CARBON NANOPARTICLES FORMED ON THE SURFACE OF PITCH-DERIVED MOLECULAR SIEVE CARBON FIBER DURING ACETYLENE DECOMPOSITION

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Introduction

Carbon nanoparticles (CNP) – fullerenes, nanotubes, nanofibers, and nanowalls – are promising materials possessing a number of unique ion-exchange, electrophysical, magnetic, adsorptive and mechanical properties [1-3]. Carbon nanotubes and nanofibers can be prepared on the surfaces of catalytically active nanophase particles (including fulerenes [4]), which sizes are close to those of carbon nanoparticles formed.

Molecular sieve carbon fiber (MSCF) is another very perspective material having a number advantages over granular carbon adsorbents (e.g., higher sorption/desorption rates, lower values of hydro- and aerodynamic resistance, more effective use of adsorbent volume in the processes of heatingless short-cycle adsorption, etc.) [5,6,7]. Pore sizes (slit sizes) in various origin MSCFs are of about 0.3 nm, or of nm values divisible by 0.3 (0.6, 0.9, etc.). Pore volume and pore size distribution of carbon fibers can be controlled by both conditions of their preparation and subsequent modification.

In the present work we have tried to modify molecular pore structure of pitch-derived carbon fiber by the deposition of pyrocarbon on its surface during acetylene decomposition. This work was aimed to prepare MSCF adsorbents with improved characteristics for separation of helium and oxygen.

Experimental

MSCF samples were obtained from isotropic coal tar pitch (ash content < 0.1 wt.%). Spinned pitch fibers were stabilized by oxidation in air and then carbonized in inert atmosphere and thermally treated at 500°C in the presence of water steam.

Modification of molecular pore sizes in MSCFs was performed by deposition of pyrocarbon on the fiber surfaces during acetylene pyrolysis at 300°C. This process was

controlled by variations in kinetics of He(H$_2$)-by-O$_2$ and O$_2$-by-He(H$_2$) substitutions. In these experiments a MSCF sample was placed in a quartz ampoule for ESR measurements and then dried in a flow of helium (or hydrogen) at 300°C. ESR spectra of MSCFs were registered with a RadioPAN SE/X 2543 ESR spectrometer (Poland) in the X-band at room temperature. The processing of gas substitution kinetic curves was conducted using a computer WIN-EPR program (Bruker, Germany). Diphenylpicrylhydrazyl (DFPG) and Mn^{2+}-doped MgO were used as the standards (for determination of g-values and estimation of ESR peak intensities, respectively). The substitution rates were calculated from the changes in amplitudes of the ESR spectra of MSCFs (see Fig. 1) occurred due to interactions of unpaired electrons of fibers with O$_2$ during the substitution of adsorbed probe gases (He or H$_2$) by oxygen [8]. Pyrocarbon deposition was controlled by mass excess of MSCF sample during pyrolysis, by changes in ESR intensities of MSCF-derived unpaired electrons interacting with O$_2$ (Fig. 2), and by pyrocarbon ESR spectra obtained by subtraction of the initial MSCF ESR spectrum from its spectra after C$_2$H$_2$ treatment at 300°C for a definite period (Fig. 3). Pyrolysed samples were analyzed in every 10-20 minutes of C$_2$H$_2$ treatment.

