

Catalytic Synthesis of Nanosized Feathery Carbon Structures via the Carbide Cycle Mechanism

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Abstract—The morphology of carbon nanostructures obtained by 1,2-dichloroethane decomposition on the 90% Ni/Al₂O₃ catalyst under different reaction conditions was studied by high-resolution transmission electron microscopy. A new carbon product was discovered, which received the name of feathery carbon. The product has an extremely loose disordered structure consisting of separate fragments of a graphite-like phase. The structural disordering is assumed to be caused by the variation of chlorohydrocarbon decomposition conditions on the frontal face of the metal particle. This changes the character of carbon atom diffusion from the frontal face to the backside face of the nickel particles and finally results in a feathery morphology of the carbon phase. The specific surface area of feathery carbon is 300–400 m²/g.

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A topical problem of present-day materials science is that of designing new materials with unique properties. These include materials based on carbon filaments and fibers. Their production and applications [1–3] are presently based on the carbonization of textile and pitch materials [1].

In recent years, carbon materials have attracted particular interest because of the rapid progress in nanotechnologies and the widening of the variety of available nanostructured carbon products.

Nanosized carbon filaments and fibers have found their own special niche in the spate of publications in this area [2, 4, 5]. Among the nanofilament and nanofiber synthesis methods of interest [2], the catalytic decomposition of various hydrocarbons on fine particles of iron-family metals and their alloys with other metals seems to be the most promising [4, 5]. The sequence of stages in this synthesis has been made clear and is known as the carbide cycle mechanism [4–6]. Understanding of the nature, stages, and regularities of this mechanism makes it possible to control the process and knowingly address the problem of obtaining carbon nanofibers and nanofilaments with various crystallographic and morphological characteristics. Three base structures can be distinguished in the totality of possible carbon nanofilaments (Fig. 1), each forming at particular catalyst compositions under particular synthetic conditions. By combining these structures and their synthesis conditions, it is possible to obtain a wide variety of nanosized carbon objects with new properties. Therefore, there is the independent problem of broadening the variety of carbon nanostructures with new special properties in order to provide a wide choice of carbon materials for various applications.

In earlier publications [7, 8], we considered the possibility of utilization of chlorinated hydrocarbons using Ni/Al₂O₃ and Co/Al₂O₃ catalysts. The feasibility of the following two technologies was demonstrated:

decomposition of chlorinated hydrocarbons of various natures and structures via the carbide cycle mechanism to obtain carbon with unconventional crystallographic and morphological characteristics and HCl;

hydrodechlorination of individual chlorinated hydrocarbons to obtain unsaturated or saturated hydro-

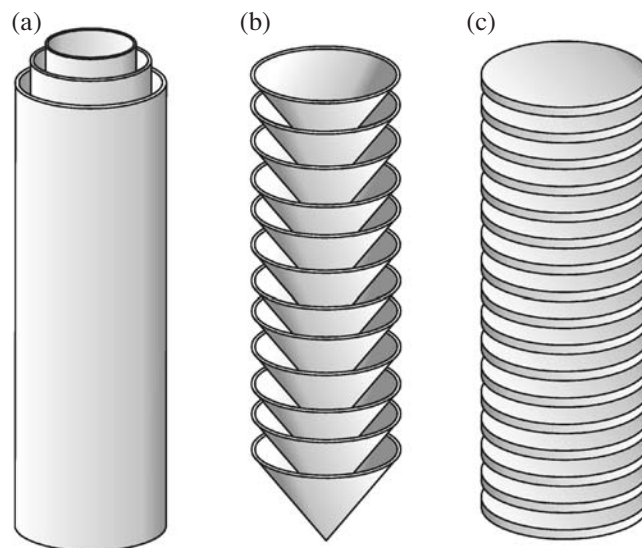


Fig. 1. Structures of graphite filaments with different arrangements of basal planes: (a) coaxial cylinders, (b) coaxial cones, and (c) plane-parallel (piled) structure.

carbons, depending on the degree of dilution of the reaction atmosphere with hydrogen.

It was found that the resistance of metals against deactivation by HCl decreases in the order $\text{Ni} > \text{Co} > \text{Fe}$.

