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Investigation of N-doped Graphene as an Absorbent for some Gases: A DFT Study

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ABSTRACT: At the present theoretical study, DFT calculations were performed for elucidating the reaction, absorption energy and the quantum molecular descriptors including electronic chemical potential, chemical hardness, Homo, Lumo, band gap energy (E_g) and finding the most active nitrogen-doped graphene sheet (N-G) for absorption H_2S, CH_4, N_2 and CO_2 gases. Finally it found that nitrogen-doped graphene absorbs most of the H_2S gas.

Keywords: *DFT, Different Properties, Nitrogen-doped graphene sheet, Some gases.*

INTRODUCTION

Since the development of waste-derived nanoporous carbon, especially from petroleum wastes, as a challenging type of contaminants, has drawn tremendous attention during the past decade [1]. In the meantime, using Computational methods in materials design can lead to significant progresses toward optimization of novel responsive adsorbents and sensors. Density functional theory (DFT) calculations are useful for studying various catalysts and adsorbents evaluating interactions between different catalytic sites and gas molecules in selective oxidation reaction [2-5]. DFT studies could also provide insights on the interactions between different gas molecules and nitrogen-doped graphene sheet, thereby elucidating the role of various graphene sheets on the catalyst activity toward gas molecules selective adsorption.

In this regard, the DFT method based calculations has been used to investigate the adsorption mechanism of each gas on adsorbent at the molecular level. DFT calculations were performed to determine the most active atoms of nitrogen-doped graphene sheet toward CO_2, H_2S, CH_4 and N_2 selective adsorption and to provide mechanistic insights about this reaction over graphene sheet. The results of this work can provide valuable insights toward the development of tailor-made carbon-based catalysts with enhanced catalytic performance for CO_2, H_2S, CH_4 and N_2 removal applications.

Also, the prominent results can shed light on an appealing avenue in the synthesis of micro-meso porous carbon and can pave the way for mass-production of

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high value-added nanoporous carbons for industrial applications.

COMPUTATIONAL DETAILS

Methods

We want to predict interaction between N-G and some gases have been studied with DFT using b3lyp method and 6-31g basis set. All DFT calculations were performed using Gaussian software.

RESULTS AND DISCUSSION

In the DFT calculations, initially the structures of pristine nitrogen-doped graphene sheet and gas molecules (CO_2, H_2S, CH_4 and N_2) were optimized. Activity of different gas molecules on nitrogen-doped graphene sheet were then evaluated based on quantum mechanical methods. Optimized structures of CO_2, H_2S, CH_4 and N_2 adsorbed on nitrogen-doped graphene sheet are shown in Fig. 1.

According to our DFT analysis (as shown in Table 1), the higher activity of H_2S toward N-G selective absorption can be attributed to this capability in H_2S dissociation. Also, based on the obtained quantum molecular descriptors, the proposed N-G shows a good selectivity for absorption gases. From Eg calculations, it can be seen that Eg are decreased in the order: N-G to H_2S > N-G to CO_2> N-G to N_2> N-G to CH_4. Decrease of Eg promise more stable compound. So, N-G beside the CH_4 can act as a better electron donor to higher electrical conductivity. Finally it is predicted that the N-G was determined as the most active phases

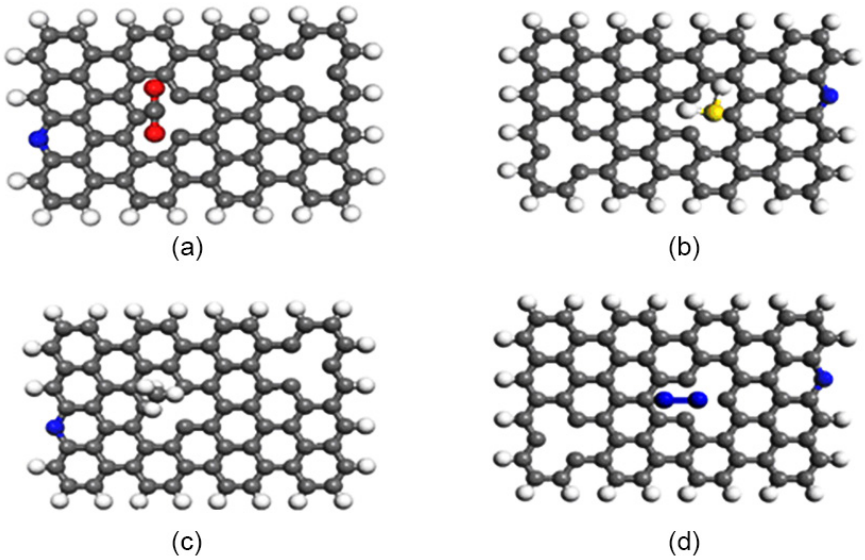

Fig. 1. Geometries of a) CO_2, b) H_2S, c) CH_4 and d) N_2 adsorbed on nitrogen-doped graphene sheet.

Table 1. Energetics of H_2S, N_2, CO_2 and CH_4 adsorbed on N-G, obtained from DFT calculations.

