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Metal oxide catalysts for low-temperature template CCVD synthesis of carbon nanotubes

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Abstract: Using the method of polymerized complex precursors (PCP) and a wide range of chelating agents, we synthesized metal oxide catalysts (MOCs) with a general composition of Me_2Co / $CaCO_3$ (CaO, MgO, NaCl, Me – Fe, Ni) and a molar ratio of Me_2Co / carrier from 0.06 : 1 to 0.55 : 1; the effectiveness of such MOCs in the synthesis of carbon nanotubes by catalytic chemical vapor deposition was determined from the gas phase (CCVD synthesis). The dependence of the specific yield and morphology of the carbon product on the MOCs composition and the nature of the chelating agent, being a decisive factor in the process of preorganization of the catalyst structure, has been established. The use of catalysts for the growth of CNTs with the composition of Ni_2Co / $CaCO_3$ (CaO) allows the CCVD process to be carried out at low temperatures (450–500 °C) in contrast to 800 °C for MOCs with the composition of Fe_2Co / $CaCO_3$ (CaO) and leads to the formation of structurally homogeneous arrays of multi-walled carbon nanotubes. At the same time, the specific yield of CNTs decreases with an increase in the temperature of the process, but an increase in the mole fraction of active metals in the catalyst leads to an increase in the specific yield of CNTs. Yet, the dependence has the form of a curve with a tendency to reach a plateau, which indicates an increase in the processes of agglomeration of metal nanoparticles, increasing their size and, due to this, reducing the possibility of nucleation of carbon nanotubes. It has been suggested that low-temperature CCVD synthesis using MOC composition Ni_2Co / $CaCO_3$ (CaO, MgO, NaCl) is realized due to the unique magnetic and electronic properties of the Ni – NiO system, which makes it possible to initiate the process of nucleation and then growth of nuclei of catalytic nickel particles at temperatures exceeding the Curie point Ni (> 360 °C).

Keywords: carbon nanotubes; CCVD synthesis; metal oxide catalysts; chelating agent.

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Металлоксидные катализаторы для низкотемпературного темплатного CCVD синтеза углеродных нанотрубок

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Аннотация: Методом полимеризованных комплексных предшественников (ПКП) с использованием широкого ряда хелатных агентов синтезированы металлоксидные катализаторы (МОК) общего состава Me_2Co / $CaCO_3$ (CaO, MgO, NaCl, Me – Fe, Ni) с мольным соотношением Me_2Co / носитель от 0,06 : 1 до 0,55 : 1, определена эффективность действия таких МОК в синтезе углеродных нанотрубок методом каталитического химического осаждения углерода из газовой фазы (CCVD – Catalytic Chemical Vapor Deposition). Установлена зависимость удельного выхода и морфологии углеродного продукта от состава МОК и природы хелатного агента как решающего фактора в процессе предорганизации структуры катализатора. Применение катализаторов роста углеродных нанотрубок (УНТ) состава Ni_2Co / $CaCO_3$ (CaO) позволяет проводить CCVD процесс при низких температурах (450…500 °С) в отличие от 800 °С для МОК состава Fe_2Co / $CaCO_3$ (CaO) и приводит к образованию однородных по структуре массивов многостенных углеродных нанотрубок. При этом удельный выход УНТ уменьшается с ростом температуры процесса, а увеличение мольной доли активных металлов в катализаторе хотя и приводит к росту удельного выхода УНТ, но зависимость имеет вид кривой с тенденцией к выходу на плато, что свидетельствует об усилении процессов агломерации наночастиц металлов, увеличении их размеров и снижении за счет этого возможности нуклеации углеродных нанотрубок. Сделано предположение, что низкотемпературный CCVD синтез с использованием МОК состава Ni_2Co / $CaCO_3$ (CaO, MgO, NaCl) реализуется благодаря уникальным магнитным и электронным свойствам системы Ni – NiO, позволяющим инициировать процесс зародышеобразования, а затем и роста зародышей каталитических частиц никеля при температурах, превышающих точку Кюри Ni (> 360 °С).

Ключевые слова: углеродные нанотрубки; CCVD синтез; металлоксидные катализаторы; хелатные агенты.

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1. Introduction

Iijima's discovery of carbon nanotubes (CNTs) in 1991, followed by the isolation and study of graphene (by A. Geim and I. Novoselov in 2004), the establishment of their extraordinary properties and the resulting possible practical applications stimulated a huge amount of research into determining the patterns of processes of producing carbon nanomaterials (CNMs) with specified properties [1–3]. At the same time, the researchers' attention was focused on finding optimal conditions for the synthesis of such CNMs as graphene, nanocarbon (NC), and CNTs.

The most common and commercially attractive method for producing CNTs is CCVD (*Catalytic Chemical Vapor Deposition*) – a process that is characterized by simplicity of instrumentation, low process temperatures (600–1100 °C); it does not require creating reduced or increased pressure, and can be scaled up to industrial installations [3]. However, in our opinion, the simplicity and advantages are apparent compared to other methods of CNTs synthesis – laser ablation and synthesis in an arc discharge. The problem is that the result of CCVD synthesis depends on many parameters – elemental composition, dispersion and texture of metal oxide catalysts (MOCs), the nature of the catalyst support, carbon precursor, carrier gas, gas flow rate and their ratio, process temperature and even design features reactor. As a result, a huge number of researchers are working to find general patterns of the mechanism of formation of CNTs.