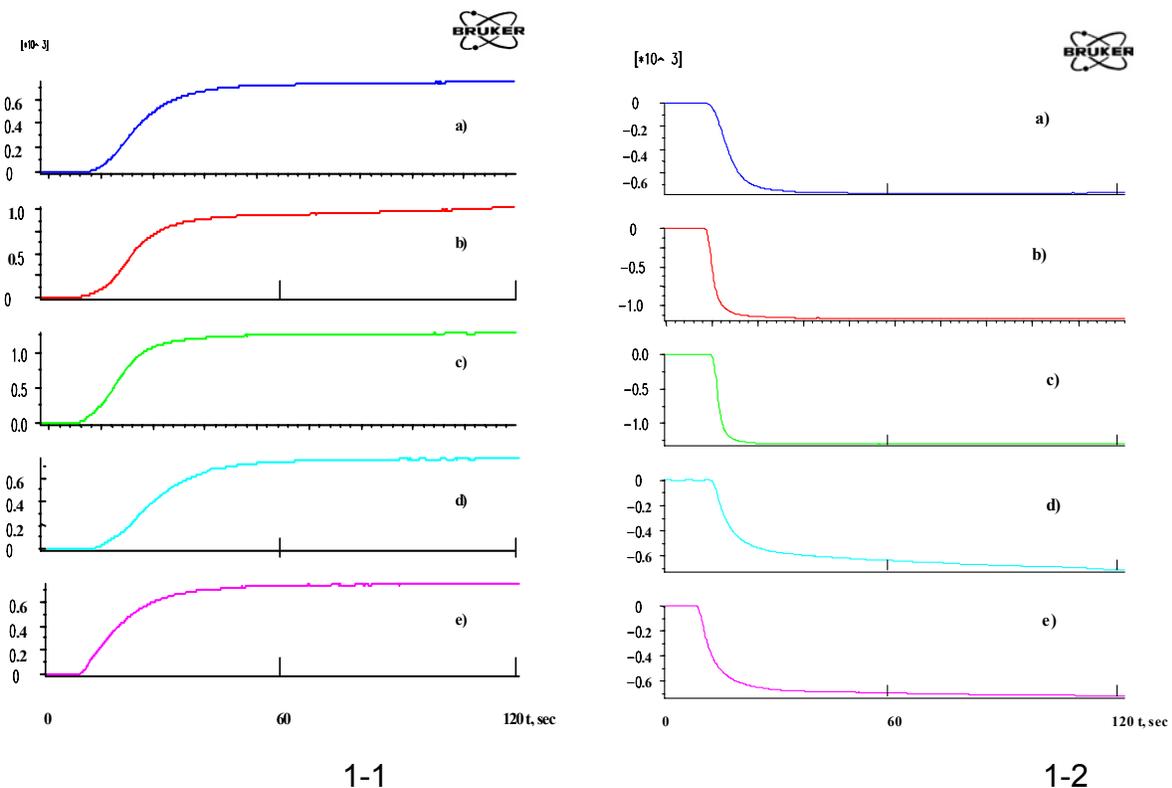1-1   1-2

Figure 1. Variations in intensities of ESR spectra of MSCFs during substitution of oxygen by helium (1-1) and helium by oxygen (1-2) in their pores:
a) – initial (air wetted) MSCF; b) – MSCF dried in argon; c) – MSCF treated with hydrogen;
d) – MSCF treated with C$_2$H$_2$ for 10 min; e) – MSCF treated with C$_2$H$_2$ for 40 min.

Surface texture of MSCFs was analyzed by SEM (BS-340, Tesla, Chechia) and TEM (TEM-125, Sumy, Ukraine). Simultaneously, the sizes of textural elements were evaluated from small angle X-ray scattering (SAXS) diffraction patterns obtained with a DRON-2.0 instrument (Russia). The elemental composition of ash from as-received fiber-forming coal tar pitch was determined by X-ray fluorescence (XRF) analysis (VRA-30, Carl Zeiss Jena, Germany).

Results and Discussion

As it can be seen from Fig.1, the rate of helium substitution by oxygen after 10 and 40 minutes of C_2H_2 treatment tended to slower (i.e., retention time of He in the C_2H_2-treated MSCFs became higher than that in the untreated ones). But in contrast, after one-hour acetylene treatment, the retention time of He was lower than that before MSCF modification. An ESR spectrum of pyrocarbon after 10 minutes of C_2H_2 treatment consists of two signals (a narrow line and a broad line, respectively) (see Fig. 3). A g-factor of the latter signal has a somewhat greater value than that of the narrow one. The centrum of the narrow line is slightly shifted to higher magnetic fields.
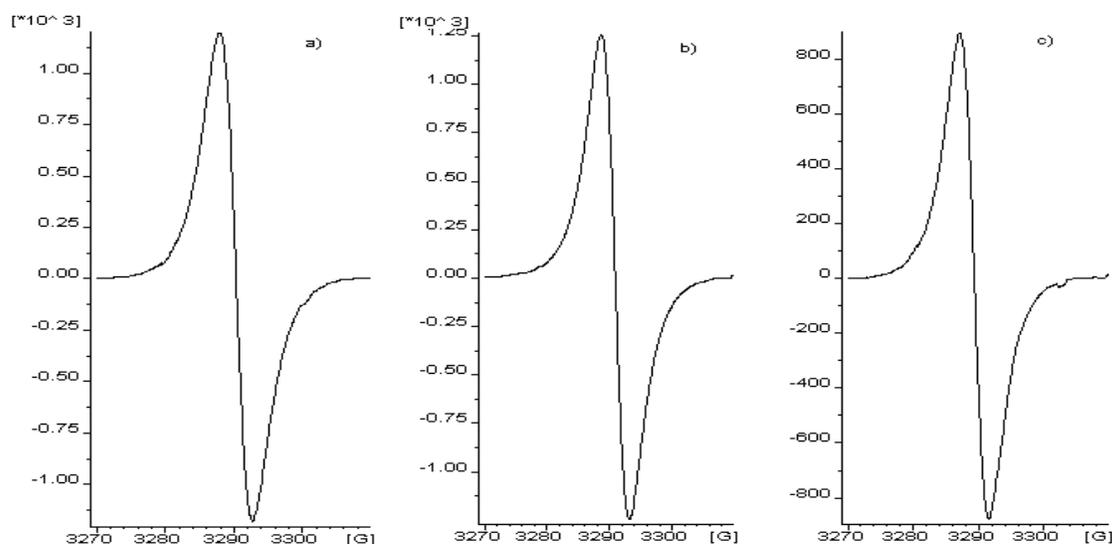

