Doped CNTs for Removal and Monitoring of Li, Na, K, Zn, Cd, Hg Chromate Molecular Complexes: a DFT Computational Study

V. Borysiuk[1,*], S. Nedilko[1], Yu. Hizhnyi[1], A. Shyichuk[2]

[1] *Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska Str., 01601 Kyiv, Ukraine*
[2] *University of Wrocław, 14, Joliot-Curie, 50-383 Wrocław, Poland*

Electronic structures and adsorption characteristics of CrO_4^{2-} molecular anions, $M^I_2CrO_4$ (M^I = Li, Na, K) and $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) molecular complexes on the surface of undoped, B- and N-doped (5,5) carbon nanotube (CNT) fragment, were studied using density functional theory within molecular cluster approach. Stable adsorption geometries, binding energies and values of electronic charges transferred from the adsorbents to the CNTs were calculated and analyzed. It is found that both undoped and B- or N-doped CNTs form stable adsorption configurations with $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) molecular complexes. The B-doped CNTs bind $M^I_2CrO_4$ (M^I = Na, K) complexes. The results indicate that the doped CNTs can find a potential application in removal of the respective chromate molecular compounds. Neither undoped nor B/N-doped CNTs would effectively bind Li_2CrO_4 molecule. The calculated changes in the electronic charges of the bound chromate(IV) indicate that undoped CNT-based materials can potentially serve as gas sensors for $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) complexes. However, they are less perspective for resistivity sensing of $M^I_2CrO_4$ (M^I = Li, Na, K) compounds.

Keywords: Electronic structures, Hexavalent chromium, Cr(IV). Chromate, Doped carbon nanotubes, Adsorption.

1. INTRODUCTION

It is known that hexavalent chromium, Cr (VI), is very harmful to living organisms. Chromium (IV) oxoanions are, in particular, carcinogenic, since they are able to modify the DNA transcription process in living cells [1-3]. Cr (VI) compounds cause nausea, diarrhea as well as kidney, liver, and gastric damage, internal hemorrhage, lung cancer, ulcer formation, respiratory problems, etc. [3-6]. Human activities primarily responsible for increase of the Cr (VI) content in environment, in particular in the atmosphere, are metallurgy, refractory bricks manufacturing, galvanic production, fuel combustion and the production of chemicals containing Cr(VI), mainly chromates and dichromates, chromium trioxide, etc. [7-9].

Removal of heavy metals, in particular Cr(VI) compounds, from the environment is an important technological problem. One of the most efficient methods of such removal is adsorption of heavy metals on artificial adsorbents [10, 11]. Materials based on carbon nanostructured materials, in particular carbon nanotubes (CNTs) are considered as promising adsorbents for such application [12-14]. Among other adsorbent materials, the CNTs are advantageous in sufficient adsorption capability with respect to many kinds of toxic molecules, large surface area and chemical stability [12, 15, 16].

The properties of CNTs as adsorbent materials of Cr(VI) compounds have been studied for the last decade and the CNT-based materials have been recognized as perspective adsorbents of Cr(VI) compounds [15, 17-23].

In the recent years, the first-principles quantum-mechanical calculations had become a powerful tool for quantitative description of the adsorption characteristics of various molecules on carbon materials, in particular, CNTs ([24] and references therein). High predictive power of *ab initio* calculations is rather generally accepted. In our previous papers [25,26] we have studied computationally some characteristics of XO_4^{2-} (X = Cr, Mo, W) anions adsorption on the surface of undoped, B/N-doped and functionalized CNTs and graphene. However, in the real environment, charged CrO_4^{2-} anions can attach some cations due to electrostatic attraction. In this paper, the electronic structure and adsorption characteristics of CrO_4^{2-} molecular anions on the surface of undoped, B- and N-doped CNT (5,5) are compared to corresponding results for $M^I_2CrO_4$ (M^I = Li, Na, K) and $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) molecular complexes. As it was found earlier, CNT doping with boron and nitrogen impurities can significantly change the adsorption capabilities of CNT [27-30]. Therefore, we consider B- or N- doping of CNTs as a method for tuning the adsorption properties of materials in respect to Cr(VI) compounds. To the best of our knowledge, adsorption of $M^I_2CrO_4$ (M^I = Li, Na, K) and $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) molecular complexes on carbon nano-structure (CNS) compounds (CNTs, fullerenes, graphene) has never been studied so far by *ab initio* calculations.