Our major interest is the problem of the MOCs synthesis, which makes it possible to produce CNTs with a high degree of selectivity in low-temperature CCVD synthesis, which is quite an urgent problem [1, 4–6]. The disadvantage of most catalysts for this process (mainly based on Fe, Co) is the fact that they begin to work in the high temperature zone (800–1000 °C), where the formation of a non-catalytic flow product is most likely [7, 8]. Therefore, reducing the temperature of CCVD synthesis of CNTs is an important technological task and enables to bring the conditions for CNTs growth closer to the conditions of processes occurring in planar technology [9]. One solution to this issue is the introduction of Ni or (Ni – Co) into the MOCs composition, which reduces their surface tension, as well as the use of oxides with low surface energy as a substrate [10]. Thus, MOCs of the composition Ni / SiO_2 make it possible to reduce the synthesis temperature to 625 °C [10], those of Ni / MgO reduce it to 600–650 °C [11–13] and even to 550 °C, using camphor as a carbon precursor [14]. In [9], Ti and Ni films deposited by electron beam sputtering onto a substrate of oxidized single-crystalline silicon made it possible to achieve CNTs growth in a flow of argon, acetylene and ammonia at 500 °C. In a more complex process with atomic deposition of Ni on a ZrO_2 substrate and plasma enhanced chemical vapor deposition (PECVD) synthesis of CNTs, the temperature can be reduced to 340 °C [15], but issues arise with scalability. Taking into account the rather modest information on this issue, an important task, in our opinion, remains the further development of such catalytic systems that would operate under mild conditions and allow the CNTs production with the required quality parameters.

We developed a method using polymerized complex precursors (PCP) to synthesize MOCs of the general composition Me_2Co / $CaCO_3$ (CaO, MgO, NaCl, Me – Fe, Ni) and studied their effectiveness in the CCVD synthesis of CNTs. The PCP method for the MOCs synthesis was chosen because it allowed one to obtain highly dispersed and highly porous MOCs powders with low bulk density and high catalytic activity. In essence, the MOCs synthesis technique we use is a superposition of the two most commonly used methods – the sol-gel method and the thermal decomposition method. The difference is that the PCP method makes it possible to implement the stage of preorganization of the spatial structure of the catalyst due to the intermediate stage of the formation of a highly porous polymer-organic matrix of the precatalyst, isolated in solid form.

2. Materials and Methods

2.1. Reagents

Metaloxide catalysts (MOCs–PCP) of the general composition Me_2Co / $CaCO_3$ (CaO, MgO, NaCl, Me – Fe, Ni) with a molar ratio Me, Co / carrier equal to 0.12 : 1 were prepared by the PCP method using nitrates of crystalline metal hydrates Fe^{3+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, sodium chloride; chelating agents – sucrose, fructose, glucose, ethylene glycol (EG), pure; diethylene glycol (DEG), pure; glycerol (GLY), pure; 1,2 – propylene glycol (PG), pure; 1,4 – butylene glycol (BG), pure; polyethylene glycol (PEG); polyvinyl alcohol (PVA), pure; pentaerythritol (PET), pure; food gradecitric acid (CA); glycine (GLYC), pure; and distilled water. MOCs-PCP obtained using two chelating agents, one of which is citric acid, are designated EG + CA, DEG + CA, GLY + CA, PG + CA, BG + CA, PVS + CA, PET + CA, GLYC + CA.

2.2 A method for the synthesis of supported MOCs for the CNTs growth using the PCP method

The essence of the PCP method is to use the ability of 3d-group metal cations to form stable complexes with carbohydrates (mono-, di- and polysaccharides, polyalcohols, oxy- and amino acids, etc.) of the composition $Me(NO_3)_xL$, where L is organic ligand [16]. Thermolys is of such a complex above 130 °C leads, as a result of the polyesterification reaction, to the formation of a three-dimensional polymer organic matrix in which the metal ions that make up the catalyst are evenly distributed throughout its entire volume. Subsequent controlled burning of the organic part leads to the formation of a nanodispersed system of mixed oxide structures, which are precursors for catalysts for the growth of multi-walled carbon nanotubes (MWCNTs).

The synthesis of metal oxide catalysts was carried out in several successive stages, presented in Table 1.

Thus, the method we developed earlier [17] is as follows: solutions of nitrates of active metals and carriers in the required stoichiometric ratios using the minimum possible amount of water were mixed with a carbohydrate solution (sucrose, glucose, fructose) at a molar ratio of carbohydrate : Me from 5 : 1 to 10 : 1. After dissolving and mixing all components, the mixture was heated to 70–80 °C with stirring until a violent reaction began with the release of brown NO_2 vapors, as a result of which the color of the reaction mass changed from light brown to dark

Table 1. Stages of MOC synthesis using the PCP method

Stage	Temperature, °C	Time, min	Process
1. Dissolution of components, homogenization	70–80	15	Formation of the carbohydrate – Me^{n+}, redox reaction
2. Production of viscous syrups	100–115	10	Dehydration
3. Formation of a solid precatalyst matrix	130–200	180	Thermal oxidation under gentle conditions
4. Precatalyst decomposition	250–450	20	Thermal oxidation of the carbon matrix
5. Annealing	550–650	180	Removal of residual organic carbon matrix
6. Mechanical activation	25	5	Increasing the reactivity of MOCs

green or blue (cobalt). After gas evolution ended, the mixture was kept at 105–115 °C to remove excess water and prepare viscous syrup. Next, a small portion of the syrup was placed in a porcelain cup with a capacity of 350 cm^3 and kept for three hours in a muffle furnace at 200 °C. During this time, the mixture increased significantly in volume (50–100 times) and hardened into fine-celled foam. The foam thus obtained was placed in a muffle furnace and controlled annealed at $T = 300$–650 °C for 3 hours. As a rule, when the furnace temperature reached 260–270 °C, spontaneous combustion of the foam occurred; combustion spread from the outer surface to the center of the mixture and led to a decrease in the volume of the sample. Next, the product was annealed at 500–650 °C for three hours. MOC, as a product of this process, was a light, highly porous coral-like mass with a well-developed surface, the frame of which consists of highly dispersed $CaCO_3$ particles (CaO, MgO, NaCl) and oxides of active metals.

