

MOLECULAR SIEVE CARBON FIBER NANOFRAGMENTS DESIGN

Victor P. Berveno, Lev I. Shchukin, Margarita V. Kornievich
Institute of Solid State Chemistry & Mechanochemistry, Kemerovo Division, SB RAS,
18 Sovetsky Ave., Kemerovo 650099, Russia, E-mail carbnanof@kemnet.ru

Abstract. Carbon materials are components of great importance for new generation composite and energy sources. Our studies were carried out with coal tar pitch-based carbon fiber (CF) and anthracene. Electron density distributions at atoms in single and associated arene molecules was estimated by a quantum-chemical modeling method. For reactivity measurements anthracene and pitch or carbon fibers was oxidized in low temperature oxygen plasma (LTOP).

Coal tar pitch consists of nanofragments (associates) comprising three aromatic molecules. Nanofragments of pitch fiber and pitch-based CF are formed with seven molecules locating in shells and three molecules concentrating in fibers cores. In case of three- and seven-molecule associates, the increased oxidation rates in LTOP are characteristic for central molecules of the associates. The increased reactivity of central molecules in the associates containing three and more molecules (compared to outer or lateral molecules) during their oxidation in LTOP or oxidative activation for molecular pore formation is due to the increased electron density located at the central molecules. The first stage of porous carbon materials preparation is a synthesis of carbon matrix having nanofragments required for pore structure formation. Methods of formation of carbon materials having nanofragments with 3, 5, 7 numbers of arene molecules have been developed. A possibility to create defectiveness of carbon matrix, pore sizes, specific pore volume, sorption-kinetic characteristics of molecular sieve carbon fibers (MSCFs) using molecular design of nanofragments, their functionalization, modification of electron-donating properties by doping with metal nanoparticles and variation of electron-exchange properties of nanofragments of carbon materials has been established.

Keywords: molecular sieve; carbon fiber; nanostructure tailoring, molecular design.

Introduction.

Carbon materials are components of great importance for aviation and airspace materials science and energy sources of new generation. Today they are again in a focus of an enhancing scientific interest in view of a discovery of carbon nanoparticles (nanotubes and fullerenes). In future energy science will be related with carbon materials. Lithium batteries, accumulators, electric supercapacitors, low temperature fuel cells and hydrogen storage units are based on novel developments in carbon materials science. Nevertheless, up to date, a mechanism of carbon materials nanofragments formation and a relationship between number and reactivity of arene molecules combined each others by π - π -electron interactions in these nanofragments are poorly studied. The mechanism of defects and molecular pore structure formation at an aggressive oxidative atmosphere is not yet established. This hinders developments of new generation carbon composites and molecular sieve. A lack of the plausible mechanism of molecular pore formation inhibits a creation of porous carbon materials for new generation energy sources.

Experimental

Our studies were carried out with coal tar pitch-based carbon fiber materials and anthracene as a pure constituent of coal tar pitch and other carbon materials precursors.

The calculated values of electron densities at carbon and hydrogen atoms in single and associated anthracene molecules were compared with the experimental results obtained during low temperature plasma oxidation of anthracene.

Electron density distributions at carbon and hydrogen atoms in single and associated arene molecules was estimated by a quantum-chemical modeling method using a semi-empirical approach (PM-3) and a Win MOPAC (Chem Office 2005) program package. For reactivity measurements anthracene was oxidized in low temperature oxygen plasma at 50°C and P_{O₂} up to 1 torr.

Some increase in electron density at carbon atoms of lateral anthracene molecules with a simultaneous decrease in electron density for a central anthracene molecule in the three-layer anthracene associates compared with the same values in single anthracene molecules have been found (Fig. 1). Such a redistribution of electron densities results in the change in reactivity of associate

molecules: one of three molecules will be oxidized slower while other two molecules will be oxidized faster. This conclusion was confirmed during anthracene oxidation in low temperature oxygen plasma.

Perylene and coronene were taken as the model substances for studying reactivities of arene molecules in pitch and carbon fiber nanofragments. The decrease in electron density at carbon atoms in lateral perylene molecules and the increase in electron density at carbon atoms in a central arene molecule for three-molecule associates (compared to the single perylene molecules) have been established (Fig. 2, 3).