The results of the calculations showed that the molecular complexes of $M^I_2CrO_4$ (M^I = Li, Na, K) and $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) form weak or regular covalent bonds with surface atoms of carbon nanotubes. Several issues that may contribute to the development of effective adsorption materials for the Cr(VI) compounds from the environment were emphasized. Additionally, we consider potential applicability of the CNT-based materials as sensors for chromates in gas phase.

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* borysyukviktor@gmail.com

2. METHODS

CNT clusters comprising 21 C_6 "rings" of armchair carbon nanotube CNT(5,5) were constructed for the calculations. The dangling C-C bonds in the clusters were capped with H atoms, resulting in overall composition of $C_{210}H_{20}$. Substitution of the edge C atoms by H atoms is a widely used approximation in computational studies of CNTs within the molecular cluster approach [31-33].

In order to model the B_C or N_C substitution impurities, one C atom from the central region of the clusters was substituted with either B or N.

The geometry optimization was performed using Gaussian 09 (build E01) [34] software package and B3LYP nonlocal hybrid exchange-correlation density functional [35, 36]. The split-valence double-zeta (6-31G) basis sets [37] were used for K, C and H atoms, while correlation-consistent polarized valence double-zeta (cc-pVDZ) basis sets [38-40] were applied for Li, Na, Cr and O atoms. Zn, Cd and Hg atoms were represented by cc-pVDZ-PP basis sets with pseudopotentials [41]. All calculations were carried out *in vacuo*.

Before the geometry optimization, several starting positions of $M^I_2CrO_4$ and $M^{II}CrO_4$ molecular complexes with respect to the carbon surface were considered for each adsorption case. In all cases, the anions were initially put in such a way that the shortest C/B/N – O distance was between 1.8 and 2.5 Å. The resulting structures presented and discussed below were the most stable.

The binding energy E_b of molecules (anions and molecular complexes) to adsorbents was obtained as the difference of the calculated total energies using the following expression:

$$E_b = E_{\mathrm{CNT-B(N)-mol}} - E_{\mathrm{CNT-B(N)}} - E_{mol}$$

where $E_{\mathrm{CNT-B(N)-mol}}$ is total energy of the optimized system "CNT with the molecule (the anion or a molecular complex)", $E_{\mathrm{CNT-B(N)}}$ is total energy of the optimized CNT, and E_{mol} is total energy of the optimized molecule (the anion or a molecular complex) calculated within the same approximations.

Below, we compare the calculated binding energies to energies of the respective covalent bonds. The two are not strictly corresponding, as the adsorption results in some deformations of the whole CNT fragment, not to mention the proximity of adsorption site. However, bond formation should be the most significant contribution to the binding energy, and the comparison is rather feasible from an order-of-magnitude point of view; covalent bonds and weak bond-like interactions can be distinguished.

The molecular complexes were not charged. Clusters of "undoped CNS + molecular complex" in calculations were not charged, while additional charges equal to − 1 and + 1 were assigned to the clusters describing the B- and N-doped nanotubes, respectively. By using such additional charges, we have modelled a very common situation when an "additional" electron introduced into the real CNT by the N_C impurity is compensated by an additional + 1 charge of a defect somewhere far from the N_C site (such compensating defects were not modelled explicitly in our clusters). Correspondingly, additional compensating defects can supply one

"missing" electron in the B_C case. Taking into account the − 2 charge of "free" $CrO_4{}^{2-}$ anion, additional − 2 charges were assigned to the clusters of undoped adsorbent and the chromate anion. Accordingly, additional charges of − 3 or − 1 were assigned to the B- or N-doped clusters, respectively. Consequently, the calculations were closed-shell.

