Spontaneous Adsorption, and Selective Sensing of CO, and CO₂ Greenhouse Gaseous Species by the more Stable Forms of N₄B₄ Clusters

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Carbon oxide gaseous species are potentially considered as pollutants of the earth atmosphere. Especially, carbon monoxide and carbon dioxide, which are of the well-known carbon oxides, play effective roles in the greenhouse gas emission. Moreover, these species could handle some chain reactions in the troposphere. It subsequently leads to emergence of some secondary air pollutants which may cause ozone to collapse. Due to the ultra-high volume of man-made production of pollutants, which are frequently released to the atmosphere, their effects on our environment are being increased. These concerns led scientists to perform a vast number of precious research activities for controlling, eliminating, and detecting these pollutants. In this regard, in the present project, I have made attempts to examine the possibility of using the more stable forms of N_4B_4 clusters in sensing, and adsorbing CO and CO_2. The results showed that the N_4B_4 cluster both in forms (A) and (B) could adsorb (and react with) CO and CO_2 in a very fast and spontaneous process.

Keywords: N_4B_4 cluster, Carbon dioxide, Carbon mono oxide, Selective sensing, Adsorption, Nano sensor

INTRODUCTION

Pollution of air and its subsequent impacts (especially its direct effects on the quality of the life and creating disease) are of the most important issues in the environmental science [1,2]. Indeed, the air pollution, especially in this level, is a new and man-made phenomenon which is being considered in the recent decades; somehow, many researchers throughout the world are interested in studying and controlling this phenomenon [3,4]. Greenhouse effect and chain reactions, which lead ozone to collapse or create dangerous species, are among the main problems related to the air pollutant species [5]. Carbon oxides are of the main pollutants of the troposphere which intervene in many atmospheric problems; however, what makes them very important for researchers is their impact on the greenhouse phenomenon [6]. Carbon di- and mono oxides are the well-known carbon oxides which have

been considered as two of the main greenhouse gases [7]. These two gases are produced by different types of human activities like power plants, factories, automobiles exhausts, burning forests and fossil fuels. This means that hundred tons of these two carbon oxides are annually sent into the earth atmosphere [8].

Theoretical investigations and physiochemical approximations based on quantum mechanics and molecular dynamic simulations (which their results are much closed to the real reaction condition), would increase our knowledge about the especial species which play roles in polluting troposphere [9-11]. Also, in the recent years, scientists have proposed a number of approaches especially use of nano-sized compounds for controlling those type of gases *via* sensing or adsorption of these gaseous species [12,13].

Accordingly, in the present research, I have examined the possibility of using a nitrogen-boron N_4B_4 cluster [14a], which was experimentally synthesized by Wentorf [14b], for sensing CO and CO_2, in one hand, and adsorbing or destructing them, on the other hand. The results of the work showed that the N_4B_4 cluster in form (A) could sense (and

