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TECHNOLOGY FOR OBTAINING CARBON NANOCOMPOSITE MATERIALS

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ABSTRACT

The kinetics of the formation of carbon nanotubes on a catalyst during the pyrolysis of carbon-containing gases is rather peculiar and little studied. Its main provisions proposed in the literature are debatable. The complexity of studying the kinetics of NT synthesis is confirmed by the use of about 10 parameters when creating a model. The kinetic regularities of the formation of carbon nanotubes during the pyrolysis of methane are studied in terms of the yield of carbon at the optimal composition of the catalyst.

Keywords: Nanotube, Nanotechnology, Bentonite, Carbon Nanotubes, Component Concentration, Diffusion Coefficient.

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INTRODUCTION

The development of new technologies, in particular nanotechnologies, opens up great prospects for the improvement of new materials. The developed mathematical model makes it possible to determine the rate of formation and the amount of the resulting product depending on the temperature of the reaction medium, the composition of the initial gas mixture (namely, the concentrations of methane and hydrogen in it), and the type of catalyst used (Ni - bentonite, Mo - bentonite, Co - bentonite).[3]

EXPERIMENTAL

To describe the process of formation of nanotubes from methane, a mathematical model of a nanotube laboratory reactor with a catalyst located in the central zone of the reactor has been developed. When constructing a mathematical model, a two-phase system is considered: a dispersion (gas) medium and a dispersed phase (catalyst), where various reactions can occur both within the medium and between the phases. The number of reactions is determined by the kinetic scheme used, which describes all chemical transformations occurring in the system.[2-4] When constructing a mathematical description of a tubular methane pyrolysis reactor, partial differential equations were used - for the dispersed phase. Since the methane pyrolysis regime is isothermal, the heat balance equations are not taken into account in the mathematical description.

RESULTS AND DISCUSSION

The equations for changing the concentrations of the components of the gaseous medium have the form:

$$\frac{\partial C_i}{\partial t} + \nu_1 \frac{\partial C_i}{\partial x} = D_i \frac{\partial^2 C_i}{\partial x^2} + D_i \frac{\partial^2 C_i}{\partial r^2} + \frac{D_i}{r} \frac{\partial C_i}{\partial r} + J_i \qquad (1)$$

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Where, v_1 - is the linear velocity of the gas mixture m/s; C_i - concentration of the i th component of the gas phase (i=1… n_1), mol/m^3; D_i - - diffusion coefficient of the i th component of the gas phase, m^2/s; J_i - - the rate of formation or consumption of the i th component according to the reactions occurring in the gas phase, mol/(m^3·s); t- time, s; x and r are the longitudinal and transverse coordinates of the reactor, respectively, m (the origin for the x-axis is the point of entry of the gas phase into the apparatus, for the r-axis it is the axis of the apparatus).[5]

The equations for changing the concentrations of the components of the dispersed phase are written as follows:

$$\frac{\partial \widetilde{C}_i}{\partial t} = \widetilde{J}_i \qquad (2)$$

Where, $\widetilde{C}_i$ - surface concentration of the solid phase component, reduced to a unit mass of the catalyst, mol/kg; $\widetilde{J}_i$ - the rate of formation or consumption of the i -th component of the dispersed phase according to reactions occurring on the surface on the surface of the catalyst, mol/(kg· s).

The initial condition for equation (3) has the form:

$$\widetilde{C}_i(t=0) = \widetilde{C}_i^0, \qquad (3)$$

Where, $\widetilde{C}_i^{\,0}$ - concentration of the i component of the dispersed phase at the initial moment of time, mol/kg (as a rule, the concentrations of all components at the initial moment of time are equal to zero, while the activity of the catalyst is maximum).[6] The activity of the catalyst is taken into account by using the so-called "active site concentration", which is actually the molar adsorption capacity per unit mass of the catalyst, provided that one molecule is located on one active site. At the initial moment of time, this concentration has a maximum value and is calculated by the relation:

$$\widetilde{C}^0_{K_t} = S_{Kt} \cdot L` / N_A \qquad (4)$$

Where, S_{Kt} - the specific surface area of the catalyst, m^2 / kg; $L^{/}$ - the total number of active centers per unit surface, 1/ m^2 / kg; N_A - Avogadro's number 1/ mol. The greater the value of this value, the correspondingly higher the activity of the catalyst.

