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Physicochemical Nano-Robot in Nanotechnology

R. A. BUYANOV¹, I. V. MISHAKOV^{1,2}¹*Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia**E-mail: buyanov@catalysis.ru*²*Novosibirsk State University, Novosibirsk, Russia*

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Abstract

Within the methodology of perception of the fundamentals and regularities of nano-dimensional world functioning, the phenomenon “physical and chemical nano-robot” (PCNR) has been proposed. Its purpose consists in the investigation and organization of nanotechnologies to produce novel substances and materials. The system capable to perform the PCNR functions is offered, evidence-based and realized in the form of the working model. This model is the nanodispersed polycrystalline particle of Ni, one of the metals of iron subgroup (Fe, Co, Ni). We have studied the specific conditions under which such Ni particles possess a set of various functions crucial in the operation of nanotechnologies focused on the synthesis of new substances and materials. The multistage mechanism of PCNR action in the nanotechnological synthesis of materials with different functions is discovered. Scientific bases for the organization of new PCNR as well as the short review of already characterized PCNR-based nanotechnologies have been presented. The basic model of PCNR nanoscale system allowing one to operate technology and control the range of nano-products is developed.

Key words: nanotechnologies, synthesis, physics, chemistry, metals, solid solutions, nano-robots, mechanisms, carbides, thermodynamics

1. INTRODUCTION

At the end of the XX century, science survived a kind of bifurcation in its development. A vast area of the nanometer-sized world has opened. The specificity and diversity of this world have not yet been arranged as adequate programmes of research and development works in the directions of priority. However, a specific problem has already appeared. It turned out that the traditional methods and procedures for the cognition of the laws of macro-world and the entire philosophy of their perception did not get

adapted in some cases to the processes of microworld cognition.

There is a boundary between these worlds, at which the terms and notions are not always identical. Here we should mention a marvellous book entitled “Nanotechnology. Alphabet for Everybody” [1]. In this book, a comprehensive and professional review of the whole range of ideas and trends of the development of this young area of science is presented.

In this paper, we discuss the results of the investigation of a new object that appeared within the science studying the nanometer-

sized world. This object was called nano-robot [1, p. 204].

2. NANO-ROBOTS TODAY IN BRIEF

The term “nano-robot” was introduced into science together with the prefix “nano”. It is slightly older than thirty years, and it is still in its infancy. Because of this, we will give only a brief description of our evaluations and expectations in this area of science.

Initially, this kind of machine was almost fantastic work of humans. It was assumed that this robot with the functional structure will be created through molecular assembling and it will possess the ability to manufacture new generations of functional materials according to a special programme. These nanometer-sized robots were called molecular robots (MR).

The very idea of MR is fascinating. However, its implementation meets enormous difficulties and expenses. It is assumed that the MR will be created by man. However, at the level of modern civilization, total expenses for the creation of such machines will turn out to be many orders of magnitude higher than the value of the products manufactured by them. As we know, only a skilled left-handed craftsman from a fairy tale – Levsha – succeeded to shoe a flea.

The difficulties in the creation of MR stimulated us to search for an alternative version of a solution to the problem. And we found such a version. We supposed that the nature itself, in its infinite diversity, makes functional structures governing nanotechnologies. It should be specially stressed that the nature tends to find the simplest solutions in its creations. This is why one speaks that greatness is in simplicity.

By that time, we possessed a sufficient amount of the information allowing us to give a general formulation of the contents of such a robot. We represented it as a system of natural origin, possessing physical and chemical properties (functions determining the type of their interaction with the environment). We called this system a physicochemical nano-robot (PCNR).

It follows from the very intention and purpose of the PCNR that the range of its manufacturing possibilities is determined by the coherent set of functions involved in nanotechnological control. It should be stressed that a principal difference of the PCNR from MR is in the nature of their functions.

However, all these considerations are rightful only on the condition that it is better to launch

the research relying on an erroneous hypothesis rather than try to find the truth by trials and errors without any direction.

3. FROM THE HYPOTHESIS AND DEDUCTIVE FIGURE TO A REAL PCNR MODEL

In this section, we discuss research results proving that the hypothesis concerning the nature and structure of PCNR has been confirmed and has become an actual object for a more thorough investigation.

The very idea of a nano-robot could have appeared only after the prefix “nano” has won its citizenship in science. Before this event, since early 1960-es, carbon as the subject appeared in the research plans of the Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR.

