KINETIC LAWS OF THE REACTION OF OBTAINING NANO-CARBON AND HYDROGEN FROM THE PROPANE-BUTANE FRACTION

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ABSTRACT

In the study, the process of obtaining monoglycerides and hydrogen from the propane-butane fraction was studied in the presence of a catalyst containing 15% Ni· 5% Co·5% Fe·5% Cu·2% Mo/HSZ with high catalytic activity and selectivity. The work aims to create catalysts with high catalytic activity for the production of nano-carbons and hydrogen from carbon compounds and to study the catalytic activity of this catalyst. The assessment of the effect of technological parameters of the process on the specific yield of the product and the properties of the obtained materials was carried out by the gravimetric method under isothermal conditions. IR-spectroscopy, X-ray phase analysis, benzene adsorption methods studied the pre- processing and subsequent structural characteristics of the first high-silicon zeolite and modified samples, the acidic properties of the catalysts - temperature- programmed desorption of ammonia. The qualitative and quantitative composition of the reaction products were analysed by the gas-liquid chromatographic method. The size and morphology of the catalyst were determined by illuminating electron microscopy, scanning electron microscopy, adsorption (BET) methods. Mesogeneity was assessed based on the study of texture characteristics.

KEYWORDS: *Carbon-Retaining Compounds, Catalyst, Temperature, Contact Time, Nanocarbon, Hydrogen.*

INTRODUCTION

Hydrogen can change any type of fuel, energy, transportation and industry due to its energy versatility. The growing needs of the chemical industry and energy are helping to increase hydrogen production. For example, over the past decade, global hydrogen production has grown at an annual rate of 4.5%, and the current level of production exceeds 100 million tons per year. Demand for hydrogen is expected to rise sharply in the near future. Depth of oil refining, increase in ammonia and methanol production, production of refined or synthetic liquid fuels, etc. The main contribution to the global demand for hydrogen is expected in the automotive and

energy supply systems, where hydrogen serves as an energy carrier, it can be 2 stored and transported as natural gas. Unlike methane, hydrogen has no resource limit and does not produce greenhouse gases. At the same time, the use of carbon nanotubes is increasing in various fields such as the development of filters for water purification, the synthesis of multi-purpose hydrogels, the delivery of drugs, and the biosensor. Multi-walled carbon nanotubes **[1, 2]** are promising materials with low toxicity and adsorption capacity. The production of multi-walled carbon nanotubes is cheaper, and is also preferred in the production of biosensors with high electrical conductivity **[3-6].** The term carbon nanotubes bonded to each other by sp2 hybridization refers to nanomaterials composed of carbon atoms with a tubular structure, and many works on carbon nanotubes began to be published 27 years ago after Lijima published the first concrete study. Many results have highlighted the successful use of carbon nanotubes in practice in many areas of science, such as energy, construction, cleaning, and environmental protection **[4-9].**

Hydrogen is currently a valuable chemical product and is widely used in a number of important industrial processes, such as the production of ammonia **[10],** methanol **[11, 12],** hydrazine **[13],** and synthetic hydrocarbons **[14].** Hydrogen is of great importance in the food industry and is used in the hydrogenation of vegetable oils **[15,16].** On the other hand, hydrogen is one of the most environmentally friendly sources of thermal energy **[17].** On an industrial scale, hydrogen is produced by steam methane reforming, heavy oil oxidation, coal gasification, and water electrolysis **[18–20].** It should be noted that biomass is also a potential source of hydrogen **[21].** All of these technologies, despite the number of shortcomings, have long been used for commercial purposes. No approach involving the efficiency and environmental safety of hydrogen production is being implemented. An alternative process that produces hydrogen is the catalytic pyrolysis of hydrocarbons, which is traditionally used to synthesize carbon materials. In general, the process can be expressed by the following equation:

$$C\ n\ H\ m \rightarrow nC + (m/2)H\ 2 \quad (1)$$

This process is widely used to obtain carbon nanotubes **[22].** The main advantage of this method in hydrogen production is the absence of carbon monoxide compounds in the produced hydrogen mixture, which does not require an additional stage of deep purification from CO and CO 2 . Pure hydrogen is obtained by catalytic decomposition of carbon compounds into carbon and hydrogen **[23-43].**

