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INVESTIGATION OF FORMALDEHYDE ADSORPTION ON $B_{12}N_{12}$, $B_6N_6C_{12}$, $B_{12}N_6C_6$, AND C_{24} NANOCAGES: DENSITY FUNCTIONAL THEORY CALCULATIONS

FORMALDEHİTİN $B_{12}N_{12}$, $B_6N_6C_{12}$, $B_{12}N_6C_6$ VE C_{24} NANOKAFESLERİNE ADSORPSİYONUNUN İNCELENMESİ: YOĞUNLUK FONKSİYONEL TEORİSİ HESAPLAMALARI

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ABSTRACT

In the last years monitoring of air pollutants become more important. Formaldehyde is one of these pollutants. It has been used in lots of purposes, but its toxic nature necessitates sensing and removing it from environment. In this work capture and/or sensing capabilities of $B_{12}N_{12}$, $B_6N_6C_{12}$, $B_{12}N_6C_6$, and C_{24} nanocages for formaldehyde are investigated. The calculations are conducted at the M06-2x/6-311g(d,p) level of Density Functional Theory. The structure and electronic properties of nanocages before and after formaldehyde adsorption, the adsorption energies are investigated and analyzed in detail. The changing of electronic properties and reactivity of nanocages are discussed. Hence, active regions of the nanocage are determined for increasing numbers of formaldehyde molecules. The results indicate that possibility of using $B_{12}N_6C_6$ nanocage to sense formaldehyde in the environment.

Keywords: Formaldehyde, nanocages, adsorption, Density Functional Theory, electronic structure

ÖZET

Son yıllarda hava kirleticilerinin izlenmesi daha önemli olmuştur. Formaldehit bu kirleticilerden bir tanesidir. Pek çok amaçla kullanılmaktadır, ancak toksik doğası tespit edilmesini ve çevreden giderilmesini gerekli kılmaktadır. Bu çalışmada $B_{12}N_{12}$, $B_6N_6C_{12}$, $B_{12}N_6C_6$ ve C_{24} nanokafeslerinin formaldehit tutma ve/veya tespit etme yetenekleri incelenmiştir. Hesaplamalar Yoğunluk Fonksiyonel Teorisi M06-2X/6-311g(d,p) seviyesinde yapılmıştır. Formaldehit adsorpsiyonundan önce ve sonra nanokafeslerin elektronik ve yapısal özellikleri, adsorpsiyon enerjileri incelenmiş ve ayrıntılarıyla analiz edilmiştir. Nanokafeslerin elektronik özelliklerinin ve reaktivitelerinin değişimi tartışılmıştır. Buna ek olarak, nanokafeslerin artan formaldehit molekülü sayısına göre aktif bölgeleri belirlenmiştir. Sonuçlar $B_{12}N_6C_6$ nanokafesinin formaldehitin çevrede tespit edilmesinde kullanılabileceğini göstermektedir.

Anahtar Kelimeler: Formaldehit, nanokafesler, adsorpsiyon, Yoğunluk Fonksiyonel Teorisi, elektronik yapı

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INTRODUCTION

Undoubtedly formaldehyde (FA) is one of the most important chemicals that is used for daily life and lots of industrial purposes such as producing dye, plastic, disinfectants etc. (Harismah, Nassar et al. 2023; Kadhim et al., 2023). It is generally used in its liquid state. It has a high tendency to vaporize, and therefore it can be found in its gas phase (Harismah et al., 2023). It is reported that FA possibly has a carcinogen nature, besides to its toxic property (Shakerzadeh, 2016). As FA has no detectable color with low threshold harm, after exposure for human it can lead to lots of health problems and even death (Al-Nadary et al. 2024; Badran et al. 2023; Tang et al. 2014). Accumulation and distribution of FA vapor in the environment is also one of the climate change reasons (Al-Nadary et al., 2024). Therefore, monitoring and importantly removing of FA is needed. Accordingly, up to now there are lots of studies that have been conducted experimentally concerning sensing and/or removing FA from environment (Chu et al. 2009; Geetha Sadasivan Nair et al. 2024; Hu et al., 2018; Li et al., 2021; Tang et al., 2014; X. Wang et al., 2015). Unfortunately, experimental methods are expensive with requiring instruments and needing long sampling intervals (Shakerzadeh, 2016). In order to explore the properties of materials Density Functional Theory methods can be more suitable than expensive experimental techniques. These methods are not time consuming like experimental ones and provide insight into the electronic properties of materials (Aydogdu & Hatipoglu, 2022a, 2023; Borji & Vahedpour, 2023). For all of these reasons, finding suitable materials theoretically before experimental methods is prime necessary.

