Applying the B_{12}N_{12} nanoparticle as the CO, CO\textsubscript{2}, H\textsubscript{2}O and NH\textsubscript{3} sensor

Rubabeh Rostamoghli\textsuperscript{a}, Mahshad Vakili\textsuperscript{b}, Alireza Banaei\textsuperscript{a, *}, Eslam Pourbashir \textsuperscript{a}, Khadadad Jalalierad \textsuperscript{a}

\textsuperscript{a} Department of Science, Payame Noor University, P. O. Box: 19395-4697 Tehran, Iran
\textsuperscript{b} Young Researchers and Elite club, Miyaneh Branch, Islamic Azad University, Miyaneh, Iran

ABSTRACT

In this study, the various properties including the stability energies, structural and electronic aspects of the hydrazine (N\textsubscript{2}H\textsubscript{4}), carbon monoxide (CO) water (H\textsubscript{2}O) and ammonia (NH\textsubscript{3}) molecules adsorptions on the top of the boron nitride nanoparticles (BNn) were studied through the Minnesota Functionals computations, DFT/M06-2X. The calculations clarifies that the most stable adsorption configurations are those in which the oxygen, carbon, oxygen and nitrogen atoms of CO\textsubscript{2}, CO, H\textsubscript{2}O and NH\textsubscript{3} are closed to the boron atom of the nanoparticle, respectively. The absorption energies were obtained about -0.14, -0.15, -0.87 and -1.54 eV for absorption of CO\textsubscript{2}, CO, H\textsubscript{2}O and NH\textsubscript{3} gasses. The geometry optimizations, energy calculations and NBO charge transfer were used to evaluate the sensing ability of BNn for different analytes. The computed density of states (DOS) clarifies that a strong orbital hybridization take place between CO\textsubscript{2}, CO, H\textsubscript{2}O and NH\textsubscript{3} and BNn in adsorption process. Finally, it is concluded that the BNn nanoparticle has greater response selectivity toward NH\textsubscript{3} compared to CO, CO\textsubscript{2} and H\textsubscript{2}O.

Keywords

carbon monoxide, carbon dioxide, water, ammonia, BNn, M06-2X

1. Introduction

Boron is one of the very interesting elements in the periodic Table. Pure boron molecules are intermediate compounds between the materials with purely nonmetallic and metallic characteristics. This feature results into high chemical flexibility of boron rich molecules and it motives many researchers to search the ground-state geometries of boron rich molecules and reveal their unique characteristics [1-8].During the last decade, various experimental and theoretical efforts have been devoted to found the fullerene-like structures which formed of non-carbon elements [1–6]. In particular, the non-carbon elements in periodic table from III to V have been extensively applied in the fullerene-like cage and nanotube [7–13]. Especially, the group III nitrides have considerable importance to the science and technology aspects [14–16]. Boron nitride (BN) nanostructures such as nanotubes [17], nanocapsules [18] and electronic industry [19] have received much attention. The boron nitride nanostructures either nanocage or nanotubes are important due to their having temperature stability, high thermal conductivity and high resistance [17, 20–22]. The polar characer of the B–N bonds in the boron nitride nanoparticles leads to a higher reactivity than their carbon homologues. In addition, the considerable charge difference between the nitrogen and boron atoms, the boron and nitrogen atoms can play as a Lewis acid and base role, respectively. Therefore, we can conclude that the boron nitride nanoparticles can be regarded as a non-metal catalyst. In the boron nitride category, B\textsubscript{12}N\textsubscript{12} (BNn) was reported to be the smallest stable nanocage particles. Recently, the scrutiny of the poisonous gasses is of the most importance in both industrial and living environments [24–27]. The presence of gases like carbon monoxide, carbon dioxide, nitrogen oxides and ammonia at any concentrations are damaging in the living environments. In the present research, we investigate the interactions between carbon monoxide (CO) carbon dioxide (CO\textsubscript{2}), water (H\textsubscript{2}O) and ammonia (NH\textsubscript{3}) molecules and the BNn nanoparticle using M06-2X calculations. Evaluation of these gases is the basic function of the gas sensors [28]. The main purpose ofhis research is to obtain the fundamental outlooks into the efficacy of adsorbed gasses on the electronic
aspects of the nanoparticles. The most valuable efforts are to use these effects to design more sensitive gas sensing devices.

