high content of nickel and aluminum corresponds to NiAl.

Obtained SHS catalysts tested for catalytic activity in the carbon dioxide dry reforming of methane in the temperature range 750 – 900 °C. CO₂ and methane conversion, H₂/CO ratio in the reaction products as well as hydrogen and CO yields for the studied SHS catalysts on the base of system NiO – Al - α -Al₂O₃ shown in Figure 4. Figure 4 shows that the best results for SHS catalysts based on systems NiO – Al - Al₂O₃ are: 93 % CH₄ conversion, 100 % conversion of CO₂, product yield reaches 92 % H₂ and 99 % CO. Ratio hydrogen to carbon monoxide in the reaction product varies in the range of 0.7 – 1.35. Increasing the reaction temperature, in most cases, increases the ratio of H₂/CO due to the amplification of dehydrogenation reaction.

Effect of catalyst composition on the conversion of CH₄, CO₂ and the ratio of H₂/CO seen in relation to the concentration of aluminum in the starting material. To maximize the yield of methane the optimum aluminum content in the initial batch is 51% and for carbon dioxide – 51 – 56 % of Al in the initial batch.

Effect of catalyst composition on the conversion of CH₄, CO₂ and the ratio of H₂/CO also seen in relation to nickel oxide, because from nickel oxide concentration depends content of nickel spinel - active catalyst component.

The optimum concentration (maximum conversion of CO₂) of nickel oxide in the starting material is 24 – 30 %, and for the conversion of methane - optimum is clearly revealed 29 % of nickel oxide.

Comparing these data with those in Figure 1 and Figure 2, it can be concluded that the catalyst with 29 % nickel oxide and 51 % aluminum in the starting material, after the SHS reaction contains a maximal concentration of NiAl, NiAl₂O₄ active phases into carbon dioxide reforming of methane.

The study of catalysts of similar composition but prepared by the traditional method of wetness impregnation and further their comparison with SHS catalysts is very interesting. A series of catalysts was prepared by impregnation method: 24.1 % NiO + 55 % Al + 20 % Al₂O₃, 25.7 % NiO + 54.2 % Al + 20 % Al₂O₃, 27.5 % NiO + 52.5 % Al + 20 % Al₂O₃, 29.2 % NiO + 50.8 % Al + 20 % Al₂O₃. Investigation of catalysts was carried out under the following conditions: CH₄ : CO₂ : Ar = 1 : 1 : 1, GHSV - 860 h⁻¹. The research results are shown in Figure 5. Analysis of the data shows that the conversion of feedstock has similar values both on SHS catalysts, and on traditional supported samples. However, target products yield is significantly higher for SHS catalysts: hydrogen yield is about 48 – 51 % on the supported catalysts, and ~ 80 % on SHS catalysts; CO yield is about 40 – 42 % on supported catalysts, while about 90 % on SHS catalysts. These data indicate a

significant advantage of the new composite materials produced by combustion synthesis process. The obtained target products on above-mentioned catalysts are cleaner, which do not require additional treatment.

