Bulgarian Chemical Communications, Volume 46, Number 3 (pp. 576 – 579) 2014

Adsorption of toxic gases by an open nanocone coupled with an iron atom

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Received October 25, 2013; Revised January 13, 2014

Density functional theory (DFT) calculations were used in order to study the adsorption of some toxic gases in the air by an open nanocone coupled with an iron atom (FeCNC). The BSSE (basis set superposition error) counterpoise correction (CP) was included during the geometry optimization for all systems. The results indicated that the effect of inclusion of BSSE-CP correction during the optimization is very important in the adsorption of some toxic gases by FeCNC.

Keywords: Nanocone; Toxic gases; BSSE-CP

INTRODUCTION

Carbon nanotubes (CNTs) have attracted considerable interest since their discovery by Iijima [1]. These nanomaterials have quickly developed into some of the most fundamental structures in nanotechnology and nanoscience due to their specific structures and unique properties. Many promising applications, including energy storage, nanoelectronic devices, chemical probes, biosensors, gas sensors, etc., have been reported in the literature [2-4]. In recent years, the investigation of the adsorption of different gases on CNTs has been found to be one of the most momentous subjects, and a number of researches have been performed on these systems [5,6]. For example, the physisorption of He, Ne, Ar, Kr, Xe and CH_4 in cylindrical pores, single-walled carbon nanotubes (SWNTs) and SWNT bundles has been inspected both experimentally and theoretically [7-17]. In addition to carbon nanotubes, a new form of carbon nanostructure, namely, carbon nanocone (CNC) has been discovered wherein a single pentagonal ring or community of nearly pentagonal rings defines a conical apex [18-21], i.e., a single walled carbon nanocone (SWNC) consists of a single layer of graphene sheet twisted into a cone. The cones can be classified by their disclination angle, which is defined as the angle of the sector removed from the flat sheet to form a cone [22]. CNCs with a disclination angle of 19°, 39°, 60°, 85° and 113° have been detected in the carbon samples in the pyrolysis of hydrocarbons [23]. Both SWNTs and SWNCs are tube-like made of single graphene sheets with hollow spaces inside. The SWNCs have larger internal pore space and surface area than SWNTs, and therefore gas storage on CNCs has some advantages compared with that in CNTs [24]. These materials are useful for many practical applications, such as gas storage and adsorption processes [21].

Within this work, density functional theory (DFT) calculations are performed to investigate the electronic and structural properties of a representative model of FeCNC. To this aim, the structural models of FeCNC with toxic gases were optimized to reach the minimum energy levels (Fig.1). The subsequent adsorption energy between FeCNC and the toxic gases was investigated. The adsorption energy was calculated at the same level with and without correction for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise (CP) technique [25].

COMPUTATIONAL DETAILS

The main model of this work is a conical structure with 39° disclination angle, in which the apex tips are saturated by iron atoms. A number of toxic gases in the air (carbon monoxide, carbon dioxide, chlorine, carbonyl chloride, hydrogen sulfide, sulfur dioxide, cyanogen) each one separately, were adsorbed

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on the structure of an open nanocone coupled with the iron atom (Fig. 1).

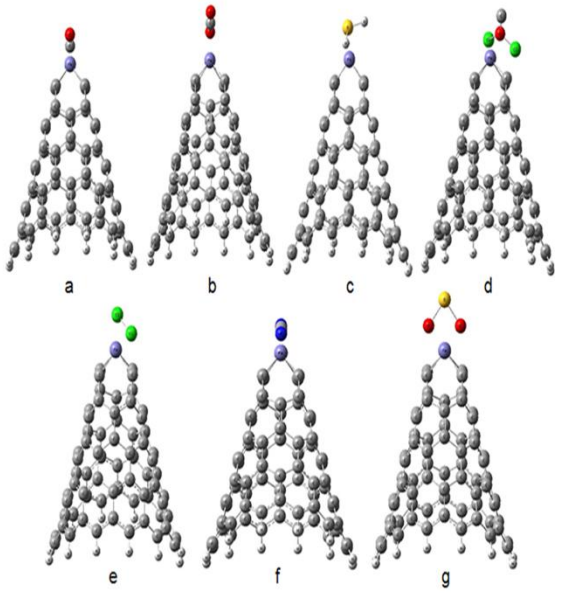

Fig. 1. Optimized absorptive structures of FeCNC with: (a) CO (b) CO_2 (c) H_2S (d) $COCl_2$ (e) Cl_2 (f) C_2N_2 (g) SO_2

All calculations were performed using the Gaussian 98 plan package [26]. GaussView 3.07 [27] was utilized to build molecular structures, display molecular geometry convergence and generate molecular graphics of all related species. The full geometry optimizations of all complexes were carried out using density functional theory (DFT) with the Beck's three parameter hybrid functional (B3) with the Lee-Yang-Parr correlation functional (LYP) called as B3LYP [28,29] with the basis set LANL2DZ [30]. For comparison, the two-layered ONIOM hybrid method [31] of calculations was also attempted.