The Δq charge transferred to/from the adsorbent was determined (using Mulliken population analysis) from the changes of total charge of the bound $CrO_4{}^{2-}$ anions (where free chromate anion charge is − 2) or the bound molecular complex $M^I_2CrO_4$ and $M^{II}CrO_4$ (free complex charge is zero). Positive or negative Δq indicates electron density transfer to or from the bound specie, respectively.

3. METHODS

3.1 Adsorption of $CrO_4{}^{2-}$ Anions

The binding energies, the shortest interatomic distances between the adsorbent and the adsorbate, as well as the transferred charges Δq are presented in Table 1. The binding energy for the chromate anion adsorbed on the surface of undoped CNT is − 4.71 eV. The shortest distance between the chromate anion oxygen atom and the carbon atom of the CNT surface (C-O bond length) is 1.44 Å. This value is quite close to the typical length of C-O covalent bond, 1.42 Å [42,43]. Δq is − 0.9, indicating significant electron density transfer to the CNT.

For the $CrO_4{}^{2-}$ chromate anion adsorption on the of boron-doped carbon nanotube CNT(5,5)-B, we have found the binding energy of − 2.3 eV with the shortest B-O distance of 1.48 Å – a typical length of a B-O covalent bond [43]. Apparently, chromate anion adsorption energy is lower in the case of B-doped CNT. Δq is − 0.64, indicating smaller electron density transfer to the adsorbent, in respect to the pristine CNT.

For the adsorption of chromate anion, $CrO_4{}^{2-}$ on the surface of the nitrogen-doped carbon nanotube, CNT(5,5)-N, we have obtained the binding energy of − 6.68 eV, and the N-O bond length of 1.52 Å (again, typical for covalent bonds [43]). Consequently, the nitrogen doping enhances binding of the anion to the nanotube, as compared to the undoped CNT. Δq is − 1.12: doping with nitrogen increases electron density transfer to the adsorbent in respect to the undoped CNT.

Taking into account the values of binding energies, we can conclude that the chemisorption mechanism is realized for all the above considered cases of $CrO_4{}^{2-}$ adsorption. Therefore, both undoped and boron-/nitrogen- doped carbon nanotubes can be considered as promising materials for removal of chromate anions $CrO_4{}^{2-}$ from gas phase. Below we consider the influence of various cations on the adsorption characteristics of the respective metal chromate molecular complexes on the surface of CNSs.

3.2 Adsorption of $M^I_2CrO_4$ (M^I = Li, Na, K) Molecular Complexes

The geometry-optimized structures of molecular complexes $M^I_2CrO_4$ (M^I = Li, Na, K) adsorbed on the surface of undoped CNT (5,5) are shown in Fig. 1 and corresponding parameters are listed in Table 1. In general,

Table 1 – Binding energies E_b(eV), transferred charges Δq(e) and the shortest internuclear distances R^{min} between molecular complexes and adsorbents ($\mathring{A}$) of chromate anion CrO_4^{2-} and molecular complexes $M^I_2CrO_4$ (M^I = Li, Na, K), $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) adsorbed on undoped and B/N-doped CNT