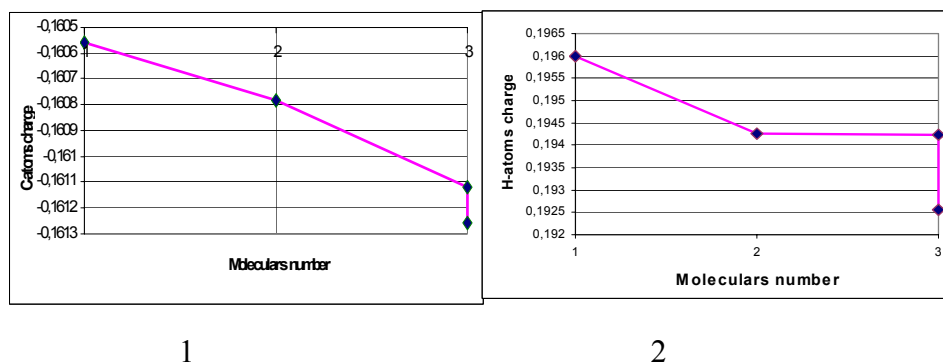


Fig. 1. Charges at carbon (1) and hydrogen (2) atoms in a single anthracene molecule and in an anthracene associate.

Such a redistribution of electron densities results in the changes in reactivities of aromatic molecules in associates: one of three molecules (a central molecule) must be oxidized faster than other two molecules.

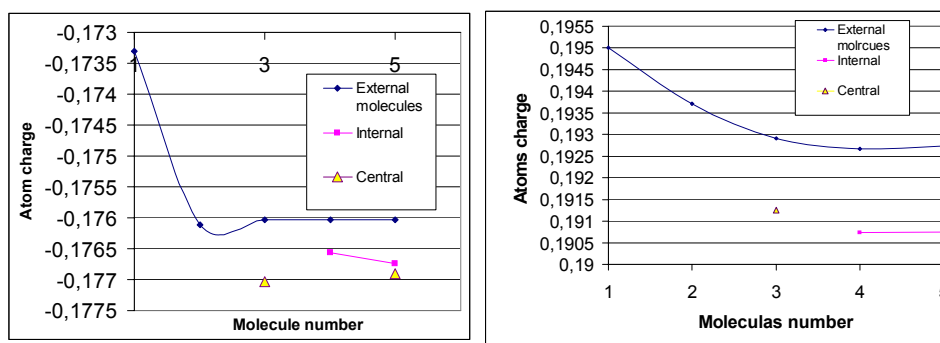


Fig. 2. Charges at H and C atoms in single and associated perylene molecules.

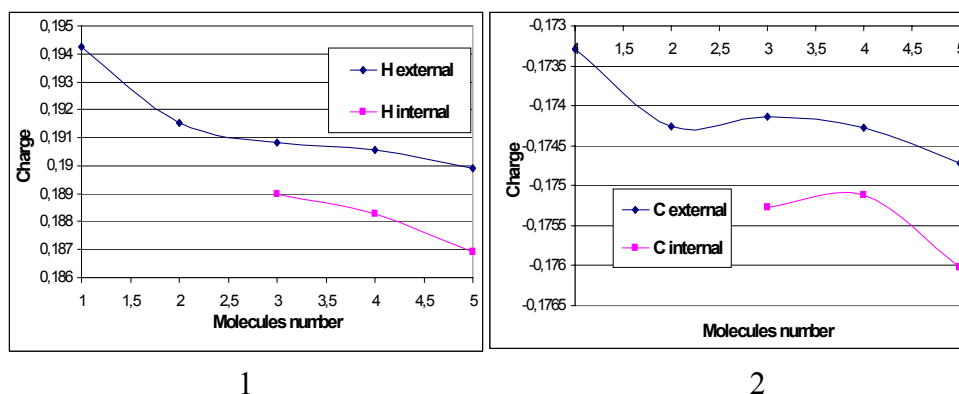


Fig.3. Charges at H and C atoms in single and associated coronene molecules

As a result of investigations of the formation of coal tar pitch-based carbon fiber (CF) nanofragments and some peculiarities of aromatic molecules reactivity in them using experimental data on low temperature oxygen plasma (LTOP) oxidation of the synthesized CF materials and calculated electron density values of associated molecules in carbon matrix nanofragments (quantum-chemical modelling), the following has been revealed.