2.3. CCVD synthesis

The CCVD synthesis of CNMs was carried out in a tubular quartz reactor at 500–800 °C and flow rates of carrier gas (Ar) and carbon precursor gas (propane – butane mixture in compliance with Russian Standard 27578-87) 60 and 30 cm^3·min^{-1}, respectively. The process time is 60 min. The laboratory installation diagram is shown in Fig. 1.

Specific yield of carbon product (η_C, g·g$_{cat}^{-1}$), as a relative quantity characterizing the efficiency of the process, was calculated as the ratio of the weight of the resulting carbon product to the weight of the template (catalyst) according to equation (1):

$$\eta_C = \frac{m_C}{m_T}, \tag{1}$$

where m_C is weight of carbon product, g; m_T is template mass (for CNTs synthesis m_T is the template weight with a deposited metal oxide catalyst, determined taking into account the mass loss in the “zero” experiment, g.

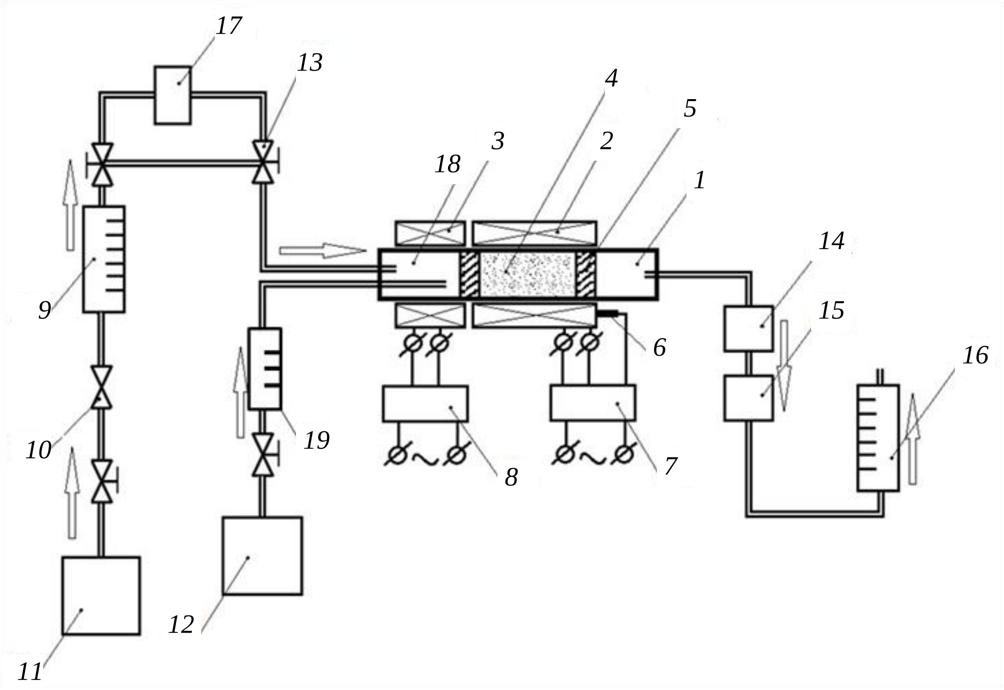


Fig. 1. Diagram of a laboratory installation for CNTs CCVD synthesis:
1 – tubular quartz reactor; *2* – pyrolysis zone heating furnace; *3* – preheating furnace; *4* – template; *5* – porous carbon inserts; *6* – thermocouple; *7* – measuring and regulating device; *8* – preheating furnace voltage regulator; *9* – rotameter; *10* – needle valve; *11* – carrier gas cylinder; *12* – carbon precursor gas cylinder; *13* – manual adjustment valve; *14*, *15* – absorbers; *16* – bubble gas flow meter; *17* – liquid supply system; *18* – steam–gas mixture input and mixing unit; *19* – rotameter for supplying carbon precursor gas

2.4. Isolation of CNMs

CNMs were isolated by treating the carbon-mineral product with 30 % HCl or 30 % HNO_3 or a mixture of them in a ratio of 3 : 1 (by volume). The mixture was heated and kept at boiling for 2 hours, then cooled to room temperature, left for 24 hours, then filtered on a glass filter, washed with deionized water to pH ≈ 7, with acetone, and dried at 105 °C to constant weight.

2.5. Analytical methods

The structural features of CNMs were studied by X-ray diffraction (XRD) using a DRON-3 diffractometer using CuK$_\alpha$ radiation, with a wavelength λ_α = 1,54181 Å (U = 30 kV, I = 20 мA).

Studies of the morphology of carbon nanotubes and template nanomaterials were carried out using transmission and scanning electron microscopy using a JEM-200A microscope from JEOL (Japan) and a JSM-6490LV scanning electron microscope (Japan) with an energy-dispersive INCA Penta FETx3 attachment (OXFORD Instruments, UK).

