Carbon Dioxide Conversion of Methane into Synthesis-Gas on Glass Cloth Catalysts

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Abstract

The catalytic activity of nanostructurized low per cent (≤1%) Co-Ni catalysts on the basis of glass cloth, obtained by "solution combustion" (SC) method, in the reaction of carbon dioxide of methane was studied. The physico - chemical characteristics of the obtained species were studied by the methods of X-ray phase analysis, SEM, TEM, TGA. It is found that SC method allows to obtain an active component on the surface of glass cloth in the form of nanopaticles. A high activity of the catalyst, the active component of which is cobalt, is revealed; the decrease in Co concentration in the matrix of glass cloth results in the decrease of activity in the reaction of carbon dioxide conversion of methane.

Introduction

Annual decrease in oil reserves in the world necessitates the search for new sources of alternative pure fuel. It is known that dimethyl ether which may be obtained from synthesis gas by the method of carbon conversion of methane (CDCM) can serve as such a fuel.

The process of carbon dioxide of methane, which up to now has not been realized in industry yet,

$$CH4 + CO2 = 2CO + 2H2$$
$$\Delta H^0_{298} = 247 \text{ kj/mole}$$

allows obtain the equimolar ratio of the components.

Among the studied catalytic systems of CDCM reaction and other hydrocarbons, mention should be made of supported nickel (Ni/Al_2O_3, Ni/SiO_2 and Ni_3Al) and cobalt-nickel catalysts [1-4], coprecipitated Ni-Mg contacts ($Ni_{0.03}Mg_{0.97}O$) [5], catalysts on the basis of noble metals [6]. Quite many data [7-9] on the use of catalysts on the basis of glass cloth in many other chemical processes have appeared lately. It is shown that catalysts on the basis of glass cloth are highly active even at a low content of the active component on the surface of nickel.

This paper deals with the influence of the conditions, under which synthesized glass cloth Ni, Co catalysts are prepared, on the physico-chemical parameters; their catalytic properties in the reaction of carbon dioxide conversion of methane were studied.

Experimental

Synthesis of catalysts

To prepare the basis for catalysts, Na-Si-glass cloth of the label KC-11-JIA (88) was used as a carrier (the temperature range for this label of glass cloth is 1000-1200 ^{0}C). Oxides of Ni and Co metals were deposited onto the surface of a glass cloth matrix by the method of "solution combustion" (SC) which is one of the variants of a self propagating high temperature synthesis [10].

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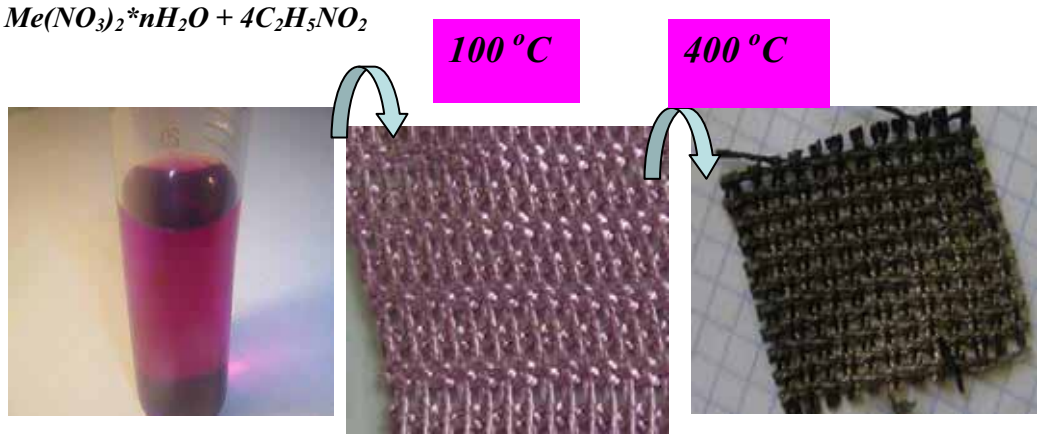


Fig. 1. The sequence of preparation fiberglass catalysts

Low percentage (not more than 1%) species were synthesized by SC method (Table 1, IK1-IK5). Glass cloth of a definite size was impregnated with solution of cobalt and nickel nitrates, then it was dried during 30 minutes in air at 100 ^{0}C and then calcined in a thermostat at 400 ^{0}C. At this temperature self propagating high temperature synthesis took place resulting in formation of nanoparticles with the sizes from 30 to 100 nm [11, 12]. The SC method between the initial components corresponds to the following reaction.

$$Me(NO_3)_2*nH_2O + 4C_2H_5NO_2+2.5O_2 = 8CO+16H_2O+3N_2+MeO,$$

where $C_2H_5NO_2$ is glycine playing the role of an oxidizer. Additional oxygen is up taken from air.