The value of the resulting products as such and the properties and origin of exotic crystallographic and morphological modifications were not discussed, because these issues were beyond the scope of the earlier works. Now that the problem of obtaining carbon nanomaterials has arisen, these issues are of independent significance. In view of this, we have carried out a preliminary study of the syntheses of these materials from chlorinated hydrocarbons [9]. The resulting unusual forms of the carbon phase were given the name of feathery structures.

In this article, knowing the carbide cycle mechanism and the regularities of the formation of filamentous carbon materials, we consider the feasibility, conditions, and specific features of the synthesis of these feathery carbon nanostructures.

FEATHERY CARBON NANOSTRUCTURES: THEORETICAL BACKGROUND AND SYNTHETIC CONDITIONS

Let us consider the basic stages of the formation of carbon nanofilaments and nanofibers catalyzed by fine particles of iron-family metals and their alloys with other metals [4, 5].

The carbide cycle mechanism of these processes consists of the following two basic stages:

(1) Chemical stage: catalytic decomposition of the hydrocarbon into carbon and hydrogen via the formation of carbide-like intermediate compounds on some faces of the fine metal particles. The faces with the most pronounced catalytic properties are called frontal faces.

(2) Physical stage: diffusion of carbon atoms through the metal particle bulk from the frontal face to the backside face, graphite phase nucleation on the latter, and the growth of carbon filaments and fibers with various crystallographic and morphological characteristics.

The following kinetic factors governing the growth of carbon products via the carbide cycle mechanism can be distinguished [5]:

hydrocarbon decomposition and free carbon atom formation rates;

rate (intensity) of the diffusion transfer of carbon atoms through the metal particle bulk from the frontal face to the backside face;

ratio of the carbon atom formation rate to the rate at which the resulting carbon atoms are transferred from the frontal face to the backside face by diffusion, which determines the rate-limiting step of the overall process;

size and shape of the fine metal particles, as well as the distribution of the carbon atom diffusion flux in them, which determines the places and specific features of carbon phase condensation on the backside face;

properties of the surface layers of the frontal and backside faces of the metal particles, which govern the processes occurring there.

Knowledge of these factors and earlier data [10] enabled us to formulate the synthetic conditions necessary to obtain the most perfectly organized carbon nanostructures (base structures):

(1) The rate of the diffusion transfer of carbon atoms from the frontal face to the backside phase should exceed the carbon atom formation rate; otherwise, the frontal face will be blocked by carbon in the course of time and the synthesis will be terminated.

(2) The carbon atom diffusion flux through the metal particle should be low so that the condensing carbon atoms can have sufficient time to form a structure with the least possible concentration of distortions and defects.

(3) Both the intensity and the distribution of the carbon diffusion flux should be constant.

(4) The surface layers of the frontal and backside faces of the metal particle should be as homogeneous as possible.

The metal particles should have clear-cut, symmetric shapes.

Note that the carbon atom diffusion flux through the metal particle makes structural elements of its crystal lattice mobile. As a consequence, the particle undergoes reconstruction and gradually changes its shape to acquire a more stable, symmetric morphology [10, 11]. The more intensive the diffusion of carbon atoms, the more labile the crystal lattice of the metal particle. However, if the carbon diffusion flux varies continually, it will break the symmetric morphology of the particle.

Obviously, the morphological and crystallographic properties of nanosized carbon products can be diversified by deviating from the above carbide cycle conditions.

We assumed that, with a chlorinated organic compound as the precursor of the carbon phase, we would be able to disturb the stationarity of the decomposition process on the frontal face of the metal particle, the uniformity of the carbon diffusion flux, and the graphite structure formation conditions on the backside face. In this way, it is possible to violate all of the above five conditions necessary for the stable growth of organized carbon structures. As will be demonstrated below, the results exceeded our expectations.

EXPERIMENTAL

The catalyst was 90 wt % $\text{Ni}/\text{Al}_2\text{O}_3$ synthesized by a standard coprecipitation method from nickel and aluminum nitrate solutions at a constant pH [9].