This is explained by the discovery of previously unknown carbon forms with many useful properties and different crystallographic and morphological characteristics.

The major goal of the works of a number of foreign research teams was directed at the empirical selection of the methods to obtain carbon products. Works aimed at the development of production technologies and model installations for manufacturing these products were also carried out.

A distinguishing feature of the works in the Institute of Catalysis was the focus on the mechanism of the catalytic synthesis of carbon materials and the methods to govern these technologies.

In 1952, the results of the studies of the formation and properties of carbon with previously unknown morphology were published [2]. This carbon was formed through thermal decomposition (600 °C) of carbon (II) oxide at the contact with iron. The carbon product was composed of worm-like particles with the internal empty channel and a constant diameter over the whole its length. The diameter of carbon particles was within the range of 0.2–0.5 μm, and their length reached 7 μm.

The contents of the paper allowed us to formulate the most significant results.

- catalytic formation of carbon was discovered only on three contacts – with iron, cobalt, and nickel.

- Carbon formed an ordered structure similar to that called a tubular nanostructure nowadays.

- Each tube has a particle of active metal on its end, and carbides were detected in the phase of the forming carbon.

It is difficult to explain today why the authors of that work, having obtained such significant re-

sults, had not continued the studies of the mechanism of this phenomenon. Maybe, for this reason, their publication was underestimated and forgotten for two decades.

Historical fairness induced us to recollect that this publication was the first to report on the formation of carbon materials of micron size with unknown morphology. This publication was an inspiring event for us. It seemed that the nature gave us a gift – a simplified model of the functional structure that we imagined as a working hypothesis. The deductive method has worked.

These results allowed us to draw a general scheme of a multistage nanotechnology of the synthesis of carbon nanomaterials. According to this scheme, gaseous hydrocarbon at a temperature of 600–900 K is chemisorbed on the surface of dispersed particles (1–100 nm) of the iron-group transition metals (Fe, Co, Ni) and gets decomposed with the formation of atomic carbon. The latter migrates to the regions of particle surface where the formation of carbon nano-sized material (CNM) occurs.

So, PCNR is a polyfunctional nano-sized structure (PNS) having the appearance of a crystal (1–100 nm) metal particle. Under definite conditions, it may switch its functions into the management of separate stages of the nanotechnology. Passing from the imaginary PCNR model to an actual one, the goal of the work was determined as the development of a demonstration model of the nanotechnology under the control of PCNR. In the model of nanotechnology chosen by us, two participants interact: a PCNR and carbon. Below we will consider them both.

Among all the elements of Mendeleev's Periodic Table, perhaps the most surprising one is carbon. Its unique properties and their diversity are due to the electronic configuration (structure) of ${}_6\text{C}$ atoms – $1s^2 2s^2 2p^2$, in which the entire chemical diversity is determined by the electrons of the second orbit ($2s^2 2p^2$).

This electronic configuration predetermined the existence of three allotropic modifications of carbon:

1. Spatial polymer with sp^3 -hybridization of electrons (diamond).
2. In-plane polymer with sp^2 -hybridization of electrons (graphite).
3. Regular polymeric carbines with a large variety of the forms of carbon and allotropic modifications with mixed types of bonds arising in sp^1 -hybridization of electrons.

For a deeper understanding of the mechanism of CNM, the information on the properties of

PCNR functions involved in nanotechnologies was attracted. Let us start with metals.

All metals may be divided into three groups:

- a) metals of groups III–VII of the Periodic Table of elements, forming thermodynamically stable carbides with carbon;
- b) metals of the subgroup of the first transition row (Fe, Co, Ni) of group VIII, forming thermodynamically unstable carbides;
- c) all other metals of group VIII and those forming no carbides at all.

It becomes clear that only unstable reactive carbides are suitable for PCNR functioning. This feature is connected with the unfilled 3rd electron shell. With an increase in the number of electrons in this shell above five, the crystal chemical affinity of these metals to carbon and their ability to form compounds with carbon possessing close structural motives decrease sharply from Fe to Co and Ni.

