РАЗДЕЛ X. ХИМИЯ

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Nature of 3d – transition metals chemical bond of in carbon nanotubes

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doi: 10.18411/lj-09-2018-70

idsp: 000001:lj-09-2018-70

Abstract

Communication of affinity degree to an electron and anti-oxidizing activity of a number of the aromatic polycondensed compounds, bakminsterfullerene (C₆₀) and multiwall carbon nanotubes is studied. The research was conducted on the model of the initiated cumene oxidation reaction. It has been determined that anti-oxidizing activity of the specified substances of the aromatic polycondensed compounds grows with increase in degree of their affinity to an electron, reaching the maximum value for fullerene C₆₀ and multiwall carbon nanotubes.

Electronic states of 3d-metals entered into the volume of carbon nanotubes (NT) have been studied. The analysis of an electronic structure, charging distributions and parameters of interatoms interactions in the specified nanostructures depending on structure of NT or the location of metal atom have been carried out. Possible changes of some physico – chemical properties of nanotubes containing 3d – metals have been discussed.

Keywords: affinity to an electron, anti-oxidizing activity, multi-phase carbon nanotubes, fullerenes, polycondensed aromatic compounds.

Urgent problem of the present stage of researches of carbon (fullerenes and nanotubes), also metal – carbon nanostructures is their functionalization. The solution of this problem means development of the methods allowing directly to regulate their physico – chemical properties. One of effective ways of a functionalization is change of the chemical composition of initial nanoobjects by introduction of alien atoms.

At present the greatest success has been achieved in researches of functionalized fullerenes, in particular the endocomplexes formed at the introduction of one or several metal atoms in the carbon cage volume [1 – 3].

Works on synthesis of nanotubular composites – carbon a nanotubes, completed by atoms or molecules are known [4].

So far questions of an electronic structure of nanotubular composites are most in detail studied for the systems including atoms of alkaline metals (Li; K) and Al [4] and single works on the evaluation of introduction energy of atoms and S atoms into the carbon nanotube [5] and study of density of some transitional metals electronic states [6 - 8].

In the present work electronic states and the nature of interatomic communications in carbon nanotubes and metal – carbon nanostructures content in the structure of transitional metals are systematically investigated. All carbon nanotubes depending on their structure are divided into two classes – unchiral ($\Theta=00$ and 300) and chiral ($00<\Theta<300$) NT. Here Θ is a chiral angle, defining type of ordering of carbon hexagons C₆ forming tube walls. Feature of carbon nanotubes is strict dependence of their electronic structure on the structure. When depending on angle Θ and diameter – D nanotubes display semiconductor or metal properties.

In this work metalsimilar and semiconductor nanotubes are considered. As research objects unchiral (9,0) and (4,4) NT are chosen. The first of them – (9,0) NT belongs to family zigzag-type nanotubes, angle $\Theta = 00$, D = 7,0510Å. In their structure C – C bond is focused

parallel to a cylindrical axis . The second – (4,4) represents family of "armchair-type" tubes where C – C bond is perpendicular to angle $\Theta = 300$ and $D = 5,428 \text{ \AA}$.

Metals Ti, Cr, Fe, Cu were placed in two positions on a cylinder axis: in the planes of carbon rings "cut" and "center" of NT are positions I and II fig.1 imitating initial and final stages of their introduction in the volume of tubes. The used models allow to observe formation of electronic states of M – centers depending on the nature of metal atom, its position in a tube, its surrounding and distances of M – C (diameter of NT).

Thus, for M(9,0) NT metal atoms are located in the center of the ring formed by 9 atoms of carbon, distance M – C makes $3,525 \text{ \AA}$, and for M (4.). NT metal atoms are surrounded with 8 atoms of carbon, and distance M–C is equal to $2,714 \text{ \AA}$.

Calculations of an electronic structure of all specified nanostructures have been carried out using the method of a discrete variation [9; 10] with expanded basis of numerical atomic orbitals (AO). Basic AO determined by Hartry-Fok-Slater equation for the isolated atoms.

Fig. 1. Structures of composites of M(9,0) NT (a) and M(4,4) NT (b) with the introduced metals – M in positions I and II.