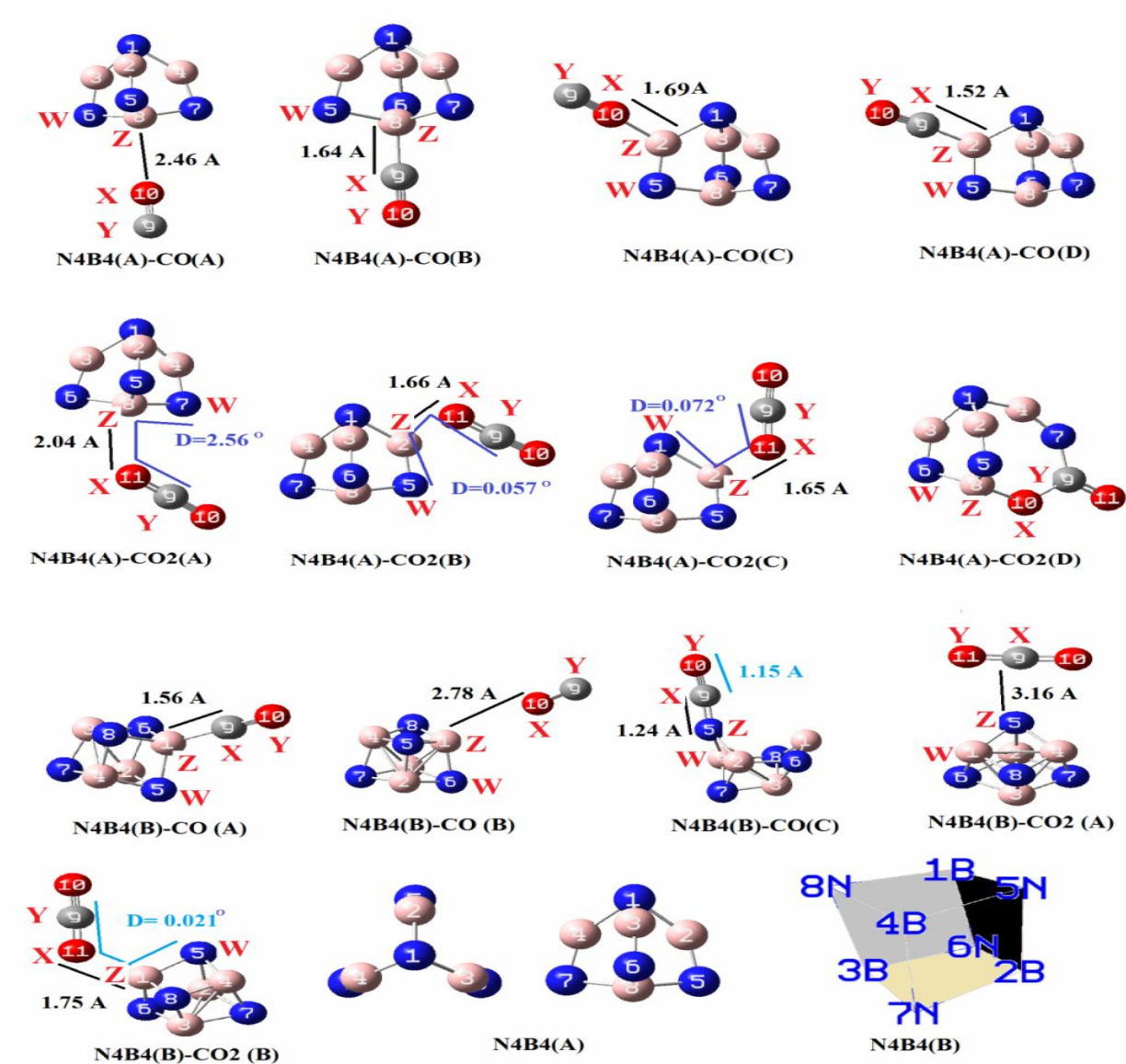_____
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Fig. 1. Geometrical situations for the adsorption systems optimized at the B3LYP/6-311++G(d,p) level of theory.

adsorb) CO and CO_2 by a ΔE_g of 0.620 eV (N_4B_4(A)-CO (B) adsorption state; E_{ads} = -13.9 kcal mol^{-1}), and 1.02 eV (N_4B_4(A)-CO_2(D) adsorption state; E_{ads} = -179 kcal mol^{-1}), respectively. Also, the N_4B_4 cluster in form (B) could sense (and adsorb) CO and CO_2 by a ΔE_g of -1.88 eV (N_4B_4(B)-CO(C) adsorption state; E_{ads} = -150 kcal mol^{-1}), and 0.550 eV (N_4B_4(B)-CO_2(B) adsorption state; E_{ads} = -102 kcal mol^{-1}), respectively.