A special role is played by the stages of dissolution and carbon diffusion in metal nickel, as well as in Fe and Co. These transition metals having small atomic radii (0.124–0.125 nm) may form solid solutions with the atoms of equal or smaller size. Carbon atoms (with a radius of 0.077 nm) form interstitial solid solutions with nickel. Under these conditions, the diffusion of carbon atoms proceeds through sequential transitions of the atoms from one interstice to another without exchanging places with metal ions. To diffuse in this manner, carbon atoms should possess activation energy sufficient to overcome the energy barrier along the route of carbon atoms from one interstice to another. The frequency of transitions and diffusion coefficient depend on this energy. The electronic structure of carbon atom allows it to act both as a donor and an acceptor of electrons. Interacting with the 3d electronic shell of the metals of the transition period (Fe, Co, Ni) carbon exhibits donor properties lending some of its electrons into the vacant 3d shell. So, carbon atoms in the carbides of transition metals act as cations [5].

It should also be reminded that gases (N_2 , O_2 , H_2) dissolved in metals are in the atomic state with increased reactivity. Hydrogen dissolved in metals is present there in the form of proton with the radius 10^5 times smaller and diffusion coefficient 10^{12} times larger than the corresponding values for carbon or nitrogen atoms [7].

The functions of PCNR may also include some exotic properties, for example, the difference in the properties of the faces of crystal metal PNS particles. In this case, each face plays the part of a separate function [12, 13]. Another special ex-

ample worth mentioning: we succeeded in creating conditions for the formation of supersaturated solutions of carbon in metals. It turned out that this state of the substance may play the role of a separate function [14].

To reveal the role of carbides in the formation of carbon materials, the kinetics of the formation and decomposition of metal carbides was studied for the metals of the iron subgroup (Fe, Co, Ni) in the atmosphere of butadiene [8–11]. The critical temperature T_{cr} was discovered. In the case of $T < T_{cr}$, the rate of carbide formation was higher than the rate of its decomposition. Because of this, the limiting stage of the formation of carbon deposits is the decomposition of carbide. As a result, a metal particle is transformed into carbide. In the case of $T > T_{cr}$, the rate of carbide decomposition becomes higher than the rate of its formation. The metal phase becomes stable. It was proved that the common limiting stage for both cases ($T < T_{cr}$ and $T > T_{cr}$) is the formation of an intermediate surface carbide compound of the type of $[\text{Fe}-\text{C}]$. These results are presented in Fig. 1. In this scheme, depending on conditions, either carbide phase or metal phase may be present.

The scheme describes the mechanism of the catalytic homolytic rupture of bonds in hydrocarbon molecules with the formation of carbon atoms.

At the moment of carbon formation in the subsurface layer of a massive metal particle, it possesses increased reactivity and may either recombine with the formation of the amorphous carbon phase or be absorbed in the process of atomic assembling of CNM.

In addition to the mentioned information, at the end of 1970-es, we succeeded in deciphering the multistage synthesis of CNM through atomic assembling, which proceeds according to the mechanism of carbide cycle (MCC). Detailed information on this subject was published in [15, 16, 18].

The final goal of the work on this subject was to make our hypothesis concerning an imaginary natural phenomenon of PCNR gain all its natural properties. We chose to focus on the hypothesis of an imaginary robot which was to be brought to life with the elixir of scientific cognition on its nature and the laws of functioning. The source of this knowledge was physics and chemistry of the functions of the imaginary robot. We collected the necessary information for such a revival. However, before starting this procedure, the peculiarity of this start is to be stressed.

Historically, investigation of the demonstration sample of PCNR proceeded in two directions independent of each other. The first of them was developing within the programmes of traditional carbon themes formed even before the discovery of the nano-sized world. Only with the development of works in this area and after deciphering the mechanism of carbide cycle of CNM formation, it turned out unexpectedly that the studies in this direction led to the birth of that demonstration sample of PCNR.

The second direction formed and developed as a new object for the science of nano-sized world. Thus the idea to supplement the paper with two more finishing sections appeared:

– About scanning some properties of the matter of which PCNR consists, and its functions.