The rate of formation or consumption of components in a continuous medium in gas-phase reactions is determined by the ratio:

$$J_i = \sum_{j=1}^{m_i} \nu_j^i W_j \qquad (5)$$

Where, ν_j^i - coefficient of the j th component in the j th reaction; W_j - j th reaction rate; chemical gas-phase reaction, mol/(m^3·s).

The rates of chemical reactions occurring in a gaseous medium are calculated by the ratio:

$$W_j = k_j^+ \prod_{i=1}^{n_1} C_i^{\nu^+_{i,j}} - k_j^- \prod_{i=1}^{n_1} C_i^{\nu^-_{i,j}} \qquad (6)$$

Where, k_j^+ and k_j^- - respectively, the rate constants of the forward and reverse reactions; $\nu_{i,j}^+$ and $\nu_{i,j}^-$ - stoichiometric coefficients of the j th component in the direct and reverse reactions, respectively.

The direct reaction constant is determined by the Arrhenius equation:

$$k_j^+ = k_j^0 \exp\left(\frac{E_j}{RT}\right) \qquad (7)$$

Where, k_j^0 - pre-exponential multiplier; E_j - activation energy of the jth reaction, J/mol; R- universal gas constant (R= 8.31441 J/(mol·K).

The feedback constant can be calculated using the formula:

$$k_j^- = \frac{k_j^+}{K_P^j} \qquad (8)$$

Where, Kp - equilibrium constant of the yth reaction, which can be calculated at a given temperature, knowing the standard change in enthalpy (AHj) and entropy (AS, -) for this chemical reaction.

The rate of formation or consumption of the dispersed phase component in surface reactions is determined by the relation:

$$\widetilde{J}_i = \sum_{j=1}^{m_2} \widetilde{\nu}_j^i \widetilde{W}_j \qquad (9)$$

Where, ν_j^i - stoichiometric coefficient of the jth component of the dispersed phase in the jth surface reaction; $\widetilde{W}_j$ -the rate of the jth surface reaction, mol/(kg·s).

In turn, the surface reaction rate is determined by the formula:

$$\widetilde{W}_j = \widetilde{k}_j \prod_{j=1}^{n_2} \widetilde{C}_i^{\widetilde{\nu}_j^i} \qquad (10)$$

Where, $\widetilde{k}$ —the rate constant of the j-th surface reaction, is determined by the Arrhenius equation.

These equations (1)-(9) are a general mathematical description of a flow tubular reactor with a catalyst located in its center. To construct a kinetic scheme for the catalytic pyrolysis of methane with the formation of carbon nanotubes, it is also necessary to take into account the chemical reactions between the components in the system.[7-8] The kinetics of the formation of carbon nanotubes on a catalyst during the pyrolysis of carbon-containing gases is rather peculiar and little studied. Its main provisions proposed in the literature are debatable. The complexity of studying the NT synthesis kinetics is confirmed by the use of about 10 parameters when creating the model. It was noted that there are two mechanisms of NT catalytic formation: root and vertex. The vertex mechanism is characterized by HB and MNT, which occurs at temperatures of 500–700°C, and the root mechanism, by ONT, at a temperature of 800–1200°C. The kinetic regularities of the formation of carbon nanotubes during the pyrolysis of methane were studied by the yield of carbon on the optimal composition of the catalyst

Co(Ni) : Mo : bentonite = 1:3:80.

The determination of the temperature regime and the behavior of the catalyst during its heating in an atmosphere of CH_4**:**H_2=1**:**4 was studied at temperatures from 25°C to 1000°C. It was found that the mass of the catalyst decreases to 800°C, then sharply increases, which is associated with the formation of NT, becomes constant, and then decreases at 1200°C. The influence of the partial pressure of methane on the formation of carbon was studied according to the equation, which shows that the reaction with respect to CH_4 belongs to the first order:

$$V_0 = K \cdot P_{CH4} - A \qquad (11)$$

Where, V_0 - the initial rate of carbon accumulation;

К = 1,0394·10^{-5}[mg · Pa^{-1}·s^{-1}] – carbon accumulation rate constant;

A = 0,067911 [mg ·s^{-1}] – empirical coefficient.

