DOI: 10.17344/acsi.2016.2702 Acta Chim. Slov. 2017, 64, 40–44

Scientific paper

Computational Investigation of the Dissociative Adsorption of Dichloroacetylene (C_2Cl_2) on N Functionalized Carbon and Carbon Germanium (CGe) Nanocone Sheets in the Gas Phase and Dimethyl Sulfoxide

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Received: 25-06-2016

Abstract

The possibility of dichloroacetylene-sensing on carbon nanocone sheet and carbon germanium nanocone sheet surfaces has been investigated. The effects of nitrogen functionalization and dimethyl sulfoxide on the adsorption of dichloroacetylene gas on carbon nanocone sheet and carbon germanium nanocone sheet surfaces were investigated. Results reveal that adsorption of dichloroacetylene on studied nanocone sheets were exothermic. Results show that, adsorption energy value of dichloroacetylene on carbon germanium nanocone sheet surface were more negative than corresponding values of carbon nanocone sheet. Results reveal that, N functionalization and dimethyl sulfoxide, increase and decrease the absolute adsorption energy value of dichloroacetylene on studied nanocone sheets, respectively. These results show that, there were good linearity dependencies between adsorption energy and orbital energy values of studied nanocone sheets.

Keywords: COSMO, DMSO, nanocone sheet, C_2Cl_2, sensor

1. Introduction

Dichloroacetylene is an oily pyrophoric chemical compound with the chemical formula C_2Cl_2. The compound is volatile at standard temperature and pressure and explodes on contact with air. It is a toxic compound.[1–3] It displays nephrotoxic effects to rats, but not to humans. It can be made from the compound trichloroethylene.[1–3] The most common effect that the compound has on humans is the development of disorders.[1–3]

These disorders can persist for any amount of time between a number of days and a number of years. Exposure to the chemical can also cause a large range of other symptoms, including a headache, vomiting and nausea, jaw pain, cranial nerve palsy, appetite loss and acute lung edema. C_2Cl_2 level of carcinogenetic in humans is not classifiable, although there are small amounts of evidence that suggest that the chemical is carcinogenic in animals.[4,5]

Studies on male rats and rabbits have shown that inhalation of C_2Cl_2 can cause tubular necrosis, focal necrosis, and other nephrotoxic effects.[6,7] Additionally, the rabbits that were given C_2Cl_2 experienced hepatotoxic and neuropath logical effects. Inhalation of C_2Cl_2 also causes benign tumors of the livers and kidneys of rats. The chemical increase the incidences of lymphomas.[9–10]

In recent years, Carbon nanocone sheet (C-NCS) and their functionalized derivatives as gas toxic sensors have been used, widely. In addition to C-NCS, there are other nanocone sheets which are found experimentally such as carbon germanium nanocone sheets (CGe-NCS).[11–19] In the current study, the interactions of C_2Cl_2 gas with C-NCS and CGe-NCS with disclination angles of 240° exploring its potential application as C_2Cl_2 gas sensor will be theoretically investigated. The N functionalization of nanostructures is very important and it can effectively change the electronic structures of nanostructures.[19,20]

Ibrahim and et al.[21] in previous study, polymerization of aniline by Cu (II) montmorillonite studied using attenuated total reflection Fourier-transform infrared

(ATR-FTIR) spectroscopy. Also experimental spectra were compared with that calculated by AM1, PM3, PM5, MINDO, Hartree-Fock, HF/6-31G(d), as well as Density Functional Theory, BLYP/DZVP and B3LYP/6-31g(d,p). Ibrahim and et al.[22] used Density functional theory (DFT) to investigate both the structure and vibrational frequencies of acetate group. A model of B3LYP with four basis set was used to optimize and locate the energy minimum of the acetic acid molecule. Ibrahim and et al.[23] studied molecular structure of gelatin by using Fourier transform infrared spectroscopy FTIR. The spectrum was subjected to deconvolution in order to elucidate the constituents of the molecular structure. Ibrahim and et al.[24] promised nanomaterials in the field of optical sensors due to their unique properties. Emeraldine base of polyaniline (Nano EB-PANI) was prepared, characterized and applied as an optical formaldehyde sensor.