2. Computational details

The theoretical calculations on the CO, CO₂, H₂O and NH₃ gases and their complexes with BNₙ including CO₂–BNₙ or HₓX–BNₙ systems were carried out using a hybrid functional closed-shell M06-2X and 6-31+G** basis set, employing the Gaussian program pakage [16]. All the calculations were carried out in the gas phase under 1 atm pressure and 298K temperature. The frequency calculations were performed at the mentioned level. No any pure imaginary frequency was obtained for the ground state at the same level of theory. Theoretical studies [17,18] proposed that the M06-2X method can give the best results to compute the absorption energies, strength of noncovalent interactions, and thermochemistry properties. The adsorption energies (E_{ad}) of the systems were computed using the M06-2X/6-31+G** level of theory. The E_{ad} was obtained via differences between the total energies of the CO₂–BNₙ or HₓX–BNₙ systems and the energies of each monomer. The interaction energies were corrected for the basis set superposition error (BSSE) in all the complexes using the full counterpoise method [19]. The density of states (DOS), molecular electrostatic potential surface (MEP) and frontier molecular orbital analyses were calculated and presented using the M06-2X/6-31+G* level of theory.

3. Results and discussion

3.1. Adsorptions in the COn–BNₙ (n = 1 and 2) or HnX–BNₙ (n = 2 and 3) systems

The fully optimized structure of isolated BNₙ nanoparticle is presented in Fig. 1a. The bond length of B–N shared between two six-membered rings is about 1.48 Å and that is shared between a four-membered ring and a six-membered rings is 1.43 Å. The calculated HOMO-LUMO gap energy (E_g) of pure BNₙ nanoparticle is to be about 9.15 eV, showing an insulator character. As shown in Fig. 3a, the HOMO and LUMO orbitals of pure BNₙ are localized on the N and B atoms, respectively. Thus, the electron deficient boron atoms can be regarded as a Lewis acid, whereas the electron-rich nitrogen atoms play the role of a Lewis base. These are consistent with the results obtained in Ahmadi et al. studies [36]. Because of the large difference in electronegativity between B and N, ionic bonding is predominant in the BNₙ nanoparticles. This can be seen from the surface electrostatic potentials (Fig. 2), where N sites receive electrons from B sites, resulting in positively charged B ions. These positively charged B ions on the cage surface become the available sites for adsorption of CO₂, CO, H₂O and NH₃ molecules. Also, the negatively charged N sites seem to be appropriate for adsorption H atoms of H₂O and NH₃ molecules. The interactions between the optimized structures of the BNₙ nanoparticles and CO₂, CO, H₂O and NH₃ is shown in Fig. 1 at the M062X/6-31+G* level of calculations. The calculated equilibrium molecule–cluster distance (d_{molecule/B_N_Nₙ}), adsorption energy (E_{ad}), NBO charge transfer, HOMO and LUMO energies, HOMO-LUMO gap energy (E_g) and change of E_g (ΔE_g) for each complex are presented in Table 1.

3.1.1. Adsorption of NH₃ on the nanoparticle

After the geometry optimization of the H₃N–BNₙ complex, two stable configurations were obtained for NH₃ from its N-side and H-side close to the B and N atoms of BNₙ nanoparticle, respectively which are presented in Figs. 1b and c. The adsorption energy and equilibrium distance of NH₃ from its N-side adsorption on the boron atom of BNₙ nanoparticles is -1.54 eV and 1.62 Å, respectively. The adsorption energy and equilibrium distance for H-side of NH₃ adsorption on the nitrogen atom of cage was -0.07 eV and 2.43 Å, respectively that can be defined as a hydrogen bond (Table 1). The boron atoms of nanoparticle acts as Lewis acid site and the nitrogen atom of NH₃ molecule acts as Lewis base site. In Fig. 2, we represented electrostatic potentials at the 0.001 electrons per Bohr⁻³ isodensity surfaces of NH₃ adsorption on the BNₙ were calculated at the same level of theory with WFA surface analysis suite [37], Natural bond orbital (NBO) analysis for N-side and H-side are 0.56 and -0.01 e, respectively. The results clarify that the hydrogen bond leads to decrease in the intensity of electrons at a particular position. For molecule adsorption on the cage surface can be explained by considering the fact that the highest occupied molecular orbitals (HOMOs) of the BNₙ are centered on the N sites, and the lowest unoccupied molecular orbitals (LUMOs) are located on the B sites (Fig. 3h). The NH₃ molecule can transfer the electrons to the LUMO on the N site of the cage through the electron lone pair of nitrogen atom and also hydrogen atom of NH₃ can accept electron from HOMO on the B site of the cage (Fig. 3i). The E_g for N-side and H-side of NH₃ are 7.72 and 5.91 eV, respectively (Table 1).

