

# Nanosized Co-Ni/Glass Fiber Catalysts Prepared by “Solution-Combustion” Method

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**Abstract** Nanostructured low percent Co-Ni catalysts on the basis of glass fibers (GF) were synthesized by a “solution combustion” (SC) method. Catalytic activity of prepared samples was studied in the reaction of dry reforming of methane (DRM) with CO<sub>2</sub>, CO and butane oxidation reactions. Physico-chemical characteristics of obtained species were studied by XRD, TEM, TGA, AFM, H<sub>2</sub>-TPR and DR UV-Vis. The active component was shown to be dispersed in the near-surface layer of the support as nanoparticles of size 10–20 nm, which have a Co<sub>3</sub>O<sub>4</sub> or (Co,Ni)Co<sub>2</sub>O<sub>4</sub> spinel structure depending on the catalyst composition. The spinel structure of the active component strongly interacting with the carrier is resistant to carbonization and provides high catalytic activity in DRM, and high activity and stability in oxidation reactions.

**Keywords** Dry Reforming of Methane, CO Oxidation, Butane Oxidation, Co-Ni-Catalyst, Glass Fiber Catalyst, Self-Propagating High Temperature Synthesis

## 1. Introduction

The high interest to nanosized objects is caused by unusual chemical and physical properties, which are connected with so-called “quantum size effect”. One of the main reasons of changing particle properties by a decrease of their size is a rise of a number of surface atoms, which are under different conditions (coordination number, local symmetry etc.) in comparison with bulk atoms. From the energetic point of view, a decrease of the particle size leads to an increase of the surface energy in chemical potential and, thereby, to an increase of the activity. These unique properties have the importance in the use of metal or metal oxide particles in catalysis. On the other hand, excess energy of nanoparticles can lead to the irreversible aggregation. Thus, an urgent task is the development of new synthesis methods providing the stabilized nanodispersed state of active components in the support matrix and their study in various catalytic reactions. Nanosized catalytic systems can be effectively used for the solution of ecological problems of the processes of CO and hydrocarbon combustion as well as for the utilization of components, which causes the so-called “greenhouse effect” [1, 2]. Main components of a greenhouse

gas are water vapor, CO<sub>2</sub>, CH<sub>4</sub> and O<sub>3</sub> [3]. Utilization of CO<sub>2</sub> and CH<sub>4</sub> is of great interest because these substances can be used as reactants for dry reforming of methane to yield hydrogen or synthesis gas [4-6], which are a valuable feedstock for the production of ultraclean fuels [7]. Rostrup-Nielsen [8] reported most of the catalysts for the DRM process to consist of Ni, Co and noble metals supported on oxide supports. Nickel catalysts exhibit high activity in the carbon dioxide reforming of methane, however, when using such catalysts, a serious problem is evolution of a great amount of carbon, which blocks active sites resulting in a rapid deactivation of catalysts [9]. Noble metal catalysts are much more stable [10, 11], but their high cost limits a wide commercial use of these systems.

Different methods are used to suppress carbon deposits on nickel catalysts. First of all, attention should be paid to works on the minimization of acid sites of the carrier. It is stated that the coke formation decreases on carriers with high Lewis basicity [12]. Additives of alkaline and alkaline-earth elements [13] and uranium oxides [14], special methods of the preparation and bimetallic systems [15] are used. The main idea of the work [16] is based on supposition that carbon is deposited on large nickel particles. Small particles interact with the carrier and are highly stable to aggregation, thus, creating preconditions for the high stability of the catalyst. The authors [16] developed a stable low percentage nickel catalyst with Ni particles of the size less than 4 nm in the system of Ni<sub>0.03</sub>Mg<sub>0.97</sub>O.

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One may suppose that a steric factor will play an important role in prevention of blocking the active sites by carbon. When applying low concentrations of the active component on the developed geometric surface of materials, separation of the carbon product and active sites is possible. Glass-fibers are the special interest due to the peculiarities of the macrostructure of the fibrous carrier with the high total surface of numerous fine elementary filaments. Besides, a glass cloth is highly strong and easily transforms, this allows to integrate catalysts into devices and reactors of diverse firms.

Quite many data[17, 18] on the use of catalysts on the basis of glass fibers in many other chemical processes have appeared lately. It is shown that catalysts on the basis of glass fibers are highly active even at a low content of the active component on the surface of the support.

The aim of our work is to create nanodispersed catalysts by forming low percentage Co-Ni- and Co- contacts on the carrier from a glass cloth by the “solution-combustion” method which is one of variants of a self-propagating high temperature synthesis[19] and their study in various catalytic reactions.

The chosen method of the preparation will allow uniform heating of the catalyst at low temperature (400°C) initiating the combustion front on the surface of the catalyst, and the low content of active components will limit the development of a high temperature wave by preventing the overheat of the catalyst.

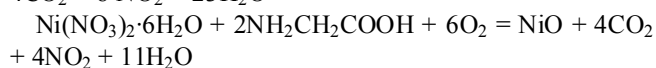
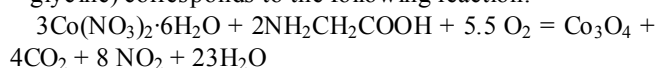
This paper deals with the influence of conditions, under which synthesized glass fibers of Co- Ni-catalysts are prepared, on physico-chemical parameters and their catalytic properties in the reaction of dry reforming of methane, oxidation of CO and butane.