3. Results and Discussion

The method we have developed for the synthesis of metal oxide catalysts for the CNTs growth by the PCP method involves the stage of preorganization of the catalyst structure by creating a solid 3d pre-catalyst matrix (a system of mixed oxide phases) with a developed system of meso- and macropores. Therefore, not only the precursors of carrier oxides and active metals, but also the chelating agents used can play an important role in this process.

To compare the efficiency of catalysts obtained using various chelating agents, catalysts of the composition $Me_2Co / CaCO_3$ (CaO, Me – Fe, Ni) with the same molar ratio of $Me_2Co / CaCO_3$ equal to 0.12 : 1 were synthesized (section 2.1). CCVD synthesis of CNMs was carried out according to the method described above in section 2.2 in a tubular quartz reactor at 500 and 800 °C and flow rates of carrier gas (Ar) and carbon precursor gas (propane – butane mixture) of 60 and 30 $cm^3 \cdot min^{-1}$, respectively. The process took 60 min.

Data on the specific yield of CNMs in the CCVD process and the bulk density of the corresponding MOCs are presented in Table 2.

According to the data presented in Table 2, catalysts obtained by the PCP method, compared with catalysts obtained by other methods, are characterized by low bulk density values (ρ = 0.01–0.25 $g \cdot cm^{-3}$) [18].

Table 2. Specific yield of CNMs

Chelates names	Specific yield of CNMs η_C, $g \cdot g_{cat}^{-1}$	Bulk density of CNTs catalyst ρ, $g \cdot cm^{-3}$
Sol	0.118	0.985
Sucrose	2.82	0.032
Fructose	2.75	0.069
Glucose	3.17	0.085
EG	0.13	0.217
EG + CA	1.07	0.104
DEG	0.25	1.109
DEG + CA	1.89	0.049
GLYC	0.11	0.146
GLYC + CA	0.88	0.133
PG	0.63	0.216
PG + CA	1.35	0.104
BG	1.31	0.164
BG + CA	1.76	0.163
PEG	1.36	0.184
PEG + CA	3.31	0.061
PET	1.15	0.558
PET + CA	4.28	0.051
PVA	0.56	0.182
PVA + CA	1.29	0.340
GLYC + CA	1.35	0.157
Sucrose*	5.13	0.023
Fructose*	5.59	0.056
EG + CA*	3.16	0.048
GLYC + CA*	2.48	0.065
BG + CA*	1.65	0.163
PEG + CA*	2.90	0.061
PVA*	4.18	0.182

Note: Items marked in the table with * refer to catalysts of general composition $Ni_2Co / CaCO_3$.

Bulk density is the most important parameter of catalysts for heterophase processes, since it clearly affects the progress of the process (gas diffusion rate, heat transfer, resistance to gas flows), especially in vertical versions of reactor equipment.

Table 2 and the dependence presented in Fig. 2 clearly indicate the dependence of the specific yield of CNMs on the nature of the ligand used in the process of pre-organization of the catalyst for the growth of CNTs.This means that, firstly, in terms of their efficiency, such MOCs are an order of magnitude higher than MOCs synthesized using traditional sol-gel technology; secondly, the productivity of MOCs obtained using two ligands (the second is citric acid) is significantly higher than that for monoligand samples; thirdly, the specific yield of CNMs obtained in the CCVD process using $Ni_2Co / CaCO_3$ catalysts is either the same or significantly higher compared to iron-cobalt MOCs, but such indicators are achieved at much lower synthesis temperature parameters (500 *vs*. 800 °C).

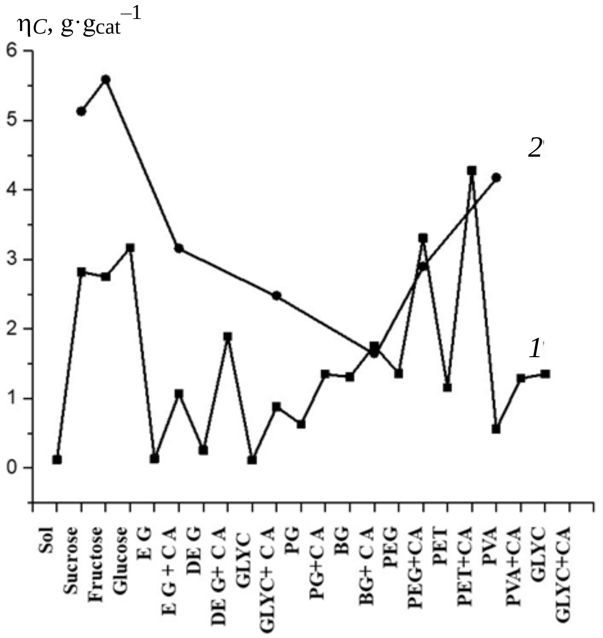


Fig. 2. The dependence of the efficiency of the MOCs – PCP of the total composition of Me_2Co / $CaCO_3$ (CaO) (Me – Fe, 800 °C, curve *1*, Me – Ni, 500 °C, curve *2*) in the CCVD synthesis of CNTs on the nature of chelating agents

