

A DFT Study on CO₂ Interaction with a BN Nano-Cage

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Received May 3, 2012, Accepted July 16, 2012

Covalent functionalization of a B₁₂N₁₂ nano-cage with CO₂ molecule has been investigated using density functional theory in terms of energetic, geometric, and electronic property analyses. Results show that besides two physisorption configurations, CO₂ preferably tends to perform [2+2] addition on B-N bonds of the cluster which are shared between six-membered and four-membered rings, releasing energy of 14.99 kcal/mol for adsorption of the first CO₂ and of 15.45 kcal/mol for the second one (per each molecule). On the basis of calculated density of states, we have found that the electronic properties of the physisorbed B₁₂N₁₂ by CO₂ have not changed, while slight changes have been predicted in the functionalized cases. Present results might be helpful to provide an effective way to modify the B₁₂N₁₂ properties for further purifications and applications.

Key Words : *Ab initio*, Carbon dioxide, Boron nitride nano-cage, DFT, B3LYP

Introduction

Carbon dioxide (CO₂) is the most important constituent of greenhouse gases (GHG) due to dependence of the world economies on fossil fuels as energy source, which has led to increase its emission into the atmosphere.¹ Sequestration of the CO₂ emitted from coal-fired power stations or industrial manufacturing plants is thus one of the most pressing issues in the environmental protection.² An ideal CO₂ sequestration material should have large surface area and strong adsorption sites that are accessible for ambient CO₂ gas.

Nanostructures are intriguing for both scientific research and future device applications, such as cluster protection, nano-ball bearings, nano-optical magnetic devices, catalysis, gas sensors, and biotechnology.³⁻⁶ Small molecule interaction with nanostructures is an important issue for both fundamental research and technical application. For example, the adsorption of gas molecules on nanostructures has the considerable potential for applications in surface modification,⁷ fuel cell,⁸ gas sensor,⁹⁻¹¹ and hydrogen storage.^{12,13}

BN nanostructures have a wide range of attractive properties, such as high-temperature stability, low dielectric constant, large thermal conductivity, and oxidation resistance, leading to a number of potential applications as electronic materials.^{14,15} Heteropolar nature of the BN nanostructures offers higher binding energies for hydrogen storage compared to the carbon based materials.¹⁶ However, the relatively large band gap and lack of solubility in solvents impose great restrictions on wider applications of BN nanostructures.¹⁷ It has been shown both experimentally¹⁸ and theoretically¹⁷ that covalent sidewall functionalization can modify the structural and electronic properties of BN nanostructures.

The geometries and stability of (BN)_n (n = 4-30) nano-clusters have been already studied by many research groups. Fowler *et al.*¹⁹ have found that B₁₂N₁₂ stands out as “magic”

BN-fullerene, and appears to be more stable relative to the others. Oku *et al.*²⁰ have synthesized the B₁₂N₁₂ cluster and characterized it by laser desorption time-of-flight mass spectrometry. The favored B₁₂N₁₂ cluster has a structure based on a decoration of the truncated octahedron in which all B vertices remain equivalent, as do all N.^{21,22} Recently, we have shown that the B₁₂N₁₂ may be a promising candidate for detection of carbon monoxide.²³ In the present work, the interaction of CO₂ with B₁₂N₁₂ will be theoretically investigated based on analyses of structure, energies, HOMO-LUMO gaps (E_g), stability, etc. Our results are likely to be useful for further studies related to functionalization of BN nanoclusters and also construction of a CO₂ storage material.

Computational Methods

Geometry optimizations, and density of states (DOS) analysis were performed on a nano-cluster of B₁₂N₁₂ and different CO₂/B₁₂N₁₂ complexes at the spin unrestricted B3LYP/6-31G(d) level of theory as implemented in GAMMES suite of program.²⁴ The B3LYP/6-31G(d) is demonstrated to be a reliable and common used level of theory in study of different nanostructures.²⁵⁻²⁷ Vibrational frequencies were also calculated at the same level to confirm that all the stationary points correspond to true minima on the potential energy surface. All frequency calculations were performed using numerical second derivatives and verified that all of the structures are true minima by frequency analysis and obtained all positive Hessian eigenvalues. We have defined the adsorption energy (E_{ad}) of CO₂ as follows:

$$E_{ad} = E(\text{CO}_2/\text{B}_{12}\text{N}_{12}) - E(\text{B}_{12}\text{N}_{12}) - E(\text{CO}_2), \quad (1)$$

where E(CO₂/B₁₂N₁₂) is the total energy of the adsorbed CO₂ molecule on the pristine B₁₂N₁₂ surface, and E(B₁₂N₁₂) and E(CO₂) are the total energies of the pristine B₁₂N₁₂ and a free

CO₂ molecule, respectively. By the definition, negative values of E_{ad} correspond to exothermic adsorption processes.