Features of an electronic power spectrum of initial (9, 0) NT and (4,4) NT are shown in fig. 2. (9,0) NT electronic spectrum typical for metalsimilar systems has been received, curves I and II clearly show increase of orbital-sp hybridization effects at transition from "end" to the "central" rings.

Essential distinctions of electronic states of carbon atoms show also an electronic spectrum (4,4) NT. It is visible that the electronic density of states of "end" C atoms are concentrated close to E_f (Ferm level), reflecting existence of the "torn-off" relations. Availability of "torn-off" relations for the NT "end" atoms defines weakening of interatomic C-C bonding in the area of "cut" of nanotubes that can play a crucial role in the course of their introduction "connecting" interductant near the end of a tube and interfering their penetration into nanotube volume.

Fig. 2. Full (a, b) and partial (Ia, IIa, Ib, IIb) densities of states (9,0)NT (a, Ia, IIa) and (4,4)NT (b, Ib, II b). Deposits to of C2s -(...) and C2p- states (---) of carbon atoms which are on the "cut" area (I a, Ib) and in "center" of NT (IIa, IIb) are given. The vertical line is Fermi level.

Results of calculations of systems M (9,0) NT and M (4,4) NT are given in table 1 and in figure 3,4 for atoms – interductants beginning (Ti)- and end of 3d – row (Cu).

Fig. 3. Model density of states for Ti (9,0) NT (a-d) and Cu (9,0) NT (e-h) are given for atoms Ti (b,d), Cu (f,h) and the carbon atoms surrounding them (a, c, e, g) (C2s (...), C2p (---)), on "cut" (a,e) and in the center (c,g) areas of NT.

Fig. 4. Model density of states Ti (4,4) NT for atoms of g Ti (b,d) and carbon atoms (a, c) (C2s (...) and C2p (---)), being on "cut" (a,b) and in the NT center (c,d) are presented.

It is visible that atom orbitals Ti as a part of M (9,0) NT most actively interact with the "torn-off" relations of carbon atoms of NT "cut", forming the allocated DS peak lying below EF, when placing atom Ti in the center of a tube its states are localized near DS. NT minimum noted earlier and as a result, relations Ti – C will be much weaker, than for Ti on NT "cut". With growth of atomic number (Z) metal (Cr (9,0) NT → Fe (9,0) NT → Cu (9,0) NT) of M state systematically move down a scale of energy, forming for Cu(9,0) NT atom-like peaks in the area – 1,7 – 3,5 eV (fig. 3).

Even more noticeable are distinctions of electronic states of polytypical interductants for series Ti (4,4) NT ... Cu (4,4) NT. In this case tube radius (2,714 Å) decreases in comparison with (9,0) NT by 30% and distance of M – NT approaches relation of lengths of metal – carbon

bond in steady compounds, and effects of chemical interactions of $M - NT$ have the most expressed character. At the same time again relations of $M - C$ with "end" atoms NT are much stronger (fig. 4). States of atoms Ti, Cr, Fe the center of the model cylinder settle down close EF, and their hybridization with $C2p$ – orbitals leads to emergence of set of the filled levels and transition of system $M(4,4)NT$ to a metalsimilar state.

Table 1

Partial and general occupancy of relations of $M - C$ and effective charges of atoms – metals (Q_e) in NT depending on the position of M atoms on the "cut" (I) or in the "center" of NT (II)

NT	Metal position	AO	M = Ti				M = Cr			
			4s	4p	3d	general	4s	4p	3d	general
M (4,4)NT	I	C_{2s}	-	-	0,068	0,216 1,71	-	-	-	0,030 1,03
			0,046	0,176			0,040	0,170	0,074	
		C_{2p}			0,265					
	II	Q	0,068	0,370			0,082	-	0,130	
								0,046		
		C_{2p}								
M (9,0)NT	I	C_{2s}	-	-	-	- 0,298 2,38	-	-	-	- 0,312 1,90
			0,122	0,409	0,039		0,106	0,386	0,049	
		C_{2p}			0,186		0,053	0,034	0,142	
	II	Q	0,028	0,058						
		C_{2p}								