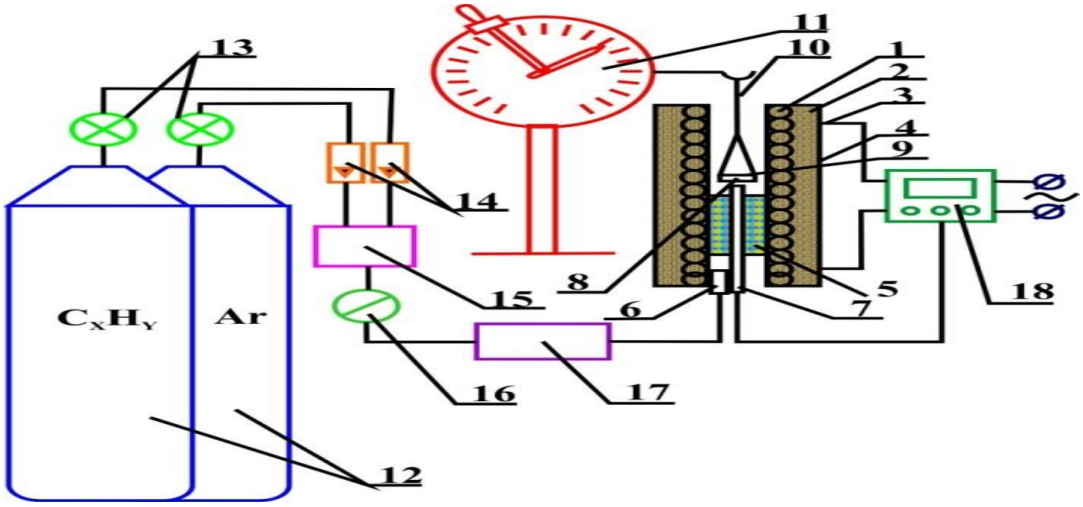
In recent years, the issue of nano generation and hydrogen extraction from carbon- containing compounds has become a very topical issue. Based on the above, this work aims to create catalysts with high catalytic activity for the production of nano-carbons and hydrogen from carbon compounds and to study the catalytic activity of this catalyst.

EXPERIMENTAL PART

The studies in the formation kinetics of carbon nanotubes. Intermediate metal-based catalysts were used to obtain carbon nanotubes by catalytic pyrolysis of 3 carbon-containing organic and inorganic compounds in the air. The results of theanalysis of the literature show that the use of Ni-based catalyst allows to carry out the pyrolysis process at relatively low temperatures of 550 ÷ 650 ℃.

The experiments were performed on a flow laboratory device (Fig. 1) operating in a differential mode consisting of a vertical reactor made of stainless steel with an inner diameter of 32 mm and a length of 500 mm. The gas mixture is sent from the bottom of the reactor. The bottom of the catalyst is filled with a nozzle (quartz particles) 150 mm below to evenly heat the gas mixture supplied from the bottom of the reactor and distribute the gas flow across the cross-section of the reactor. A catalyst-dusted substrate was placed at the bottom of the reactor and hermetically sealed. During the heating of the reactor, it was filled with argon.

The catalyst was distributed on the surface of a flat "LA77-2" brass mesh "boat" made of 77% copper, 2% aluminium and 21% zinc and fastened to a stainless steel wire 09Г2С. The propane-butane mixture of gases was sent to the reaction zone heated to operating temperature, and the heating circuit of the reactor was driven by an inert gas, which allowed atmospheric air to be expelled from the reaction zone. The torsional balance readings, which record the change in mass of the substance in the boat, were measured at 15 s intervals. After the formation of carbon nanotubes stopped, the hydrocarbon was squeezed out of the reactor with an inert gas.



1 - Reactor for nanoglerode extraction; 2 - heating element; 3 - thermal insulation; 4 - kojux; 5 - nozzle; 6 - nozzle for gas delivery; 7 - thermocouple; 8 - boat; 9 - catalyst layer; 10 - hook wire; 11 - torsion scales; 12 - gas cylinders (Ar, C3H8 + C4H10); 13, 16 - valves; 14 - rotamers; 15 - mixer; 17 - filter; 18 - PID regulator.