Results and Discussion

Geometry and Adsorption Energy of the Adsorbed CO₂ on B₁₂N₁₂. Generally, a B₁₂N₁₂ nano-cage is formed from eight 6-membered rings (6-MR) and six 4-membered rings (4-MR) with T_h symmetry. Each of the calculated B-11 and N-15 NMR spectra consists of one single peak, confirming the T_h symmetry because it is obvious that according to this symmetry the cluster must contain one kind of either B or N atom. Optimized structure and geometrical parameters of the B₁₂N₁₂ are shown in Figure 1, where two types of B-N bonds can be identified, one with the bond length of 1.43 Å which is shared by two 6-MRs (B₆₆), and the other which is shared between a 4-MR and 6-MR (B₆₄) with the length of 1.48 Å. They are both shorter than the single bond in H₃B-NH₃ (1.66 Å), but longer than the double bond in H₂B=NH₂ (1.39 Å) at B3LYP/6-31G(d). This indicates that B₁₂N₁₂ is stabilized by π electron conjugation. The results are in good agreement with those obtained by Wu *et al.*²⁸ The calculated IR frequencies are found to be in the range of 323.9-1446.3 cm⁻¹, indicating that this structure is a true stationary point on the potential energy surface. The range of calculated vibrational frequencies within the density functional based tight binding method in Ref. 12 is 320-1456 cm⁻¹ which is rather in good agreement with our results.

In order to determine the minimum energy adsorption structure for CO₂ on the surface of the cluster, a number of distinct starting structures have been used for optimization

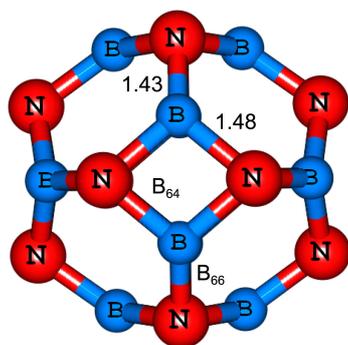


Figure 1. Geometrical parameters of the optimized B₁₂N₁₂. Distances are in Å.

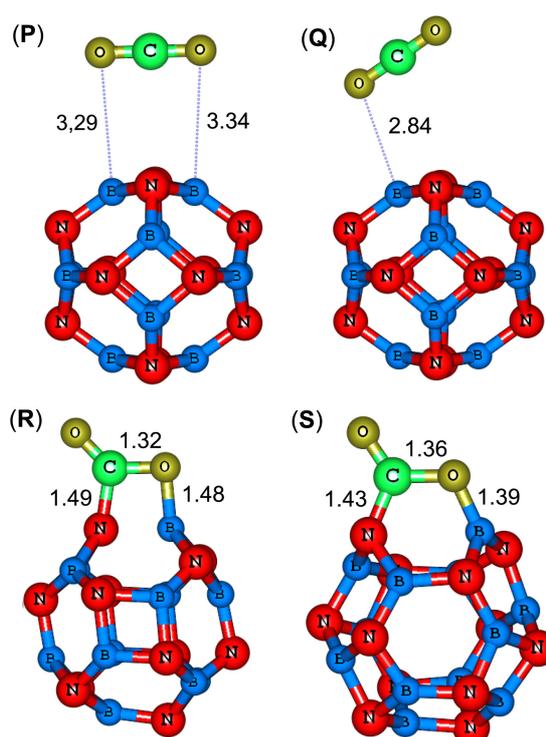


Figure 2. Models for two different physisorption (P and Q) and two covalent functionalization (R and S) of CO₂ molecule on B₁₂N₁₂.

including both the carbon and oxygen atoms of CO₂ close to B₆₆ and B₆₄, oxygen atom close to B atom, two oxygen atoms locating top of the two B atoms of a 6-MR or 4-MR and one of the oxygen atoms above the center of 4-MR or 6-MR. After careful structural optimizations, re-orientation of the molecule has been observed in some cases, and finally four stable CO₂/B₁₂N₁₂ complexes are obtained (Fig. 2). We have divided the interactions into two categories named physisorption and chemical functionalization.