Kinetic experiments were carried out at atmospheric pressure in a horizontal setup. The bulk density of the catalyst was 0.666 g/sm^3, and the specific surface area was 160 m^3/g. The average pressure during the experiments was 750 mm Hg. or 99992 Pa. The behavior of the catalyst was studied when it was heated in an atmosphere of CH_4 and H_2 (1:4 volume). The heating rate was 10^0/min at a gas mixture feed rate of 350-400 ml/min. It was found that the formation of carbon is affected by the partial pressure of methane and the reaction proceeds in the first order. It was found that carbon accumulations below 5% vol. in a mixture of CH_4 and H_2 are not observed. To determine the hydrogen order, the partial pressure of CH_4 was at the level of 9940 Pa (10% vol.), and the hydrogen pressure was varied from 89510 (90% vol.) to 59670 (60% vol.), replacing part of the H_2 supplied to the reactor with argon.[9] Experimental results show that increasing the hydrogen pressure reduces the rate of carbon accumulation. The resulting dependence is described by the equation

$$V_0 = K \cdot \frac{1}{P_{H_2}} - B \ , \qquad (12)$$

Where, K = 617830[mg · Pa $^{-1}$ · min^{-1}] - effective carbon accumulation rate constant, B = 5,716 [mg.min^{-1}] - empirical coefficient. It was found that the hydrogen pressure should not exceed 0.108 MPa. The order in H_2 is the reverse of the first. The overall equation, taking into account the dependence of the initial rate of carbon accumulation on the partial pressures of methane and hydrogen, can be represented as:

$$V_0 = K(P_{CH_4} - P^*_{CH_4})(\frac{1}{P_{H_2}} - \frac{1}{P^*_{CH_4}}), \qquad (13)$$

Where, K - effective carbon accumulation rate constant (K = 18250 mg. min $^{-1}$)

$P^*_{CH_4}$, P_{H_2} - minimum and a maximum pressure of methane and hydrogen, respectively.

The experimentally obtained kinetic dependences show that the initial rate of carbon accumulation is constant but then decreases exponentially with the time of the pyrolysis process, which is apparently associated with catalyst deactivation. It is probably associated with a change in the phase composition of particles during the growth of carbon NT, which will be studied in further studies of the adsorption-structural characteristics of the catalyst.[11-12] Based on experimental data and literature sources, the authors of this work propose a kinetic scheme for the formation of carbon nanotubes in methane pyrolysis, taking into account the main chemical reactions in the gas phase and on the surface of the Ni(Co)-Mo-bentonite catalyst.[10] Table-1 shows the kinetic scheme for the formation of carbon nanotubes during methane pyrolysis, taking into account chemical reactions in the gas phase and on the catalyst surface.

Table-1: Kinetic Scheme for the Formation of Carbon Nanotubes During Methane Pyrolysis

№	stages	A	B	E, kj/mol
	Reactions taking place in the gas phase			
1	$2H \leftrightarrow H_2$	200	-1	0
2	$CH_4 \leftrightarrow CH_3 + H$	$1{,}00 \cdot 10^{-7}$	3	54.470
3	$CH_4 + H \leftrightarrow CH_2 + H_2$	$2{,}20 \cdot 10^{-8}$	3	36.663
4	$CH_3 + H \leftrightarrow CH_2 + H_2$	0,9	0	63.269
5	$C H_2 + H \leftrightarrow CH + H_2$	1000	-1.56	0
6	$CH + H \leftrightarrow C + H_2$	1,5	0	0
7	$2 CH_3 \leftrightarrow C_2 C_6$	903	-1.18	2.740
	Reactions taking place on the surface of the catalyst			
1	$Kt + CH_3 \rightarrow [CH_3 - Kt]$			
2	$[CH_3 - Kt] + H \rightarrow [CH_2 - Kt] + H_2$			
3	$[CH_2 - Kt] + H \rightarrow [CH - Kt] + H_2$			

4	$[CH-Kt]$+H→$[C-Kt]$+ H_2			
5	$[C-Kt]$→C_{HT}+Kt			
6	$[C-Kt]$→$[C_A-Kt]$			
7	Kt+H→$[H-Kt]$			
8	$[H-Kt]$+H→Kt+ H_2			

Where,
C_{nt} – carbon NT; C – carbon deposited on the NT surface;
Kt – catalyst in active form;
C_{nt}-Kt – deactivated form of the catalyst;
C_{nt}-C – HT with carbon deposited on their surface.