The chlorinated hydrocarbon was 1,2-dichloroethane. The decomposition of 1,2-dichloroethane in order to obtain carbon with a feathery morphology was carried out in a quartz reactor. The diameter of the reac-

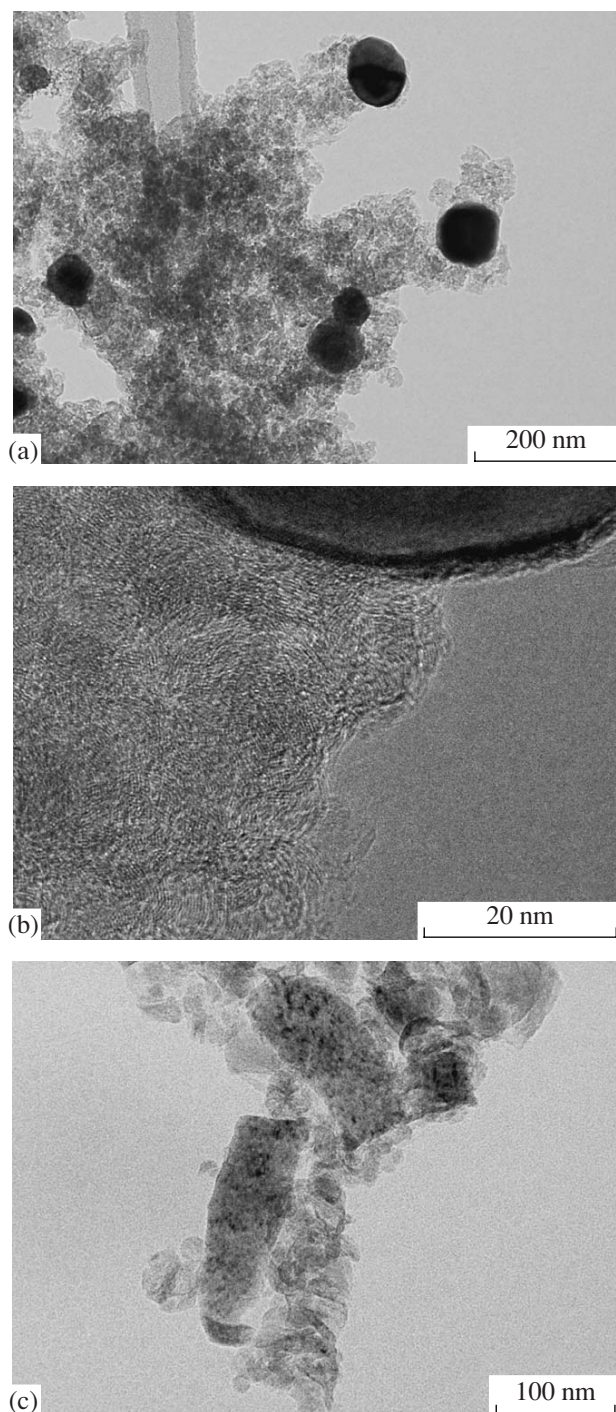


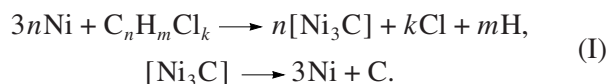
Fig. 2. Electron micrographs of the carbon structures obtained by the decomposition of the gas mixture H_2 (35%) + Ar (58%) + $\text{C}_2\text{H}_4\text{Cl}_2$ (7%) at 500°C: (a) morphology of the carbon mass formed on separate catalyst particles; (b) fine, unordered structure of graphite formed on the backside faces of separate catalyst particles; (c) breaking of the carbon phase on the backside faces of catalyst particles.

tor insert was 9 mm, the catalyst weight was 100 mg, and the catalyst pellet size ranged between 0.1 and 0.5 mm. The feed flow rate was 9 l/h.

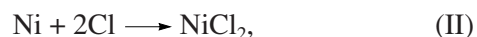
The morphology of the resulting carbon was studied by high-resolution transmission electron microscopy (HRTEM) using a JEM-2010 electron microscope (JEOL, Japan) with a lattice resolution of 0.14 nm at an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

In the decomposition of chlorohydrocarbons via the carbide cycle mechanism, the following basic reactions take place on the frontal face of a nickel particle:



Here, $[\text{Ni}_3\text{C}]$ is a carbide-like surface intermediate [4, 5].



As was noted in earlier works [7, 9], for each iron-family element (Fe, Co, Ni), there is a critical temperature below which chlorohydrocarbon decomposition poisons the catalyst through the formation of a bulk metal chloride phase by reaction (II). In the case of 1,2-dichloroethane decomposition on nickel, the critical deactivation temperature is 550°C. The critical point of the stable operation of the nickel catalyst can be lowered by about 200 K by adding hydrogen to the reaction mixture [8].