Properties	N-G to H_2S	N-G to CO_2	N-G to CH_4	N-G to N_2
Interaction Energy (kcal/mol)	-95.5055	-94.9407	-90.4227	-90.7985
E_{Lumo} (eV)	-1.4682	-1.3429	-1.3483	-1.2963
E_{Homo} (eV)	-5.8130	-5.6713	-5.6441	-5.6032
E_g (eV)	4.3447	4.3257	4.2957	4.3085
Chemical Hardness (eV)	3.6406	3.5071	3.0736	3.4506
Chemical Potential (eV)	2.1710	2.1628	2.1465	2.1541

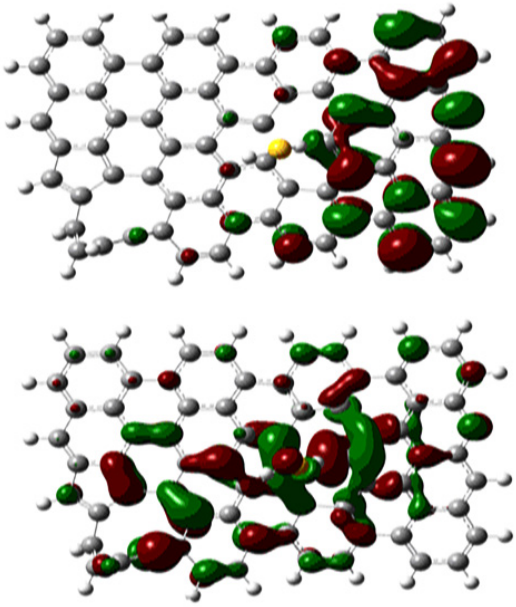

Fig. 2. The frontier molecular orbitals of the modeled Nitrogen-doped graphene sheet unit structure (Upper image shows the LUMO orbitals and bottom image presents the HOMO molecules).

toward H_2S adsorption.

Chemical hardness and chemical potential of the proposed structures were also calculated. Chemical hardness of all the samples the nitrogen-doped graphene are in the same range. However, nitrogen-doped graphene sheet to H_2S possesses the most chemical hardness indicating that nitrogen-doped graphene sheet interaction with H_2S is harder than the others. So, the increase in global hardness and energy gap suggest the increasing of stability and decrease reactivity of the H_2S/nitrogen-doped graphene sheet complex. The same trend is observed for chemical potential of the modelled structures where nitrogen-doped graphene sheet to H_2S provides the highest chemical potential and nitrogen-doped graphene sheet interaction with CH_4 shows the lowest. In the gas molecules (CO2, H_2S, CH_4 and N_2)/nitrogen-doped graphene sheet complex, ΔN values are positive, indicating that the gas molecules act as electron acceptor. In general, as previously stated in the in the literature [6], interaction energy is considered as the determining factor related to the complex activity. Structure and frontier orbitals of the modeled Nitrogen-doped graphene sheet are shown in Fig. 2. The band gap of the modeled Nitrogen-doped graphene sheet unit was 3.7373 which was increased to 4.3447 by adding the H_2S molecules indicating that the during the H_2S adsorption process, the conductivity of the Nitrogen-doped graphene sheet decreases.

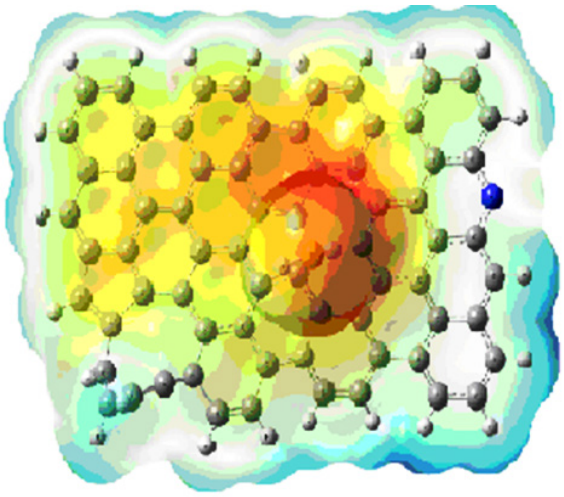

Fig. 3. The molecular electrostatic potential (MEP) of the nitrogen-doped graphene sheet and H_2S.

In addition, the Molecular Electrostatic Potential (MEP) is shown for Nitrogen-doped graphene sheet and H_2S which represents information about the potential of all nuclei and electrons in these structures. As shown in Fig. 3. Various colors are assigned to different values of electrostatic potentials in which the red color is related to the attraction of proton and the blue color indicates the repulsion of the electrons. In order to investigate the electrostatic potential of each atom, the transparent MEP is shown for nitrogen-doped graphene sheet and H_2S.

CONCLUSIONS

CO_2, H_2S, CH_4 and N_2 selective adsorption was studied via DFT calculations. According to the DFT calculations, it was observed that the most active phases of nitrogen-doped graphene sheet toward H_2S selective adsorption. The dissociation of H_2S which is an important step in catalytic oxidation of H_2S occurs more preferably on nitrogen-doped graphene sheet. These results imply that nitrogen-doped graphene sheet which has not been considered experimentally for H_2S adsorption, can be used for efficient adsorption and removal of H_2S.

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