Figure 1. A device for studying the kinetics of the process of formation of carbon nanotubes

An experimental study of the production of carbon nanotubes used a catalyst containing 15%Ni·5%Co·5%Fe·5%Cu·2%Mo/HSZ. The thermal decomposition method was used in the preparation of the catalyst. The thermal decomposition method is one of the most efficient methods of catalyst preparation. The catalyst powder was obtained by the thermal decomposition of metal nitrates. The essence 4 of the method is the nitrates of metals (Ni(NO 3) 2 ·6H 2 O, Co(NO 3) 2 ·6H 2 O, Fe(NO 3) 2 ·9H 2 O, Cu(NO 3) 2 •3H 2 O, (NH 4) 2 MoO 4 •24H 2 O, ammonium molybdate, which are part of the catalyst. It consists of the interaction of a mixture of high silicon zeolite (HSZ) and organic matter (for example, a mixture of glycine and citric acid) from bentonite imported from Navbahor district, Navoi region, Uzbekistan at a temperature of ≥500 ℃ in the air. . Physicochemical and texture characteristics of high-silicon zeolites have

been studied **[32-35]** and in the aromatization of natural gas, petroleum gases and propane-butane fractions **[36-41]** and used in the Fisher-Tropsh process as well as in the production of olefins from dimethyl ether **[42-43].** High-silicon zeolite forms a well-developed porous structure, on the surface of which Ni, Co, Fe, Cu, Mo particles are distributed.

During the experimental studies of the process of synthesis of carbon nanotubes, propane-butane mixture (S3N8 / S4N10 = 50% / 50%) and inert gas stored in the cylinder - argon (Ar) were used as carbon-retaining compounds. The removal of catalyst particles from the synthesized carbon nanotubes was carried out by the acid washing method.

Investigation of the process of obtaining carbon nanotubes in reactors with a fixed layer of catalyst. This series of experimental studies aimed to determine the possibility of a large-scale transition from a laboratory device to an industrial device, as well as to determine the rational values of the basic model parameters of synthesis used in the subsequent design of carbon nanotubes. Pyrolysis of the propane-butane mixture (C 3 H 8 /C 4 H 10 =30%/70%) was carried out at atmospheric pressure and at a temperature of 600-650 ℃, in laboratory and pilot reactors operating periodically on a stationary layer of catalyst. A zeolite-based filter was used to clean the gas mixtures from impurities and to dry them from moisture. The exhaust gas was examined on a chromatograph - Crystal 7000 chromatograph.

RESULTS AND DISCUSSION

Experimental studies to determine the dependence of the specific yield ē of carbon nanotubes on the processing time were carried out at a rate of 550 to 700 ℃ and a flow rate of hydrocarbons of 15 to 20 l/h (Figure 3).

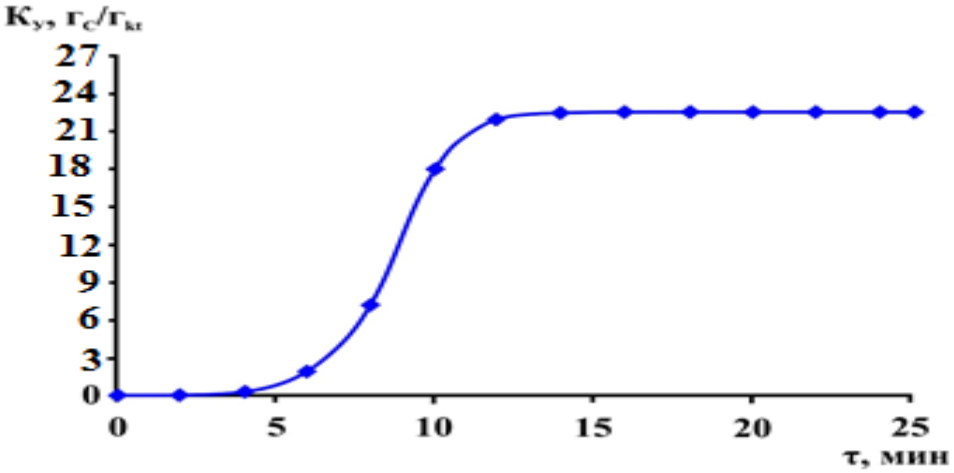


Figure 3. Dependence of specific yield of carbon nanotubes (ē) on pyrolysis time (t)

The initial period of time (≈10 min) describes the phase of reduction of Ni, Co, Fe, and Mo oxides to metal, the accumulation of free carbon, and the formation of carbon nanotube particles. The active phase of the synthesis lasts 9 ÷ 10 minutes and ensures that η is in the range of 22 g s /g cat . Then the growth of nanostructures stops. To determine the effect of the thickness of the catalyst layer on the yield, etc., different traction of the catalyst was placed on the "boat" (average pile density ρ c ≈480 kg/m 3) and distributed evenly over the entire surface (S boa = 0,1·10 -3 m 2). The thickness of the catalyst layer was changed in the range h c = 0.1 ÷ 2 mm,

the mass of the loaded catalyst was determined as m c =ρ c S boa h c . The experiments were performed for 10 min at a flow rate of 550 to 700 ℃ and a flow rate of 15 to 20 l/h of hydrocarbons. The timing of the process was chosen based on previous experimental data.

