

NOVEL CARBON NANOSTRUCTURES PRODUCED BY ELECTROCHEMICAL METHOD

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Introduction

The efficiency of many synthetic methods is often based on the creation of a reaction zone under non-equilibrium conditions of synergism of physical and chemical actions. The use of charge separation and transfer processes, stimulated by an external electric field, in electrolytic cell allowed us to obtain a new nanostructured form of carbon.

Results and Discussion

Carbon nanostructures are synthesized by the method developed by us at room temperature on the surface of an oxidized valve-metal (Al, Ta, Ti) anode by the action of electric current on aromatic compounds in the presence of an electrolyte and a catalyst [1]. The general reaction scheme includes oxidation of benzene by one-electron mechanism, formation of cation radical, attachment of next molecules with proton detachment, etc. A peculiarity of the method is the possibility of reaction chain branching not only in the *para*-position but also in the *ortho*-position of benzene molecule, which diversifies greatly the form of substances obtained [3].

The carbon-bearing reaction products may be divided into four main groups:

1) carbon features in the anode surface layer, which have a fairly high adhesion to the electrode material;

2) carbon fibers, which grow in the course of synthesis from the electrode surface into the reaction space and can be easily separated by washing with water or another solvent;

3) benzene-soluble substances, mainly nonpolar polycyclic hydrocarbons;

4) polar compounds which accumulate in the electrolyte.

The carbon coating on the electrode is a semitransparent electrically conductive film, in which numerous dark fractal bulk structures have been formed, whose topology depends on the nature of metal and the type of aromatic compound. The geometrical structure of the fractal features has been investigated by electron microscopy. The presence of subparticles of

50-100 nm size, which include elements in the form of interlaced fibers, spheres, truncated spheres, tori, cones, etc (Fig.1, for more detailed information see [2]), was noted.

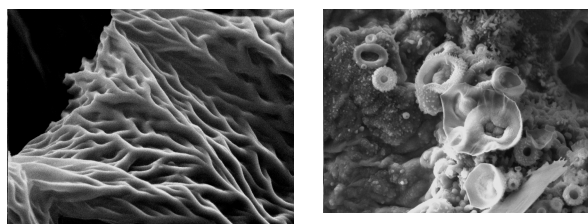


Fig 1. Micrographs of some carbon structures obtained on the aluminium oxide surface under different electrochemical conditions. X 1500 magnification.

The electronic structure of the structures found has been analysed by X-ray photoelectron spectroscopy. The spectrum contains peaks that are characteristic C-C (284,5 eV) and C-H (285,45 eV) bonds.

To analyse the chemical composition of reaction products (groups 2 and 3), field desorption mass spectrometry was employed.

Molecular ions of 720 and 1157 amu mass have been found in the composition of carbon fibers, which agrees with the molecular formulas C_{60} and C_{96} of the fullerenes. A number of molecular ions have also been found which corresponded to the empirical formula C_nH_{2n+2} , where n varied sequentially from 32 to 38 and had values of 40, 42, 44, 45, 61, 63 [4]. It is likely that molecular complexes of fullerenes with long-chain aliphatic hydrocarbons are formed in carbon fibers during synthesis, these complexes being stable under normal conditions. These complexes break down by the action of field ionization at elevated temperatures.

In the mass spectra of a benzene solution of reaction products, molecular ions have been found in the range $m/z = 75 - 1176$ amu (Fig. 2).

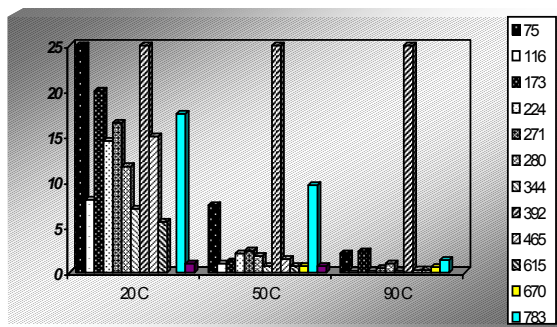


Fig 2. Composition of the hydrocarbon fraction of carbon features (according to the results of mass spectrometry at 20, 50, 90°C). On the y axis and in the table: peak intensity, V. On the x axis: mass numbers of peaks (m/z), amu.

The composition of the mixture and mixture ratio vary greatly as a function of temperature and field desorption. On the basis of mass values, the presence in the mixture of indene, triphenylene, diphenylnaphthalene, benzfluoranthene, tetra (peri-naphthylene)anthracene, and other polycyclic hydrocarbons with five- and six-membered rings in the molecule may be assumed. A compound with a molecular mass of 392 amu predominates among the substances found. The model, proposed by us, of such a molecule with the molecular formula $C_{32}H_8$ is a rather rigid structure (Fig.3), in which six-membered rings form a three-dimensional quasi-cylindrical tube.

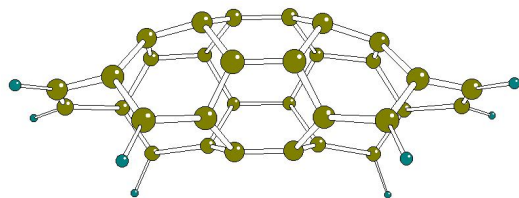


Fig 3. Model of the hydrocarbon molecule $C_{32}H_8$ of 392 amu mass.

Such a molecule can be stabilized by a system of delocalized π -electrons, which is closed into a toroid of 10 aromatic rings. Reactive sites are four CH groups, which are at the ends of this molecular tube. Such substances belong apparently to a new class of organic compounds, which is intermediate between planar polycyclic aromatic hydrocarbons and three-dimensional fullerenes, nanotubes. Quantum-chemical calculations of the electronic and spatial structure of $C_{32}H_8$ and some other molecules indicate that they have an increased reactivity and semiconductor properties.

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References

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