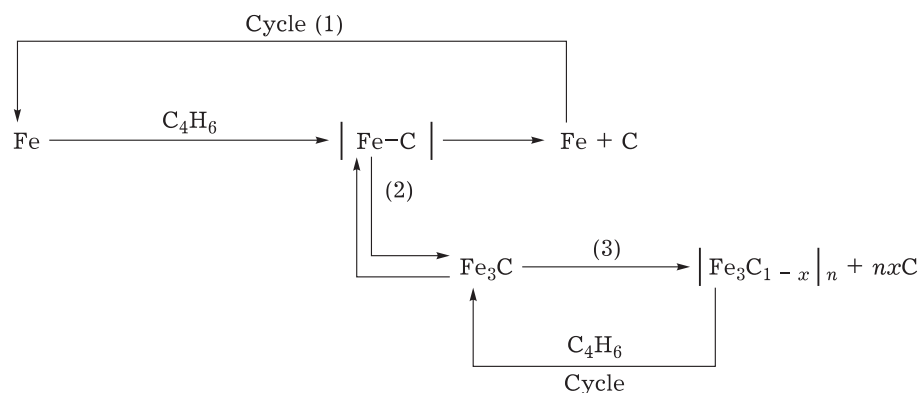


Fig. 1. Scheme of catalytic formation of atomic carbon during the decomposition of hydrocarbons through intermediate carbide-like compounds. Cycle (1) – splitting (dissociation) of hydrocarbon molecules on the surface of metal particles (Fe, Co, Ni); reaction (2) – the effect of reaction medium and reaction conditions on the catalyst (phase and chemical transformations); reaction (3) – carbon formation on the carbide phase (n – dimensions of the region on carbide surface losing one carbon atom, that is, average surface area corresponding to one catalytic centre, $xn = 1$, $[\text{Fe}-\text{C}]$ – carbide-like intermediate compound, $[\text{Fe}_3\text{C}_{1-x}]_n$ – carbide state with disturbed stoichiometry).

– About the possibility to affect the behaviour and role of PCNR functions in the nanotechnologies of the production of the target material.

4. PCNR SCANNING

The term ‘scanning’ has not been determined in the methodology of cognition. However, in this specific case, it is adequate in expressing the essence and meaning of its participation in the scientific search. In our case, scanning means the collection of information over the whole range of properties and functions of the object under investigation.

The synthesis of CNM according to the regulations of nanotechnology is finally reduced to the recovery of atomic carbon from the structure of hydrocarbons and molecular assemblage into the CNM structure (the synthesis from below).

In the process of scanning, the problem concerning the significance and potency of the methodological participation of the PCNR phenomenon in scientific experiments and special significance of its special functions and mechanisms of operation arose.

We carried out scanning and scientific analysis at all the stages and processes of PCNR over all the stages of nanotechnology and polyfunctional activity of the robot. As a result, the knowledge enriching the methodology of the search for new types of PCNR was obtained. Below we will consider the most important scanning results.

It follows from the above considerations that PCNR is a polyfunctional nano-sized (1–100 nm) structure (PNS) having the appearance of the crystal particles of the metals of the iron subgroup (Fe, Co, Ni).

Scanning results will be commented adhering to the sequence of stages of PCNR in the technology of the synthesis of CNM.

To start scanning the multistage technology, it was necessary to specify what we accept to be the starting point. Scanning results should not disturb the coherence of the structure under investigation. In our case, the start is connected with the state of the dispersed metal particle, which may play the role of PNS and PCNR and be present in different thermodynamic relations with the environment [20]. In the equilibrium state, molecules and nanoparticles behave independently of each other, each of them ignores the others. Particles in this state are called somnambulists (or hypnones) [20].

Hypnones are metal particles in the state resembling lethargic sleep. Their functional abilities are not oriented at any object of the non-equilibrium world. The transition to the non-equilibrium state wakes hypnones and established the coherency in the system. This transition occurs when the reactor with a filler composed of nickel nanoparticles is filled with hydrocarbons. The system of PNS – hydrocarbon is thus formed. It is ready for switching on the nanotechnology of CNM production. Its activity is due to the non-equilibrium state. The involvement of this system into the work occurs by its activation as a result of temperature rise in the reactor. After activation, the whole technology is controlled by the functions of the robot.

In Section 3, we collected the information on the physical and chemical properties of the participants of the nanotechnological synthesis of CNM. Scanning results were obtained through the generalization of numerous experiments with different compositions and regimes of the synthesis of nano-products.

Scanning the functions we studied the specific features of their physical and chemical properties.

In our case, synthesis and its scanning start from the stage [X] – chemisorption of hydrocarbons on the faces of the crystal nickel nanoparticle (robot). This is the starting chemical function entering the technological process of synthesis. The intensities of chemisorption of hydrocarbons at different faces of the robot differ. Thus, it was reported [7] that methane decomposes on the (100) and (110) faces of nickel crystal to form carbon, while methane is not sorbed on the (111) face, and carbon is not released. However, all of them work synchronously for the same final goal.