Table 1
Conditions for synthesis of glass cloth catalysts

№	$C_{cat.}$(%)	Co/Ni, %	Glycine, Mole
IK1	1,0	100/0	4,0
IK2	1,0	70/30	4,0
IK3	1,0	50/50	4,0
IK4	1,0	30/70	4,0
IK5	1,0	0/100	4,0

Investigation of the catalytic activity of the synthesized glass cloth species in the process of carbon dioxide conversion of methane into synthesis gas was carried out chromatographically on a gas-liquid chromatograph Cristall 2000M of the firm «Hromatec» (Russia). Detector on thermal conductivity was used, its column length being equal to 2.5 m, internal diameter – 3 mm, the sorbent – activated carbon, carrier gas – argon.

It was used a quartz reactor with the internal diameter of 10 mm placed horizontally in a cylindric electric furnace with the length of 20 cm switched on to a thermoregulator RPN-3 with an isolated chromium-alumel thermocouple which directly in the layer of a catalyst.

Consumption of initial gases was designed with the help of mass flow controller. The experimental conditions are: CH_4 – 70%; CO_2 – 30%; temperature in the reactor 600-800 ^{0}C; the catalyst volume: 1,6-2,0 cm^3; consumption of the mixture – 60 cm^3/m; the total flow rate of gases – 1800-2250 h^{-1}; the time for carrying out an experiment for 1 sample – 2-4 h.

The physico-chemical study of the samples was carried out at G.K. Boreskov Institute of catalysis of SB of RAS (Novosibirsk, Russia).

The specific surface (S_s, m^2/g) of samples was determined by the method of thermal desorption of argon (BET method) on the device SORBI N.4.1. by comparing volumes of gas – adsorbate (argon), being sorbed by the sample under study and the standard sample of the material with the known specific surface.

The elemental composition of deposited active components on glass cloth samples was determined by the method of atomic – emission spectroscopy with inductively – coupled plasma (OPTIMA-4300 DV, USA).

X-ray phase analysis was carried out on the device HZG-4 with emmitance CoK_α in the range of angles 20-80^0 by 2Θ with the scanning rate of 1 d/m. The phases were indentified according to the radiographic data base JCPDS.

The morphology of particles was studied by the methods of scanning (SEM) and transmission electron microscopy (TEM)on the device JSM 6460LV (JEOL, Japan) with accelerating of 25 kv and JEM 2010 (JEOL, Japan) with the resolution on the grid 0.14 nm

The thermogravimetric analysis (TGA) was carried out on the device NETZSCH STA 449C.

Results and discussion

Characteristics and properties of the system under study

The specific surface of the studied samples made up ≤1,0 m^2/g which is close that of the catalyst carrier – glass cloth owing, partially, to the fact that the amount of the deposited components did not exceed 1% mass.

To study the sample by X-ray phase analysis, the sample with the active component deposited onto the surface of the support was ground to powder. The diffractogram of ИК2 sample (Figure 2) shows the presence of two phase: 1-X-ray amorphous phase of the support (glass cloth – a characteristic line of grade), 2 – spinel phase $(Co,Ni)Co_2O_4$ with the size of particles D=200A (the most characteristic line of 42,73 grade and weaker ones of 35.72, 69.99, 77.15 grade). Study of the oxide film without active components (without a glass cloth matrix) by X – ray phase analysis also showed the presence of spinel phase $CoCo_2O_4$ and this can serve as verification of the obtained data.