## 2. Experimental

### 2.1. Synthesis of Catalysts

A silica glass fiber (SGF) used in experiments consists of filaments with the diameter of 6-7  $\mu\text{m}$ . After removal of a lubricant, the glass fiber was leached in a 5.5% solution of nitric acid for 1 h at 90°C, washed with water to obtain pH = 5.5-7, dried and calcined at 400°C in air. The properties of the SGF after the pretreatment are as follows:  $S_{\text{BET}}$  is 1.0  $\text{m}^2/\text{g}$ ,  $V_{\text{pore}}$  is 0.0006  $\text{cm}^3/\text{g}$ , amorphous phase in XRD.

Low percentage species were synthesized by the SC method (Table 1). The glass cloth of a definite size was impregnated with the solution of cobalt and nickel nitrates, then it was dried during 30 minutes in air at 100°C and then calcined in the air atmosphere at 400°C. The SC method between initial components (mixed Co nitrate and Ni nitrate + glycine) corresponds to the following reaction.



**Table 1.** List of Catalysts on Glass Cloth

No. of the sample	Glass cloth catalysts	Total content of MeO, %	CoO/NiO, % / %
1	0.2Co	0.2	100/0
2	0.5Co	0.5	100/0
3	0.8Co	0.8	100/0
4	1.0Co	1.0	100/0
5	1.2Co	1.2	100/0
6	1.5Co	1.5	100/0
7	0.25Co-0.25Ni	0.5	50/50
8	0.4Co-0.4Ni	0.8	50/50
9	0.3Co-0.7Ni	1.0	30/70
10	0.6Co-0.4Ni	1.0	60/40
11	0.6Co-0.6Ni	1.2	50/50
12	1.2 Ni	1.2	0/100

### 2.2. Study of Catalytic Activity

The catalytic activity in the DRM process was examined using a fixed bed quartz reactor with the inner diameter of 10 mm under the following conditions:  $\text{CH}_4$ , 50%;  $\text{CO}_2$ , 50%; temperature, 600-800°C; flow rate, 60  $\text{cm}^3/\text{min}$ ; gas hourly space velocity, 1440  $\text{h}^{-1}$ ; and time of activity measurement, 2-4 h.

The catalytic activity in CO and  $\text{C}_4\text{H}_{10}$  oxidation reactions was examined using a fixed bed quartz reactor under the following conditions: CO or  $\text{C}_4\text{H}_{10}$ , 1 vol. % in air; gas hourly space velocity, 1000  $\text{h}^{-1}$ .

### 2.3. Physicochemical Examination of Samples

The specific surface area ( $S_{\text{BET}}$ ,  $\text{m}^2/\text{g}$ ) 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 area.

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

X-ray diffraction (XRD) patterns were recorded using a HZG-4C diffractometer with  $\text{CoK}\alpha$  ( $\lambda=1.79021\text{\AA}$ ) radiation. Sample patterns were taken by point scanning with 0.05 degrees with accumulation of 18 s at each point in the range of angles 20-80°. To make the certain phase composition and to determine parameters of the lattice, we additionally carried out the point scanning with the step of 0.05° with the accumulation of 36-60 s at each point in the range of angles 70-80°. The average size of crystallites was estimated in accordance with the Sherrer equation. The analysis of the crystalline structure of samples was carried out using the JCPDS Database.

The particle size and the state of the active components were estimated by HRTEM using a JEM 2010 (JEOL, Japan) microscope with the lattice resolution 0.14 nm connected to a Phoenix EDAX spectrometer for microanalysis. An additional assessment of the catalyst dispersion was made by AFM using a SolverP47Bio instrument.

The H<sub>2</sub>-TPR studies of catalysts pretreated *in situ* in O<sub>2</sub> or Ar at 400 °C were carried out with 10 % H<sub>2</sub>/Ar mixture, feed rate 30 cm<sup>3</sup>/min, heating rate 10 °C/min from 30 to 800 °C.

DR UV-Vis spectra of glass-fiber samples were registered by a UV-2501 PC (Shimadzu) spectrophotometer equipped with a ISR-240A DR unit in the range 11000-54000 cm<sup>-1</sup>. The spectra are presented in coordinates: Kubelka-Munk function vs. wavenumber.

The carbon content was determined using an Elementar Vario EL Cube analyzer.

### 3. Results and Discussion

#### 3.1. Characteristics and Properties of Catalysts

The specific surface area of the studied samples does not exceed 1.0 m<sup>2</sup>/g, which is close to that of the catalyst carrier – glass fibers owing, partially, to the fact that the amount of the deposited components does not exceed 1 wt. %.

To study samples by the X-ray analysis, samples with the active component deposited onto the surface of the support were ground to powder. The XRD patterns of samples 1.0Co (Figure 1) and 0.3Co-0.7Ni (Figure 2) show the presence of a X-ray amorphous phase of glass fibers and phases of CoO-NiO catalytic systems. In case of the 1.0Co catalyst, a spinel phase Co<sub>3</sub>O<sub>4</sub> with the size of particles 20 nm has been observed.