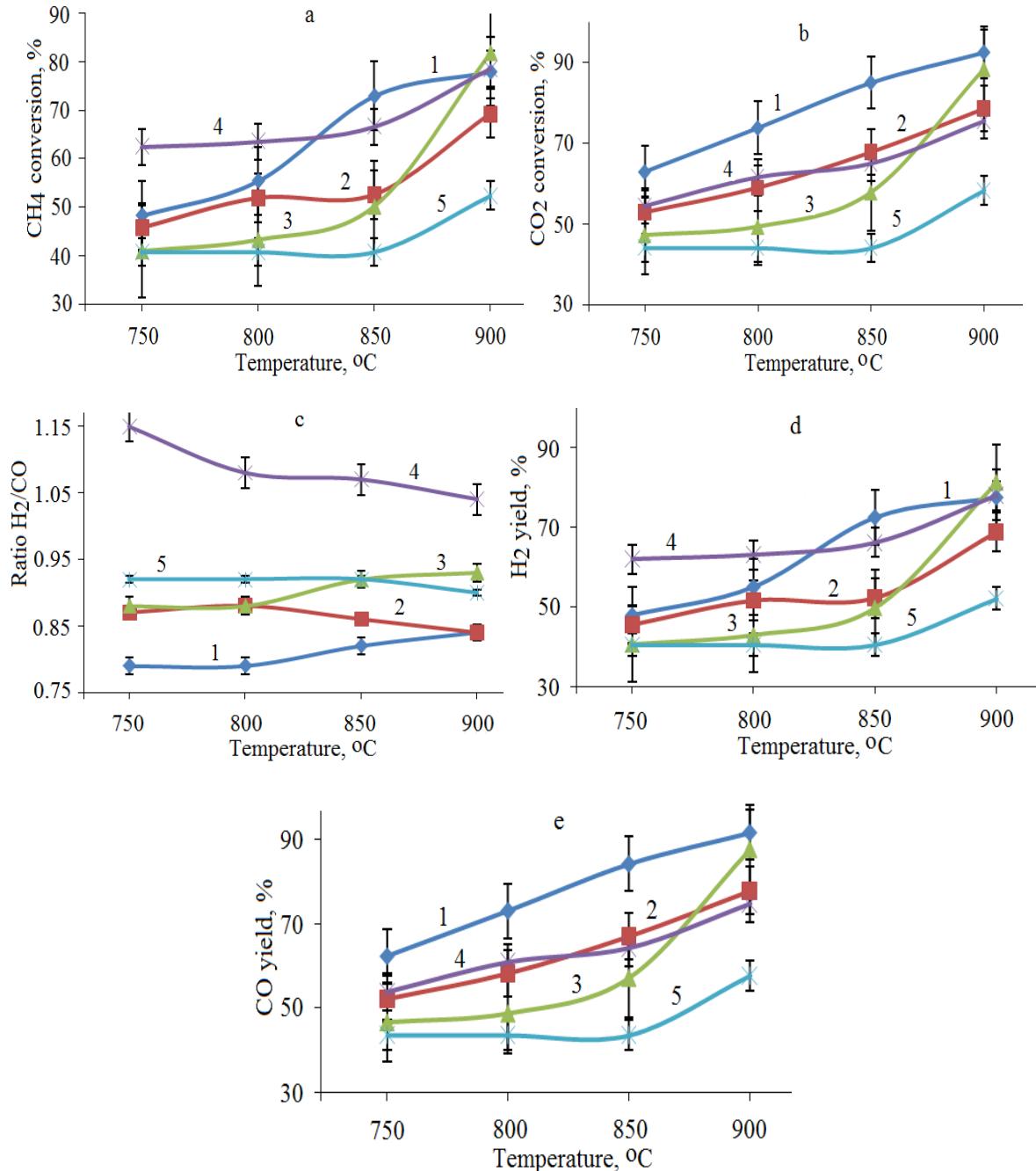


Figure 4: The indicators of CO₂ reforming of methane according to the reaction temperature for SHS catalysts on the base of system NiO - Al - Al₂O₃. 1 – 31 % NiO + 19 % Al + 50 % Al₂O₃, 2 – 28 % NiO + 42 % Al + 30 % Al₂O₃, 3 – 39 % NiO + 10 % Al + 30 % Al₂O₃ + 7 % Mg + 14 % MgO₂, 4 – 87 % NiO + 12.6 % Al + 0.4 % H₃BO₃, 5 – 10 % NiO + 28 % Al + 40 % Al₂O₃ + 22 % MoO₃; GHSV – 860 h⁻¹

The catalysts of NiO - Al - α-Al₂O₃ series prepared by SHS method and by incipient wetness supporting were tested in the partial oxidation of methane in the following conditions: GHSV = 2,500 h⁻¹, composition of the reaction mixture: 34 % CH₄ + 17 % O₂ + 50 % Ar (Table 1).