As shown in Figure 2, configuration P shows the interaction between both of the oxygen atoms of CO₂ molecule and the B atoms of a 4-MR of the cluster. In this configuration, a net charge of 0.017 electrons is transferred from the molecule to the cluster and the calculated E_{ad} value is about -1.61 kcal/mol (Table 1). The smallest distance of molecule to the cluster is found to be about 3.29 Å. All above indicate that this interaction is weak and should be considered as a physisorption. Another CO₂ physisorption approach has

Table 1. Calculated adsorption energy (E_{ad} , kcal/mol), activation energy (E_{act} , kcal/mol) of CO₂ adsorption on the B₁₂N₁₂, HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), and HOMO-LUMO energy gap (E_{g}) of systems in eV

System	E_{ad}	E_{act}	${}^aQ_{\text{T}}$ (e)	E_{HOMO}	E_{LUMO}	E_{g}	${}^b\Delta E_{\text{g}}$ (%)
B ₁₂ N ₁₂	-	-	-	-7.70	-0.86	6.84	-
P	-1.61	0.00	0.017	-7.73	-0.89	6.84	0.0
Q	-2.30	0.00	0.023	-7.68	-0.85	6.83	0.1
R	-9.45	12.15	-0.143	-7.80	-1.51	6.29	8.0
S	-14.99	11.17	-0.147	-7.65	-1.66	5.99	12.4
2CO ₂	-15.45	-	-0.179	-7.92	-1.96	5.96	12.8

^a Q_{T} is defined as the average of total Mulliken charge on the acetylene molecule. ^bThe change of HOMO-LUMO gap of B₁₂N₁₂ after CO₂ adsorption.

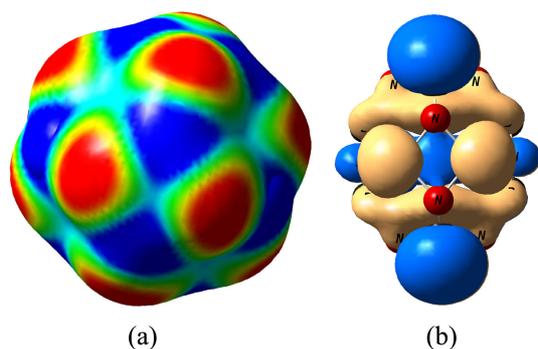


Figure 3. (a) Calculated molecular electrostatic potential surface, and (b) the lowest unoccupied molecular orbital (LUMO) of $B_{12}N_{12}$ cluster. The red color is referred to the high electron density and the blue one is referred to the positive sites. Distances are in Å.

been shown as configuration **Q**, in which one of the oxygen atoms of CO_2 is close to a B atom of the cluster by a distance of 2.84 Å. This configuration has an E_{ad} of -2.30 kcal/mol and a charge of $0.023 e$ is transferred from the molecule to the cluster. As shown in configurations **P** and **Q**, CO_2 can be physisorbed on the $B_{12}N_{12}$ surface so that only its oxygen atom(s) interact with B atom(s) of the cluster. This phenomenon is discussed by MEP and FMO analyses. Based on the Mulliken population analysis, the point charge of boron and nitrogen in the $B_{12}N_{12}$ cluster is $+0.44 e$ and $-0.44 e$, respectively, which is in agreement with our calculated MEP. As shown by the mapped-MEP of $B_{12}N_{12}$ in Figure 3(a), the B atoms are positively charged (blue colors) while the N atoms are negatively charged (red colors) in B-N bonding, so it seems that these atoms are suitable sites for nucleophilic attack of CO_2 molecules. As shown in Figure 3(b), calculated LUMO for the $B_{12}N_{12}$ cluster reveals that it is more localized on the boron atoms in energy level of -33.89 kcal/mol. Also, as can be seen in Figure 3(c) the HOMO of CO_2 molecule is located on the O atoms, thus, it prefers to lie on the B atom of the cluster from its O head.

The calculated frequencies for configuration **Q** are ranging from 10.8 to 2430.4 cm^{-1} . The stretching mode of O-B (the distance between the O atom of CO_2 and a B atom of the cluster) is approximately 71.5 cm^{-1} , demonstrating the weakness of this interaction in comparison with the other bonds along the complex which typically are about 327.6 – 2430.4 cm^{-1} . The largest frequency value of 2430.4 cm^{-1} belongs to the stretching mode of C-O bonds in the adsorbed CO_2 molecule. The calculated frequency for C-O mode of the free molecule is 2436.4 cm^{-1} , indicating that the length of the C-O bond has no significant change after physisorption on the $B_{12}N_{12}$.