The synthesis of nanotubes (NT) was carried out in accordance with the block diagram shown in Fig.-1. In accordance with the scheme shown in Fig.-1, in the continuous apparatus (1), the Mo-Co(Ni) / bentonite catalyst of a given composition is synthesized by the bentonite impregnation method. The resulting flue gases enter a cyclone (not shown in the diagram) to separate the catalyst particles from the flue gases, which are either after burned or released into the atmosphere. The catalyst from the installation (1) is combined with the catalyst from the cyclone and the conveyor is fed into the storage hopper (2), from which it is transported to the airlock (3), purged with a methane-hydrogen mixture, then by the dispenser into the reactor.

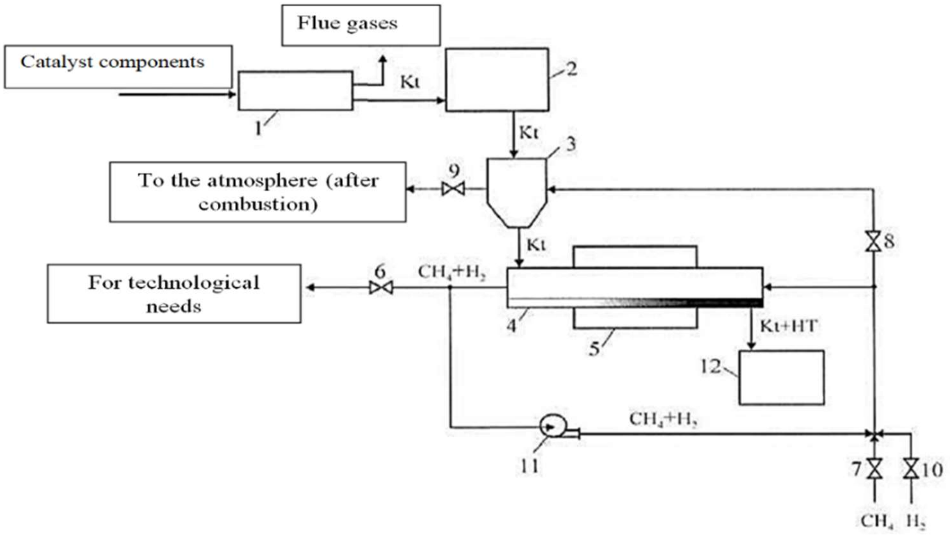

Fig.-1: Schematic Diagram of NT Synthesis by Catalytic Pyrolysis of Methane with Recirculation of Methane-Hydrogen Gas

1- catalyst synthesis unit;
2- catalyst storage bin;
3- sluice for removing air from the catalyst;
4- continuous reactor;
5- furnace with resistive heating;
6,7,8,9,10 - valves;
11 - compressor for recirculation of methane-hydrogen gas;
12- receiver.

Experimental data were obtained in the designed semi-industrial laboratory reactor of continuous action.
The development is a continuous installation with a tubular screw reactor. Quartz tube 5 with an inner diameter of 4.2 cm and a length of 90 cm is mounted on holders 4. The middle part of the reactor (pyrolysis zone) is heated to the required temperature using an electric furnace 8. The catalyst is forced to move using a screw 6. The reactor ends are cooled using a cooling system 7. From the cyclone tank, the

catalyst is fed into the furnace by rotating the dispenser 10, after heating in the pyrolysis zone, the catalyst with the obtained carbon nanotubes enters the receiver 1. The rotation of the screw is carried out using a motor with a reduction gear 14 and then a damper 13. A mixture of methane with hydrogen is fed into tube 3 on the receiving holder and tube 2 lowered to the bottom of the receiver. The exhaust mixture of gases is discharged through the tube 9, located on the supply holder, and the tube 15, located on the tank-cyclone.