Type of doping	Configuration	E_b	Δq	R^{min} (bond type)
undoped	CNT(5,5)-CrO$_4^{2-}$	− 4.71	− 0.9	1.44 (C-O)
	CNT(5,5)-Li$_2$CrO$_4$	− 0.39	− 0.13	2.43 (C-Li)
	CNT(5,5)-Na$_2$CrO$_4$	− 0.36	− 0.13	2.85 (C-Na)
	CNT(5,5)-K$_2$CrO$_4$	− 0.43	− 0.03	2.84 (C-O)
	CNT(5,5)-ZnCrO$_4$	− 1.46	− 0.3	2.13 (C-Zn)
	CNT(5,5)-CdCrO$_4$	− 1.33	− 0.32	2.35 (C-Cd)
	CNT(5,5)-HgCrO$_4$	− 2.9	− 1.06	1.43 (C-O)
B - doped	CNT(5,5)-B-CrO$_4^{2-}$	− 2.3	− 0.64	1.48 (B-O)
	CNT(5,5)-B-Li$_2$CrO$_4$	− 0.77	− 0.3	2.37 (C-Li)
	CNT(5,5)-B-Na$_2$CrO$_4$	− 1.03	− 0.07	1.59 (B-O)
	CNT(5,5)-B-K$_2$CrO$_4$	− 1.65	0.19	1.56 (B-O)
	CNT(5,5)-B-ZnCrO$_4$	− 1.85	− 0.47	1.57 (B-O)
	CNT(5,5)-B-CdCrO$_4$	− 2.47	− 0.5	2.39 (C-Cd)
	CNT(5,5)-B-HgCrO$_4$	− 3.96	− 1.32	1.47 (B-O)
N - doped	CNT(5,5)-N-CrO$_4^{2-}$	− 6.68	− 1.12	1.52 (N-O)
	CNT(5,5)-N-Li$_2$CrO$_4$	− 0.31	− 0.08	2.53 (C-Li)
	CNT(5,5)-N-Na$_2$CrO$_4$	− 0.44	− 0.04	2.88 (C-Na)
	CNT(5,5)-N-K$_2$CrO$_4$	− 0.76	0.05	2.73 (C-O)
	CNT(5,5)-N-ZnCrO$_4$	− 1.17	− 0.29	2.13 (C-Zn)
	CNT(5,5)-N-CdCrO$_4$	− 0.89	− 0.36	2.32 (C-Cd)
	CNT(5,5)-N-HgCrO$_4$	− 3.62	− 0.98	1.38 (C-O)

the obtained results indicate that $M^I_2CrO_4$ molecular complexes have a weaker bonding with CNTs compared to CrO_4^{2-} anions. However, some peculiarities are worth discussing in more detail. As our calculations show, the binding energies of $M^I_2CrO_4$ (M^I = Li, Na, K) molecular complexes adsorbed on an undoped CNT(5.5) range from − 0.36 to − 0.43 eV (see Table 1). On the one hand, such values are too small for covalent bonding. On the other hand, it is rather not surprising: apparently, metal cation interacts with delocalized π-density of the CNT. A careful analogy with ferrocenes can be drawn, although it seems that the CNT density is not well shaped to form strong π bonds with alcali cations.

When M^I = Li and Na, the shortest inter-nuclear distance is formed between the carbon atom of the CNT and Li or Na cation of $M^I_2CrO_4$ complex. Whereas for K_2CrO_4, the shortest inter-nuclear distance is C-O. Typical covalent bonds length of Li-C, Na-C and C-O are 2.35 Å, 2.47 Å and 1.42 Å, respectively [42, 44-46]. As we see from Table 1, the shortest Li-C, Na-C and C-O distances are 2.43 Å, 2.85 Å and 2.84 Å, respectively. Consequently, the shortest distances in all three cases are longer or much longer than it should be in the case of covalent bonding.

For adsorption of $M^I_2CrO_4$ complexes on the surface of boron-doped carbon nanotubes, we obtain higher absolute values of binding energies (Table 1). In general, boron doping enhances the bonding between the nanotube and $M^I_2CrO_4$ complexes if compared to the undoped CNTs. The binding energies range from − 0.77

to − 1.65 eV. These values correspond to the lower boundary of the covalent bond energy region [43].

For Li_2CrO_4 complex adsorbed on CNT(5.5)-B, the shortest inter-nuclear distance is Li-C equal to 2.37 Å. The Li-C was the shortest bond also in the case of Li_2CrO_4 adsorption on undoped CNT(5.5). Apparently, doping with boron does not change the type of adsorbent-to-adsorbate bonding in Li_2CrO_4 case. It is different for Na and K cations: the B-O bond lengths are 1.59 and 1.56 Å for Na_2CrO_4 and K_2CrO_4 respectively. These values are quite close to the length of B-O covalent bond (1.37 Å) [42]. Consequently, boron doping leads to the formation of covalent bonds between the carbon nanotube and Na_2CrO_4 and K_2CrO_4 molecular complexes.

The binding energies of the $M^I_2CrO_4$ (M^I = Li, Na, K) molecular complexes adsorbed on the nitrogen-doped CNT(5.5)-N range from − 0.31 to − 0.76 eV. The shortest inter-nuclear distances are 2.53 Å (bond type: Li-C), 2.88 Å (bond type: Na-C) and 2.73 Å (bond type: C-O) – too long to assume covalent bonding (the same conclusion was drawn for the undoped carbon nanotubes above).