Figures 2 and 3 show electron micrographs of the carbon phases resulting from 1,2-dichloroethane decomposition under different conditions. As compared to the base structures (Fig. 1), the observed structure is a loose and disordered individual modification consisting of defective graphene layers. The formation of this product could be predicted based on the concept of the carbide cycle mechanism. It follows from this concept that the main cause of the disordering of the carbon structure in this case is the deviation of the chlorohydrocarbon decomposition conditions on the frontal face of the metal particle from the conventional carbide cycle conditions. This affects the character and trajectories of the carbon diffusion fluxes from the frontal faces to the backside faces of the nickel particles and finally results in the observed feathery morphology of the carbon phase.

The process begins with the adsorption of 1,2-dichloroethane molecules on Ni particles followed by the decomposition of the chlorohydrocarbon (reaction (I)). The C–Cl bond breaks first because it is the weakest in the 1,2-dichloroethane molecule. The chlorine atom, a very reactive species, oxidizes the nickel surface via reaction (II). At the same time, chlorine interacts continuously with hydrogen (reaction (IV)) and leaves the surface as HCl, thereby regenerating the nickel surface

(reaction (III)). Thus, two opposite competing reactions, namely, reactions (II) and (III), take place in the system. Depending on the ratio of their rates, nickel chloride cluster “islands” blocking the supply of carbon atoms resulting from 1,2-dichloroethane decomposition can appear or disappear on the surface of nickel particles.

It is likely that this competition causes autooscillation-like phenomena on the frontal face of the nickel particle. Some parts of the surface are periodically covered by nickel chloride, blocking reaction (I). As a consequence, once the area of these parts has reached a certain value, their growth begins to decline. The regeneration of the metal surface via reaction (III) takes place over the entire chloride phase surface. The chloride surface area is determined by the competition between reactions (II) and (III). Thus, nickel chloride islands appear and disappear alternately on the frontal faces of the Ni particles. The smaller the size of the blocked parts of the surface, the more discrete, mosaic, and labile the structure of the frontal face of the nickel particle. The destructive effects cause erosion of the surface layers and continuous changes in the surface of the nickel particles. All of this causes permanent variations of the conditions under which the carbon atom diffusion flux to the backside face forms. This results in a carbon structure consisting of defective graphene layers.

Now we will dwell on the effect of the diffusion flux through the bulk of a metal particle on the state of this particle. Earlier [4, 5], it was demonstrated that carbon diffusion makes the particle labile, thick-flowing, and, in some cases, liquidlike. Due to the high chemical affinity of carbon atoms for Ni, an intensive carbon diffusion flux forces Ni atoms to move in the same direction, specifically, from the frontal face to the backside face [12]. This motion causes permanent changes in the relief and topography of the backside face and in the carbon phase formation conditions. In addition, it should be taken into account that the random condensation of carbon atoms into a phase gives rise to mechanical stresses in the bulk of the phase and causes its loosening and breaking into fragments. This yields a carbon product with the so-called feathery morphology, which cannot be assigned to any of the base structures shown in Fig. 1.

These considerations are in full agreement with our experimental data (Figs. 2, 3). The carbon phase imaged in Fig. 2 resulted from the decomposition of 1,2-dichloroethane in a mixture of H_2 (35%), Ar (58%), and $\text{C}_2\text{H}_4\text{Cl}_2$ (7%); the carbon phase in Fig. 3, from the decomposition of $\text{C}_2\text{H}_4\text{Cl}_2$ (10%) + Ar (90%).

It is clear from a high-resolution image (Fig. 2b) that the structure of the product is so fragmented that it does not reveal even a small graphene-layer area. The general morphology of this carbon sample is uncertain (Fig. 2a).

The structure of the carbon phase shown in Fig. 3 is more ordered. It exhibits separate areas with a graphitic