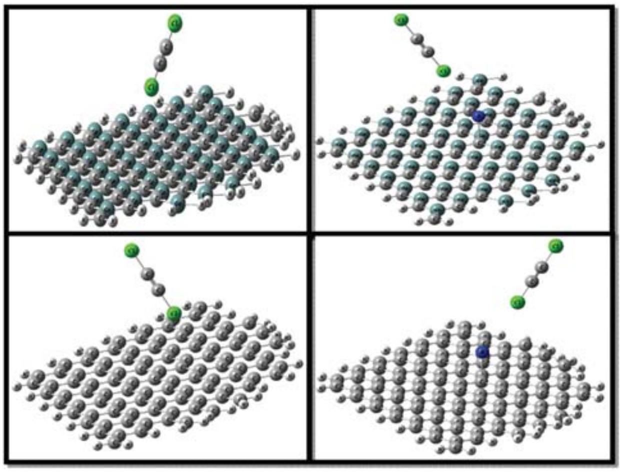

Figure 1. Complexes of C_2Cl_2 with C-NCS, CGe-NCS, N-C-NCS and N-CGe-NCS.

In previous study, Warshel and et al.[25] utilized computer simulations to elucidate the true molecular basis for the experimentally observed effect. They start by reproducing the trend in the measured change in catalysis upon mutations. They discuss the role of flexibility and conformational dynamics in catalysis, once again demonstrating that their role is negligible and that the largest contribution to catalysis arises from electrostatic preorganization.

In previous studies, Warshel and et al.[26,27] described a general approach for exploring the energetics of different feasible models of the action of CcO, using the observed protein structure, established simulation methods and a modified Marcus' formulation. They start by reviewing our methods for evaluation of the energy diagrams for different proton translocation paths and then present a systematic analysis of various constraints that should be imposed on any energy diagram for the pumping process.

In previous study, Warshel and et al.[28] considered the current state of simulations of electrostatic energies in macromolecules as well as the early developments of this field. They focused on the relationship between microscopic and macroscopic models, considering the convergence problems of the microscopic models and the fact that the dielectric 'constants' in semimacroscopic models depend on the definition and the specific treatment.

In previous study, Warshel and et al.[29] described application of the calculated geometry and vibrations to the analysis of vibronic structure. A preliminary account of the use of observed vibronic structure for determination of the geometry of excited electronic states was given.

In previous study,[30] it be observed that the predominant initiation reaction for oxidation of methane, propene, and o-xylene under fuel lean conditions involved hydrogen abstraction of the methyl hydrogen by molecular oxygen forming hydroperoxyl and hydrocarbon radical species.

The study of adsorption of toxic gas on the solid surface of nanostructures in order to identify the suitable sensor to remove or reduce the toxic gas are important in environmental issue. C_2Cl_2 has a toxic effect on humans who are exposed to it.

Therefore adsorption C_2Cl_2 by nano structures is important and fundamental objects of present paper are: (1) to investigate the C_2Cl_2 adsorption on C-NCS and CGe-NCS surfaces; (2) to compare the C_2Cl_2 adsorption ability of C-NCS and CGe-NCS; (3) to identify the effect of N functionalization of studied C-NCSs and CGe-NCSs on adsorption of C_2Cl_2; (4) to explore how the solvent alter the C_2Cl_2 adsorption on studied C-NCS and CGe-NCS surfaces; (5) To find the C-NCS and CGe-NCS with highly effective detection of C_2Cl_2.

2. Computational Details

In this paper, structure of C-NCS (constructed of 108 C atoms) and CGe-NCS (constructed of 54 C and 54 Ge atoms) with disclination angles of 240° and their N functionalized derivatives were geometry optimized in the gas phase and solvent. Also the structure of complexes of studied C-NCSs and CGe-NCSs with C_2Cl_2 molecule were geometry optimized in gas phase and solvent (structures were shown in figure 1). In order to avoid boundary effects, atoms at the open ends of the studied C-NCSs and CGe-NCSs were saturated with hydrogen atoms.[19] All the calculations were performed using the DFT/B3LYP method and 6-31G(d,p) basis set within the GAMESS package.[19,31,32]

Also, harmonic vibrational frequencies have been calculated, enabling us to confirm the real minima. Solvation effects were included through the use of the polarized continuum model (PCM).[19,33] The B3LYP is a reliable and common used level of theory in the study of different nanostructures.[19,34–36] A dielectric constant of 46.7 was used corresponding to that for dimethyl sulfoxide (DMSO) as the solvent.