3.3 Adsorption of $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) Molecular Complexes

The calculated binding energies, the transferred charges Δq and the shortest internuclear distances for adsorbed $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) complexes are presented in Table 1. The corresponding optimized structures are presented in Fig. 2.
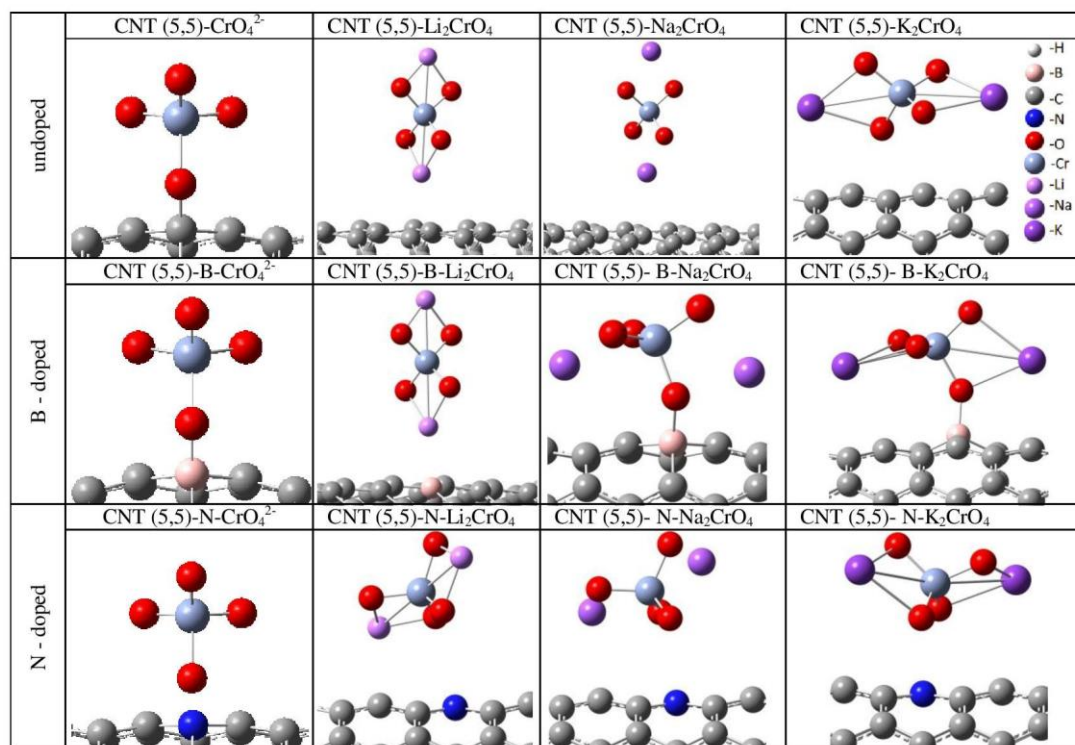
Fig. 1 – The geometry-optimized structures of undoped and B/N-doped CNTs with adsorbed molecular complexes $M^I_2CrO_4$ (M^I = Li, Na, K)

The binding energies of $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) complexes adsorbed on undoped CNT(5.5) range from -1.33 to -2.9 eV (see Table 1). In the case of M^{II} = Zn and Cd, the shortest inter-nuclear adsorbent-adsorbate distance is between the carbon atom of CNT and Zn or Cd cation of the complex, 2.13 and 2.35 Å respectively. For $HgCrO_4$, the shortest inter-nuclear distance is O-C, 1.43 Å. Typical distances for the Zn-C, Cd-C, and C-O covalent bonds are 1.96, 2.23 and 1.42 Å, respectively [43, 46, 49]. Thus, in all three cases, the binding energies and the shortest inter-nuclear distances correspond to covalent bonding [43].