COMPUTATIONAL

Isolated forms of the more possible states of the N4B4 cluster, containing forms A and B (Fig. 1) were drawn as input files and were then optimized to give the best energy minima. During the calculations, it was found that for some systems, there was more than only one orientation, while for some other cases, there was only one stable geometry. The

Table 1. The Key Geometrical Parameters for the Adsorption Systems (X is the O or C Atom of Carbon Oxides, and the Distances are in Angstrom)

System	N-X	B-X	C-O	Y-X-Z	Dihedral angle (Y-X-Z-W)
$N_4B_4(A)$-CO(A)	-	2.46	1.13	1.53	3.32
$N_4B_4(A)$-CO(B)	-	1.64	1.12	0.061	143
$N_4B_4(A)$-CO(C)	-	1.69	1.14	172	0.956
$N_4B_4(A)$-CO(D)	-	1.52	1.13	175	179
$N_4B_4(A)$-CO$_2$(A)	-	2.04	1.16	115	2.56
$N_4B_4(A)$-CO$_2$(B)	-	1.66	1.19	115	0.057
$N_4B_4(A)$-CO$_2$(C)	-	1.65	1.18	128	0.072
$N_4B_4(A)$-CO$_2$(D)	-	1.40	1.44	125	0.079
$N_4B_4(B)$-CO(A)	-	1.56	1.12	180	110
$N_4B_4(B)$-CO(B)	-	2.78	1.13	178	7.60
$N_4B_4(B)$-CO(C)	1.24	-	1.15	173	114
$N_4B_4(B)$-CO$_2$(A)	3.16	-	1.16	91.1	31.8
$N_4B_4(B)$-CO$_2$(B)	-	1.75	1.19	121	118

Gaussian 03 quantum chemical package was used to perform the required calculations [15] and the related parameters were extracted accordingly. Studies on all stationary points along with the reaction channels, in addition to the other calculations, were performed using B3LYP/6-311++g(d,p) level of theory [16-18], and the frequency of each structure was extracted to give the thermodynamic and kinetic parameters of each geometry. The natural bond orbital (NBO) analysis [19,20] was subsequently used to give the electrical charge of each atom in the proposed states, and the Global Electron Density Transfer (*GEDT*) was calculated using the following formula [21,22],

$$GEDT = -\Sigma q_A \qquad (1)$$

Where, q_A is the net Mulliken charge as well as the sum of the entire atoms of dipolarophile species.

The related partial bond order was also extracted by using Pauling relation [23], Eq. (2),

$$n_X = n_0 \exp\left(\frac{(r_0 - r_X)}{c}\right) \qquad (2)$$

where, the bond order n_x of a bond length r_x is a function of the standard bond of length r_o whose bond order is defined as n_o.

RESULTS

At the first step, each isolated species containing N_4B_4 in form A, N_4B_4 in form B, CO, and CO$_2$ species were drawn as input files and were then optimized, separately. Then, each of CO and CO$_2$ molecules were placed near to

Table 2. The Key Adsorption and Frontier Molecular Orbital, FMO, Parameters of the Adsorption Systems at the B3LYP/6-311++G(d,p) Level of Theory

System	E_{ads} (kcal mol^{-1})	GEDT	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	E_g (a.u.)	E_g (eV)	ΔE_g (eV)
N_4B_4(A)	-	-	-0.265	-0.155	0.110	2.97	-
N_4B_4(B)	-	-	-0.318	-0.160	0.158	4.26	-
N_4B_4(A)-CO(A)	-0.526	0.024	-0.262	-0.152	0.110	2.99	0.022
N_4B_4(A)-CO(B)	-13.9	0.152	-0.247	-0.114	0.133	3.62	0.647
N_4B_4(A)-CO(C)	-2.34	0.066	-0.244	-0.131	0.113	3.07	0.104
N_4B_4(A)-CO(D)	-39.6	0.061	-0.258	-0.143	0.115	3.13	0.158
N_4B_4(A)-CO_2(A)	-1.93	0.086	-0.260	-0.148	0.112	3.05	0.076
N_4B_4(A)-CO_2(B)	-10.9	0.223	-0.235	-0.114	0.121	3.29	0.321
N_4B_4(A)-CO_2(C)	-7.85	0.174	-0.236	-0.119	0.117	3.18	0.212
N_4B_4(A)-CO_2(D)	-179	0.075	-0.294	-0.146	0.148	4.03	1.06
N_4B_4(B)-CO(A)	-190	0.134	-0.290	-0.125	0.165	4.49	0.228
N_4B_4(B)-CO(B)	-170	0.043	-0.325	-0.148	0.177	4.81	0.554
N_4B_4(B)-CO(C)	-150	0.286	-0.204	-0.116	0.088	2.39	-1.87
N_4B_4(B)-CO_2(A)	-170	-0.009	-0.332	-0.157	0.175	4.76	0.500
N_4B_4(B)-CO_2(B)	-102	0.098	-0.296	-0.118	0.178	4.84	0.582