NT	Metal position	AO	M = Fe				M = Cu			
			4s	4p	3d	general	4s	4p	4d	general
M (4,4)NT	I	C_{2s}	-	-	0,025	0,130 1,30	-	-	-	- 0,036 0,96
			0,033	0,130			0,032	0,131	- 0,027	
		C_{2p}			0,099					
	II	Q	0,127	0,044			0,158	0,028	- 0,032	
		C_{2p}								
M (9,0)NT	I	C_{2s}	-	-	-	- 0,194 1,72	-	-	-	- 0,279 1,61
			0,090	0,307	0,011		0,097	0,334	- 0,018	
		C_{2p}			0,104		0,150	0,053	- 0,033	
	II	Q	0,047	0,063						
		C_{2p}								

		C2p	0,031	0,015	0,041		0,015	0,007	0,001	
		Q				1,24				1,61
	II	C2s	-	-	-		-	-		
		C2p	0,027	0,037	0,007	0,001	0,021	0,037	- 0,005	- 0,090
		Q	0,014	0,013	0,045	0,36	- 0,018	- 0,012	0,003	1,08

The general regularities of change of interatomic interactions in the given systems proceeding from the size of the general and partial occupancy of relations of $M - C$ have been considered. From table 1 it is seen for $M(9,0)$ NT an overlapping of AO $M - NT$, occurs only for Ti, Cr and Fe atoms on NT cut considerably decreasing with the growth of Z metals. For atoms M in the NT center interaction of $M - NT$ is absent. For a nanotube of small diameter systems $M(4,4)$ NT the strongest relations $M - NT$ are formed for atom of the titan in position I. In all cases of relations $Cu - C$ does not arise. Besides, from tab. 1. it is seen that the main contributions to occupancy of relations of $Ti - C$ are made by hybridization of $M3d - C2p$ AO. With growth of Z metals the role of an overlapping of $M4s - C2p$ AO increase.

Thus, binding of metal in NT decreases – the first, with growth of Z , secondly, with growth of NT diameter, and the third, when finding metal in NT volume.

Hence, it is possible to assert that formation of nanocomposites with copper participation will be the most probable.

In the case of the titan, formation of strong relations of $Ti - C$ will interfere introduction of titan atoms in NT volume and promote formation of end structures of closing NT cut. When placing Ti in NT volume these bonds can lead to local deformation and destruction of NT walls forming carbide nanoparticles.

The regularities received in work are coordinated with the general tendencies of solidphase interactions in systems $M - C$ where it is well known that carbide forming ability of $3d$ – transitional metals sharply decreases with the growth of their atomic number Z . Thus, metals VII and VIII groups, most inert in relation to carbon will be optimum as the introduced metals not causing destruction of nanotube structure.

1. Nakale T., Xu Z.D, Yamamoto E. Et al//Fullerene Sci.Tecnol.1997 V.5 N5 p 289
2. Degiorgi L//Adv.Phys. 1998 v.47 N 2 p 207
3. Prato M//Topics Current Sci. 1999 v.199 p 173
4. Ivanovsky A of L//Achievements of chemistry. 1999. T. 68 N_o 2 with.119
5. Wu J, Wang N.L, Lu R, Duan W//Inteen.J Modern Phys.1998 V B 12 N 15 p 1601
6. Kenno O.M, Dyachok I.I.N. // Chemical. Physics. 1998 T.17 N_o 16 with 118
7. Dyachkov I.I.N Kenn O.M//Dokl. AH 1999 T.365 N3 with 215
8. Sextons P.N//Zhurn. Neorgan.Khimm 2001.E.46 N1 with 10
9. Baerends T.Y, Ellis D.E Ros.P.P//Chem Phys. 1973 v.5 N_o 1 p 41
10. Press.M.R., Ellis DE.//Phys. Rev.B.1976 v.13 N_o10 p 4438

Минакова Т.А., Калужина С.А., Введенский А.В.
Термодинамический анализ взаимодействий в системе Al-H₂O

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doi: 10.18411/lj-09-2018-71
idsp: 000001:lj-09-2018-71

Аннотация

В настоящей работе проведен термодинамический анализ системы Al-H₂O в диапазоне температур 25°-65°С с учетом возможности образования трех