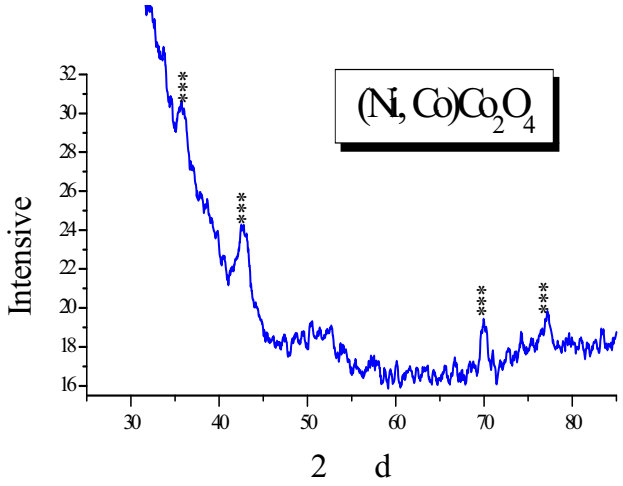


Fig. 2. The diffractogram of ИК2 catalyst

Quantitative elemental analysis of the active components deposited on the surface of glass cloth showed (Table 2) that the ratio Co : Ni lasts, however there are small losses which are likely due to the losses in the process of preparation of the designed content of active components on glass cloth on account of small moisture capacity of the support.

So, it follows according to the data of chemical analysis that the working amount of the active phase varies in the range of 0.6-0.8%.

Table 2
Estimated data and the data of chemical analysis for some samples

№	Co, weight % estimation	Co, weight %. chem. analysis	Ni, weight % estimation	Ni , weight %. chem. analysis
ИК2	0,70	0,45	0,30	0,20
ИК3	0,50	0,43	0,50	0,44
ИК4	0,30	0,21	0,70	0,51

Study of catalysts by SEM and TEM methods

The surface of fibers of the initial glass cloth (Figure 3a) and the glass cloth with the deposited active component (Figure 3b) was studied by SEM method.

As is seen in Figure 3a, the initial sample of glass cloth is fibers with the diameter of 7-8 μm, on the surface of which there are inclusions, probably, impurities. Comparison with Figure 3b shows that deposition of cobalt and nickel oxides onto surface by SC method results in formation of a film covering the whole surface of glass cloth.

Spectral analysis (EDX) of IK3 sample (Figure 3) verifies the presence of both Co and Ni in the basis of the oxide film, this corresponding to the conditions of synthesis of the given sample (the ratio of Co:Ni corresponds to 1:1).

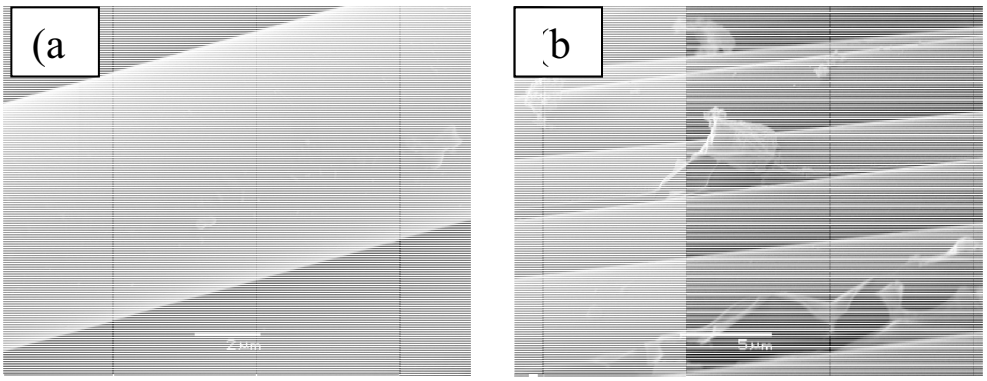


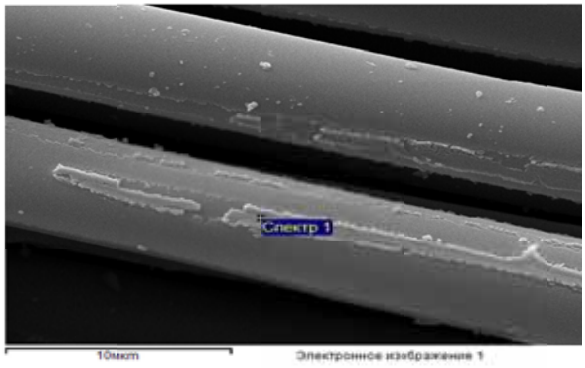
Fig. 3. SEM pictures: (a) – pure glass cloth, (b) – sample of IK1(b)

As the probe beam penetrates to the depth of 1-2 microns of the catalyst basis, in the elements found by this method there are, alongside with the introduced active components, the elements contained in the glass cloth matrix (Table 3).