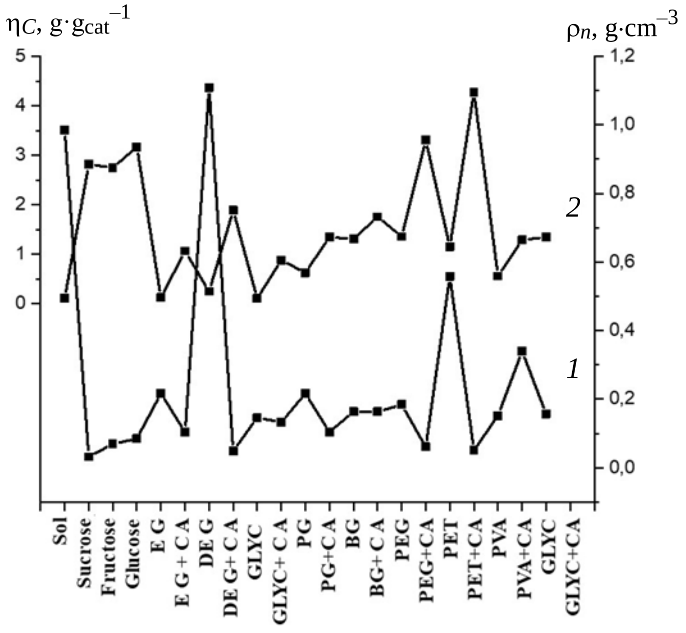
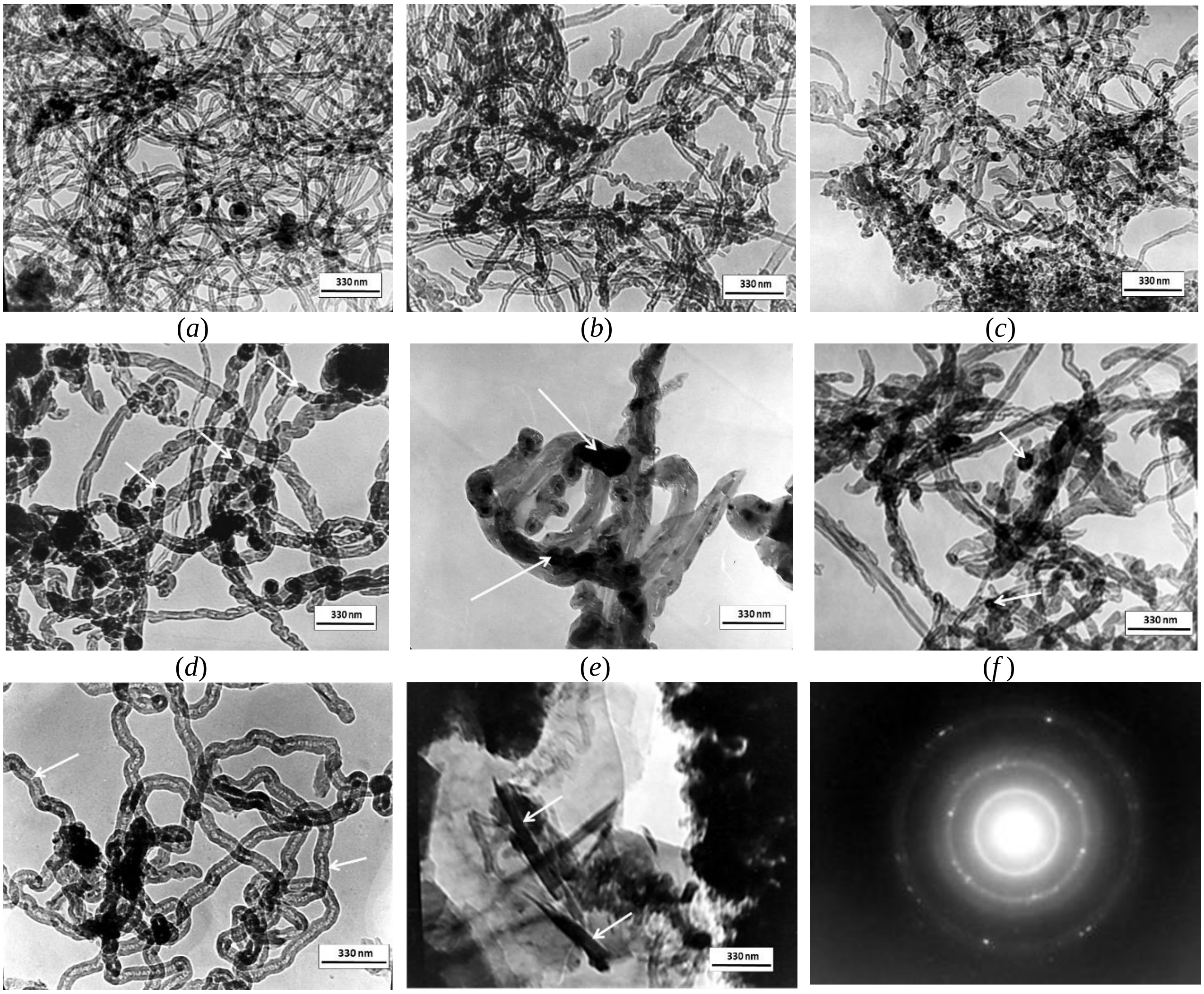


Fig. 3. Dependence diagrams of bulk density (*1*) and specific yield of CNMs (*2*) on the nature of the ligand

This type of dependence with minima for monoligand and extrema for bigand compositions correlates well with the dependence of such a significant indicator for heterogeneous catalysts as bulk density on the nature of the ligand, as shown in Fig. 3.

From a comparative analysis of the data presented in Fig. 3, it follows that MOCs with lower ρ are more effective compared to MOCs with higher ρ (the minima on curve *1* coincide with the maxima on curve *2* and vice versa). It has been established that the use of a second chelating ligand (citric acid) in almost all cases leads to the production of MOCs with low ρ. This fact is explained by the fact that when using citric acid, the degree of homogenization of metal ions in the MOCs matrix increases due to an additional complexing agent, as well as an increase in the depth of the polyesterification process and the formation of a cross-linked spatial network of the pre-catalyst. Ultimately, this leads to the formation of homo- or heterogeneous clusters of active metal particles of small sizes and homogeneous composition in the reducing atmosphere of the reactor [19]. The latter circumstance is a decisive factor in the process of initiation and growth of carbon nanotubes, since it determines both the morphological parameters of CNTs and the possibility of their formation.