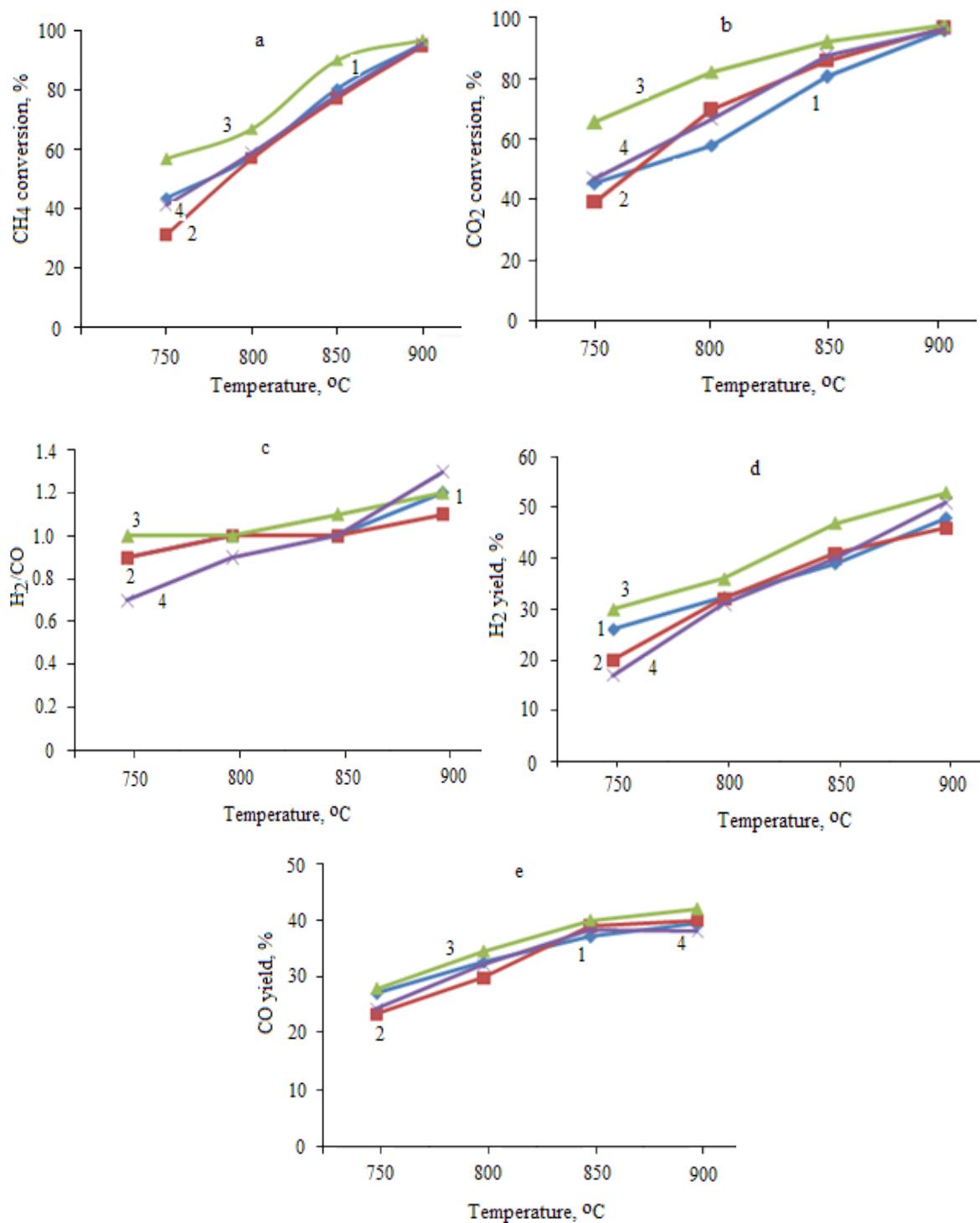


Figure 5: Indicators of carbon dioxide reforming of methane depending on the reaction temperature on the catalysts based on $\text{NiO} - \text{Al} - \text{Al}_2\text{O}_3$ system, prepared by incipient wetness supporting. 1 – 24.1 % $\text{NiO} + 55.9\%$ Al + 20 % Al_2O_3 , 2 – 25.8 % $\text{NiO} + 54.2\%$ Al + 20 % Al_2O_3 , 3 – 27.5 % $\text{NiO} + 52.5\%$ Al + 20 % Al_2O_3 , 4 – 29.2 % $\text{NiO} + 50.8\%$ Al + 20 % Al_2O_3 . GHSV – 860 h^{-1}

SHS catalysts show higher activity in CH_4 partial oxidation, H_2 yields (52.0 - 67.0 %) are higher compared with supported samples (53.9 - 57.2 %), and for CO - (21.0 - 27.1 %) instead of (21.9 - 24.2 %). Ratio of $\text{H}_2/\text{CO} = 2.0 - 2.9$. The ideal ratio of $\text{H}_2/\text{CO} = 2$ was obtained for the SHS sample (29.2 % $\text{NiO} + 50.8\%$ Al + 20 % Al_2O_3).

Table 1: Oxidative conversion of CH₄ on the NiO - Al - α -Al₂O₃ catalysts prepared by SHS (I) and incipient wetness supporting methods (II)

Starting mixture	CH ₄ conversion, %		H ₂ yield, %		CO yield, %		H ₂ /CO	
	I	II	I	II	I	II	I	II
24.1 % NiO 55.9 % Al 20 % Al ₂ O ₃	90.0	78.8	61.5	54.9	21.0	21.9	2.9	2.5
25.8 % NiO 54.2 % Al 20 % Al ₂ O ₃	84.2	66.9	62.0	57.2	26.4	22.4	2.3	2.6
27.5 % NiO 52.5 % Al 20 % Al ₂ O ₃	96.0	69.4	67.0	53.9	27.1	24.2	2.5	2.2
29.2 % NiO 50.8 % Al 20 % Al ₂ O ₃	81.7	73.7	52.0	55.7	25.9	22.8	2.0	2.4

4. Conclusions