According to our calculations, doping with boron substantially enhances bonding between the CNT and $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) molecular complexes, in respect to the undoped carbon nanotubes. The binding energies of $M^{II}CrO_4$ to CNT(5.5)-B range from -1.85 to -3.96 eV, which is typical for covalent bonds [44]. In the cases of the $ZnCrO_4$ and $HgCrO_4$ the B-O bonds are formed (1.57 Å and 1.47 Å, respectively, typical for B-O covalent bonds [42]). For $CdCrO_4$ adsorption on CNT(5.5)-B, the shortest inter-nuclear distance is Cd-C, 2.39 Å, which is close to the typical value of covalent bond (see above).

In respect to the undoped CNT, the $ZnCrO_4$/CNT(5.5)-B binding energy increases, and the bond type is changed from Zn-C to B-O. For $HgCrO_4$, the binding energy also increases and the bond type is also changed from C-O to B-O. In the case of $CdCrO_4$, the bond type is not changed, while the binding energy increases. Therefore, boron doping strengthens chemical bonds between the carbon nanotube and $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) molecular complexes.
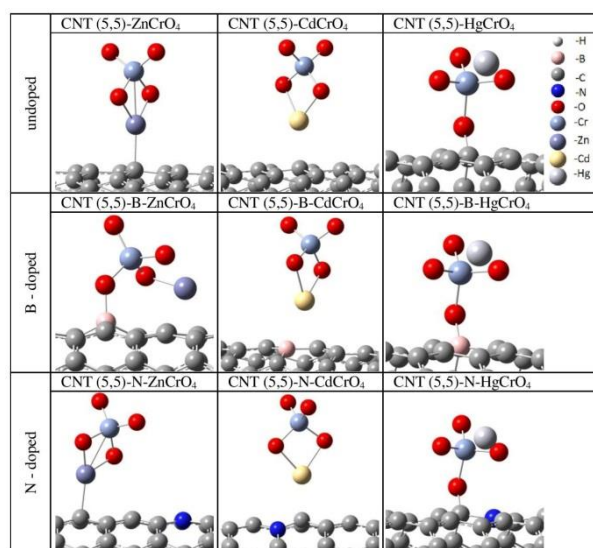

Fig. 2 – The geometry-optimized structures of undoped and B/N-doped CNTs with adsorbed molecular complexes $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg)

The binding energies between adsorbed $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) molecular complexes and CNT(5,5)-N range from -0.89 to -3.62 eV and fall into the lower boundary of the covalent bond energy scale [43]. For $ZnCrO_4$, the Zn-C bond is formed at a considerable distance (~ 5 Å) from the N dopant site. Consequently, the nitrogen impurity interferes deconstructively with adsorption of $ZnCrO_4$ molecular complex on the surface of CNT(5,5). The respective binding energy is slightly weaker in comparison to the undoped CNTs (Table 1).

For $HgCrO_4$ adsorption on CNT(5,5)-N, the absolute

value of the binding energy increases in respect to the undoped CNT. The bond type (covalent C-O) is the same. For the CdCrO₄ case, the binding energy weakens substantially, while the bond type is the same (Cd-O in both CNT(5,5) and CNT(5,5)-N cases).

3.4 Prospects for Use of CNTs as Materials for Removal and Monitoring of Cr(VI) Containing Molecular Complexes

The discussed adsorption characteristics of CrO_4^{2-} anions, $M^I_2CrO_4$ and $M^{II}CrO_4$ molecular complexes lead to the following conclusions. It is rather clear that covalent bond (chemisorption mechanism) is realized in the following cases: chromate anion and HgCrO₄ complex on the surface of the undoped CNT(5,5); chromate anion, chromates of Na, K, Zn(II), Hg(II) on the B-doped CNT(5,5); chromate anion and Hg(II) chromate on the N-doped CNT(5,5). These cases are characterized by rather high binding energies and covalent bonds between oxygen of the chromate anion and the adsorbent. It is likely that both undoped and B/N-doped CNT-based materials can be used as adsorbents for removal of the respective (strongly-binding) chromates from gas phase.