The adsorption energy (E_{ad}) of C_2Cl_2 molecule on the C-NCS and CGe-NCS is obtained using the following equation:

$$E_{ad} = E\ (\text{nanocone sheet}/C_2Cl_2) - E\ (\text{nanocone sheet}) - E\ (C_2Cl_2) + E_{BSSE} \quad (1)$$

where E(nanocone sheet/C_2Cl_2) is the energy of C-NCS or CGe-NCS–C_2Cl_2 complex, and E(nanocone sheet) and E(C_2Cl_2) are referred to the energies of C-NCS or CGe-NCS and C_2Cl_2 molecule, respectively. The negative value of E_{ad} indicates the exothermic specificity of the adsorption. The basis set superposition error (BSSE) has been corrected for all of the interactions.[37]

3. Results and Discussion

3. 1. The Ead values of C_2Cl_2 Gas on Studied Nanocone Sheet Surfaces in Gas Phase and DMSO

The calculated E_{ad} values of C_2Cl_2 gas on C-NCS and CGe-NCS and their N functionalized derivatives (N-C-NCS and N-CGe-NCS) in gas phase and DMSO were reported in the table 1. Results in table 1 show that, the E_{ad} values of C_2Cl_2 on C-NCS and CGe-NCS in gas phase were –3.13 and –3.48 eV, respectively. Also the E_{ad} values of C_2Cl_2 on C-NCS and CGe-NCS in DMSO are –2.94 and –3.25 eV, respectively.

Results in table 1 show that, the E_{ad} values of C_2Cl_2 on N-C-NCS in gas phase and DMSO were –3.66 and –3.48 eV, respectively. Also the E_{ad} values of C_2Cl_2 on N-CGe-NCS in gas phase and DMSO were –4.06 and –3.87 eV, respectively.

Results reveal that, N functionalization of C-NCS increase the absolute E_{ad} values of C_2Cl_2 in comparison to C-NCS ca 0.53 and 0.54 eV in gas phase and DMSO, respectively. Results indicated that, DMSO decrease the absolute E_{ad} values of C_2Cl_2 on N-C-NCS and N-CGe-NCS in comparison to gas phase ca 0.18 and 0.19 eV, respectively.

Results indicate that the absolute E_{ad} values of the C_2Cl_2 on studied nanocone sheets decreased in the following order in gas phase and DMSO: C-NCS < N-C-NCS < CGe-NCS < N-CGe-NCS. In according to obtained E_{ad} values of C_2Cl_2 on studied nanocone sheet surfaces in gas phase and DMSO, it can be concluded that N-CGe-NCS and C-NCS have higher and lower ability to adsorption of C_2Cl_2, respectively.

Table 1. Calculated E_{ad} (in eV) of C_2Cl_2 on C-NCS, CGe-NCS, N-C-NCS and N-CGe-NCS surfaces in gas phase and DMSO.

DMSO	Gas phase	Nanostructure
–2.94	–3.13	C-NCS
–3.25	–3.48	CGe-NCS
–3.48	–3.66	N-C-NCS
–3.87	–4.06	N-CGe-NCS

These results in this section can be interpreted with a known fact that Ge atoms in studied CGe-NCS stabilize the CGe-NCS and their C_2Cl_2-CGe-NCS complexes; hence, these results in increased absolute E_{ad} in comparison to studied C-NCS in gas phase, DMSO.[19]

Also results show that in compare to gas phase, DMSO attenuate the absolute E_{ad} values of C_2Cl_2 on studied nanocone sheet surfaces ca 0.197 eV. Fundamental reason for decrease in absolute E_{ad} values in DMSO, could be an unequal stabilization/destabilization of the studied nanocone sheets and their complexes with C_2Cl_2 in DMSO.[19]

Therefore results in this study show that, the N-CGe-NCS and C-NCS have the most and less absolute E_{ad} values of C_2Cl_2 on studied nanocone sheet surfaces.

3. 2. The E_{HOMO} and E_{LUMO} of Studied Nanocone Sheets

In this work the E_{HOMO}, E_{LUMO} and E_{HLG} values of C-NCS and CGe-NCS and their N functionalized derivatives were calculated and reported in table 2. In this section the dependencies of between E_{ad} corresponding E_{HOMO}, E_{LUMO} and E_{HLG} values of studied nanocone sheets were investigated.

Results show that, calculated E_{HOMO} values of studied nanocone sheets range from –5.58 to –6.12 eV. Therefore obtained absolute E_{HOMO} values of studied nanocone sheets show that the N-CGe-NCS and C-NCS have higher and lower tendency to lose electron, respectively.[19]

Results reveal that, calculated E_{LUMO} values of studied nanocone sheets range from –3.57 to –3.94 eV. Therefore obtained E_{LUMO} values of studied nanocone sheets show that the N-CGe-NCS and C-NCS have higher and lower capacity to accept electrons, respectively. [19]

Results indicated that, calculated E_{HLG} values of studied nanocone sheets range from 1.64 to 2.55 eV. Therefore E_{HLG} values of studied nanocone sheets show that the N-CGe-NCS have lower stability and higher reactivity and C-NCS have lower reactivity.[19]

