ELECTRONIC AND MAGNETIC PROPERTIES OF GRAPHENE-LIKE MATERIALSWITH DOUBLE VACANCY DOPED BY IRON AND/OR NITROGEN ATOMS

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Graphene and graphene-like materials (GLM) are widely used in various fields: as energy production, as energy storage and accumulation [1], as platinum-free catalysts in fuel cells [2].This versatility is partly due to the electronic structure of these two-dimensional materials. The density of states at the Fermi level is exactly zero (Dirac point) – is the easy way to changing the electronic properties of graphene and its derivatives. From a geometric point of view follows: as the size of the graphene sheet increases, the specific number of its edge atoms decreases, which critically affect the unique properties of graphene. Therefore, the introduction of single-atom and multi-atom vacancies in the interior of the graphene sheet can provide an additional ways of graphene functionalization, which will expand the areas of its application greatly.

Currently, platinum is the most active cathode electrocatalyst in oxygen reduction reactions in fuel cells, but it is expensive and lose its stability during operation. Therefore, the nitrogen-functionalized graphene derivatives containing inexpensive transition metal atoms are used to develop the electrocatalyst [3].

This report present the results of quantum chemical calculations (DFT, B3LYP/6-31G**) of the structural relaxations and electronic structure of the GLM – polycyclic aromatic hydrocarbons (PAH)$C_{96}H_{24}$ and its derivatives. The derivatives were obtained by removing of two adjacent carbon atoms (was formed single double vacancy, DV) from interior area of PAH. Two and four carbon atoms (which surrounding the DV) were replacement by two and four nitrogen atoms, respectively. The single iron atom in 0, +2 and +3 oxidation states was placed into the DV. The magnetic moment of the iron-containing samples was significantly increased compared to iron-free N-PAH sample with single DV.

The DV formation (the removal of a double C_2 molecule from the PAH) is an endothermic process with a reaction energy (E_{react}) of 16.73 eV. The value of E_{react} replacing of two carbon atoms surrounding the DV in the defect molecule $C_{94}H_{24}$ by two nitrogen atoms is 5.98 eV (the $C_{92}N_2H_{24}$ molecule is formed). The value of E_{react} for a similar reaction with the replacement of four C atoms in $C_{94}H_{24}$ by four nitrogen atoms is 7.77 eV (the $C_{90}N_4H_{24}$ molecule is formed). According to carried out calculations, the ground electronic state (GES) of $C_{96}H_{24}$, $C_{94}H_{24}$, $C_{92}N_2H_{24}$ and $C_{90}N_4H_{24}$ molecular systems is singlet, i.e. their multiplicity (M) is equal to one.

All iron-binding reactions in 0, +2 and +3 oxidation states are exothermic and the GES of the formed complexes is different from the singlet state. So for the complexes $[C_{94}H_{24}Fe]^0$ E_{react}=-3.91 eV, M=3; $[C_{94}H_{24}Fe]^{+2}$ E_{react}=-15.26 eV, M=5; $[C_{94}H_{24}Fe]^{+3}$ E_{react}=-36.75 eV, M=6. For the nitrogen-containing complexes $[C_{92}N_2H_{24}Fe]^0$$E_{react}$=-7.73 eV, M=3; $[C_{92}N_2H_{24}Fe]^{+2}$ E_{react}=-19.35 eV, M=3; $[C_{92}N_2H_{24}Fe]^{+3}$ E_{react}=-40.85 eV, M=4; $[C_{90}N_4H_{24}Fe]^0$ E_{react}=-7.37 eV, M=3; $[C_{90}N_4H_{24}Fe]^{+2}$ E_{react}=-18.80 eV, M=5; $[C_{90}N_4H_{24}Fe]^{+3}$ E_{react}=-40.49 eV, M=2.

The obtained E_{react} values of nitrogen-containing systems complexation are two times higher than the similar values for the nitrogen-free carbon system $C_{94}H_{24}$.

The relative energies for different spin states of iron complexes (in zero oxidation states) with defect-containing PAH $C_{94}H_{24}$, $C_{92}N_2H_{24}$ and $C_{90}N_4H_{24}$ are presents in the table. We can make several important conclusions. First, the complexes in the non-singlet magnetic states have the lowest energy. Second, the singlet state (M=1) energy of complexes and the GES energy are located on the comparatively large distance from each other in comparison with distance between GES energy and another non-singlet energy. Third, the eigenvalues of the total spine operator (S^2) is slightly differs from the theoretical integer value (bold type), indicating that the single-determinant wave function in the DFT approximation is quite accurate.