In the last years organic nano materials have gained lots of attention from researchers for developing new functions and applications (Da'i et al., 2023; Vishwkarma, Yadav, Pathak, & Brahmachari, 2023). After the development of the fullerene structure, many fullerene-like nanomaterials with high surface-to-volume ratio have been developed for environmental purposes (Harismah et al., 2023; Soltani et al., 2019). These nanomaterials are used in lots of areas like sensing material, optoelectronic, drug delivery, catalysis etc. The earlier studies, the adsorption of FA molecule with some of nano materials have been investigated (Ibrahim et al., 2023; Kadhim et al., 2023; Louis et al., 2022; R. S. Roy et al. 2024). They are mainly investigated adsorption property of FA to nano material (Abbasi et al. 2016; Badran et al., 2023; Da'i et al., 2023; Harismah et al., 2023; Kadhim et al., 2023; Noorizadeh & Shakerzadeh, 2012; Shakerzadeh, 2016; Soltani et al., 2019; Soltani et al. 2020; Vessally et al. 2017; R. Wang et al. 2008; Yoosefian et al. 2015). However, there is no conducted study in the literature that investigates the efficiency of different numbers of carbon containing nanocage for FA adsorption, and the effect of increasing number FA molecules to the adsorption efficiency of these materials.

For all these reasons, this study on environmental pollutants also aims to determine the electronic and adsorption properties of nanocages. Furthermore, the potential use of $B_{12}N_{12}$, $B_6N_6C_{12}$, $B_{12}N_6C_6$, and C_{24} nanocages for sensing and/or removing FA are investigated. The nature of interactions, electronic, and thermodynamic properties related to adsorption are analyzed. Furthermore, the effect of FA number on the adsorption process is also investigated. As a novel purpose different nanocage performances have analyzed to find better adsorbate system.

MATERIALS AND METHODS

According to literature survey M06 type functionality gives better results for molecular interaction than B3LYP type of functionality (Walker et al. 2013; Zhao & Truhlar, 2008). These computational methods have used for analyzing adsorption properties of different type of chemicals (Geetha Sadasivan Nair et al., 2024). In this study, modelling of FA gas and adsorbent nanocage systems have been performed by using Density Functional Theory M06-2X functionality with 6-311g(d,p) basis set (Geetha Sadasivan Nair et al., 2024). The nature of the structures as global minimum are determined by frequency calculations as all positive values. The Natural Bond Orbital (NBO) calculations are used to interpret interactions. All the calculations are performed by using Gaussian 09 (Frisch et al. 2019).

The adsorption energies of related adsorption systems are determined by given formula below.

$$E_{ads} = E_{complex} - (E_{nanocage} + E_{FA}) + E_{BSSE} \quad (1)$$

In this equation $E_{complex}$, $E_{nanocage}$, E_{FA}, and E_{BSSE} are energies of complex, nanocage, FA, and basis set superposition effect respectively. Basis set superposition effect is determined by counterpoise method (Vessally et al., 2017).

The Density Functional Theory global reactivity indices of the systems are calculated Koopman's Theorem in which it is stated that ionization potential and electron affinity can be found by using negative values of Frontier Molecular Orbital Energies. The used formulas for chemical potential (μ), hardness (η), electrophilic index (ω), and softness (S) are given below respectively (Parr, Szentpály, & Liu, 1999; R. K. Roy, Pal, & Hirao, 1999).

$$\mu = \frac{E_{LUMO}+E_{HOMO}}{2} \quad (2)$$

$$\eta = \frac{E_{LUMO}-E_{HOMO}}{2} \quad (3)$$

$$\omega = \frac{\mu^2}{2.\eta} \quad (4)$$

$$S = \frac{1}{2.\eta} \quad (5)$$

RESULTS AND DISCUSSION

Adsorption of FA onto the Nanocages

The optimized molecular geometries and some of the geometrical parameters for nanocages ($B_{12}N_{12}$, $B_6N_6C_{12}$, $B_{12}N_6C_6$, and C_{24}) are illustrated in Figure 1.