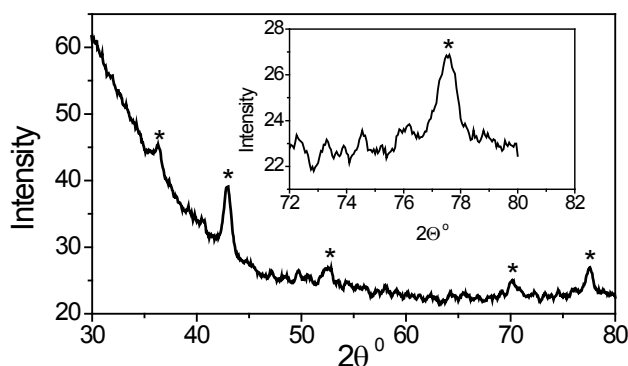


Figure 1. XRD pattern of the catalyst 1.0Co; \* - Co<sub>3</sub>O<sub>4</sub> phase

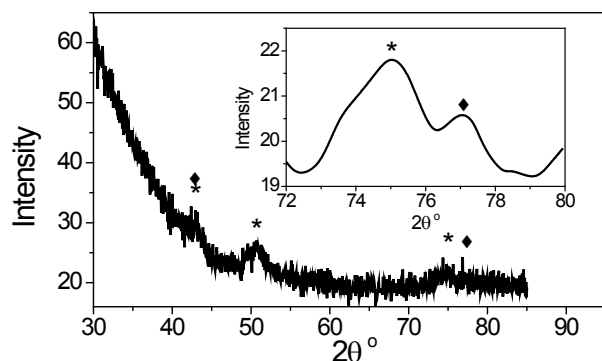


Figure 2. XRD pattern of the catalyst 0.3Co-0.7Ni: \* - NiO phase, ◆ - (Ni,Co)Co<sub>2</sub>O<sub>4</sub> phase

The study of the oxide film without the support (without a glass fibers matrix) by the X-ray phase analysis also showed

the presence of the spinel phase Co<sub>3</sub>O<sub>4</sub> and this can serve as the verification of the obtained data. Addition of NiO to CoO in the catalyst 0.4Co-0.4Ni (Co/Ni=50/50) leads to dilution of NiO in Co<sub>3</sub>O<sub>4</sub> and formation of a substituted spinel phase (Ni, Co)Co<sub>2</sub>O<sub>4</sub>. Increasing of the NiO amount in the catalyst 0.3Co-0.7Ni (CoO/ NiO= 30/ 70) results in formation of two phases: spinel (Ni, Co)Co<sub>2</sub>O<sub>4</sub> and NiO (Figure 2) with the same size of particles equal to 20 nm. NiO is a single phase in the sample 1.2Ni (Co/Ni=0/100).

One can see in pictures made by TEM (Figure 3) that the active component is dispersed on the surface of the fiber mainly in the form of separate particles with the size of about 10-20 nm. Figure 4a presents a HR-TEM picture of separate particles and a digital diffraction from the selected area (black square). The morphology of particles is a characteristic for spinel structures. Observed interplanar distances are close to interplanar distances of NiCo<sub>2</sub>O<sub>4</sub> (111) 4.6846Å, (222) 2.3423Å, (311) 2.4465Å, (331) 1.8615Å (JCPDS diffraction data). It is seen in the picture that some particles are on the surface of SGF, the others are localized inside the glass cloth matrix.

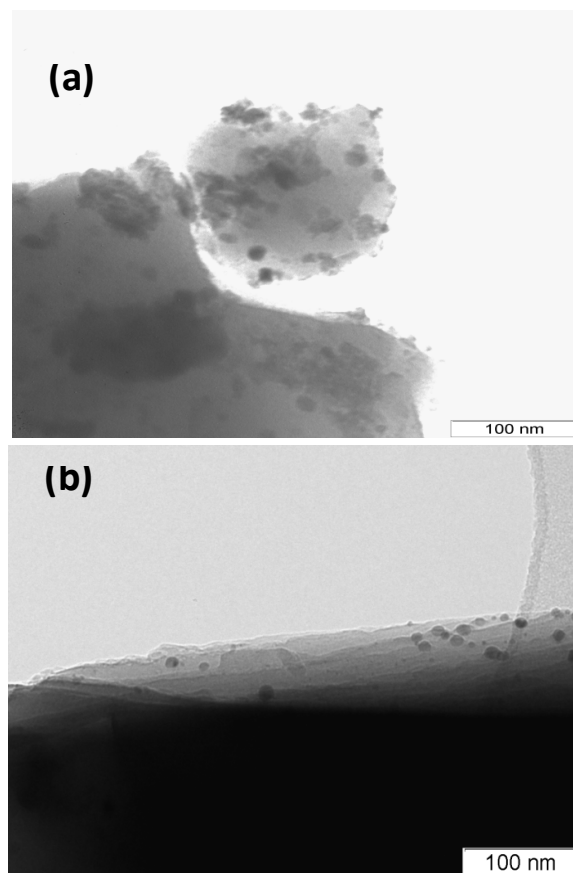
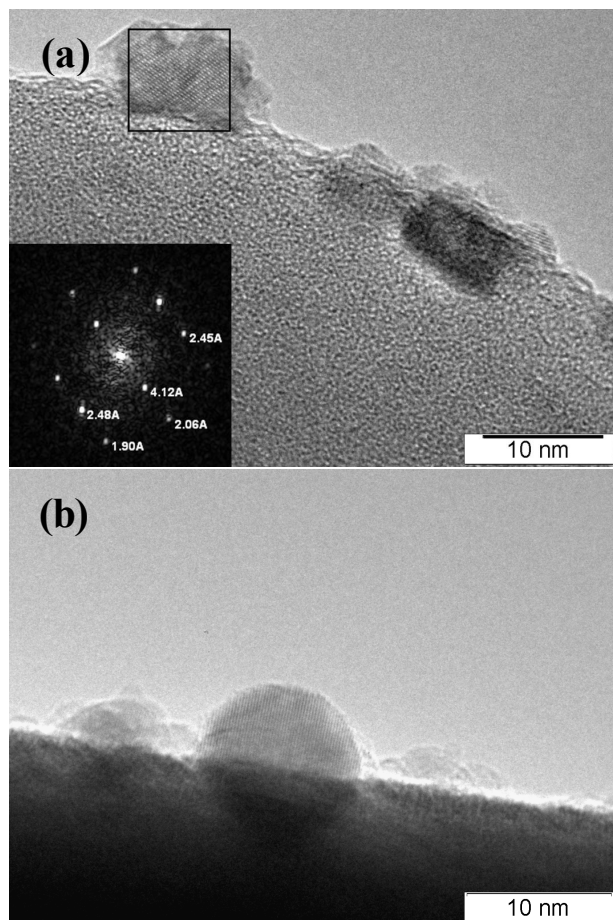