3.1.2. Adsorption of H₂O on the nanoparticle

The DFT calculations on the H₂O–BNₙ complex indicate that there are two adsorption sites between the oxygen and hydrogen atoms of H₂O (O-side and H-side) and the B and N atoms of BNₙ (Fig. 1d and 1e). In the H₂O adsorption systems, the bond lengths of B–O and N–H decrease by about 1.64 and 2.07 Å, respectively, that the adsorption energy (E_{ad}) are -0.87 and -0.18 eV, respectively (see Table 1). The NBO analysis shows that the oxygen and hydrogen atoms acquire positive and negative charges, respectively. This reveals that the charge is transferred from the H₂O molecule to the cage in the B–O bond formation while the in the N–H bond
formation the charge transferred from the cage to the H$_2$O molecule (Table 1). Fig. 2 presents the molecular electrostatic potentials $V(r)$ on the surface of the BN$_n$–H$_2$O, which are computed on the 0.001 au contour of the molecule’s electronic density. The calculated HOMO-LUMO gap ($E_g$) for H$_2$O–BN$_n$ (O–B) and BN$_n$–H$_2$O (N–H) systems are 7.88 and 9.19 eV. The results clarify that the $E_g$ of H$_2$O–BN$_n$ (O–B) is significantly decreased through the adsorption process.

3.1.3. Adsorption of CO$_2$ on the nanoparticle

It is found two configurations through adsorption of CO$_2$ at top of the nanoparticle surface: (i) the carbon side (configuration d) and (ii) the oxygen side (configuration e) of CO$_2$ adsorption on the top of the boron atom of the nanoparticle (Fig. 1d and 1e). The M062X calculations indicate that the adsorption of the CO$_2$ molecule from the carbon side and oxygen side on the cages (d and e) are an exothermic processes with negative $E_{ads}$ of -0.14 and -0.03 eV and the interaction distances are 2.54 and 4.19 Å, respectively (Fig. 1a). The NBO analysis indicates the charge transfers are 0.00 and 0.04 e from CO$_2$ to the BN$_n$ nanoparticles surfaces in the configurations d and e (Table 1). This charge transfer indicates that the boron atoms of nanoparticle acts as Lewis acid site and the carbon and oxygen atoms of CO$_2$ molecule acts as Lewis base site. Fig. 2 reveals the electrostatic potential map of the BN$_n$-CO$_2$ system that indicates the locations of the various most positive and most negative potentials, designated as $V_{S,max}$ and $V_{S,min}$, respectively. The DFT calculations indicate that in the configuration e, the interaction between the molecule and cage is much stronger in comparison to that of the d configuration. The calculated HOMO of CO$_2$ molecule is mainly located on the oxygen atom; thus this reveals that the electrons are transferred from CO$_2$ molecule to the BN$_n$ nanoparticle (Figs. 3d and 3e).

3.1.4. Adsorption of CO on the nanoparticle

Two configurations were selected to investigate in adsorption of CO at top of the nanoparticle. In the configuration b, the carbon atom of CO attaches to the boron atom of the cage and in the configuration c, the oxygen atom of CO binds to the boron atom of the cage (Fig. 1b and c). The computed adsorption energies ($E_{ads}$) and the equilibrium molecule–cage distance ($d_{Molecule/B12N12}$) for the two molecular adsorption configurations are -0.15 eV and 1.81 Å for configuration b and -0.09 eV and 2.66 Å for configuration c (Table 1). The interface between CO and BN$_n$ leads to a charge transfer of 1.20 and 0.02 from the carbon and oxygen sides of CO to the nanoparticle, respectively (Table 1). There is a positive electrostatic potential and negative electrostatic potential for this configuration (Fig. 2). The HOMO of CO molecule is mainly occurred on the carbon atom respect to oxgen atom which leads to the stronger interaction in configuration b in comparison to the configuration c. Comparative investigation of the adsorption energy in the CO–BN$_n$ (n = 1 and 2) or HnX–BN$_n$ (n = 2 and 3) systems reveals that BN$_n$ has greater response to NH$_3$ (from N side) than that of CO$_2$ (from C side), CO$_2$ (from O side), CO (from C side), CO (from O side) and H$_2$O (from O side) (Table 2). A relatively large difference of adsorption energy between CO–BN$_n$ or HnX–BN$_n$ complexes can be described based on the electronegativity difference, $p$ character, and dipole moment in the molecules (see Table 2).

### Table 1. Calculated adsorption energy ($E_{ads}$, eV), HOMO energies ($E_{HOMO}$), LUMO energies ($E_{LUMO}$) and HOMO–LUMO energy gap ($E_g$).