The other cases (Li, Na, K, Cd(II), Zn(II) chromates and the undoped CNT(5,5); Li, Cd(II) chromates and the B-doped CNT(5,5); Li, Na, K, Cd(II), Zn(II) chromates and the N-doped CNT(5,5)) can be also considered as chemisorption – with a certain care. The formed bonds are quite long carbon-metal kind, and should not be strong given the participation of the carbon electrons in delocalized orbitals of the CNT. It is likely, that these weak interactions (note the low binding energies) are only possible due to curvature of the CNT surface (which reduces the C-C p-p orbital overlap) and would not happen (or be much weaker) in graphene. The binding energies are still negative, and it might be worth checking the gas-phase absorption capabilities of the undoped, B- or N-doped CNTs towards the complexes mentioned above in this paragraph.

In general, boron doping enhances the adsorption properties of CNT(5,5) with respect to CrO_4^{2-} chromate anions, $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) and $M^I_2CrO_4$ (M^I = Li, K) molecular complexes if compared with the undoped CNT(5,5). Doping with nitrogen seems to have no positive effect on adsorption capabilities of CNT(5,5) with respect to studied Cr(VI)-containing molecular compounds (with the exception of HgCrO₄).

The prospects for use of the CNT-based materials for elaboration of gas sensors of the Cr(VI)-containing molecular complexes can be examined if we formulate some general criteria using existing literature data. The results of the DFT-based calculations of adsorption of several types of molecules on the surface of the CNT were analyzed recently [27, 28, 48-51] from a viewpoint of the potential application of CNT-based materials in gas sensing. Gas sensing materials must form weak (reversible) bonds with the detected molecules, and result in some changes that might be interpreted as signal. It was shown previously [26] that electronic transitions of chromate anion might undergo changes due to its chemisorption on CNS. It was also concluded that if the calculated binding energies are above -0.7

eV (i.e. $|E_b| < 0.7$), the respective CNT-based materials are suitable for elaboration of gas sensors for the corresponding molecules. If the amount of (Mulliken) charge $|\Delta q|$ transferred from/to the adsorbates is larger then 0.12 e, it is expected that resistivity of the adsorbent would change enough to facilitate a resistivity-based gas sensing. Principles of gas sensing using CNT mixes and measurements of resistivity were described in brief in [54] and references therein. These criterions are visualized in Figure 3 by the dashed lines (one for E_b and another one for Δq) against the results of our calculations.
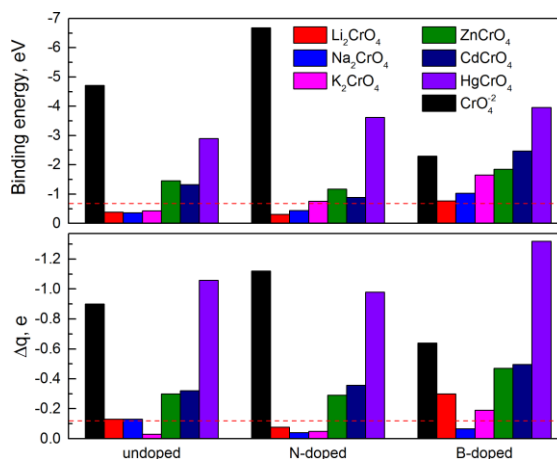

Fig. 3 – Dependencies of the binding energies E_b and absolute values of transferred charges Δq on type the CNT doping

As Figure 3 shows, the absolute values of binding energies of $M^I_2CrO_4$ (M^I = Li, Na, K) complexes adsorbed on the undoped CNT(5,5) are smaller then 0.7 eV and are below the line. The respective $|\Delta q|$ are larger then 0.12 (except for K₂CrO₄), meaning that resistivity sensing is potentially possible for Li₂CrO₄ and Na₂CrO₄ in gas phase using undoped CNT(5,5). As for adsorption of $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) and CrO_4^{2-} on the undoped CNT (5,5), $|\Delta q|$ values are above the threshold, also indicating the possible sensing application. However, the values of E_b are far above the dashed line (that is, binding is too strong).

For the case of adsorption on the N-doped CNTs, the absolute values of binding energies of $M^{II}CrO_4$ and chormate are too large (far above the line), while $|\Delta q|$ are suitable (above the line). For the $M^I_2CrO_4$, $|\Delta q|$ are too small (below the line), while $|E_b|$ are fine (below or almost below the line). That is, doping with nitrogen would not enhance the gas sensing capabilities of the CNT(5,5)-based materials with respect to CrO_4^{2-}, $M^I_2CrO_4$ and $M^{II}CrO_4$ molecular compounds.