each designed derivative of N_4B_4, in different orientations as input files. During the initial and also the final optimization, some of the different proposed geometries turned into the same orientations. Thus, among input files, several orientations were detected after further optimizations (Fig. 1). One of the interesting points found during the calculations was that in some cases the adsorption process of CO and CO_2 proceeded in stepwise pathways for each of the considered forms. The other point was that attaching carbon of CO_2 to nitrogen or carbon of the N_4B_4 cluster, in the input file, led to the destruction of the cage structure as well as attaching oxygen of CO_2 to nitrogen of the cage. While, forming a bond between boron of the cluster and oxygen of CO_2 gives some true and stable states.

The results presented in Table 1 showed that both N_4B_4 clusters in forms A and B are able to adsorb and react with CO and CO_2 as well. These properties seem to be useful for elimination of these two well-known dangerous carbon oxides. Also, adsorption of CO and CO_2 species by each form of N_4B_4 cluster could proceed *via* two – or multi-step processes; and it is more clearly observed for the cases in which form A of N_4B_4 cluster is in interaction with CO_2; somehow, at the first step, in N_4B_4(A)-CO_2(A) state (E_{ads} = -1.93 kcal mol^{-1}), the oxygen of CO_2 approaches to the boron (B8) of the cluster in a distance of 2.04 Å, and in the second step, the other carbon of CO_2 (C9) approaches to the nitrogen (N7) of the cluster that leads to destruction of the
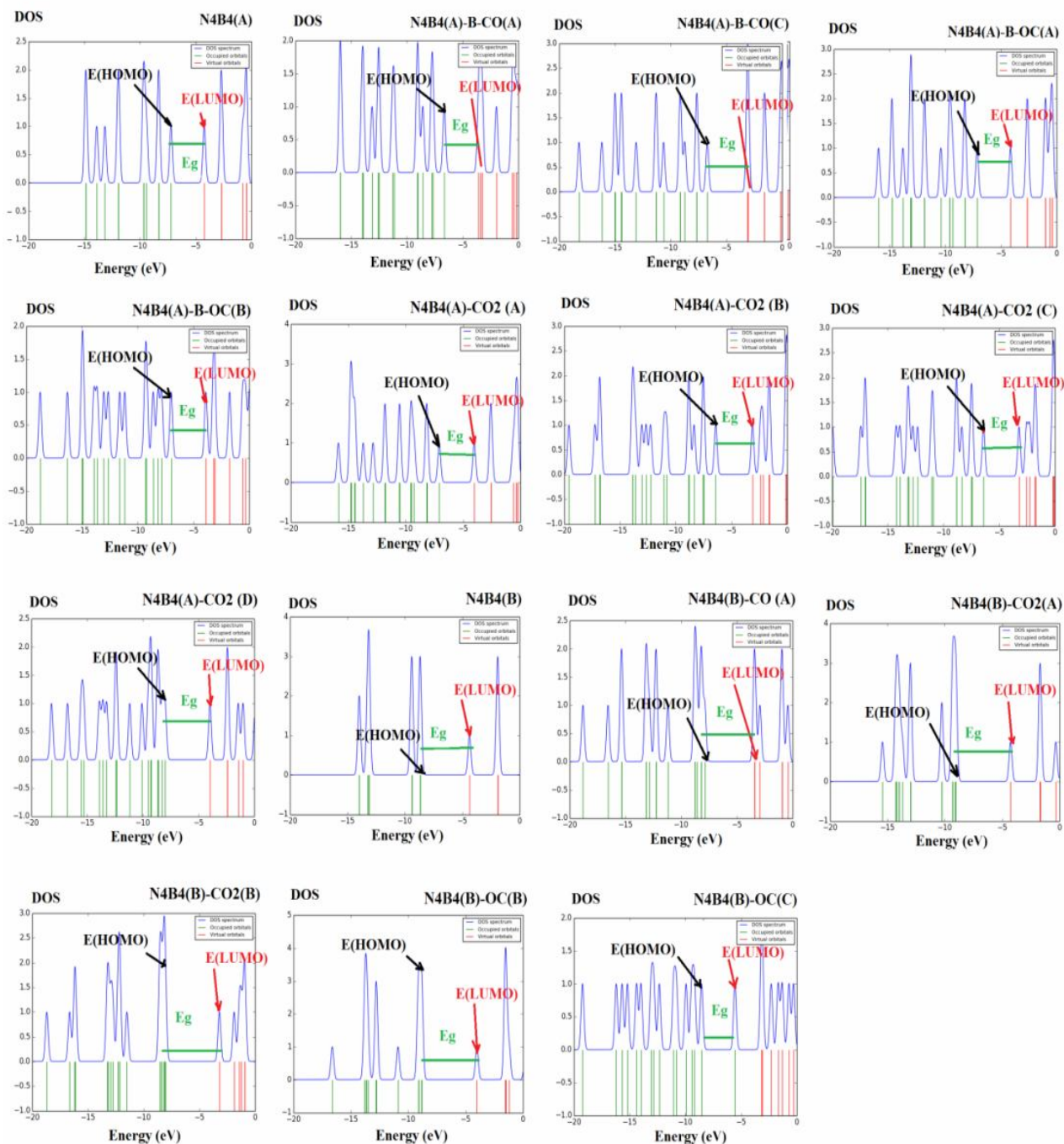
Fig. 2. The DOS plots for the adsorption systems of the graphene segments and also for the fullerenes at the B3LYP/6-311++G(d,p) level of theory.