Table 3.

The data of spectral analysis of IK3 catalyst

Element	Weight %	Atomic %
C K	10.65	17.14
O K	44.23	53.45
Al K	1.40	1.00
Si K	39.02	26.86
Co K	2.38	0.78
Ni K	2.32	0.77



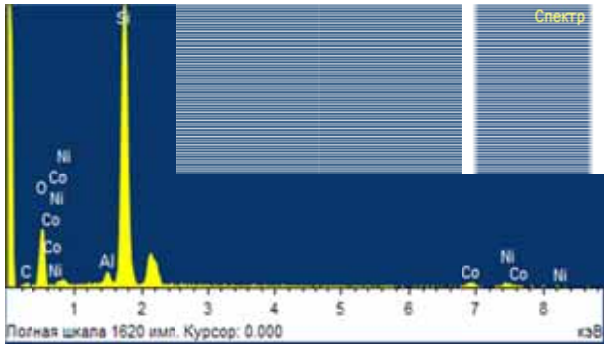


Fig. 4. SEM picture of IK3 sample (a), EDX spectrum (b)

It should be noted that the resolving power of SEM method is not sufficient for a full revelation of the picture of an oxide film covering the sample. In this connection, the structure and characteristic size of crystallites on the surface of samples was additionally studied by the method of transmission electron microscopy.

One can see in the pictures made by TEM (Figure 5) that the active component is dispersed on the surface of fiber mainly in the form of separate particles with the size of an order 10 nm. EDX analysis (Figures 5, 6) showed the presence of Ni and Co atoms in them. Figure 6 presents a TEM picture of a separate particle. Interplane distances characterize the metallic state of elements.

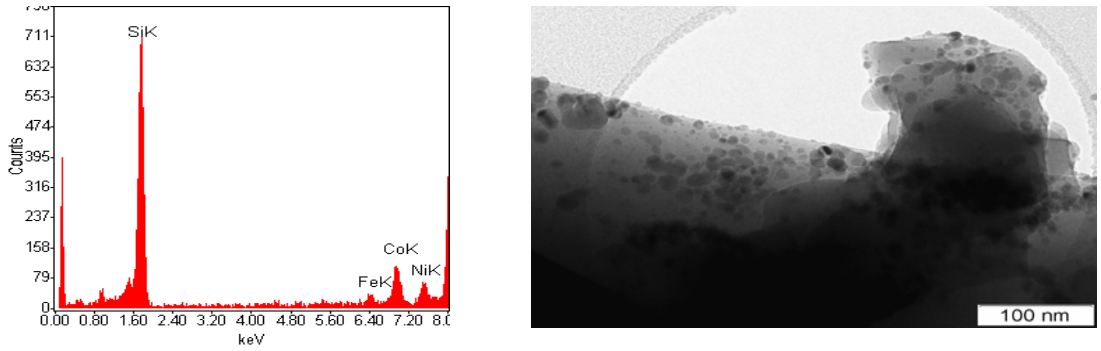


Fig. 5. EDX spectrum (a), TEM picture of Co/Ni catalyst – 0.6/0.4; 0.8% (b)