Energies* (eV) of magnetic and non-magnetic states of the considered molecular systems
with double vacancy, undecorated and decorated with nitrogen atoms,
with an single iron atom in the vacancy center

Multiplicity, M (spin number, S)	$[C_{94}H_{24}Fe]^0$	$[C_{92}N_2H_{24}Fe]^0$	$[C_{90}N_4H_{24}Fe]^0$
1 (S=0)	2.66 (S^2=0)	1.55 (S^2=0)	1.40 (S^2=0)
3 (S=1)	0.21 (S^2=2.07)	**0.00 (S^2=2.01)**	**0.00 (S^2=2.02)**
5 (S=2)	**0.00 (S^2=6.05)**	0.22 (S^2=6.04)	0.33 (S^2=6.05)
7 (S=3)	0.89 (S^2=12.09)		

*The zero-point energy of each of the three complexes – the energy of the GES.

In the complexes $[C_{94}H_{24}Fe]^0$, $[C_{92}N_2H_{24}Fe]^0$ and $[C_{90}N_4H_{24}Fe]^0$ spin density is concentrated at the iron atom (see figure), and with increasing number of nitrogen atoms in the ligand absolute value of magnetic moment decreases, due to the formation of Fe-N bonds.
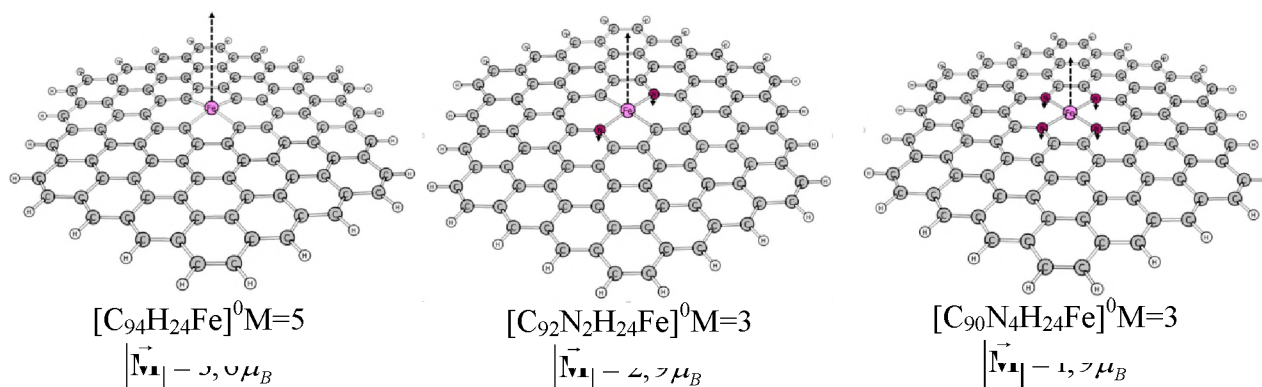

$[C_{94}H_{24}Fe]^0 M=5$
$|\vec{M}| - 5,0 \mu_B$

$[C_{92}N_2H_{24}Fe]^0 M=3$
$|\vec{M}| - 2,9 \mu_B$

$[C_{90}N_4H_{24}Fe]^0 M=3$
$|\vec{M}| - 1,9 \mu_B$

Fig. Spin density distribution of α- (dashed arrow) and β- (solid arrows) subsystems in Fe^0 complexes with defect-containing molecules $C_{94}H_{24}$, $C_{92}N_2H_{24}$ and $C_{90}N_4H_{24}$

$|\vec{M}|$ – absolute value of magnetic moment, μ_B – Bohr magneton.

Thus, the formation of DV in PAH $C_{96}H_{24}$ is accompanied by a rather high endothermic effect (16.73 eV), while the E_{react} of the substitution of two carbon atoms for two nitrogen atoms is 2.99 eV per one atom. When four C atoms are substituted for four N atoms the latter value decreases to 1.92 eV. The formation of Fe^0 complexes with the arrangement of this atom in the cavity center stabilizes the systems $C_{94}H_{24}$, $C_{92}N_2H_{24}$ and $C_{90}N_4H_{24}$ due to saturation of broken bonds of carbon atom and formation of Fe-N bonds.

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