cluster (N_4B_4(A)-CO_2(D)) state with E_{ads} = -1.93 kcal mol^{-1}).

In another two-step adsorption process, at first, an oxygen of CO_2 approaches to the B2 atom of the cluster and

forms N_4B_4(A)-CO_2(C) state with an energy release of -7.85 kcal mol^{-1}. At the second adsorption step, the dihedral angle of N5-B2-O11-C9 switches from 0.057° to 179.9° to form
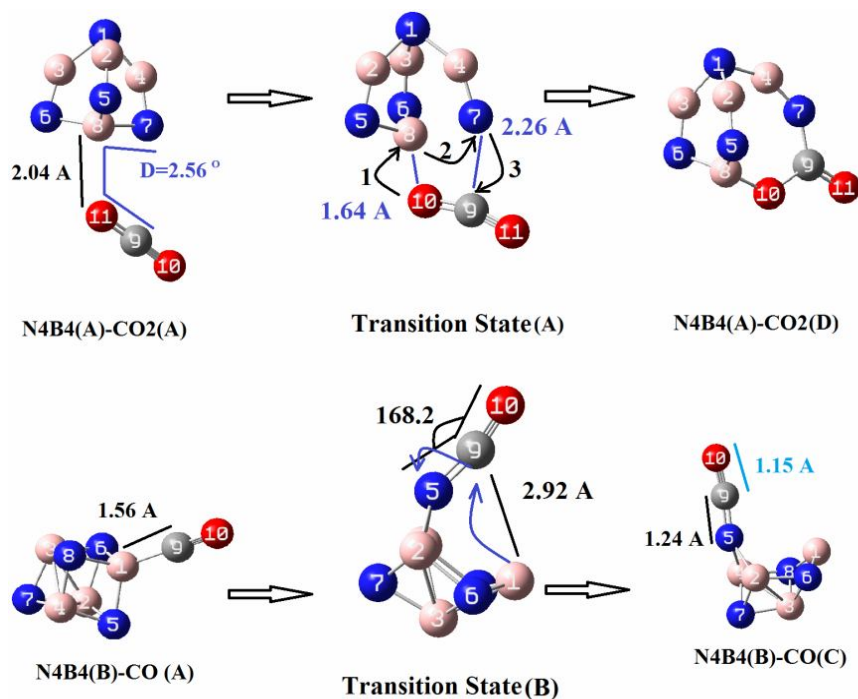
Fig. 3. The mechanistic aspects of the reactions between each cluster and the gas leading to destruction of the original form of the cluster.