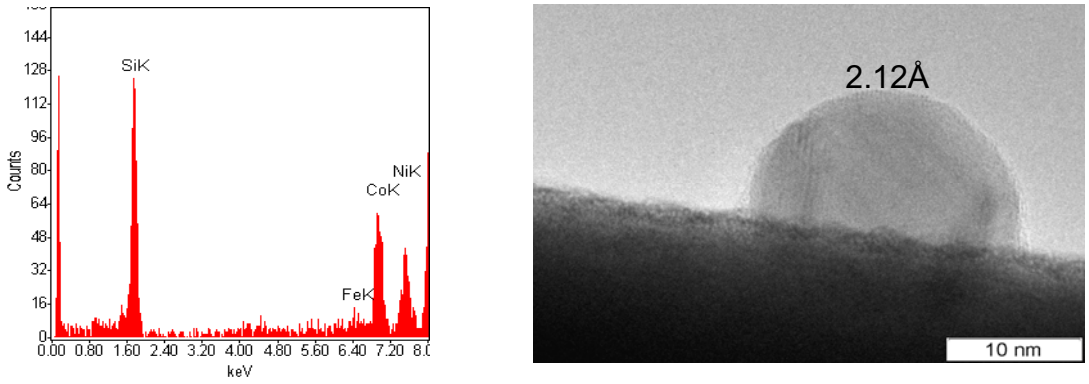


Fig. 6. EDX spectrum (a), TEM picture of a separate particle consisting of Ni and Co catalyst – 0.6/0.4; 0.8% (b)

The catalytic activity of samples in the reaction of carbon dioxide conversion of methane

The catalytic activity in the reaction of CDCM was determined out for samples of catalysts presented in Table 1. Figures 7, 8 present the results of the study on conversion dependency of initial substances, methane and carbon dioxide as well as the values of yields of the reaction target products – hydrogen and carbon monoxide on temperature and time of catalysis. Sample IK1 (Figure 7a) showed a quite high activity: it is seen that the yield of synthesis gas reaches 32% of H_2 and 46% of CO at 745^{0}C. Conversion of CH_4 makes up 30% that of CO_2 makes up 80% at the same temperature.

Considerable changes in the yield of synthesis gas with time (Figure 7b) are not observed, this indicating the fact that the work of this catalyst is stable in the studied temperature range.

This is not the case for sample IK 5 modified by nickel oxide (Figure 8a). Only reaching 720 ^{0}C, the yield of target products made up 17% of H_2 and 19% of CO. Conversion of CH_4 makes up 20%, CO_2 – 47%. After the temperature in the reactor reaches 740 ^{0}C, the catalyst considerably decreases.

Samples of catalysts IK 2,3,4 (Table 1) showed average activity in the reaction of CDCM – the decrease in cobalt oxide concentration results in the decrease in the catalyst activity.

A conventional catalyst GIAP -18 (NiO = 6-8 %, Al_2O_3 = 90 %) was studied for comparison with glass cloth catalysts in the reaction of CDCM. The ratio of initial gases was CH_4 / CO_2 = 1,25/0,75. The yield of synthesis gas made up 53% of H_2 and 24% of CO at 630^{0}C, conversion of CH_4 - 58%, CO_2 – 75%. However, the life time of GIAP -18 appeared to be short and after approximately 3 hours of work the yield of carbon oxide decreased up to 8 % and conversion carbon dioxide made up 82%, this indicating the process of carbonization. Besides, the catalyst volume after the reaction of CDCM decreased three times.

After the reaction of CDCM, the surface of glass cloth catalysts was studied by the method of TGA in the range of temperatures from the room temperature to 1000 ^{0}C with the velocity 10 ^{0}/min. according to the obtained data, carbon on the surface is formed in a small amount not exceeding 0.465 % for sample IK 1 and 0.51 % for IK 2.