1. Coal tar pitch consists of nanofragments (associates) comprising three aromatic molecules; nanofragments of pitch fiber and pitch-based CF are formed with seven molecules located in shells and three molecules concentrated in fiber cores.

2. In case of three- and seven-molecule associates, the increased oxidation rates in LTOP are characteristic for central molecules of the associates.

3. The increased reactivity of central molecules in the associates containing three and more molecules (compared to outer or lateral molecules) during their oxidation in LTOP or oxidative activation for molecular pore formation is due to the increased electron density located at the central molecules.

The purpose of the next part of this work was to characterize the sorption properties of molecular sieve carbon fibers (MSCFs), in both oxidized and reduced states, and also to study the changes in interfacial spacings in the MSCF nanofragments received at 500-800°C.

The MSCF samples were prepared from isotropic coal tar pitch activated by water *steam* at 500 (MSCF 500), 600, 700, 800°C; the materials were further reduced in H₂ at 300°C, and then oxidized under *the* ambient conditions. The properties of MSCFs were analyzed with a conventional chromatographic technique. The data received were compared to the interfacial distances determining pore widths (these values were computed using a quantum-chemical modeling method). The oxidative activation of carbon fiber (CF) with partial burning out of middle arenes in three-layer associates (nanofragments of CF matrices) and the oxidation of lateral arenes in associates in activated CFs are accompanied by shortening the interfacial distances between lateral arenes.

Changes in retention volumes of gases (V₂) and H₂/CO separation coefficients (C_s) for the MSCFs are defined by interfacial distances and sizes of molecules in arene molecule associates involved in nanofragments of carbon matrix.

The oxidized MSCF sample activated at 800°C separates a mixture of H₂/CO with C_s ~ 50, while the reduced one shows the C_s value of ~ 30. An increase in the C_s for the oxidized CF sample is explained by the fact that the sizes of entrance windows in molecular pores are closed, and their volume decreases during the functionalization (with OH-groups) of edge carbon atoms located in the lateral arene molecules of MSCF textural fragments.

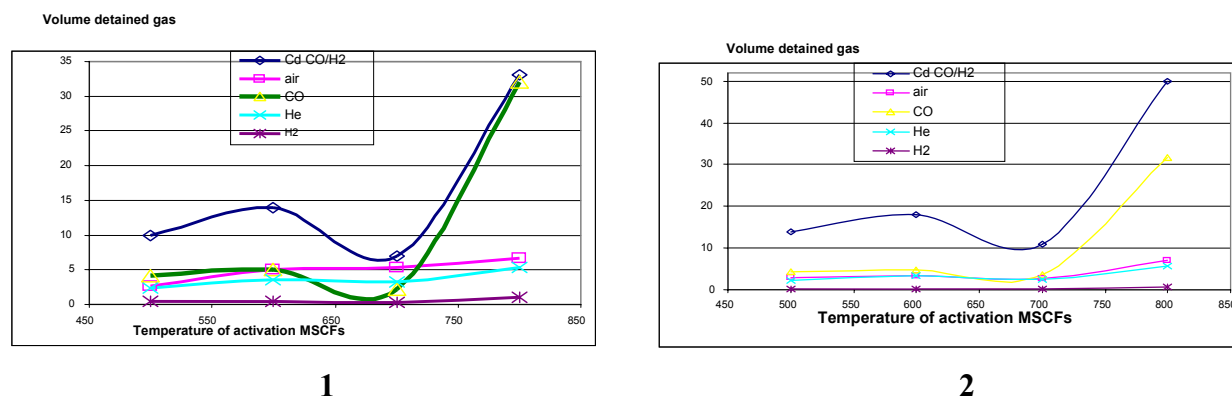


Fig.4. Specific retention volumes (V₂) for H₂ and CO and absolute retention volumes for He in CFs with reduced (1) or oxidized (2) surfaces activated at 500, 600, 700 and 800°C.