Covalent functionalization is the other type of the interaction between the CO_2 and $B_{12}N_{12}$, so that one C-O bond of the molecule is located atop the B-N bonds of the cluster and [2+2] cycloaddition of CO_2 was occurred. The E_{ad} for 1, 2 addition of C-O bond to the B_{64} bond (-14.99 kcal/mol, configuration **S**) is very larger than that to the B_{66} one (-9.45 kcal/mol, configuration **R**) with rather a significant Mulliken charge transfer of 0.147 and 0.143 e from the cluster to the

molecule, respectively (Fig. 2). It is may be due to the above mentioned fact that the B_{64} bond is shared between a 4- and a 6-MR, but the B_{66} between two 6-MRs; therefore, the B_{64} bond is thermodynamically more favorable site for the adsorption of the CO_2 because of more strain in 4-MR compared to that in the 6-MR. In the other words, the 4-MR has more tendency to react with CO_2 molecule thereby releasing its strain energy through weakening the B_{64} bonds. Based on the NBO analysis, the B_{64} bond is broken in the **S** case after the adsorption process and two new bonds are formed, namely, C-N and O-B with the bond lengths of 1.43 and 1.39 Å, respectively. This functionalization undergoes a carboxylate-like structural distortion and CO_2 π -bond breaking due to electron backdonation from the BN to CO_2 and the CO_2 molecule undergoes the structural distortion to a bent geometry. Therefore, the O-C-O bond angle is reduced to 123.0° , and the broken C-O bond is significantly elongated to 1.36 Å on top of the BN. The calculated frequencies for the **S** and **R** configurations are ranging from 70.6 to 1898.0 cm^{-1} and 94.6 to 1956.2 cm^{-1} , respectively. In the most stable configuration (**S**) the stretching mode of the C-N and O-B (the distance between the molecule and the cluster) is approximately 1166.9 and 1329.4 cm^{-1} , respectively, demonstrating that the O-B interaction is stronger than the C-N bond.

With each B_{64} bond in the $B_{12}N_{12}$ being a potential adsorption site, the possibility of the second adsorption is interesting for consideration. In this section, two CO_2 are placed on two B_{64} bonds as far as possible, which ensures the least steric repulsion between these molecules (Fig. 4). The E_{ad} of this process is found to be about -15.45 kcal/mol per CO_2 , which is slightly higher than that of one CO_2 adsorption. It may be rationalized by the fact that after the adsorption of the first CO_2 molecule, the high T_h symmetry of the cluster has been broken and also its electric dipole moment has been increased from 0.00 to 3.57 Debye, slight-

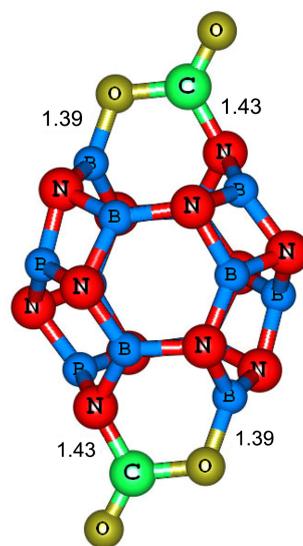


Figure 4. Model for $2CO_2$ functionalized- $B_{12}N_{12}$. Distances are in Å.

ly increasing the reactivity of the cluster. The lengths of newly formed B-O and N-C bonds are close to those of CO₂-attached B₁₂N₁₂ with individual addends discussed above.

It is noteworthy to mention that the dispersion term in comparison with the total energy may give a non-negligible contribution, especially in the calculation of the CO₂ physisorptions. Therefore, we have repeated all of the energy calculations, using Møller-Plesset perturbation theory²⁹ (MP2) with the same basis set. The calculated E_{ad} values are about -4.06, -3.99, -7.40, -11.45, and -13.02 kcal/mole for configurations **P**, **Q**, **R**, **S** and for the case of 2CO₂ adsorption, respectively. The results reveal that the E_{ad} values of MP2 are somewhat more negative than those of the B3LYP, in two cases of physisorptions (**P** and **Q**). It may be due to the fact that the MP2 includes dispersion interactions. Subsequently, kinetic favorability of the energetically possible adsorption process has been explored. As shown in Table 1, the CO₂ molecule has to overcome energy barriers of 12.15 and 11.17 kcal/mol to get into final configurations of **R** and **S** while the adsorption processes are barrierless through the two physisorption states. However, we believe that the activation energies are not large enough to hinder the adsorption processes at room temperature.

