

MOLECULAR STRUCTURE AND THERMO-OXIDIZING STABILITY OF CARBON MATERIALS CONTAINING BORON AND NITROGEN HETEROATOMS

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Introduction

It is well-known that by inserting boron or nitrogen heteroatoms into a carbon matrix, one can significantly increase the thermo-oxidizing stability of carbon materials. Three possible mechanisms for the effect of boron on the increased thermo-oxidizing stability have been discussed by one of us earlier [1]: 1) limitation to the diffusion of oxygen owing to coating an external surface by the glassy B₂O₃; 2) an inhibition effect of boron on the electronic states of condensed systems; 3) a catalytic effect on the process of graphitization of a material. In the case of nitrogen-containing carbon materials such an effect has not been explained yet.

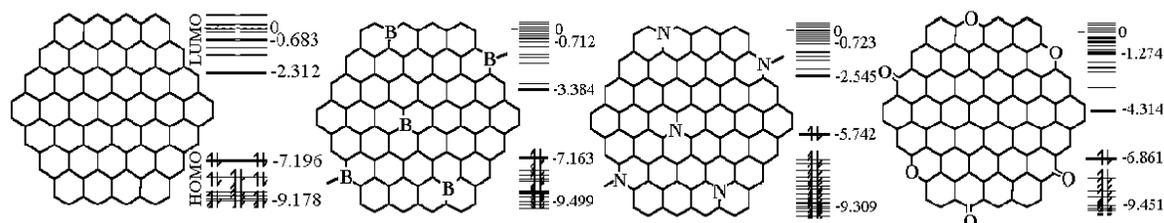
Structure of clusters and calculation method

Here we aim to study the possible influence of these factors on the thermo-oxidizing stability, a semi-empirical AM1 method is employed in order to calculate the molecular structure and donor-acceptor

properties of B- and N-containing clusters, which simulate corresponding graphite-like micro-crystallites of carbon.

It is an axiom that the primary elementary act of oxidation of any substance involves the electron transfer from oxidizing particles to oxygen, transforming it to a super-oxide anion O₂⁻. The inhibition effect of B and N may arise due to their influence on the energy levels E_{HOMO} and E_{LUMO} of the corresponding molecular clusters, simulating B- and N-containing carbons.

In the figure located below clusters formed by 37 condensed rings and containing from 0 to 6 at. % of heteroatoms, are shown. For the sake of comparison, corresponding clusters containing oxygen atoms of carbonyl (C=O) and furan (>O) types are also shown. Such O-containing clusters are taken for comparison since real carbon materials always contain 4-6% of chemically bonded oxygen in the form of C=O and >O groups.



Results and Discussion

E_{HOMO} values (Fermi level energies) are known to determine the electron donor ability of a system. Calculation results for

initial carbon cluster (C₉₆, E_{HOMO}=-7.20eV) and clusters containing 6 % of boron (C₉₀B₆, E_{HOMO}= -7.52 eV) demonstrate that E_{HOMO} for the latter is shifted to lower

energies by approx. 0.3 eV. This fact indicates the lowering of the electron donor ability of B-containing carbons which is manifested by their higher thermo-oxidizing stability when compared to clusters of an idealized graphite-like material. It is surprising, however, that clusters containing >O groups ("real" carbon) appear to be much more stronger donors of electrons ($C_{90}O_6, E_{HOMO} = -5.94\text{eV}$) than an idealized graphite-like material containing no oxygen. Carbon materials with the carbonyl-type oxygen ($C_{90}O_6, E_{HOMO} = -6.85\text{eV}$) have lower electron donor ability than materials with the furan-type oxygen. Most probably, this arises due to the fact that the furan-type oxygen, unlike other types of oxygen, donates its $2p$ -electrons to the mutual π -conjugated system of condensed rings.

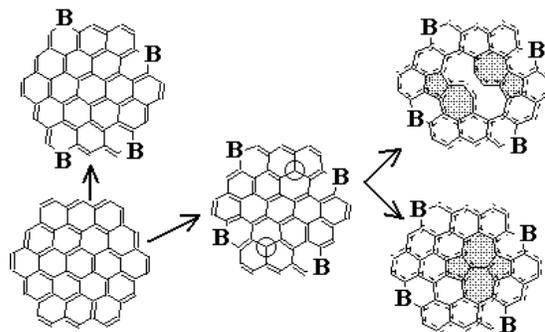
In N-containing carbons with 2-3% of nitrogen, the Fermi level ($C_{94}N_2, E_{HOMO} = -5.85\text{eV}$) is increased by 1.4 eV if compared to ordinary carbons; that is, these are better electron donors than the initial materials ($C_{96}, E_{HOMO} = -7.20\text{eV}$).

Obviously, real B- and N-containing carbons must contain some oxygen atoms in the form of C=O and >O. That is why we performed calculations of the energy of mixed clusters with heteroatoms: N (3%) and O (7%) - $C_{86}N_3O_7$ ($E_{HOMO} = -7.01\text{eV}$) and B (3%) and O (7%) - $C_{86}B_3O_7$ ($E_{HOMO} = -6.97\text{eV}$). As expected, the respective E_{HOMO} values of such clusters are 0.3-0.6 eV lower than these of B- and N-containing clusters, as well as mixed clusters containing furan-like and carbonyl-like oxygen.

Therefore, real differences in E_{HOMO} values for initial >O- and C=O-containing carbons and carbons containing both B, N and O can be as large as around 1 eV. We believe, this somehow explains an inhibition effect of boron and nitrogen atoms on the processes of thermal oxidation.

Finally, we performed calculations of the molecular structure of B-containing

clusters with an increasing number of boron atoms in the condensed system. It has been shown that at 4% and more boron content in some positions, defects may appear in the continuous π -conjugated system, and unstable azulene fragments may be formed. We guess that such defects arise due to the loss of stability of the system and, in turn,



may cause its fast crystallization and formation of graphite, which is more stable than usually turbostratic carbons

Conclusions

The data obtained enable us to explain the causes of the inhibition effect of boron and nitrogen heteroatoms on the thermal oxidation of carbon materials in terms of molecular structure and the electron donor properties of B-, N- and O-containing clusters. The results reveal that in order to obtain carbon materials of improved thermo-oxidation stability, one has to control the synthesis process so as to reach an optimal ratio of boron, nitrogen and oxygen.

References

1. Jones LE, Thrower PA. Influence of boron on carbon fiber microstructure, physical properties and oxidation behavior. *Carbon* 1991; 29(2); 251-269.