Figure 2. Δ-ESR spectra of MSCF-derived unpaired electrons reversibly interacting with oxygen (difference spectra obtained by subtraction of MSCF spectrum in O_2 from their spectra in He). These spectra are widened as a result of such interactions.
a) Δ-spectrum of MSCF after drying in argon;
b) Δ-spectrum of MSCF after treatment in hydrogen (a difference spectrum obtained by subtraction of the MSCF ESR spectrum before sample treatment from its spectrum after H_2 treatment);
c) Δ-spectrum after MSCF treatment with C_2H_2 40 min (a difference spectrum obtained by subtraction of the MSCF ESR spectrum before sample treatment from its spectrum after C_2H_2 treatment).

In the ESR spectra of pyrocarbon obtained after C_2H_2 treatment for 30 and 60 min, a narrow line (attributed to a more ordered carbon phase) is masqued (overlapped with) by a more intensive spectrum from a less ordered carbon phase. It is well known [9,10] that ESR spectrum of carbon nanotubes is a relatively narrow line shifted to higher magnetic fields, compared to ESR spectra of carbon particles having less ordered structures [10].
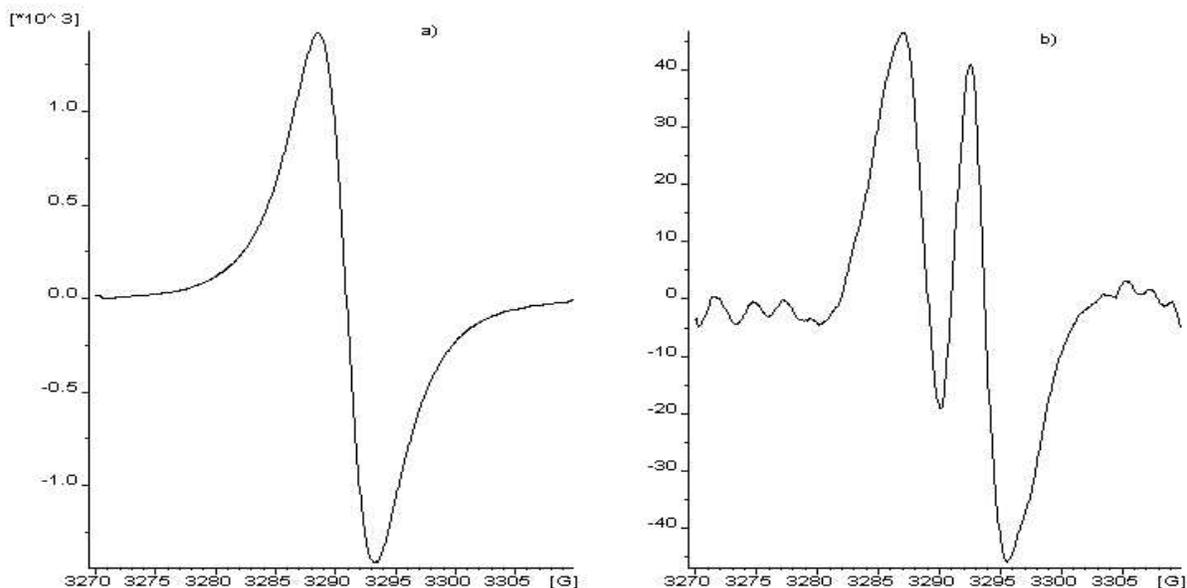

Figure 3. ESR spectra of MSCFs in hydrogen treated:
a)– ESR spectrum of the initial MSCF sample after its drying in hydrogen;
b) ESR spectrum of pyrocarbon after C_2H_2 treatment of MSCF for 10 min (a difference spectrum obtained by subtraction of the MSCF ESR spectrum before sample treatment from its spectrum after C_2H_2 treatment);