Effect of CO₂ Adsorption on the Electronic Properties of the B₁₂N₁₂. In the following, we have studied the influence of the CO₂ adsorption on the electronic properties of the cluster. The difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), E_g, was calculated from density of state (DOS) plots. For the bare B₁₂N₁₂ in Figure 5, it can be concluded that it is a semi-insulator material with a wide E_g of 6.84 eV. DOSs for different models of the CO₂-adsorb-

ed B₁₂N₁₂ have been shown in Figure 5. At physisorption configurations (**P** and **Q**) neither valence nor conduction levels of the B₁₂N₁₂ are significantly changed, thus the large E_g of B₁₂N₁₂ is completely preserved. DOSs for the functionalization cases are shown in Figure 4, indicating that upon the CO₂ adsorption on the B₁₂N₁₂, the electronic properties of the cluster are more changed compared to the physisorption cases. For example, in the most stable configuration (**S**), the DOS near the conduction level has a slightly change compared to that of the pristine cluster, which would result in an E_g reduction from 6.84 eV to 5.99 and 5.96 eV for the first and the second CO₂ adsorptions, respectively.

From comparison view, it has been previously shown that the pristine BNNT is almost inert towards the closed-shell CO₂ while on the basis of the results of *ab initio* calculations using theories of plane waves [PAW-PBE] and localized atomic orbitals [ONIOM(wB97X-D/6-31G*:AM1)], Choi *et al.*³⁰ have reported that a defect site of BNNT can capture CO₂ strongly enough to the ambient-condition sequestration with E_{ad} values approximately in the range of -0.70 to -0.85 eV (16.14 to 19.60 kcal/mol). However, the interaction of CO₂ with the B₁₂N₁₂ nanocage is somewhat stronger than that with the pristine BNNTs, while defects may increase the strength of interaction. We think that the small size of the nanocage and releasing the strain energy upon the CO₂ adsorption make it more reactive in comparison with the BNNTs. In addition, Mousavi *et al.*³¹ have shown that the adsorption of CO₂ molecules on the BNNTs causes a reduction in the E_g of the tube which is similar to our finding. However, this is due to an increasing charge carrier concentration induced by the adsorbed gas molecules.

Conclusion

The adsorption of carbon dioxide on a B₁₂N₁₂ was studied using DFT calculations. The results showed that the CO₂ prefers to be adsorbed atop a B₆₄ bond of the cluster surface rather than the B₆₆ one with binding energies of about -0.65 eV with a charge transfer of 0.147 e from the cluster to the molecule. The results also indicate that attachment of the CO₂ on the walls of the B₁₂N₁₂ induces some changes in electronic properties of the cluster and its E_g is reduced after covalent functionalization process. So we believe that the functionalization of B₁₂N₁₂ with CO₂ may be a good method for altering the properties of B₁₂N₁₂ for further application and functionalization of the nanocluster. Also, the strong adsorption of the CO₂ on the B₁₂N₁₂ indicates the potential application of the BN-based materials for carbon dioxide capture and storage.

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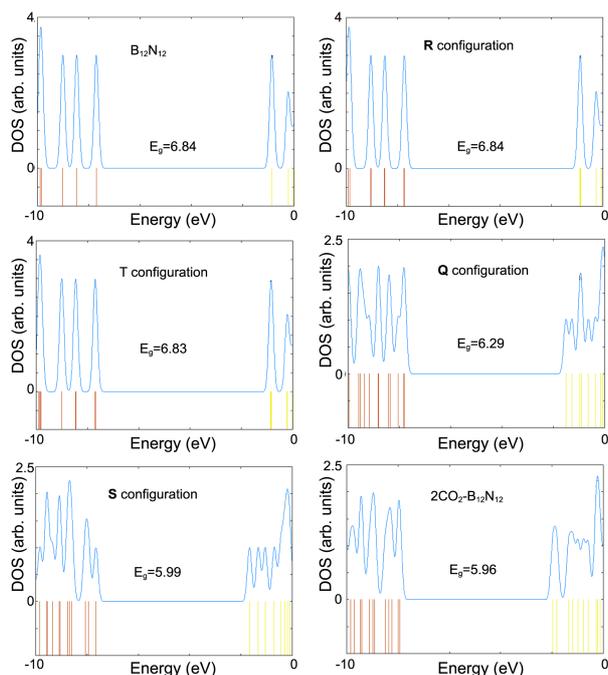


Figure 5. Calculated density of states (DOS) for pristine and different models of CO₂/B₁₂N₁₂ complexes.

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