At the next stage, chemisorbed carbon decomposes through an intermediate unstable carbide-like compound [Ni–C] in which carbon atoms (electron donors) act as cations. This compound decomposes in the subsurface layer of the nickel particle (robot) [X]. Carbon atoms are to occupy their positions in the new structure. At the moment of decomposition of the carbide-like compound [Ni–C], the released carbon atoms could recombine to form soot but they get captured by the subsurface layer of the nickel particle.

We have already mentioned that the elements of the iron subgroup (Fe, Co, Ni) possess crystal chemical affinity to carbon. In turn, carbon behaves as the donor of electrons with respect to these metals. This combination leads to the cap-

ture of carbon atoms by massive nickel. A solid solution of carbon in nickel is formed [Ø].

In our case, we scan the continuous technological chain until CNM production. The half-way formation of the solid solution of carbon appears to be a paralysis of the whole technology. A way out of this apparent blind alley is prompted by physics and thermodynamics.

The solubility of carbon in metal nickel depends on the chemical potential μ of carbon to be dissolved. According to thermodynamics, "A direct quantitative analog of temperature for the processes of substance distribution is the chemical potential of the substance to be dissolved. In other words, the driving force of isothermal diffusion is the negative gradient of the chemical potential of diffusing substance" [6, 14].

We considered the mechanism of formation, release and capture of carbon atoms by the sub-surface layer of nickel particle (PCNR). This mechanism [Ø] acts until the chemical potentials of carbon in carbon source and in its solvent (Fe, Co, Ni) become equal.

The chemical potential of atomic carbon dissolving in nickel is determined by its origin. It is formed in the decomposition of a carbide-like compound such as Ni_3C or $[\text{Ni}-\text{C}]$. As a result, a short-living mixture of nickel and carbon atoms is formed in the subsurface layer of nickel particle. It is transformed into the supersaturated solution of carbon in nickel. Carbon concentration in this solution is many times higher than its equilibrium content in nickel crystal in contact with graphite. Their ratio is 25 : 0.3.

As carbon concentration in the supersaturated solution increases, its chemical potential reaches a critical value sufficient for overcoming the potential barrier of the formation of a nucleus of the graphite phase (CNM). At this limit of system stability, bifurcation with the complete destruction of the initial structure and the formation of the new structure (a nucleus of graphite phase) occurs. Carbon from its supersaturated solution [Ø] is dumped into this nucleus.

Since then, the regime of the atomic-molecular assemblage of CNM is established due to the diffusion intake of carbon atoms through the mass of the nickel particle (PCNR) [Ø]. With the formation of the centre of carbon crystallization, the possibility of the formation of supersaturated solutions disappears. A steady regime of nanotechnology with the distribution of the faces of nickel particles according to the functional destination is established. The faces generating atomic

carbon got the name "frontal", while those on which CNM are formed are called "rear". In this deterministic regime, the process of atomic-molecular assembling of CNM is stabilized.

Scanning of the stages in their technological sequence was considered by us as one of the approaches in cognition methodology. Having no special hope for its potential possibilities, we applied it to promote the development of the scientific foundations of the synthesis of PCNR for different purposes. In the proposed work, seven different functions were used in scanning PCNR in the technology of CNM production. Each of them accompanied a separate stage in the technological sequence of the production of CNM. Four of these seven functions originated from the nucleus of PCNR while three of them originated from its surface.

Scanning allowed us to determine the structure of PCNR more accurately. It was composed of two inseparable carriers of functions: a three-dimensional, in the form of the metal nucleus, and a two-dimensional in the form of its surface. For obviousness, this robot is represented in the form of a nut composed of a metal kernel (Fe, Co, Ni) in a shell, which is its surface. The two-dimensional carrier of functions (the shell) provides chemical, catalytic stages of nanotechnologies generating substances in the atomic state. A classical example of such a generation of atomic carbon was considered above.

In the general view, a two-dimensional carrier (the shell) in the PCNR system accompanies the catalytic stages that may arise in new modifications of PCNR. In this connection, it is necessary to cite a fragment of the report made by G. K. Boreskov concerning the modern notion of this phenomenon [21]: "Bonding forces providing the formation of surface compounds essential for catalysis have the same nature as the bonding forces in usual chemical compounds. However, the manifestation of these forces in the surface interaction is characterized by a number of specific features which are due to the fact that one of the participants of the interaction is a solid body with complicated electronic structure.