The two-layered ONIOM(B3LYP/6-311++G(d,p):B3LYP/LANL2DZ) approach applied on the structure of FeCNC with toxic gases, two sections of CNC/toxic gas and iron atom were treated as the high and low levels of theory, respectively. The following relations were used in order to investigate the adsorption energy of toxic gases in the air by FeCNC :

$$\boldsymbol{E_{abs}^{(1)}=E_{FeCNC\text{-}gas}-E_{CNC}-E_{Fe}-E_{gas}} \quad (1)$$

$$\boldsymbol{E_{abs}^{(2)}=E_{FeCNC\text{-}gas}-E_{FeCNC}-E_{gas}} \quad (2)$$

RESULTS AND DISCUSSION

Based on the results calculated from Eqs.(1) and (2), it can be concluded that the amount of adsorbed sulfur dioxide is higher than that of other gases, but there is an important difference between the quantities of $E_{abs}^{(1)}$ and $E_{abs}^{(2)}$ in spite of the fact that the two systems are not very different (Table 1).

Table 1. The distance between FeCNC and toxic gases (D), bond length of toxic gas solely (***L***), bond length of adsorbed toxic gase (***L***$^{/}$), uncorrected adsorption energy ($E^{(1)}$,$E^{(2)}$) and corrected adsorption energy ($E^{*(1)}$,$E^{*(2)}$) .

System	D	L	L$^{/}$	$E_{abs}^{(1)}$	$E_{abs}^{(2)}$	$E_{abs}^{*(1)}$	$E_{abs}^{*(2)}$
FeCNC-CO	2.065	1.187	1.212	-0.3295	-0.0419	-0.2141	-0.0087
FeCNC-CO_2	1.989	1.227	1.235	-0.3322	-0.0446	-0.2303	-0.0075
FeCNC-Cl2	2.247	2.294	4.442	-0.4373	-0.1497	-0.3545	-0.1317
FeCNC-$COCl_2$	2.095	1.965	3.018	-0.4098	-0.1222	-0.2772	-0.0544
FeCNC-H_2S	2.631	1.447	1.441	-0.3036	-0.016	-0.2342	-0.0114
FeCNC-SO_2	1.821	1.735	1.830	-0.4451	-0.1575	-0.3016	-0.0788
FeCNC-C_2N_2	1.903	1.160	1.264	-0.3400	-0.0524	-0.2365	-0.0137

This shows that in the hybrid systems, there is an important effect of the basis set of a molecule on the basis set of another molecule.

So at a closer look it can be said that such an interpretation of adsorption may not be true because the interaction energy between an open nanocone with an iron atom and the toxic gas molecules is ignored. Therefore, in order to assess the basis set superposition error (BSSE) correction and its impact on the amount of energy changes during adsorption, the Boys-Bernardi counterpoise (CP) technique [25] was used. The quantities of absorbed energy with respect to interaction energy, named corrected adsorption energy, are listed in Table 1. In addition, the difference between corrected adsorption energy $E^{*(1)}$ and $E^{*(2)}$ is less than the difference between uncorrected adsorption energy $E^{(1)}$ and $E^{(2)}$ for each of the systems. So, based on the interaction energy between open nanocone, iron atom and toxic gases, the chlorine molecule has maximum adsorption (Fig. 2).