Figure 3. TEM picture of 1.0Co (a), 0.6Co-0.4Ni (b) catalysts

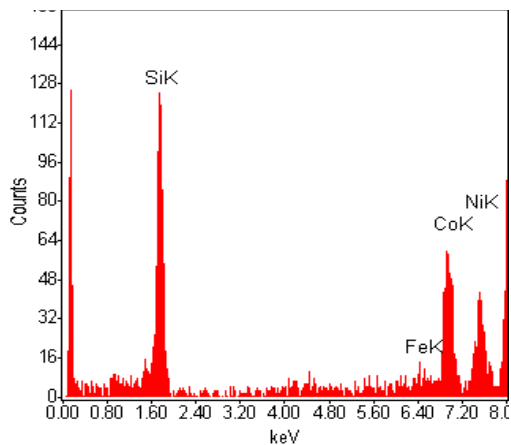
Particles of a spherical form and the size close to 10 nm were found in the same sample (Figure 4b).

According to the data of the EDX analysis, the particle contains amounts of Ni and Co corresponding to the chemical composition of this sample (Figure 5). Interplanar distances characterize the metallic state of elements. It

should be noted that, according to the data of radiographic studies, metallic phases of the active component were not detected. It is not excluded that metallic particles were obtained from oxide ones under the action of beam of electrons. Note that the particles are strongly retained on the support surface. In a special experiment with the pronounced mechanical effect followed by an ultrasonic treatment, we managed to detach some particles from the support. A TEM study of these particles shows that their size does not exceed 8 nm [20, 21].



**Figure 4.** HR-TEM picture of a separate particles consisting of  $\text{NiCo}_2\text{O}_4$  (catalyst 0.6Co-0.4Ni) and digital diffraction from selected area (black square) (a); consisting of metal Ni and Co (b)



**Figure 5.** EDX-spectrum of the spherical particle shown in Figure 4b

The  $\text{H}_2$ -TPR analysis of catalysts pretreated in Ar and having different CoO/NiO ratio of the active component, 100% CoO (1.2Co), 100% NiO (1.2Ni), and 50%CoO/50%NiO (0.6Co-0.6Ni), (Figure 6a) revealed that the temperature of the  $\text{H}_2$  consumption maximum increases in the following order:  $\text{NiO} < \text{NiO/CoO} < \text{CoO}$ . The catalysts containing the spinel phase are reduced by a two-step scheme  $(\text{Co,Ni})\text{Co}_2\text{O}_4 \rightarrow \text{CoO} + \text{NiO} \rightarrow \text{Co} + \text{Ni}$  and  $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$ . Upon treatment in an oxygen medium (Figure 6b), this trend persists; however, the  $\text{H}_2$  consumption maximum for nickel catalysts shifts by 25 °C to a high-temperature region, probably due to the interaction with the support in the oxidative atmosphere. It agrees with the lower value of the experimental  $\text{H}_2$  consumption than one of required for NiO reduction to Ni. Meanwhile, the cobalt catalysts oxidized to  $\text{Co}_2\text{O}_3$  are reduced at a 325 °C, that is the lower temperature as compared to the Ar-pretreated catalysts containing a  $\text{Co}_3\text{O}_4$  spinel. The presence of several TPR peaks for  $\text{O}_2$ -pretreated catalysts (Figure 6b, curves 1, 2) indicates the three-step reduction by a scheme  $\text{Co}_2\text{O}_3 \rightarrow \text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$ , the NiO phase is reduced together with CoO (Figure 6b, curve 2).