Thus, the catalysts were prepared by SHS and incipient wetness supporting methods based on Al – NiO - Al₂O₃ and Al – NiO - Al₂O₃ -M systems and extensive studies of their properties and activity in the reaction of carbon dioxide dry reforming and partial oxidation of methane were carried out. The analyses of Al – NiO - Al₂O₃ catalyst using XRD, SEM and BET methods provided useful information in understanding the catalytic activity of catalysts at the conversion of methane to synthesis-gas. It was found causes of optimal catalyst activity.

The increase of NiO concentration and decrease of the Al concentration in the initial charge increases combustion velocity. It is connected with approach the stoichiometric composition, and therefore a greater heat generation affects the increase in the reaction rate. High temperatures (when there is more than 27 % NiO and lower than 55 % Al in the initial batch) affect the stabilization of the crystal lattice. The change of crystal lattice parameters influences the catalytic activity. The best results for SHS catalysts based on systems NiO – Al - Al₂O₃ are: 93 % CH₄ conversion, 100 % conversion of CO₂, product yield reaches 92 % H₂ and 99 % CO. Ratio H₂/CO in the reaction product varies in the range of 0.7 – 1.35. The catalyst with 29 % NiO and 51 % Al in the starting material, after the SHS reaction contains a maximal concentration of NiAl, NiAl₂O₄ active phases into carbon dioxide reforming of methane. The optimal lattice parameter for maximum conversion of CO₂ and CH₄ are 3.48 - 3.485 Å for Al₂O₃, which plays the role of a catalyst carrier and 1.42 Å - for NiAl₂O₄ playing the role of catalyst.

Acknowledgments

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