Surface compounds are much richer in the set of possible bond energies and correspondingly they are less discrete in their properties than usual stoichiometric compounds with a very large number of atoms. This is the reason also of the difficulties with building the theory of heterogeneous catalysis and the special position occupied by it in science.

Heterogeneous catalysis is one of the most important and widespread manifestations of surface interaction, with its specific regularities. The revelation of these regularities, development of the chemistry of surface compounds are the necessary conditions for the creation of the theory of heterogeneous catalysis”.

Three-dimensional carrier of the functions (the kernel of the nut) governs the formation of CNM, that is, three-dimensional materials by the atomic-molecular assemblage (synthesis from below). The kernel is a crystal particle of one of the metals of the iron subgroup (nickel in our case). Its exotic structure should be stressed. This is a three-dimensional lattice of positive ions floating free in a dense electronic gas.

The insertion of atomic carbon into interstices causes strong electron interaction [7] and enhances the reactivity.

One can see that the nature and regularities of the action of two- and three-dimensional carriers of PCNR functions belong to different scientific objects. Two-dimensional carriers function at the chemical stages and produce chemical products. Three-dimensional carriers function at the physical stages and produce three-dimensional materials or specific chemical products.

It should be noted here that the studies of the mechanisms catalysis are carried out for more than 175 years, but the scientific foundations of the prediction of catalytic activity are still unclear. At this background, the studies of PCNR and its applied significance are only at their starting point.

Today it is possible to propose an extensive research programme. One of its directions should be the creation of the carriers (frameworks) for the rational (spatial) fixation of PCNR with required size and the methods of regulating diameters, compositions of PCNR etc.

To conclude, it should be noted that a demonstration model of PCNR has been developed, and a classical basic sample with the scientific substantiation of all the stages of the nanotechnology of CNM production has been made.

The model allows proposing new nanotechnologies, which will be the subject of the last section of this paper.

5. ABOUT THE POSSIBILITY TO GOVERN THE FUNCTIONS OF PCNR FOR THE PRODUCTION OF THE TARGET PRODUCT

We described the history and results of the studies into the mechanism and regularities of

functioning of a new phenomenon – PCNR. So, the contours of the scientific foundations for the formation of nanotechnologies accompanied by the robot were outlined.

In this section, with references for the corresponding scientific publications, we present several examples of these technologies in the form of brief annotations. To avoid misunderstanding of the essence of annotated papers, it should be stressed that some of them relate to works carried out before the science dealing with nanotechnologies had been born. These works are cited from the primary sources.

Meanwhile, a more detailed examination of this question today points to the necessity to reconsider our notions concerning the mechanisms of a number of technologies which we relate to catalytic ones. The methodology of nano-world cognition suggests that some of the so-called catalytic technologies are actually corresponding in their nature and mechanism of product synthesis to the mechanism of nanotechnology with the participation of PCNR.

We have already considered the functional possibilities of PCNR in the arrangement of a nut. They provide the generation of the atomic state of the raw material with high reactivity during the synthesis of nanoproducts. Substances that are capable of dissolving (in the atomic state) in the lattice of one of the metals of the iron subgroup (Fe, Co, Ni) are suitable as the raw material for this purpose.

In the review of brief annotations of the papers dealing with the studies of nanotechnologies, we will mention publications in which the authors chose hydrogen as the raw material. Its properties are ideally suitable for many nanotechnologies of the synthesis of various products and materials. Hydrogen dissolved in the nickel kernel of the PCNR exists in the form of a proton. Its radius is 10^5 times smaller than the radius of the atom (or ion) of carbon or nitrogen, while the diffusion coefficient in these metals is 10^{12} times larger than that for C, N and O [7].