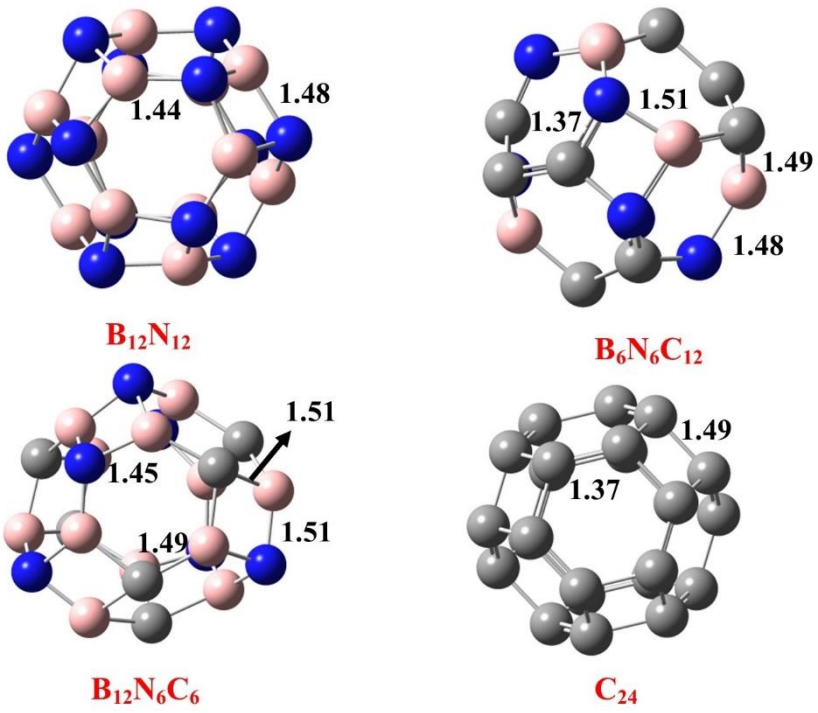

Figure 1. The Optimized Geometries of Nanocages with Their Geometrical Parameters

As understood from the figure that nanocages are composed of six tetragonal and eight hexagonal rings. In agreement with the literature that B-N bond lengths of $B_{12}N_{12}$ nanocage are found as 1.48 Å and 1.44 Å for tetragonal and hexagonal rings respectively (Geetha Sadasivan Nair, Narayanan Nair, & Sun, 2023). For the other nanocages B-N, B-C and C-C bonds are found 1.48, 1,49, and 1.36 Å respectively for tetragonal ring. The same bond lengths for hexagonal rings of nanocages are 1.51, 1.51, and 1.49 Å respectively. In Sadasivan Nayir et al. study C-C bond lengths for tetragonal and hexagonal rings of nanocage is 1.37, and 1.49 Å respectively which is also conforms to this study (Geetha Sadasivan Nair et al., 2023).

It is known from the literature that FA adsorbed from only one position that is the oxygen atom of molecules onto the different adsorbents (Harismah et al., 2023; Shakerzadeh, 2016; Vessally et al., 2017). For this reason, only

adsorption from the oxygen atom of FA is studied. The optimized geometries for complexes after adsorption are illustrated in Figure 2.