Conclusions

The first stage of porous carbon materials preparation is a synthesis of carbon matrix having nanofragments appropriate for pore structure formation. The methods for the preparation of carbon materials having nanofragments with tailored numbers of arene molecules have been developed (Fig.5)

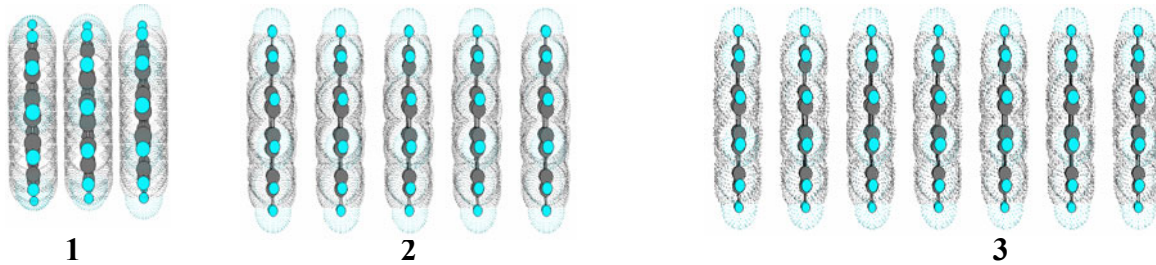


Fig. 5. Nanofragments models for traditional (1) and new generation (2, 3) CFs carbonized at 500°C.

Reactivity of molecules in nanofragments is not only determined by their structure but also by their position in nanofragments (in internal or external domains of nanofragments). Redistribution of electron densities in associated arene molecules resulted in a rise in reactivity of internal molecules and in drop in reactivity of external molecules of nanofragments has been found.

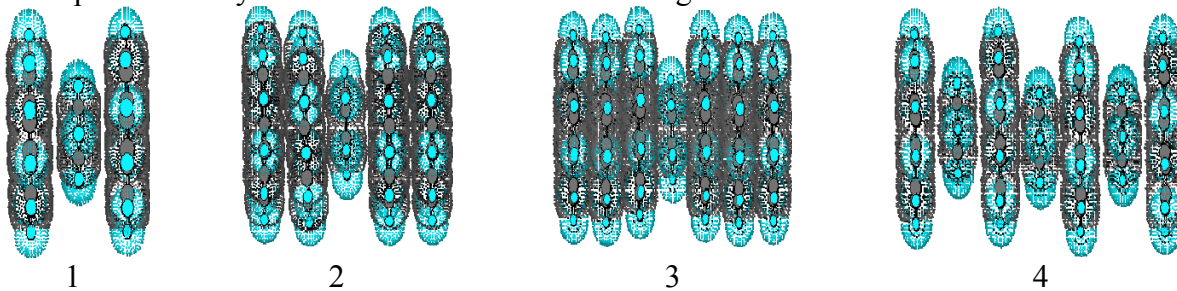


Fig. 6. Nanofragments models for traditional (1) and new generation (2, 3, 4) MSCFs activated at 500°C.

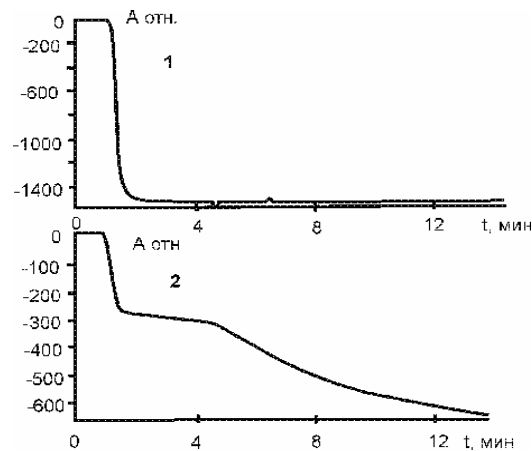


Fig. 7. Kinetics of redistribution for methane and oxygen in traditional (1) and new generation (2) MSCFs.

A possibility to create defectiveness of carbon matrix, as well as pore sizes, specific pore volume and adsorption-kinetic characteristics of the MSCFs using the molecular design of nanofragments (Fig.6,7) their functionalization, modification of electron-donating properties (by doping metal nanoparticles) and variation of electron-exchange properties of nanofragments of carbon materials has been established

References

Huttepain M, Oberline A. Microtexture of nongraphitizing carbons and TEM studies of some activated samples. Carbon 1990; 28:103-111.

Stoeckli F, Daguerre E, Gulliot A. The development of micropore volumes and widths during physical activation of various precursors. Carbon 1999; 37; 2075-7.

X. Py, A. Gulliot, B. Cagnon . Nanomorfology of activated carbon porosity: geometrical models confronted to experimental facts. Carbon 2004;42; 1743-1754.