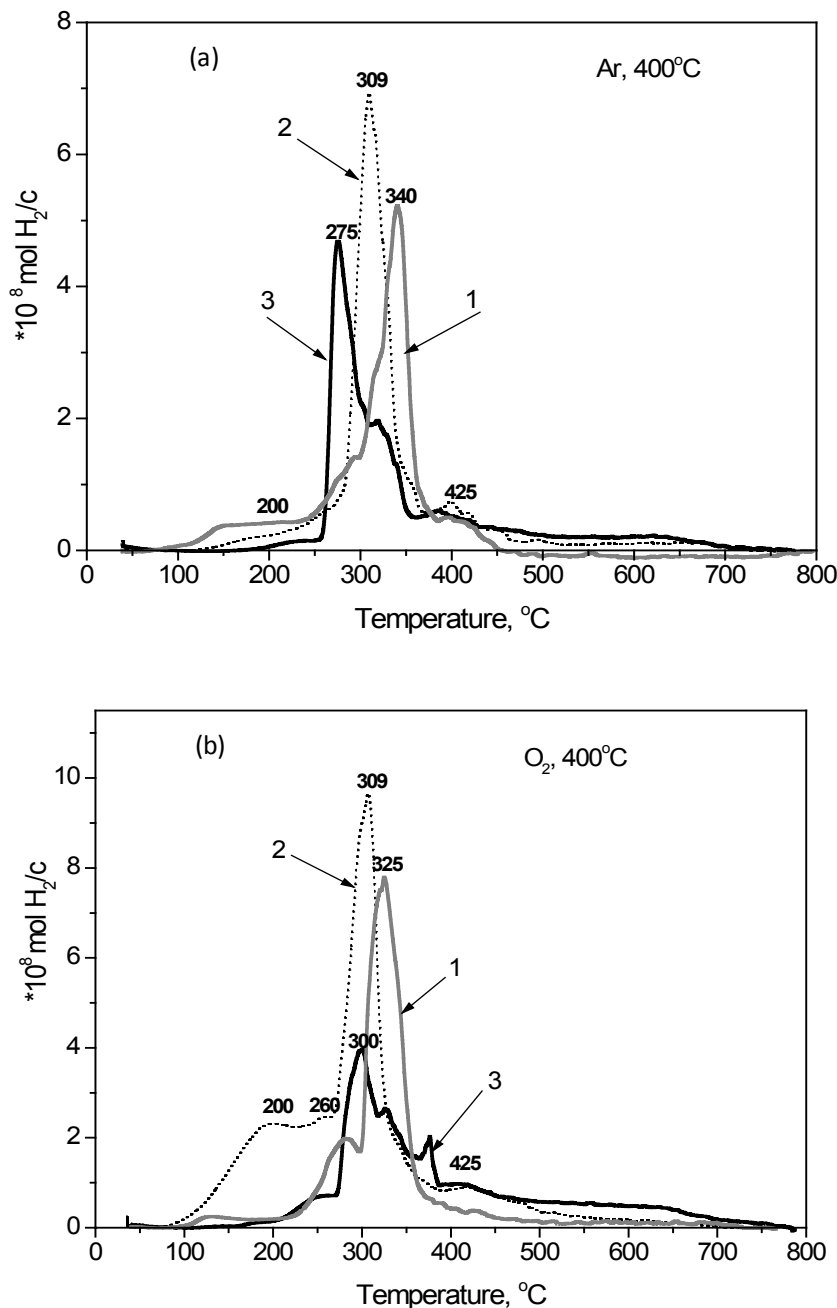
Figure 7 presents DR UV-Vis spectra of the SGF sample and Ni-, Co- and CoNi- catalysts. An intense absorption at 40000  $\text{cm}^{-1}$  is observed on the unmodified SGF sample (curve 1). This absorption can be attributed to a fundamental absorption edge (FAE). In the spectrum of the Ni- catalysts (curve 2) a doublet of the band 12900 and 13700  $\text{cm}^{-1}$  as well as a shoulder 23900  $\text{cm}^{-1}$  are observed. Energies of these bands are attributed to d-d transitions  ${}^3\text{T}_{1g} \rightarrow {}^3\text{A}_{2g}$ ,  ${}^1\text{E}_g \rightarrow {}^3\text{A}_{2g}$  and  ${}^3\text{T}_{1g}(\text{P}) \rightarrow {}^3\text{A}_{2g}$  of  $\text{Ni}^{2+}$  ions in octahedral coordination ( $\text{Ni}^{2+}_{\text{Oh}}$ ), respectively. Considerable differences of the Ni- catalyst from the well known NiO/MgO system are a shift of absorption bands to the low frequency region (about 600-1400  $\text{cm}^{-1}$ ) and a decrease of the splitting of the doublet from 1400 to 800  $\text{cm}^{-1}$ . It points out to the strong interaction of  $\text{Ni}^{2+}_{\text{Oh}}$  ions with the support.

In the DR UV-Vis spectrum of the Co- catalyst (curve 3) two intense bands 14000 and 23200  $\text{cm}^{-1}$  are observed. These bands can be attributed to d-d transitions of  ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$  of  $\text{Co}^{2+}$  ions in tetrahedral coordination ( $\text{Co}^{2+}_{\text{Td}}$ ) and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$  of  $\text{Co}^{3+}$  ions in octahedral coordination ( $\text{Co}^{3+}_{\text{Oh}}$ ), respectively. The presence of such cobalt states can indicate to the formation of spinel structures, for example  $[\text{Co}^{2+}](\text{Co}^{3+})_2\text{O}_4$  or  $[\text{Co}^{2+}](\text{Al}^{3+}, \text{Co}^{3+})_2\text{O}_4$ , during the synthesis of the catalyst. It should be noted that the intensity of these bands increases with an increase of the Co content in the sample. The difference of our Co- catalysts from known systems containing  $\text{Co}_3\text{O}_4$  is an absence of the splitting of the band 14000  $\text{cm}^{-1}$  and the shift of this band to the lower frequency region to about 1000  $\text{cm}^{-1}$  as well as a change of the ratio of intensities of the bands attributed to  $\text{Co}^{2+}_{\text{Td}}$  and  $\text{Co}^{3+}_{\text{Oh}}$  ions. The shift of absorption bands to the low frequencies region is likely to be connected with a strong interaction of  $\text{Co}^{2+}_{\text{Td}}$  ions with the support. The higher intensity of the band 23200  $\text{cm}^{-1}$  in comparison with the band 14000  $\text{cm}^{-1}$  indicates to the higher amount of  $\text{Co}^{3+}_{\text{Oh}}$  and to a high defectiveness of the