When studying the morphology of carbon products of CCVD synthesis of CNMs on catalysts obtained using various ligands, in most cases their morphological similarity was found, as shown in Fig. 4*a*–*c*, and the product is coils of MWCNTs with a diameter of 15–50 nm with a structure like “matryoshka”. The differences lie in the relative content of MWCNTs of different diameters, since when moving from saccharides to polyalcohols, the proportion of particles with a diameter greater than 40–50 nm increases. In addition, the magnetic susceptibility of MWCNT samples increases due to the encapsulation of metal particles in the internal space of the nanotubes, as well as at the growth end of the nanotube as a result of the formation of a carbon cap around the active metal particle. This phenomenon is especially characteristic of CNM samples obtained on MOC–PVA + CA (Fig. 4*d*, *e*, arrows indicate the places of encapsulation of metal particles) and MOC–PET + CA (Fig. 4*f*), although in the latter case the main a number of CNTs have open ends. Encapsulated metal particles are inaccessible to acids and cannot be removed during the isolation of MWCNTs, which is confirmed by the presence of intense reflections in the XRD-patterns at $2\theta = 44.56°$ and $64.92°$, characteristic of α-iron [20]. The diffraction pattern of MWCNTs is shown in Fig. 5.



(*a*) (*b*) (*c*)

(*d*) (*e*) (*f*)

(*g*) (*h*) (*i*)

Fig. 4. TEM-images of the products of CCVD synthesis of CNMs on the MOC – PCP obtained using ligand compounds: *a* – sucrose; *b* – diethylene glycol; *c* – polyethylene glycol; *d*, *e* – polyvinyl alcohol; *f* – pentaerythritol; *g*, *h* – diethylene glycol at $T = 850$ °C; *i* – electronogram of CNM, obtained on MOC – DEG + CA at 850 °C (*a* – *h* – magnification 30.000×)

It should be noted that these samples are also characterized by the presence of particles with other morphological features – spiral and bamboo-shaped, which indicates an increase in the defectiveness of the graphene network of CNTs due to the appearance of fragments in the form of penta- and heptagons. The use of general Ni_2Co / $CaCO_3$ catalysts obtained using fructose as a chelating agent leads to the formation of thick-walled CNTs of uniform composition with an internal channel of very small diameter (~ 5–6 nm). It was also established that when the temperature of the CCVD process increases to 850 °C, nanotubes with internal constrictions appear in the carbon products of the CNTs synthesis on MOC–DEG + CA (Fig. 4*g*), nanotubes with internal constrictions appear (Fig. 4*g*), as well as carbon nanoparticles formed by a mechanism different from the formation of CNTs and having a “papier-mâché” or nanoscroll type structure (Fig. 4*h*). The appearance of such structures becomes clear from the discovery of flat 2D-structures of few-layer imperfect nanographene in carbon products, which is confirmed by the presence in the electron diffraction pattern of the corresponding sample of reflections related to the structure of graphite (Fig. 4*i*). The latter is probably associated with an increase in the contribution of the non-catalytic flow, which, for the process of carbon deposition on calcium carbonate, increases exponentially in a given temperature range [8].

Based on the data obtained, the best indicators for the quality and specific yield of CNTs in the CCVD process at $T = 500$ °C were obtained on MOC

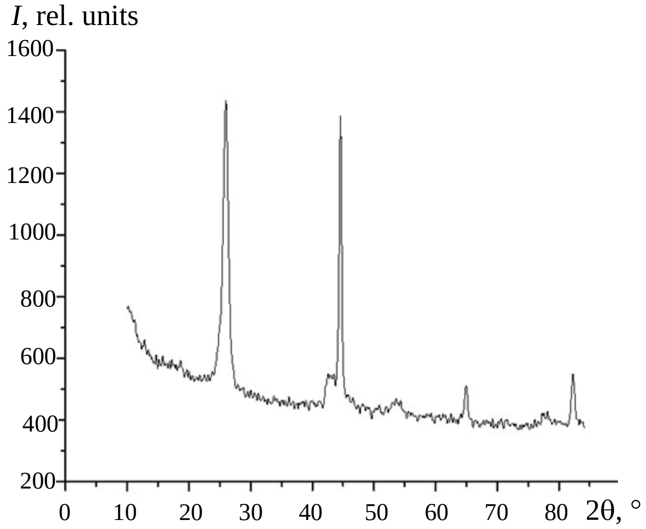


Fig. 5. Diffractogram of multi-walled carbon nanotubes obtained at the MOC–PVS

of the Ni_2Co / $CaCO_3$ composition using sucrose and fructose as a chelating agent, therefore we used the PCP (chelate - sucrose) method metal oxide catalysts (MOCs – PCP) of the general composition Ni_2Co / $CaCO_3$ (CaO, MgO, NaCl) with a molar ratio of Ni_2Co / $CaCO_3$ from 0.06 : 1 to 0.55 : 1 were obtained. To study the dependence of the specific yield of CNT_S on the temperature of CCVD synthesis, MOCs with a molar ratio of Ni_2Co / $CaCO_3$ 0.12 : 1 were used.