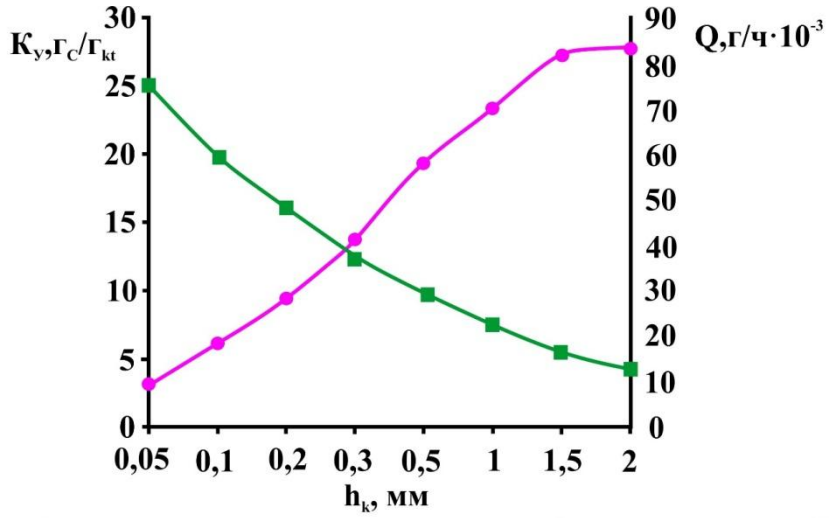


Figure 4. The relative yield of carbon nanotubes (K u) and dependence of reactor efficiency (Q) on catalyst layer thickness (h c)

The thickness of the catalyst layer h c ≈0,2÷0,3 mm was determined for conducting experiments and setting the calculation parameters of the experimental-industrial device for the synthesis of carbon nanotubes.

The effect of temperature on specific yield was studied in 10 ℃ steps in the temperature range of 550 ÷ 700 ℃. The thickness of the catalyst layer was h c ≈0.2 mm (m = 12 mg), the carbon consumption gas consumption was 9 ± 0.1 l/h, and the processing time was 12 min. The results of experimental studies (Fig. 5) showed that starting at 620 ℃, the process temperature did not affect the specific yield of carbon nanotubes, which was η≈22g c /g cat .

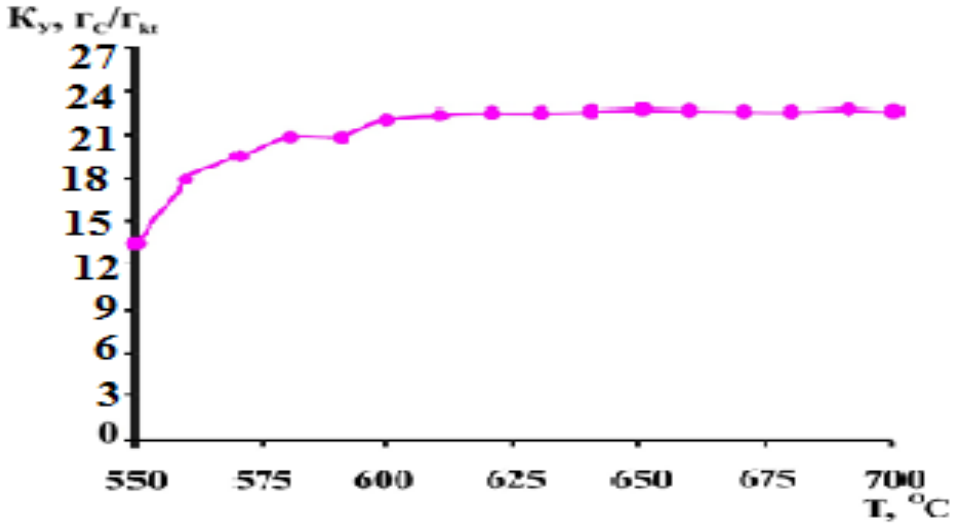


Figure 5. Graph of temperature (T) of specific gravity of carbon nanotubes (ē)

The conducted experiments allowed us to determine the dependence of the laws of the kinetics of MCN (mass of carbon nanotubes) synthesis on the basic mode parameters of η by establishing the exact conditions of its conduction in a flow- type reactor. These studies, carried out at the initial stage of the work, have shown that when using a propane-butane mixture, the synthesis of carbon nanotubes with a catalyst of this composition and the technology of production is possible.