$N_4B_4(A)$-$CO_2(B)$ with an energy release of -3.05 kcal mol^{-1} (E_{ads} = -10.9 kcal mol^{-1}). Moreover, the adsorption energy for both clusters, especially for form B, is more negative in many adsorption states (for example -179 kcal mol^{-1}, and -190 kcal mol^{-1} for $N_4B_4(A)$-$CO_2(D)$ and $N_4B_4(B)$-$CO(A)$ states, respectively) that would make the process spontaneous.

In the issue of sense of CO or CO_2 gases by the considered clusters, it should be said that due to the relatively suitable HOMO-LUMO gap of the systems (E_g = 2.97 eV for isolated $N_4B_4(A)$ and E_g = 4.26 eV for isolated $N_4B_4(B)$) the conductivity of these cluster units may be sufficient for further investigation on these units as the potential semiconducting sensors. It is observable that in more cases, changes in the HOMO-LUMP gaps, ΔE_g (eV), between the isolated states and the states in which CO or CO_2 molecules are near to the cluster is more significant when using the B from of the considered clusters (Fig. 2, Table 1). Also, the results of the density of state (DOS) plots and the frontier molecular orbital (FMO) indicate that

presence of CO or CO_2 near to the A and B forms of N_4B_4 clusters cause considerable changes in the HOMO-LUMO gap of the system. The N_4B_4 cluster in form (A) could strongly sense CO by a ΔE_g of 0.620 eV for $N_4B_4(A)$-$CO(B)$ adsorption state, and CO_2 by a ΔE_g of 1.02 eV for $N_4B_4(A)$-$CO_2(D)$ state, respectively. Furthermore, the N_4B_4 cluster in form (B) could highly sense CO by a ΔE_g of -1.88 eV for $N_4B_4(B)$-$CO(C)$ state, and CO_2 by a ΔE_g of 0.550 eV for $N_4B_4(B)$-$CO_2(B)$ state, respectively.

In the case of the destruction process of the N_4B_4 form (A) by CO_2 gas (Table 3, Fig. 3), the bond distance between O10 and B8 in the transition state structure (TS (A)) is about 1.64 Å, while, the value of this parameter for the N7 and C9 atoms is about 2.26 Å. It shows that the bond formation for O10-B8 proceeds faster than that for the C9-N7 bond. Moreover, the increase of the negative Mulliken charge in O10 and decrease of this parameter in B8 atom during the destruction process of the N4B4 form (A) cluster along with the negative charge decrease on N7 and positive charge decrease on C9, may confirm this idea. Also, the

Table 3. Key Parameters for Critical Structures of the Reactions between each Cluster and the Gas Leading to Destruction of the Original form of Cluster

Species	Interatomic distances [Å]		Mulliken charges			
	B8-O10	N7-C9	N7	B8	C9	O10
Reactants [N$_4$B$_4$(A)+CO$_2$(A)]	-	-	-0.521	0.785	0.409	-0.108
TS (A)	1.64	2.26	-0.455	0.740	0.324	-0.127
Product [N$_4$B$_4$(A)+CO$_2$(D)]	1.40	1.40	-0.433	0.769	0.336	-0.373
Species	B1-C9	C9-N5	B1	C9	N5	O10
Reactants [N$_4$B$_4$(B)+CO(A)]	1.56	-	0.229	0.122	-0.412	0.012
TS (B)	2.92	1.25	-0.546	0.310	-0.221	-0.112
Product [N$_4$B$_4$(B)+CO(C)]	-	1.24	-0.503	0.398	-0.329	-0.111

$\Delta G^{\#}$ for the formation of TS (A) form the reactant (N$_4$B$_4$ (A)+CO$_2$) is about 2.63 kcal mol^{-1} indicating that the destruction occurs very fast.