Molecular sieve carbon fiber is a composite consisting of various textural blocks (arene associates of about 1.0 nanometer scale). In the MSCFs studied, the textural blocks are of ~ 0.5 nm (Fig. 4). As it can be seen from Fig. 4, nanofibers of ~ 50-100 nm in diameter were formed on some parts of the MSCF surface during the pyrolysis of acetylene at 300°C for 1 h in the absence of catalyst (Fig. 4). The increase in sample mass was of ~ 10% per hour. No solid impurities were found in the as-received fiber-forming pitch: the solution of this pitch was easily filtered without any precipitate. However, some soluble metalloorganic compounds were present in the pitch (after its burning about 0.1 wt.% of ash was formed). As it was shown by XRF analysis, iron was the main ash component among the metals with variable valence. But its content in MSCFs was by several orders lower than that in carbon nanoparticles prepared by vapor phase deposition (CVD-method) on catalyst particles.
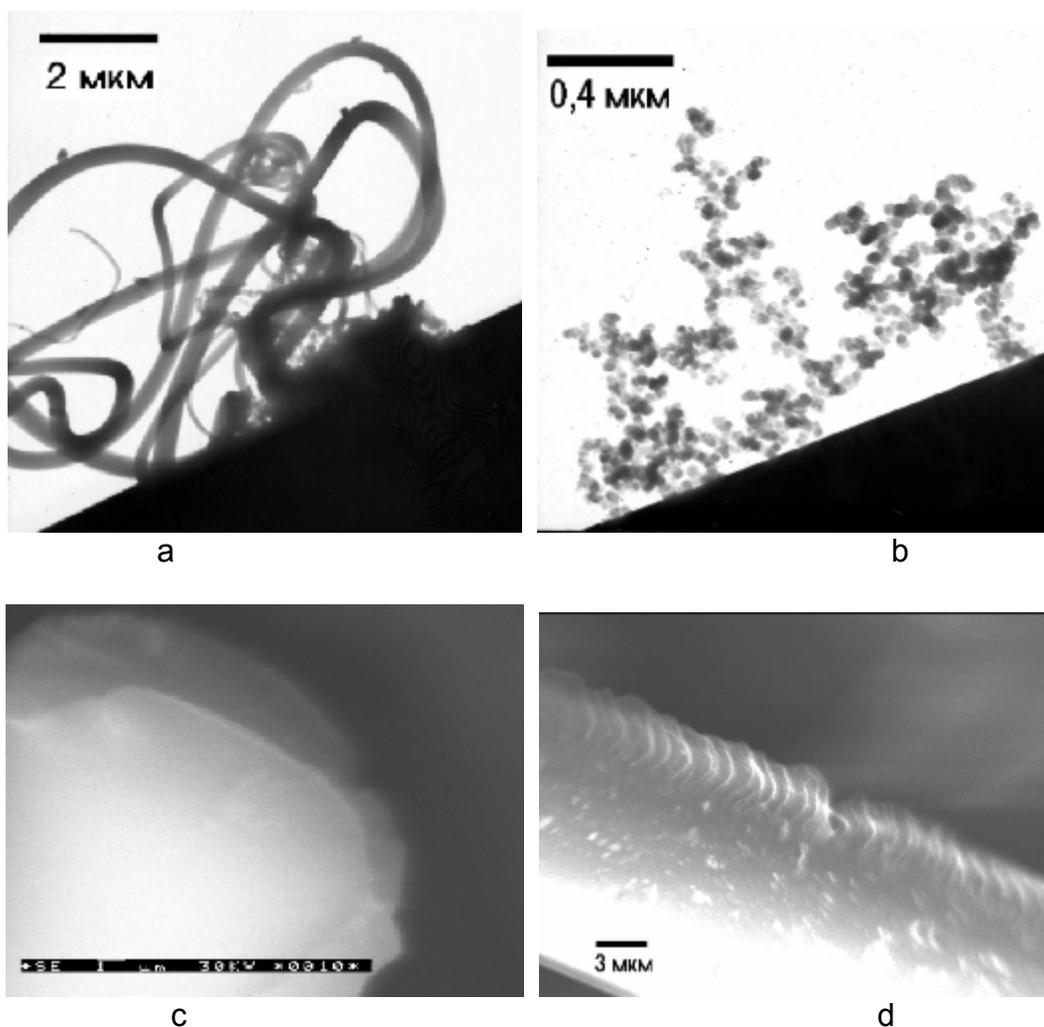
Figure 4. The texture of MSCFs and images of nanofibers formed: SEM micrographs (c,d); TEM micrographs (a,b).

Conclusions

1. Short-time pyrolysis of C_2H_2 on the surface of pitch-derived MSCFs provides some improvement in their efficiency to separate helium and oxygen.

2. Carbon nanofibers and nanoparticles are formed on the surface of nanostructured coal tar pitch-based MSCF during low temperature pyrolysis of C_2H_2 (at 300 °C).

3. Both synthesis of carbon nanoparticles on the MSCF surface and modification of MSCF pore structure can successfully be controlled using a ESR spectroscopic technique.

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