A method based on measuring the electromagnetic properties of the material being synthesized. To study the kinetics of the process of formation of carbon nanotubes, an original method was developed based on the measurement of the complex dielectric constant of a catalyst and carbon nanotubes placed in a reaction zone called electrographs. Depending on the size of the catalyst, carbon nanotubes, as well as the material placed in the reactor, the complex dielectric constant of the catalyst, carbon nanotubes, the signal coming to the computing device and reflected on the monitor screen will also change accordingly. To implement this method of studying the kinetic properties of the process of synthesis of carbon nanotubes, an original device design was developed and developed, the scheme of which is shown in Figure 6.

Figure 6. Device scheme for determining the kinetics of the process of formation of carbon nanotubes

The device allows changing the conditions of the process of obtaining carbon nanotubes by catalytic pyrolysis of organic and inorganic compounds containing carbon in the air, to monitor the change in reaction mass in the reactor cell and to monitor the information received on the monitor screen in real-time.

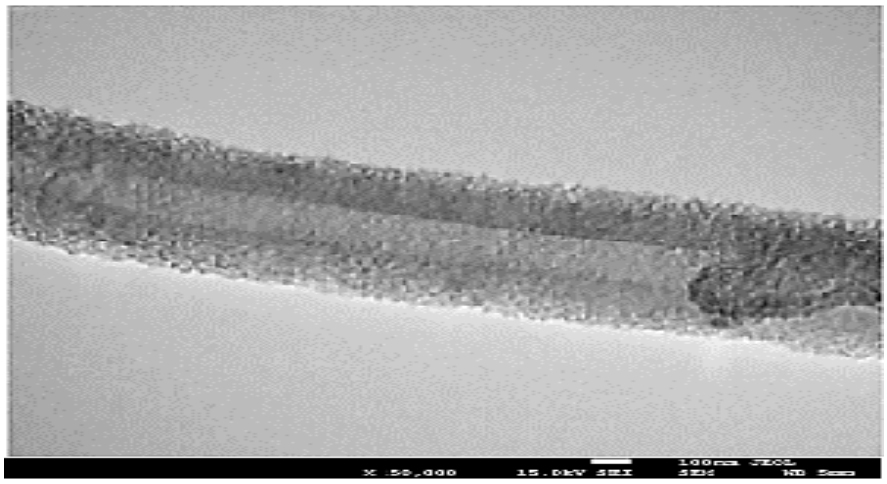


Figure 7. Microstructure of the obtained materials

The timely cessation of synthesis at the end of the growth of nanostructures, which was carried out within the framework of this experiment, not only significantly optimized the processing time but also allowed to obtaining of carbon nanotubes with high-quality properties. From the scanning microscopy data (Fig. 7), it can be deduced that the material to be synthesized consists of an almost complete tubular nano glue with a narrow range of diameters (15-20 nm) with a minimal amount of amorphous carbon (<3-5%).

The studies allow us to conclude that the synthesis of carbon nanotubes is possible by catalytic pyrolysis of the propane-butane mixture (C 3 H 8 /C 4 H 10 =50/50%) in this type of catalyst (15%Ni*5%Co*5%Fe*5%Cu*2%Mo/HSZ). The known regime parameters and the obtained dependencies underlie the recommendations for the design of laboratory reactors for the synthesis of carbon nanotubes by catalytic pyrolysis with a stationary layer of catalyst. The synthesis was carried out at atmospheric pressure in the temperature range of 500 ÷ 700 ℃, the pyrolysis time was changed in the range of 5 ÷ 30 min. At the end of the process, the reactor was cooled in an argon stream. The processing of the obtained data allows obtaining dependencies that estimate the effect of process time on the specific yield of the product (Figure 8). The maximum η was reached approximately 35 minutes after the start of the process.