About the destruction process of the N4B4 form (B) by CO gas (Table 3, Fig. 3), the results show that destruction process of C9-N5 bond with a length of 1.25 Å is significantly faster than that for the B1-C9 bond (2.92 Å), indicating that this process occurs with a highly asynchronous mechanism [24]. The highly decrease of negative charge on N5 (from -0.412 in reactant to -0.221 in TS (B)), and highly increase of negative charge on B1 (from 0.229 in reactants to -0.546 in TS (B)) show that the nitrogen atom (N5) attacks to the carbon atom of CO species leading to migration of the from B1 atom. Subsequently, the B1 atom receives the electron density of the CO species. Moreover, the $\Delta G^{\#}$ for the formation of TS (B) form the reactant (N$_4$B$_4$(B)+CO) is about 40.12 kcal mol^{-1}. It shows that unlike the first reaction ((N$_4$B$_4$(A)+ CO$_2$) is about 2.63 kcal mol^{-1}), the destruction reaction of N$_4$B$_4$(B)+CO is so unfavorable, and thus, the N$_4$B$_4$ cluster in form (B) is relatively stable against the CO and CO$_2$ gases.

CONCLUSIONS

The data presented in this project showed that the nitrogen-boron clusters, both in forms A and B, are highly able to adsorb (and react with) CO and CO$_2$. This ability could handle the elimination of these two dangerous carbon oxides. The adsorption of CO and CO$_2$ gases by each form of N$_4$B$_4$ cluster might proceed *via* multi-step processes. It is especially observed for the cases in which the form A of N$_4$B$_4$ cluster is in interaction with CO$_2$. At the first step, in N$_4$B$_4$(A)-CO$_2$(A) state (E_{ads} = -1.93 kcal mol^{-1}), the oxygen of CO$_2$ approaches to the boron (B8) of the cluster (2.04 Å). At the second step, the carbon of CO$_2$ leads to destruction of the cluster (N$_4$B$_4$(A)-CO$_2$(D) state with E_{ads} = -1.93 kcal mol^{-1}. Also, the adsorption energy, especially for the form B of the cluster, is very negative in most adsorption cases (for example -179 kcal mol^{-1} and -190 kcal mol^{-1} for N$_4$B$_4$(A)-CO$_2$(D) state and N$_4$B$_4$(B)-CO(A) state, respectively). It makes the process much favorable.

On the other hand, the results of the DOS plots and the FMO data reveal that existence of carbon monoxide or carbon dioxide near to both A and B forms of N$_4$B$_4$ clusters

lead to significant changes in the HOMO-LUMO gap of the system. The N_4B_4 cluster in form (A) could strongly sense CO by a ΔE_g of 0.620 eV for N_4B_4 (A)-CO (B) adsorption state, and CO_2 by a ΔE_g of 1.02 eV for N_4B_4 (A)-CO_2 (D) adsorption state, respectively. Also, the N_4B_4 cluster in form (B) could highly sense CO, by a ΔE_g of -1.88 eV for N_4B_4(B)-CO(C) adsorption state, and CO_2 by a ΔE_g of 0.550 eV for N_4B_4(B)-CO_2(B) state, respectively. For most of the investigated systems, N_4B_4 cluster acts as a catalyst for sensing the gases, but in the case of the CO_2+N_4B_4(A) system, the cluster is destroyed. Moreover, the $\Delta G^{\#}$ for the formation of the TS (B) form the reactant (N_4B_4(B)+CO) is about 40.12 kcal mol^{-1}. It shows that unlike the first reaction ((N_4B_4(A)+CO_2) is about 2.63 kcal mol^{-1}), the destruction reaction of N_4B_4(B)+CO is so unfavorable, and thus, the N_4B_4 cluster in form (B) is relatively stable against the CO and CO_2 gases.

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