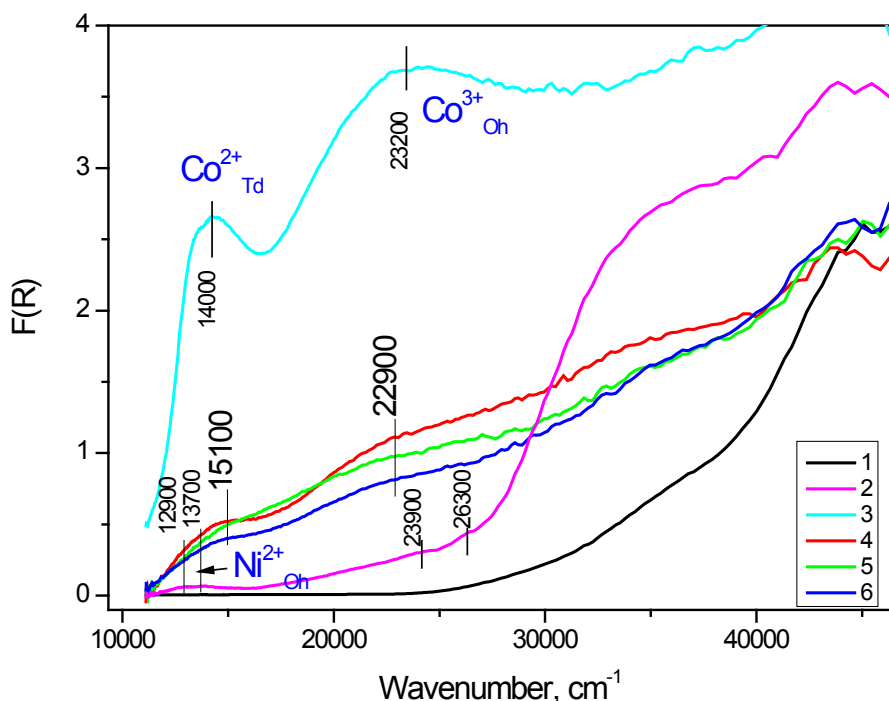
spinel structure.

The spectra of CoNi- catalysts (curves 4-6) are considerably differed from the spectra of unicomponent catalysts. In the CoNi- catalysts containing 0.5-1.2 wt.% metals an absorption as shoulders at 15100 and 23000  $\text{cm}^{-1}$  is appeared. The intensities of these bands are significantly lower than that of the Co- catalyst with the close cobalt content (curves 3 and 5). Observed bands can be attributed to d-d transitions of  $\text{Co}^{2+}_{Td}$  and  $\text{Co}^{3+}_{Oh}$  ions, respectively. From the spectra, it is practically impossible to obtain a coordination and an electron state of nickel cations, that is

why these bands can be a superposition of bands typical for  $\text{Ni}^{2+}_{Oh}$  (doublet 13000-15000  $\text{cm}^{-1}$ ) and  $\text{Co}^{2+}_{Td}$  (14000  $\text{cm}^{-1}$ );  $\text{Ni}^{2+}_{Oh}$  (25000  $\text{cm}^{-1}$ ) and  $\text{Co}^{3+}_{Oh}$  (23000  $\text{cm}^{-1}$ ). In this case, the CoNi- catalyst can contain of  $\text{Ni}^{2+}_{Oh}$  cations in NiO particles, and  $\text{Co}^{2+}_{Td}$  and  $\text{Co}^{3+}_{Oh}$  cations in the spinel structure  $\text{Co}_3\text{O}_4$ . It should be mentioned that intensities of both bands do not depend on the total amount of Co and Ni in the sample at the ratio  $\text{Co/Ni}=1/1$ . Besides, taking into account the low intensity of the band attributed to  $\text{Co}^{2+}_{Td}$ , one can consider that the  $\text{Co}^{3+}$  state is prevailed in the catalyst and the  $\text{Co}_3\text{O}_4$  spinel has a defective structure.



**Figure 6.**  $\text{H}_2$ -TPR curves for the catalysts: 1 – 1.2Co, 2 – 0.6Co-0.6Ni, and 3 – 1.2Ni after pretreatment at 400 °C in Ar (a) and  $\text{O}_2$  (b)



**Figure 7.** DR UV-Vis spectra of SGF (1), Ni- catalyst (2), Co- catalyst 0.8Co (3) and Co-Ni- catalysts with the ratio CoO/NiO=50/50: 0.6Co-0.6Ni (4), 0.4Co-0.4Ni (5), 0.25Co-0.25Ni (6)

### 3.2. The Catalytic Activity of Samples in the Reaction of Dry Reforming of Methane

The results of an investigation of catalysts in the DRM reaction are presented in Table 2. A study of Co-catalysts comprising the spinel phase  $\text{Co}_3\text{O}_4$  revealed a dependence of their catalytic activity on the concentration of active components. As seen from Table 2, the conversion of initial reactants and the yields of  $\text{H}_2$  and CO at  $750^\circ\text{C}$  are increased with increasing the content of Co oxides in the catalysts. For Co-Ni-catalysts (CoO/NiO=50/50) comprising the spinel phase (Ni, Co) $\text{Co}_2\text{O}_4$  a direct dependence of the activity on the total concentration of Ni and Co oxides is not observed. In this series, a maximum activity was shown by the catalyst 0.4Co-0.4Ni. For Ni-catalyst, which comprise only the NiO phase the conversion of initial reactants attains 75% but the yield of target products does not exceed 35-40%, due to side reactions and the formation of carbon.