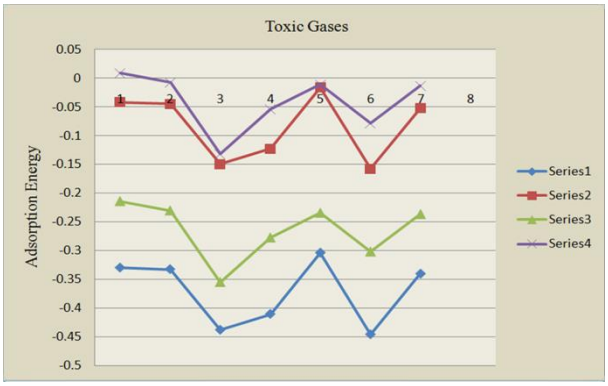

Fig. 2. Uncorrected adsorption energy $E^{(1)}$ (series 1), $E^{(2)}$ (series 2) and corrected adsorption energy $E^{*(1)}$ (series 3), $E^{*(2)}$ (series 4): *(1) FeCNC-CO (2) FeCNC-CO_2 (3) FeCNC-Cl_2 (4) FeCNC-$COCl_2$ (5) FeCNC-H_2S (6) FeCNC-SO_2 (7) FeCNC-C_2N_2*

After adsorption by FeCNC, bond lengths of toxic gas molecules were also changed, as indicated in Table 1. Unlike other toxic gases it was observed that the bond length of hydrogen sulfide was reduced in consequence of its adsorption by FeCNC, which was consistent with the calculated results.

CONCLUSIONS

In this study the structure of open nanocone coupled with an iron atom was investigated and its impact on the adsorption of some of the toxic gases in the air was assessed. The values of the uncorrected and corrected adsorption energy of the molecules of the toxic gases and the FeCNC were compared. Results showed that in the hybrid systems, there is an important effect of the basis set of a molecule on the basis set of another molecule. It was found that the adsorption of chlorine gas by FeCNC is better than that of other toxic gases while carbon monoxide has the lowest adsorption among other gases.

REFERENCES

1. Iijima, S: Helical microtubules of graphitic carbon. *Nature* **354**, 56–*58 (*1991*).*
2. Reich, S, Thomsen, C, Maultzsch, J: Carbon Nanotubes Basic Concepts and Physical Properties, Wiley-VCH Verlag GmbH and Co., KGaA, Weinheim, 2004.
3. Dresselhaus, MS, G, Dresselhaus, Eklund, PC: *Science* of Fullerenes and Carbon Nanotubes; Academic Press: New York (1996).
4. Jalili, S, Majidi, R: The Effect of Gas Adsorption on Carbon Nanotubes Properties: *J. Comput. Theor. Nanosci.* **3**, *664*–669 (*2*006*).*
5. T. Baei, M, Ahmadi Peyghan, A, Bagheri, Z, Bigdeli Tabar,M: B-doping makes the carbon nanocones sensitive towards NO molecules. *Phys. Lett.* A **377**, 107-111(2012).
6. Bagheri, Z, Ahmadi Peyghan, A: DFT study of NO2 adsorption on the AlN nanocones. *Comput. Theor. Chem.* **1008**, 20-26(2013).
7. Kuznetsova, A, Yates Jr, JT, Liu, J, Smalley, RE: Physical adsorption of xenon in open single walled carbon nanotubes: Observation of a quasi-one-dimensional confined Xe phase. *J. Chem. Phys*. **112**, 9590-9598 (2000).
8. Babaa, MR, Stepanek, I, Masenelli-Varlot, K, Dupont-Pavlovsky, N, McRae, E, Bernier, P: Opening of single-walled carbon nanotubes: evidence given by krypton and xenon adsorption. *Surf. Sci*. **531**, 86-*92 (*2003*).*
9. Simonyan, VV, Johnson, JK, Kuznetsova, A, Yates Jr, JT: Molecular simulation of xenon adsorption on single-walled carbon nanotubes, *J. Chem. Phys.* **114**, 4180-*4185 (*2001*).*
10. Talapatra, S, Zambrano, AZ, Weber, SE, Migone, AD: Gases do not adsorb in the interstitial channels of SWNT bundles. *Phys. Rev. Lett*. ***85***, 138-145 *(*2000*).*
11. Jalili, S, Majidi, R: Study of Xe and Kr adsorption on open single-walled carbon nanotubes using molecular dynamics simulations. *Physica E* **39**, 166-170 (2007).
12. Gordillo, MC, Brualla, L, Fantoni, S: Neon Adsorbed in Carbon Nanotube Bundles. *Phys. Rev. B* **70**, 245420-245427 (2004).
13. Rols, S, Johnson, MR, Zeppenfeld, D, Bienfait, M, Vilches, OE, Schneble, J: Argon adsorption in open-ended single-wall carbon nanotubes. *Phys. Rev. B* **71**,155411-155419 (2005).
14. Teizer, W, Hallock, RB, Dujardin, E, Ebbesen, TW: He Desorption from Singel Wall Carbon Nanotubes Bundles: A 1-dimensional Adsorbate, *Phys. Rev. Lett*. **82**, 5305-8 (1999)
15. Teizer, W, Hallock, RB, Dujardin, E, Ebbesen, TW: He Desorption from Single Wall Carbon Nanotube Bundles: A One-Dimensional Adsorbate, *Phys. Rev. Lett*. **84**,1844–1845 (2000)
16. Maddox, MW, Gubbins,KE: A molecular simulation study of freezing/melting phenomena for Lennard-Jones methane in cylindrical nanoscale pores, *J. Chem. Phys*. **107**, 9659-9668 (1997).
17. Cao, D, Zhang, X, Chen, J, Wang, W, Yun, J: Optimization of single-walled carbon nanotube arrays for methane storage at room temperature, *J. Phys. Chem. B* **107**, 13286-13292 (2003).
18. Iijima, S, Ichihashi, T, Ando, Y: Pentagons, heptagons and negative curvature in graphite microtubule growth, *Nature* **356**, 776-778 (1992).
19. Iijima, S, Ichihashi, T: Single-shell carbon nanotubes of 1-nm diameter, *Nature* **363**, 603- 605 (1993) .
20. Ge, M, Sattler, K: Observation of Fullerene Cones, Chem. Phys. Lett. **220**, 192-196 (1994).