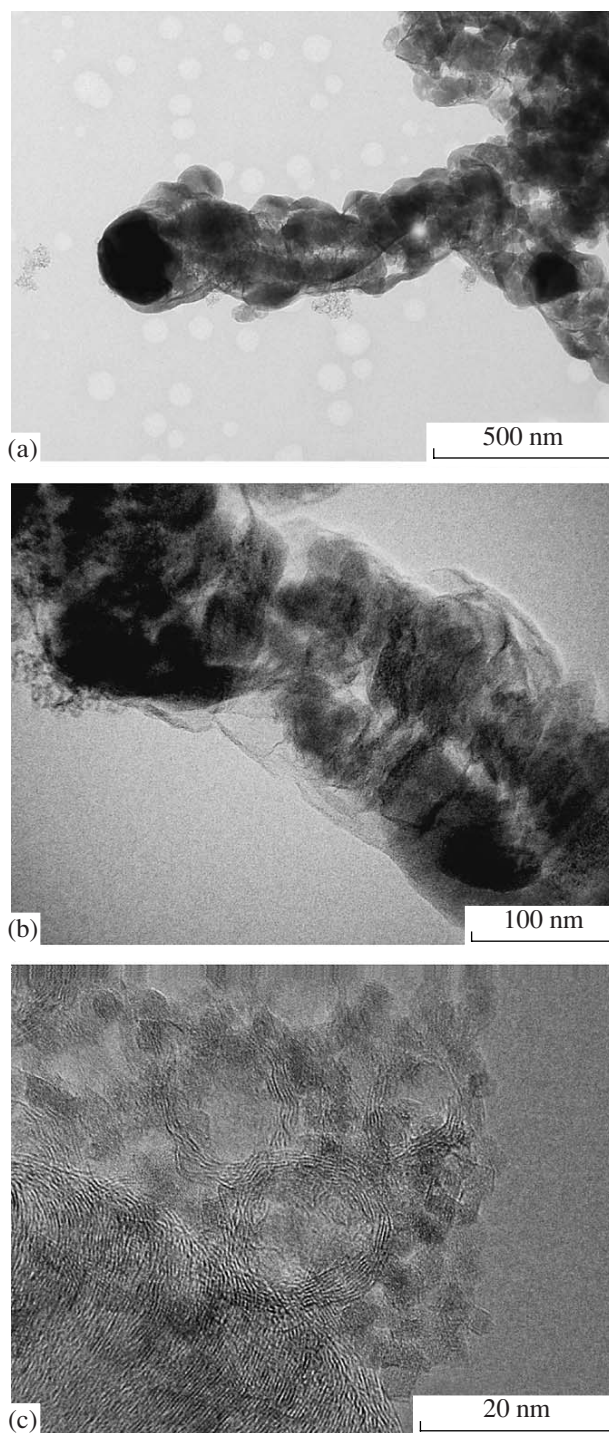


Fig. 3. Electron micrographs of the carbon structures obtained by the decomposition of the gas mixture Ar (90%) + $\text{C}_2\text{H}_4\text{Cl}_2$ (10%) at 550°C: (a) morphology of the carbon mass formed on separate catalyst particles, (b) flaky layered structure of the carbon mass on a separate catalyst particle, and (c) carbon mass with separate layered graphite structure areas.

layered structure (Fig. 3c), and the morphology of this phase resembles twisted braid fragments with a layered flaky structure (Figs. 3a, 3b).

Figure 2c depicts the mechanical breaking of the carbon phase structure. The random, constantly varying carbon diffusion flux toward the backside face of the metal particle brings about mechanical stresses in the carbon phase, which cause its disintegration.

We first obtained carbon deposits with this morphology by the decomposition of multicomponent waste from the vinyl chloride plant AO Plastpolimer (Volgograd, Russia), which consisted of 1,2-dichloroethane and a wide variety of chlorinated aliphatic and aromatic hydrocarbons. This mixture was decomposed at 550°C and a mixture/H₂ ratio of 1 : 3. The structure of the resulting carbon phase was again formed by chaotic layers of graphitic flakes and appeared as separate, regularly oriented, featherlike branches [9]. The angle between the axes of these branches was ~60°. This was further evidence of the regular variation of the carbon diffusion fluxes from the frontal faces (100) and (110) to the backside face (111) of the nickel particle.

Thus, the migration of the active areas of the frontal face and, accordingly, the variation of the direction and intensity of the carbon atom diffusion fluxes disturb the formation of the crystal structure and morphology of the carbon phase.

The above considerations are confirmed by the degree of imperfection of the feathery carbon nanostructures. According to X-ray crystallography data, the spacing between graphene layers in these structures is 3.44–3.47 Å and is somewhat larger than the standard interplanar spacing in graphite (3.35 Å).

The specific surface areas of the resulting phases are also in full agreement with the above model of the formation of defective feathery graphite. The specific surface area of the most disordered feathery structures is as large as 400 m²/g.

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