After the reaction of DRM, the carbon content of the catalyst samples was measured. According to the obtained data, the carbon content does not exceed 0.13-0.20 wt. % for catalysts with the ratio of CoO/NiO = 100/0 and 50/50, that corresponds to its content in the initial catalysts before the reaction. An appearance of the NiO phase in the catalyst

leads to heading the amount of carbon deposits on the catalyst surface to 5.7 wt. % as the concentration of NiO in the samples grows from 50 to 100%. One may suppose that the presence of the NiO phase in catalysts contributes to the formation of carbon. However, the Ni-catalyst has been stable during 3 hours of operation despite of the amount of the carbon deposition is more than the Ni amount five times. It is likely that carbon is distributed on the volume of the carrier and does not block active sites of the catalyst, that is important for its stable operation.

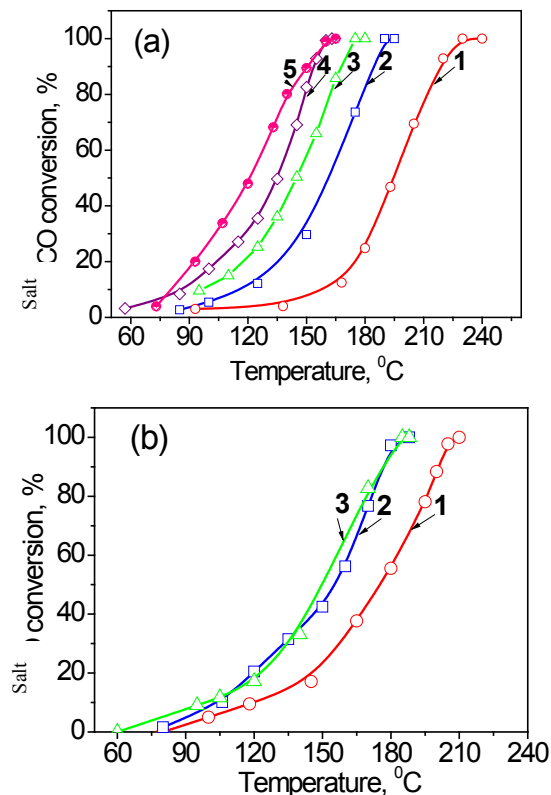
We suggest that the key factor determining the stability of active sites having the spinel structure to carbonization is strong interaction between the spinel and the carrier, that is showed by TEM and DR UV-Vis methods. This interaction prevents the sintering of activity sites and the formation of large particles required to produce carbon[16].

A comparison of the obtained results with the literature data demonstrates that the activity of the developed catalysts based on Co oxides or mixed Co and Ni oxides with the total content of the active component not higher than 1.5 wt.% is comparable with the activity of  $\text{CoO}_x/\text{MgO}$  catalysts, which contain 12-30 wt.% of cobalt oxides[22, 23].

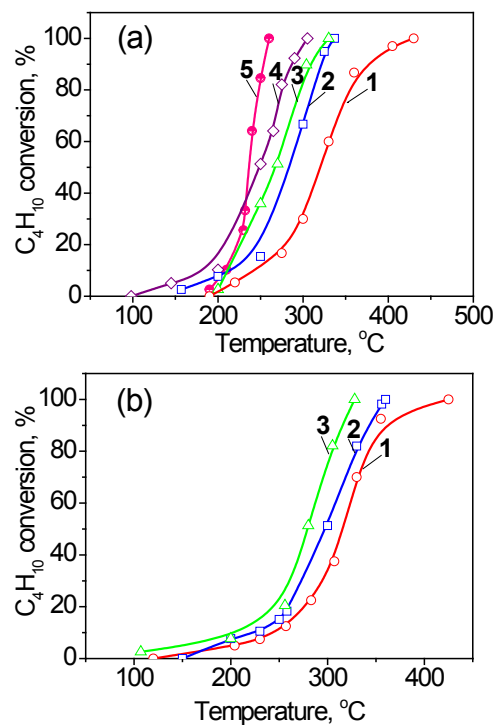
**Table 2.** The catalytic activity of samples in the reaction of dry reforming of methane

Catalyst	T, $^\circ\text{C}$	Conversion, %		Yield, %		C content in the catalysts, wt. %	
		$\text{CH}_4$	$\text{CO}_2$	$\text{H}_2$	CO	initial	after reaction
0.2Co	715	0	0	0	0	0.14	0.14
0.5Co	715	57	60	40	50	0.13	0.13
1.2Co	715	85	95	70	75	0.19	0.20
1.5Co	715	85	95	70	70	0.18	0.19
0.4Co-0.4Ni	750	90	100	82	90	0.14	0.13
1.2Ni	815	50	75	37	40	0.17	5.75