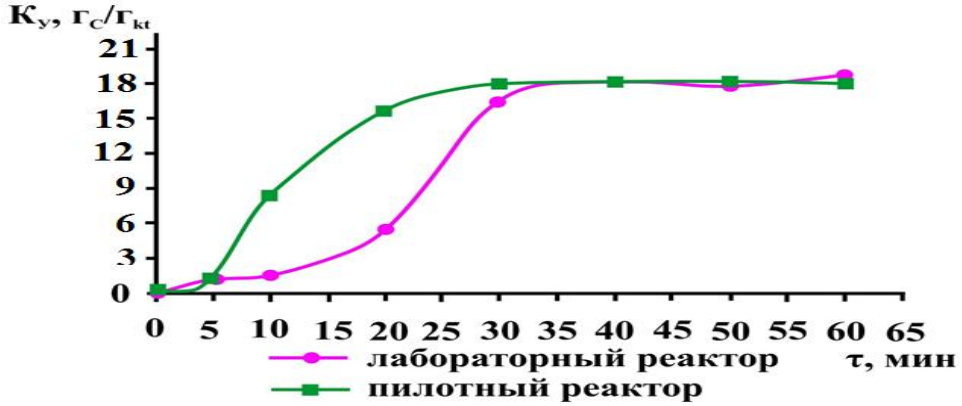
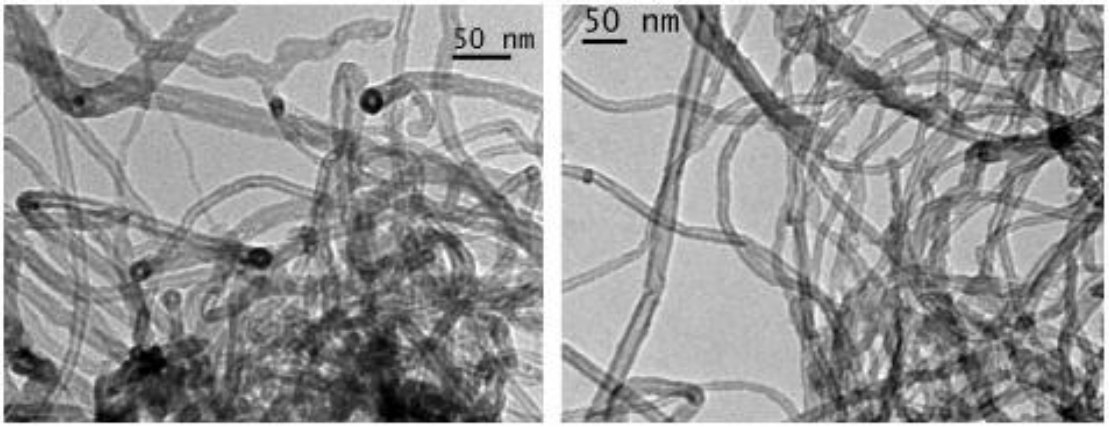


Figure 8. Graph of the dependence of the specific yield of the mass (τ) of carbon nanotubes on the pyrolysis time (t)

Despite the different characteristics of the mass growth curves of the carbon nanotubes used in the reactors, η ≈18 g s / g cat was approximately the same size. A microphotograph of the obtained nanocarbon obtained by scanning electron microscopy is shown in Figure 9 below.



(a) **(b)**

Figure 9. TEM image of nano-carbon initially (a) and treated with nitric acid for 8 hours (b)

CONCLUSION

Thus, the process of obtaining nano-carbon and hydrogen from the propane-butane fraction was studied in the presence of a catalyst containing 15%Ni*5%Co*5%Fe*5%Cu*2%Mo/HSZ with high catalytic activity and selectivity. Experimental studies to determine the dependence of the specific yield of carbon nanotubes on the processing time were carried out at a flow rate of 550 to 700 ℃ and a flow rate of hydrocarbons of 15 to 20 l/h. The initial period (≈10 min) is the phase of reduction of Ni, Co, Fe and Mo oxides to metal, accumulation of free carbon and formation of carbon nanoparticle particles, the active phase of synthesis lasts 9 ÷ 10 minutes and η is in the range of 22 g s /g cat . The effect of temperature on specific yield was studied in 10 ℃ steps in the temperature range of 550 ÷ 700 ℃. The thickness of the catalyst layer was hk≈0.2 mm (m = 12 mg), the carbon consumption gas consumption was 9 ± 0.1 l/h, and the processing time was 12 min. According to the results of experimental studies, starting from 620 ℃, the process temperature does not affect the specific yield of carbon nanotubes, it was η ≈22 g s /g cat

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