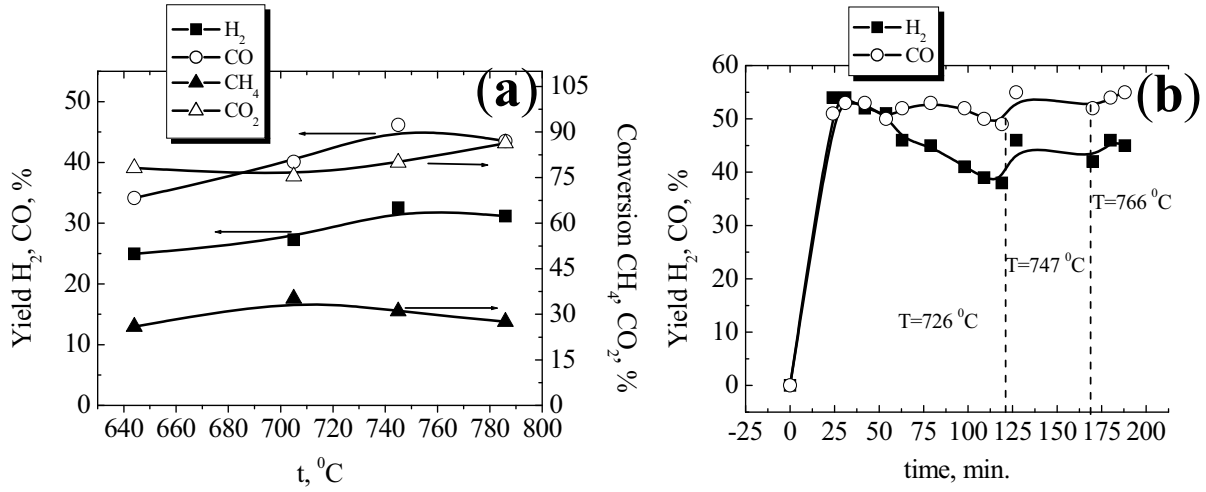


Fig. 7. Catalyst IK1. The change in the yield of the reaction products (H_2, CO), initial components of the reaction mixture (CH_4, CO_2) depending on temperature (a) and the change in the yield of the reaction products on time at different temperatures (b)

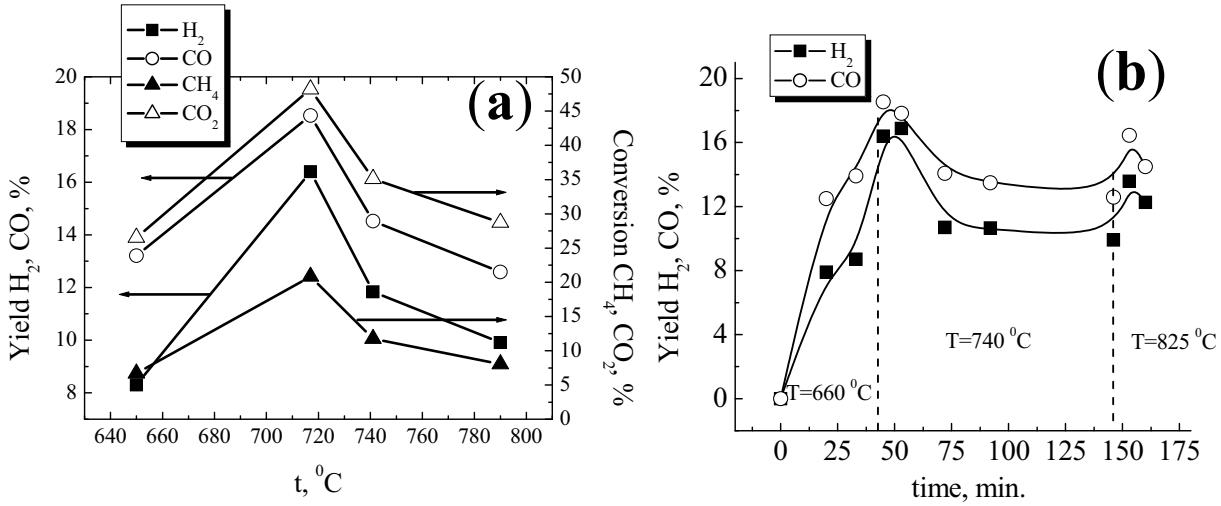


Fig. 8. Catalyst IK5. The change in the yield of the reaction products (H_2, CO), initial components of the reaction mixture (CH_4, CO_2) depending on temperature (a) and the change in the yield of the reaction products on time at different temperatures (b)

Conclusion

It follows from the presented data that glass cloth is a new, promising material which can serve as a carrier foe oxide and metallic phase and allows creating highly effective catalysts for the process of carbon dioxide conversion of methane. Due to its good gas dynamic characteristics, small concentrations of the active component will do well.

Study of the surface of a glass cloth sample by the method of SEM and TEM showed that the active component is dispersed mainly in the form of separate particles with the side of 10 nm and less which form an oxide film.

Samples of catalysts with deposited cobalt oxide show high activity in the reaction of carbon dioxide conversion of methane. It should be noted that, in comparison with the industrial catalyst GIAP-18, glass cloth catalyst IK 1 carbonizes considerably slower and after three hours of work the carbonization degree for IK 1 made up not more than 0.5%.

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