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$E_{ads}$ (eV)</th>
<th>$E_{HOMO}$ (eV)</th>
<th>$E_{LUMO}$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>%$\Delta E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN</td>
<td>-</td>
<td>-9.51</td>
<td>-0.36</td>
<td>9.15</td>
<td>-</td>
</tr>
<tr>
<td>BN–NH$_3$</td>
<td>-1.54</td>
<td>-8.68</td>
<td>-0.95</td>
<td>7.72</td>
<td>142.59</td>
</tr>
<tr>
<td>BN–H$_2$N</td>
<td>-0.07</td>
<td>-7.19</td>
<td>-1.28</td>
<td>5.91</td>
<td>324.18</td>
</tr>
<tr>
<td>BN–OH$_2$</td>
<td>-0.87</td>
<td>-8.86</td>
<td>-0.99</td>
<td>7.88</td>
<td>127.05</td>
</tr>
<tr>
<td>BN–H$_2$O</td>
<td>-0.15</td>
<td>-8.11</td>
<td>-1.41</td>
<td>6.70</td>
<td>245.29</td>
</tr>
<tr>
<td>BN–CO$_2$</td>
<td>-0.03</td>
<td>-9.53</td>
<td>-0.47</td>
<td>9.06</td>
<td>8.68</td>
</tr>
<tr>
<td>BN–O$_2$C</td>
<td>-0.14</td>
<td>-9.44</td>
<td>-0.44</td>
<td>9.00</td>
<td>14.69</td>
</tr>
<tr>
<td>BN–CO</td>
<td>-0.15</td>
<td>-9.14</td>
<td>-0.05</td>
<td>9.09</td>
<td>5.87</td>
</tr>
<tr>
<td>BN–OC</td>
<td>-0.09</td>
<td>-9.45</td>
<td>-0.01</td>
<td>9.44</td>
<td>29.01</td>
</tr>
</tbody>
</table>

3.2. Density of state (DOS) analysis

Computed density of state (DOS) maps indicate that the energy gaps of BN$_n$ is 9.15 eV and of COn–BN$_n$ or HnX–BN$_n$ with CO$_2$ (C–side interaction), CO$_2$(O–side interaction), CO(C–side interaction), CO(O–side interaction), NH$_3$(N–side interaction), H$_2$O (O–side interaction) NH$_3$ (H–side interaction) and H$_2$O (H–side interaction) complexes are 9.15, 9.06, 9.09, 9.44, 7.72, 5.91 and 6.70 eV, respectively at the M06-2X/6-31++G** method (Fig. 3).

The $\Delta E_g$ in the adsorption process is associated to the sensitivity of an absorbent for a particular molecule. As seen in Table 1, the $\Delta E_g$ of BN$_n$ is 8.68% and of CO–BN$_n$ or HnX–BN$_n$ with CO$_2$ (C–side interaction), CO$_2$(O–side interaction), CO(C–side interaction), CO(O–side interaction), NH$_3$(N–side interaction), H$_2$O (O–side interaction) NH$_3$ (H–side interaction) and H$_2$O (H–side interaction) complexes are 14.69%, 5.87%, 29.01%, 127.05%, 142.59%  324.18% and 245.29%, respectively. The computed DOS indicates that the $E_g$ amount is reduced compared to the isolated BN$_n$. It is known that the $E_g$ is a major factor in determination of the electrical conductivity of BN$_n$ which will improve in the existence of the molecules with respect to the following equation [38]:

$$
\sigma \propto \exp\left(\frac{-E_g}{2KT}\right)
$$
in where $\sigma$ is the electrical conductivity and $k$ is the Boltzmann’s constant. According to the equation, the smaller $E_g$ amount leads to increase the conductivity at a given temperature. However, it can be conclude that the BNn nanoparticle selectively acts as a gas sensor device between CO$_2$, CO, H$_2$O and NH$_3$ which acts as the most suitable gas sensor for the NH$_3$ molecule.

**Fig. 1.** Geometric parameters of isolated BNn and small molecule-adsorbed BNn nanoparticle. Distances in Å and angles in degrees.

**Fig. 2.** The molecular electrostatic potentials $V(r)$ on the surface of the BNn-Complexes.
Fig. 3. Computed density of states (DOS) for pure BNN and the BNN-CO(C), BNN-CO(O), BNN-CO₂(C), BNN-CO₂(O), BNN-NH₃(N), BNN-H₂O(O), BNN-NH₃(H) and BNN-H₂O(H) complexes

4. Conclusions

The M06-2X calculations are used to studied the equilibrium distances, stabilities, and electronic properties of CO₂, CO, NH₃ and H₂O molecules which adsorbed at top of the BNN nanoparticle. The results reveal that the CO₂, CO, NH₃ and H₂O molecules can be strongly adsorbed on the BNN with a good adsorption energies. The CO and CO₂ molecules interactions to BNN from the carbon and oxygen atoms of CO and CO₂ are more prominent compared to the interaction with the oxygen and carbon atoms, respectively. A relatively large difference of adsorption energy between COₓ–BNN (n = 1 and 2) or HₓN–BNN (n = 2 and 3) complexes can be described on the basis of electronegativity difference, p character, and dipole moment in molecules. The most stable configuration was BNN-NH₃ with Eₘd and Eₚ about -1.54 and 7.72 eV and 142.59% change of the Eₚ. Finally, it is concluded that BNN nanoparticle has greater response selectivity toward NH₃ compared to CO, CO₂ and H₂O, a wide variety of investigations have been done upon the adsorption of this molecule both theoretically and experimentally.

References