The situation is somehow similar for doping with boron. Most of the $|\Delta q|$ are fine (above the line), while $|E_b|$ are too large. Li₂CrO₄ is the only exception, with fine $|\Delta q|$ and barely acceptable $|E_b|$.

4. CONCLUSIONS

According to our calculation results, chromate anion and HgCrO₄ complex can be efficiently adsorbed by the undoped CNT(5,5) *in vacuo* (in gas). The same goes for chromate anion and chromates of Na, K, Zn(II), Hg(II) on the B-doped CNT(5,5) as well as chromate anion and

Hg(II) chromate on the N-doped CNT(5,5). Cd(II) chromate binds rather strongly to the CNT(5,5)-B despite the long Cd-C bond. The respective CNT materials are promising candidates for gas phase adsorption and removal of the respective complexes.

The Li, Na, K, Cd(II), Zn(II) chromates are less efficiently bound to the undoped CNT(5,5), and so does Li chromate on the B-doped CNT(5,5) as well as Li, Na, K, Cd(II), Zn(II) chromates on the N-doped CNT(5,5). On the other hand, weaker adsorption provides possibilities for elaboration of sensors for the respective molecules in gas phase. With resistivity sensing in mind, the best candidates are undoped CNT(5,5) for Li_2CrO_4 and Na_2CrO_4 and CNT(5,5)-B for Li_2CrO_4. Nitrogen doping does not result in any improvement in both ad-

sorption and sensing capabilities of the studied CNT(5,5). Boron doping enhances adsorption capabilities, thus effectively reducing the sensing capabilites.

With some care, these conclusions can be extended on other low-diameter CNT, where surface curvature is comparable to that of CNT(5,5). It is expected that changes in curvature would result in rather different picture, in terms of both adsorption and sensing capabilities of the respective carbon materials.

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В. Борисюк[1], С. Неділько[1], Ю. Хижний[1], А. Шийчук[2]

[1] *Київський національний університет імені Тараса Шевченка, вул. Володимирська, 64/13, 01033 Київ, Україна*
[2] *Вроцлавський університет, 14, Жоліо-Кюрі, 50-383 Вроцлав, Польща*

Розраховано електронні структури та адсорбційні характеристики молекулярних аніонів CrO_4^{2-}, молекулярних комплексів $M^I_2CrO_4$ (M^I = Li, Na, K) та $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg) на поверхні нелегованого та легованого бором чи азотом фрагмента (5,5) вуглецевої нанотрубки (ВНТ) в наближенні теорії функціоналу електронної густини (ТФГ). Розраховано і проаналізовано між'ядерні відстані в адсорбованих станах, енергії зв'язку та значення електронних зарядів, що переносяться з адсорбентів на вуглецеві нанотрубки. З'ясовано, що матеріали на основі як нелеговані, так і леговані бором або азотом вуглецевих нанотрубок можуть утворювати стійкі конфігурації з молекулярними комплексами $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg). Леговані бором вуглецеві нанотрубки зв'язуються з комплексами $M^I_2CrO_4$ (M^I = Na, K). Одержані результати вказують на те, що леговані вуглецеві нанотрубки є перспективними матеріалами для видалення відповідних молекулярних сполук хроматів. Ані нелеговані, ні B/N- леговані ВНТ не будуть ефективно адсорбувати молекулярні комплекси Li_2CrO_4. Розраховані зміни електронних зарядів досліджених сполук хроматів вказують на те, що матеріали на основі нелегованих вуглецевих нанотрубок є перспективними для розробки газових сенсорів комплексів $M^{II}CrO_4$ (M^{II} = Zn, Cd, Hg), однак вони не є перспективними для резистивних сенсорів сполук $M^I_2CrO_4$ (M^I = Li, Na, K).

Ключові слова: Електронна структура, Шестивалентний хром, Хромат, Леговані вуглецеві нанотрубки, Адсорбція.

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