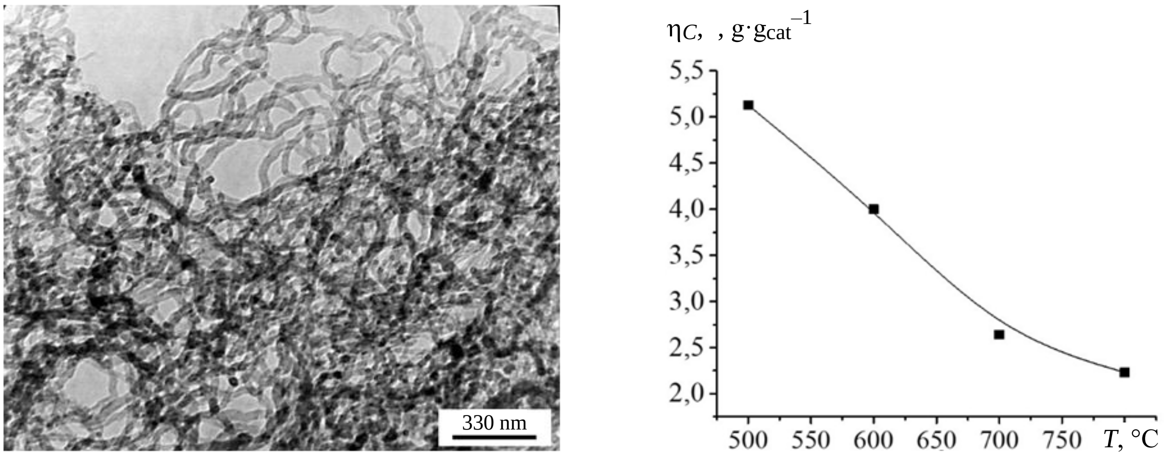
The carbon products obtained after the CCVD process and removal of the template are CNTs coils with a diameter of 20–40 nm with a low content of amorphous carbon (AC) (Fig. 6*a*).

From the obtaineddata, it follows that when using this combination of active metals in the composition of MOCs and using $CaCO_3$ as a carrier, the process of CNTs synthesis begins already at $T = 450$ °C and occurs most efficiently at $T = 500$ °C. An increase in the process temperature leads to a decrease in the specific yield of CNTs (Fig. 6*b*), and this is also typical for MOCs, where sodium chloride was used as a carrier.

An increase in the mole fraction of active metals in the composition of MOCs while maintaining a fairly high specific yield leads to a decrease in process productivity, which is expressed in the tendency for the dependence η_C – Ni_2Co / $CaCO_3$ (NaCl), mol×mol^{-1} to reach a plateau (Fig. 7*a*, *b*).

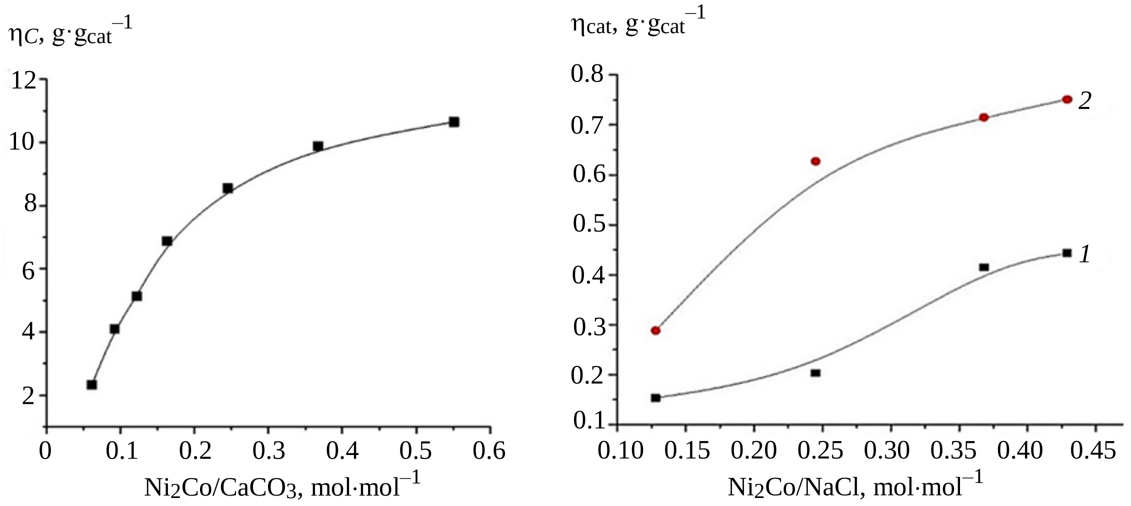
Specific yield (η_C, g·g_{cat}^{-1}) of CNMs in CCVD synthesis using MOCs with the composition Ni_2Co / carrier (carrier: $CaCO_3$, MgO, NaCl) at the same molar ratios of components and synthesis conditions (Pr-But = 30 cm^3·min^{-1}, Ar = 60 cm^3·min^{-1}, $t = 1$ h, $T = 500$ °C) decreases in the next row: 5.13($CaCO_3$) > 0.62(MgO) > 0.15(NaCl). The introduction of at hird metal Fe in to the bimetal licmix ture Ni, Co leads to a decrease in the specific yield of CNTs at the molar ratio Fe : Ni : Co = 1 : 1 : 1 and 2 : 2 : 1 to 1.02 and 1.23, respectively. Monometallic catalysts with the composition Me / $CaCO_3$ (Me = Ni, Co, Fe) also have low productivity, which leads to a decrease in specific yield to 2.08 for Ni, 0.55 for Co and 0.62 for Fe.