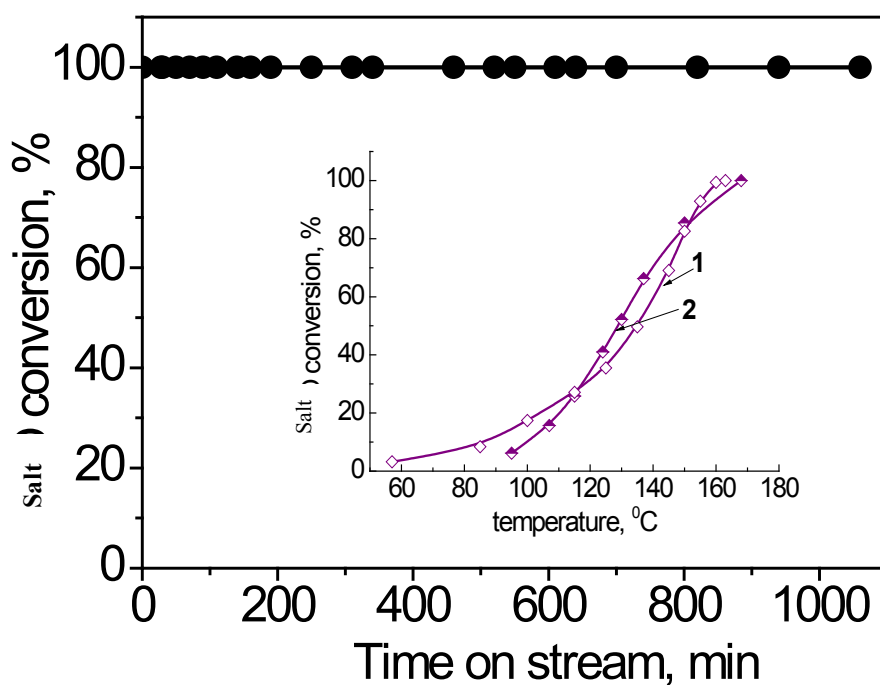
### 3.3. The Catalytic Activity of Samples in the CO and $C_4H_{10}$ Oxidation Reaction



**Figure 8.** Conversion of CO on (a) Co-catalysts: 1- 0.2Co, 2- 0.5Co, 3- 0.8Co, 4- 1.2Co, 5-1.5Co; (b) Co-Ni-catalysts (CoO/NiO=50/50): 1 – 0.25Co-0.25Ni, 2 – 0.4Co-0.4Ni, 3 – 0.6Co-0.6Ni



**Figure 9.** Conversion of  $C_4H_{10}$  on (a) Co-catalysts: 1- 0.2Co, 2- 0.5Co, 3- 0.8Co, 4- 1.2Co, 5-1.5Co; (b) Co-Ni-catalysts (CoO/NiO=50/50): 1 – 0.25Co-0.25Ni, 2 – 0.4Co-0.4Ni, 3 – 0.6Co-0.6Ni



**Figure 10.** Time course of the catalytic activity in Co oxidation at  $T = 160^\circ\text{C}$ , CO – 1% in air, GHSV=1000  $\text{h}^{-1}$  on 1.2Co catalyst. Insert displays CO conversion on 1.2Co catalyst 1- initial, 2- after long-term operation

A study of Co- and Co-Ni-catalysts (CoO/NiO=50/50) in the CO (Figure 8) and butane (Figure 9) oxidation reactions revealed a dependence of their catalytic activity on the concentration of active components. Especially this dependence is exhibited on Co-catalysts with the spinel  $\text{Co}_3\text{O}_4$  structure (Figure 8a, Figure 9a). It is shown that  $\text{Co}_3\text{O}_4$  spinel active sites are more active in the deep oxidation reactions than (Co,Ni) $\text{Co}_2\text{O}_4$  spinel (Figure 8b, Figure 9b) at the similar content of the active component.

Figure 10 presents data on a long-term operation of the 1.2Co catalyst at 160°C. It is shown that the catalyst provides the 100% CO conversion for 19 hours. The activities of the initial catalyst and the catalyst after the long-term test are also presented in Figure 10. It is shown that the high activity of the catalyst is maintained after the long-term test. That points to the high stability of  $\text{Co}_3\text{O}_4$  active sites in oxidation reactions. It is known that  $\text{Co}_3\text{O}_4$  is highly active for the low temperature CO oxidation [24-26]. It is important that the catalyst prepared by the “solution-combustion” method exhibits high activity and stability at the active component content lower than 1.2 wt. %. The selected method of the active component supporting allows a strong deposition of nanosized oxide particles on the near-surface layer of the support. That provides its high availability to reactants and prevents the aggregation of particles in reaction conditions.

## 4. Conclusions

Glass fiber catalysts based on Ni and Co oxides with the total content of oxides not exceeding 1.5 wt.% for various catalytic reactions have been developed. The catalysts were synthesized by the “solution-combustion” method providing a uniform distribution of the active component as  $\text{Co}_3\text{O}_4$  and (Co,Ni) $\text{Co}_2\text{O}_4$  spinels or as NiO in the near-surface layer of a support. They are individual nanoparticles of size 10-20 nm strongly interacting with the carrier. It was shown that nanoscale particles of the active component with spinel structure prevent the formation of carbon deposits and provide high activity of catalysts in the DRM reaction. These catalytic systems have shown high activity in CO and  $\text{C}_4\text{H}_{10}$  oxidation reactions and exhibit high stability in long-term operation. We suggest that developed approaches in the preparation of catalysts are promised for future making of low-content catalysts supported on the carrier with low surface area.

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