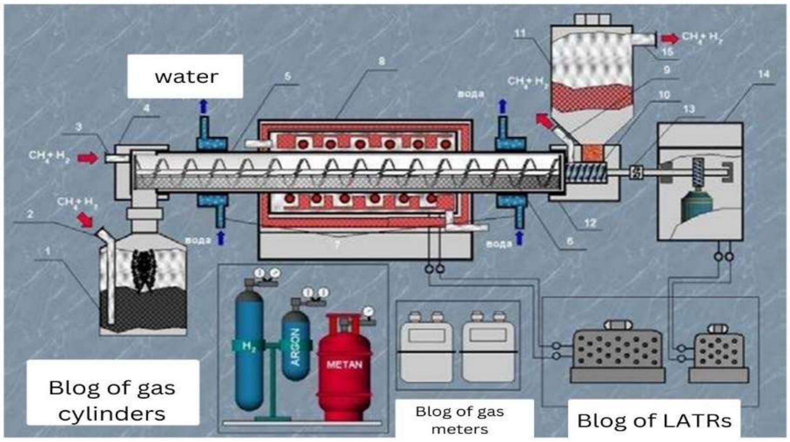

Fig.-2: Installation for the Production of Nanotubes by the Method of Carbon Synthesis in a Continuous Mode

A computer with the installed TRACE MODE program is integrated into the installation. In a continuously operating reactor, the following process characteristics are recorded

Temperature t = 900 ± 10 ^{0}C

Residence time of the catalyst in the hot zone 35 min;

Composition of the methane-hydrogen mixture (vol.%) CH_4 - 20, H_2 - 80;

Consumption of methane-hydrogen mixture 400 cm^3/min;

An increase in the productivity of the apparatus can be achieved by increasing the process temperature, the load of the reactor on the catalyst, the flow rate of the methane-hydrogen mixture, and the use of more active catalysts.

The nanotube production model developed using the TRACE MODE software product is a virtual production duplicating the functions of a laboratory facility. The main functions of control and display of information are reproduced in the virtual apparatus in a visualized form, which makes it possible to conduct visualized experiments with adjustment and monitoring of the process. By turning on virtual production and setting the parameters of the pyrolysis process using the created virtual controls, you can change the temperature of the furnace, the ratio of the supply of a mixture of gases, and, in accordance with the entered mathematical models, observe the output characteristics displayed in the form of a digital display, graphic dependence and events associated with them: a visual change in the speed of rotation of the auger, the activation of an alarm in case of overheating, etc.

CONCLUSION

Thus, based on the above results, the authors have made the following conclusions:

- a mathematical model of a laboratory-type tubular reactor with a catalyst located in the central zone of the reactor has been developed. When constructing a mathematical model, a two-phase system is considered: a dispersion (gas) medium and a dispersed phase, for which partial and simple differential equations are used, respectively. When studying the kinetics of the formation of carbon nanotubes (NT) on a catalyst, it was noted that there are two mechanisms: root and vertex;
- Studied the behavior of the catalyst and the temperature regime in the atmosphere of methane: hydrogen=1: 4 at a temperature of 25-1000^{0}C. The influence of the partial pressure of methane on

the formation of carbon was studied and it was found that the reaction of methane pyrolysis belongs to the first order;

- the influence of the partial pressure of hydrogen on the formation of carbon from 89510 Pa (90%) to 59670 Pa (60%) was revealed. The resulting dependence is described by the equation. It was found that the hydrogen pressure should not be higher than 0.108 MPa, the order in H_2 is equal to the reverse of the first;
- the experimentally obtained kinetic dependences show that the initial rate of carbon accumulation is constant, but then decreases exponentially with the time of the pyrolysis process, which is apparently associated with the deactivation of the catalyst. It is probably associated with a change in the phase composition of particles during the growth of carbon nanotubes, which will be studied in further studies of the adsorption-structural characteristics of the catalyst;
- a kinetic scheme for the formation of carbon nanotubes during pyrolysis and on the catalyst, the surface was proposed.

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