In according to obtained results in table 2, it can be concluded that N functionalization of C-NCS and CGe-NCS increase the absolute E_{LUMO} values and decrease the absolute E_{HOMO} and E_{HLG} values in comparison to C-NCS and CGe-NCS. The computed E_{ad} values of C_2Cl_2 on studied nanocone sheet surfaces are corrected against corresponding calculated E_{HOMO}, E_{LUMO} and E_{HLG} values of studied nanocone sheets. Equations obtained from the linear regression are as follows:

$$E_{ad} = -1.71 \times (E_{HOMO}) - 13.54 \quad (2)$$

$$E_{ad} = 2.49 \times (E_{HOMO}) + 5.72 \quad (3)$$

$$E_{ad} = 1.03 \times (E_{HLG}) - 5.74 \quad (4)$$

The correlation coefficients of equations 2, 3 and 4 reached ca 0.985, 0.992 and 0.990, respectively. These results show that, there are good linearity dependencies between E_{ad} and orbital energy (E_{HOMO}, E_{LUMO} and E_{HLG}) values of studied nanocone sheets. This can be useful in the selection of suitable nanocone sheets with enhanced C_2Cl_2 adsorption potential.[19]

As mentioned in tables 1 and 2, this can be concluded the calculated E_{ad} and orbital energy scales have same trends for averment C_2Cl_2 adsorption potential of studied nanocone sheets. Therefore results in this study, reveal that N-CGe-NCS has highest and C-NCS has lowest C_2Cl_2 adsorption potential among studied nanocone sheets.[19]

Table 2. Calculated E_{HOMO} (in eV), E_{LUMO} (in eV) and E_{HLG} (in eV) of C-NCS, CGe-NCS, N-C-NCS and N-CGe-NCS.

E_{HLG}	E_{LUMO}	E_{HOMO}	Nanostructure
2.55	–3.57	–6.12	C-NCS
2.16	–3.69	–5.85	CGe-NCS
2.03	–3.74	–5.77	N-C-NCS
1.64	–3.94	–5.58	N-CGe-NCS

Finally higher absolute E_{ad} and E_{LUMO} values and lower E_{HOMO} and E_{HLG} values for studied nanocone sheets are appropriate benchmarks to approval the C_2Cl_2 adsorption potential. Therefore it can be concluded the E_{ad}, E_{HOMO}, E_{LUMO} and E_{HLG} values of studied nanocone sheets can consider as important parameters to predicate and propose suitable nanocone sheets with enhanced C_2Cl_2 adsorption potential. [19]

4. Conclusion

In this study the E_{ad} values of C_2Cl_2 gas on C-NCS and CGe-NCS surfaces in gas phase were investigated using density functional theory calculations. The effects of N functionalization and DMSO on the adsorption of C_2Cl_2 gas on C-NCS and CGe-NCS surfaces were investigated. Results reveal that adsorptions of C_2Cl_2 on studied nanocone sheets were exothermic and experimentally possible from the energetic viewpoint. Results show that, E_{ad} value of C_2Cl_2 on CGe-NCS surface are more negative than corresponding values of C-NCS. Results reveal that, N functionalization and DMSO causing an increase and decrease the absolute E_{ad} values of C_2Cl_2 on studied nanocone sheets, respectively. Results show that, there are good linearity dependencies between E_{ad} and orbital energy values of studied nanocone sheets. Therefore it can be concluded the E_{ad} and orbital energy values of studied nanocone sheets can consider as important parameters to propose suitable nanocone sheets with enhanced C_2Cl_2 adsorption potential.

5. Acknowledgment

Thank colleagues for their valuable discussion on the computational affairs.

6. Abbreviations

HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), HLG (HOMO–LUMO gap), DFT (density functional theory), B3LYP (Becke 3-parameter Lee, Yang and Parr), DMSO (dimethyl sulfoxide), C-NCS (carbon nanocone sheet), CGe-NCS (carbon germanium nanocone sheet) and polarized continuum model (PCM), BSSE (basis set superposition error).

7. References

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Povzetek

S pomočjo funkcionalno gostotne teorije v plinski fazi smo proučevali možnost zaznavanja C_2Cl_2 na C-NCS in CGe-NCS površinah. Proučevali smo tudi učinke N funkcionalizacije in DMSO na adsorpcijo C_2Cl_2 na teh površinah. Rezultati kažejo, da je adsorpcija C_2Cl_2 na površini nanstožcev eksotermna in z energetskega vidika možna. Energija adsorpcije, E_{ad}, C_2Cl_2 na CGe-NCS površini je bolj negativna od E_{ad} na C-NCS. Izkazalo se je, da N funkcionalizacija povzroči zvišanje in DMSO znižanje absolutne vrednosti E_{ad} C_2Cl_2 na proučevane nanostožce. Dokazali smo tudi linearno zvezo med E_{ad} in orbitalnimi energijami nanostožcev.