Thus, from the data obtained, it follows that the most powerful factor influencing the performance of Ni–Co based MOCs, as well as for the Fe–Co system [21], is the nature of the catalyst carrier. The productivity of the CCVD process decreases when moving from a more basic oxide to a less basic



(*a*) (*b*)

Fig. 6. TEM-image of CNTs obtained in low-temperature CCVD synthesis:
a – Ni_2Co / $CaCO_3$ (0.12 : 1 mol × mol^{-1}, Pr-But = 30 cm^3·min^{-1}, Ar = 60 cm^3·min^{-1}, $T = 500$ C, $t = 1$ h, chelate sucrose);
b – dependence of the specific yield of CNTs on the temperature of CCVD synthesis (Ni_2Co / $CaCO_3$ (CaO), Pr-But = 30 cm^3·min^{-1}, Ar = 60 cm^3·min^{-1}, $t = 1$ h, chelate sucrose)



(*a*) (*b*)

Fig. 7. Dependence of the specific yield of CNTs in the CCVD synthesis on the molar fraction of active metals:
a – Ni_2Co / $CaCO_3$; Pr-But = 30 $cm^3 \cdot min^{-1}$, Ar = 60 $cm^3 \cdot min^{-1}$, t = 1 h, T = 500 °C;
b – Ni_2Co / NaCl, $mol \cdot mol^{-1}$, Pr-But = 30 $cm^3 \cdot min^{-1}$, Ar = 60 $cm^3 \cdot min^{-1}$, t = 1 h, T = 650 °C – curve *1*; 750 °C – curve *2*

oxide or ionic carrier. This fact confirms our assumption that the catalyst support is directly involved in the process of electron transfer from the catalyst to hydrocarbons and back at the phase interface.

Due to the fact that the solubility of carbon in metals, as a decisive factor in the process of nucleation and formation of CNTs, decreases in the series Fe > Co > Ni [9], the type of temperature dependence becomes quite understandable – a rapid increase in the amount of pyrolytic carbon with limited solubility and the rate of carbon diffusion in the volume of the catalytic particle leads to the deposition of carbon on the outer surface of metal particles, their carbonization and, as a consequence, a decrease in process productivity. This process becomes more pronounced the higher the temperature of the CCVD process.

In contrast to Fe, Co MOCs, where the dependence η_C – Fe, Co / $CaCO_3$ (CaO), $mol \cdot mol^{-1}$ showed an extremum with a subsequent decrease in MOC productivity as the mole fraction of active metals increased, Ni, Co MOCs tend to decrease in efficiency (Fig. 7*a*, *b*), but this occurs to a moderate extent and is predictable. However, in our opinion, in both cases a size effect is manifested – as the content of active metals increases, the processes of agglomeration of reduced particles intensify, their enlargement to sizes with a critical radius of curvature, after which the CNTs formation becomes impossible. On the other hand, the unique decrease in temperature of the CCVD process of CNTs synthesis may be associated with the characteristics of the Ni, Co catalyst. Firstly, these metals, according to their state diagrams, are unlimitedly soluble in each other and form substitutional solid solutions over a wide range of concentrations. Secondly, the Ni–NiO system is one of the few that can exist in both oxidized (oxides) and reduced (metal) forms [19]. Thirdly, in the Ni–NiO system there are phase transitions of the second order: in NiO at 250 °C (523 K) an antiferromagnet – paramagnetic transition occurs, in Ni at 360 °C (633 K – the Curie point of Ni) – ferromagnet – paramagnetic. At $T > 360$ °C, such systems are paramagnetic and contain nickel particles of a certain size (more than 1 nm). This state of the system promotes not only the formation of embryos, but also their growth. Moreover, if at $T < T_C$ (Curie temperature – T_C) the oxidation of hydrocarbon occurs due to the oxygen of the NiO crystal lattice, then at $T > T_C$ the properties of the active center of the catalyst are determined by the set of Ni atoms formed during the reduction of nickel oxide. In our opinion, Co also plays a significant role in the reduction process of Ni due to the similarity of the electronic structure of the atoms and also the possibility of reduction through the hydrogen spillover mechanism. The validity of this assumption is confirmed by the fact that, as stated above, monometallic catalysts based on Ni and Co have much lower productivity compared to bimetallic Ni–Co and the principle of additivity of contributions is not observed.

4. Conclusion

Thus, based on the data obtained, it has been established that the use of the PCP method using chelating agents of various natures in the MOC synthesis for the CCVD synthesis of CNTs makes it possible to implement the process of preorganization of the spatial structure of the catalyst due to the formation of an intermediate highly porous polymer-organic pre-catalyst matrix. The latter, as well as the uniform distribution of active metal ions in the MOC matrix, lead to a significant increase in the efficiency of catalysts compared to the sol–gel method. The high efficiency of MOCs of the composition $Ni_2Co / CaCO_3$ in the CCVD synthesis of CNTs has been established; it has been shown that, in contrast to Fe, Co – MOCs (synthesis start temperature 800 °C), for these catalysts the process begins already at 450–500 °C and leads to an increase in the specific yield of the target product by 2–3 times. The influence of the stage of preorganization of the MOC structure using chelates of different nature is manifested in the formation of carbon products that differ in morphology. It has been suggested that low-temperature CCVD synthesis using MOCs of the composition $Ni_2Co / CaCO_3$ (CaO, MgO, NaCl) is realized due to the unique magnetic and electronic properties of the Ni–NiO system, which makes it possible to initiate the process of nucleation and then growth of nuclei of catalytic nickel particles at temperatures exceeding the Curie point of Ni (> 360 °C).

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6. Conflict of interests

The authors declare no conflict of interest.

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