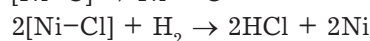
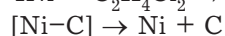
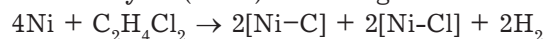
BRIEF ANNOTATIONS OF PAPERS DEALING WITH NANOTECHNOLOGIES PARTICIPATED BY PCNR

1. Regularities of the decomposition of chlorinated derivatives of hydrocarbons on the metals of iron subgroup [22].

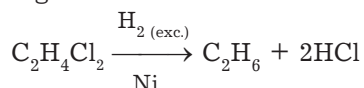
Nano-sized particles of the metals of transition row Fe, Co, Ni were tested as PCNR accompany-

ing the nanotechnologies of the decomposition of chlorinated organics – 1,2-dichloroethane and chlorobenzene in the atmosphere of hydrogen. Two reaction routes were detected:

– under the conditions of the lack of hydrogen, prevailing mechanism is the mechanism of carbide cycle (MCC) according to the scheme



– hydrodechlorination is the process prevailing under the conditions of hydrogen in excess:



2. Method of the utilization of chlorinated hydrocarbons on Ni- and Co-containing catalysts [23].

Nanoparticles of metals Ni, Ni-Pd, Co were tested as PCNR. Two methods of utilization of chlorinated hydrocarbons were followed:

– decomposition of hydrocarbons of different nature and structure according to the MCC mechanism to form carbon and HCl at $T \geq 500$ °C with total hydrogen content in the mixture not less than the amount necessary stoichiometrically for binding all Cl atoms into HCl. The method is suitable for the utilization of individual hydrocarbons and their complex mixtures;

– hydrodechlorination of the chlorinated derivatives of hydrocarbons with the formation of unsaturated or saturated hydrocarbons.

3. Conditions for obtaining the structure of disordered graphite filaments formed in the decomposition of chlorinated derivatives of hydrocarbons on Ni- and Co-containing catalysts [24].

It is shown that the formation of graphite materials with different morphological and structural characteristics proceeds according to the MCC.

The methods of controlling the technology allowing one to obtain a range of materials are considered.

4. Theoretical substantiation of the conditions of operation of a physicochemical nano-robot (PCNR) in the production of nanodiamonds and other carbon-containing nanocomposites [25].

A new term has been introduced: physicochemical nano-robot (PCNR) controlling nano-

technology. The conditions under which the synthesis of nanodiamonds from hydrocarbons is possible at the atmospheric pressure and $T < 1000$ K.

5. The method of doping carbon nanomaterials with nitrogen has been developed [26].

Carbon nanofibres doped with nitrogen up to 8 mass % were obtained. This became possible due to the simultaneous activation of C and N atoms in the Ni kernel of PCNR and their joint condensation into the synthesized fibre structure.

6. Dispersed nickel particles as polyfunctional nano-sized structures – chemical nano-robots synthesizing carbon materials [27].

With references for a number of earlier publications, the authors considered the ability of nano-sized nickel particles to carry out a set of various functions in the interaction with the medium, to initiate various chemical processes and to control them. These polyfunctional nano-sized structures (PNS) were called nano-robots.

7. New catalysts of the type of metal-filamentary carbon: from fundamental studies to the technology [28].

8. New metal-carbon catalysts.

I. Methods of preparation, area of application [29].

9. New metal-carbon catalysts.

II. Reasons for the selective action of nickel catalysts in hydrogenation [30].

New catalytic systems composed of a metal and filamentary carbon have been discovered. They have some principal differences from the known catalysts both in their structure and in the method of obtaining. Metal-carbon catalysts are formed during the decomposition of hydrocarbons on the metals of iron subgroup or on their alloys with other metals and are arranged as metal particles fixed at the ends of carbon filaments. Varying the conditions of hydrocarbon decomposition, one may render the properties that would allow the metal-carbon systems to be used as the catalysts of various reactions.

10. The process and the kinetics of carbon and diamond methanation on bulk nickel, iron and platinum in the atmosphere of hydrogen were studied [31].

Carbon is dissolved in nickel, transformed into the atomic state, and reacts with atomic hydrogen.

11. The dissolution of carbon on nickel, iron and platinum matrices was studied [32].

The process of engraving the surfaces of diamonds through selective dissolution (methanation) of diamond surface in the sites of contact with the voluminous pattern of nickel surface has been developed. The activity of metals with respect to methanation decreases as a sequence Ni > Fe > Pt.

This review of the annotations of some works may be useful for the primary evaluation of the scientific and applied significance of one of the directions in the area of nanotechnologies.

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Supplement

ABBREVIATIONS

- PNS – polyfunctional nano-sized system;
 CNM – carbon nanomaterial;
 PCNR – physicochemical nano-sized robot;
 MR – molecular robot;
 MCC – mechanism of carbide cycle;
 [Ø] – physical functions;
 [X] – chemical functions.