21. Yudasaka, M, Iijima, S, Crespi, VH: Single-wall carbon nanohorns and nanocones, *Appl. Phys.* **111**, 605-629 (2008).
22. Bourgeois, L, Band, Y, Han, WQ, Sato, T: Structure of boron nitride nanoscale cones: ordered stacking of 240° and 300° disclinations, *Phys. Rev. B* **61**, 7686-7691 (2000).
23. Krishnan, A, Dujardin, E, Treacy, MMJ, Hugdahl, J, Lynum, S, Ebbesen, TW: Graphitic cones and the nucleation of curved carbon surfaces, *Nature* **388**, 451-454 (1997).
24. Dillon, AC, Jones, KM, Bekkedahl, TA, Kiang, CH, Bethune, DS, Heben, MJ: Storage of hydrogen in single-walled carbon nanotubes, *Nature* **386**, 377-379 (1997).
25. Boys, SB, Bernardi, F: The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced error , *Mol. Phys*. **19**, 553-566 (1970).
26. Frisch, MJ, Trucks, GW, Schlegel, HB, Scuseria, GE, Robb, MA, Cheeseman, JR, Montgomery Jr, JA, Stratmann, RE, Burant, JC, Dapprich, S, Millam, JM, Daniels, AD, Kudin, KN, Strain, MC, Farkas, O, Tomasi, J, Barone, V, Cossi, M, Cammi, R, Mennucci, B, Pomelli, C, Adamo, C, Clifford, SO, Chterski, J, Petersson, GA, Ayala, PY, Cui, Q, Morokuma, K, Malick, DK, Rabuck, AD, et al.: Gaussian 98. Gaussian Inc., Pittsburgh, PA (1998)
27. GaussView 03, Revision 3.07, Gaussian, Inc., Wallingford, CT (2006).
28. Becke, AD: Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys*. **98**, 5648–5652 (1993).
29. Lee, C, Yang, W, Parr, RG: Development of the Colle-Salvetti conelation energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785–789 (1988).
30. Hay, PJ, Wadt, WR: Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **82**, 299–310 (1985).
31. Svensson, M, Humbel, S, Froese, RDJ, Matsubara, T, Sieber, S, Morokuma, K: The IMOMO method: integration of different levels of molecular orbital, *J. Phys. Chem.* **100**, 19357–19363 (1996).

АДСОРБЦИЯ НА ТОКСИЧНИ ГАЗОВЕ С ОТВОРЕН НАНОКОНУС СВЪРЗАН С ЖЕЛЕЗЕН АТОМ

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Постъпила на 25 октомври 2013 г.; коригирана на 13 януари, 2014 г.

(Резюме)

Използвани са изчисления по теорията плътностния функционал (DFT) за изследването на адсорбцията на някои токсични газове от въздуха в отворен наноконус с включен железен атом (FeCNC). BSSE (множеството от суперпосиционните грешки) е включено при оптимизацията на геометрията за всички системи. Резултатите показват, че ефектът на включване на противовесна корекция при оптимизацията е много важен при адсорбцията на токсични газове в FeCNC.