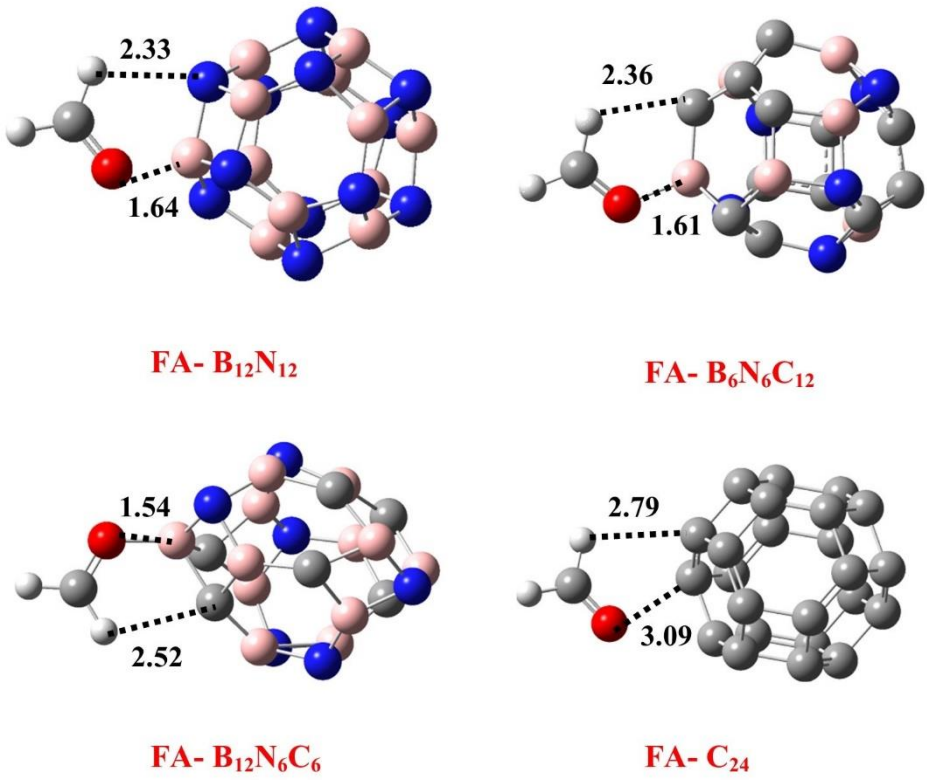

Figure 2. The Optimized FA-Nanocage Geometries

Adsorption of FA onto the nanocages occurs with the lone paired electrons of the oxygen atom of FA and empty p orbital of boron or carbon atoms of the nanocages. The structural changes occur at the interaction sites after adsorption process. The interaction bond length between the oxygen atom of FA and boron or carbon atom of nanocages are 1.64, 1.53, 1.61, and 3.09 Å for $B_{12}N_{12}$, $B_6N_6C_{12}$, $B_{12}N_6C_6$, and C_{24} nanocages respectively. Moreover, after interaction with nanocages the bond length of carbon oxygen double bond stretched. The highest elagonation of C=O bond belongs to FA-$B_{12}N_6C_6$ which is 0.029 Å higher than isolated FA molecule. The stretching percentage of C=O bonds for all complexes approx. 1.84 %. The HCH bond angle of FA molecule also changes after adsorption. Initially the value of bond angle is 116.11^0, and then it increases 5.82^0, 7.29^0, 7.34^0, and 0.68^0 higher for FA-$B_{12}N_{12}$, FA-$B_6N_6C_{12}$, FA-$B_{12}N_6C_6$, and FA-C_{24} respectively.

In the interacted structure of molecular complexes there is also another interaction in which bond length changes between 2.33 Å and 2.79 Å. These extra Van der Waals interactions can be the reason of stabilizing of interacted molecular complexes.

The NBO charge distribution results of FA-nanocages are given in Figure 3. As understood from the figure that the NBO charges of carbon and oxygen atoms of FA molecule change. This means that these atoms are crucial for charge transfer. The electron transfer occurs from these atoms of FA to the boron, or carbon atoms of nanocages. As a result of electron transfer charge distribution of solely FA molecule is different from the structure of adsorbed one. This may be the reason of stretching of the carbonyl bond of FA after interaction as discussed earlier.

Energetic Parameters

It is known that the more negative E_{ads} energy means that the more probable adsorption complex (Abbasi et al., 2016). For this sense, adsorption energies are calculated and presented with the calculated thermodynamic results in Figure 4.

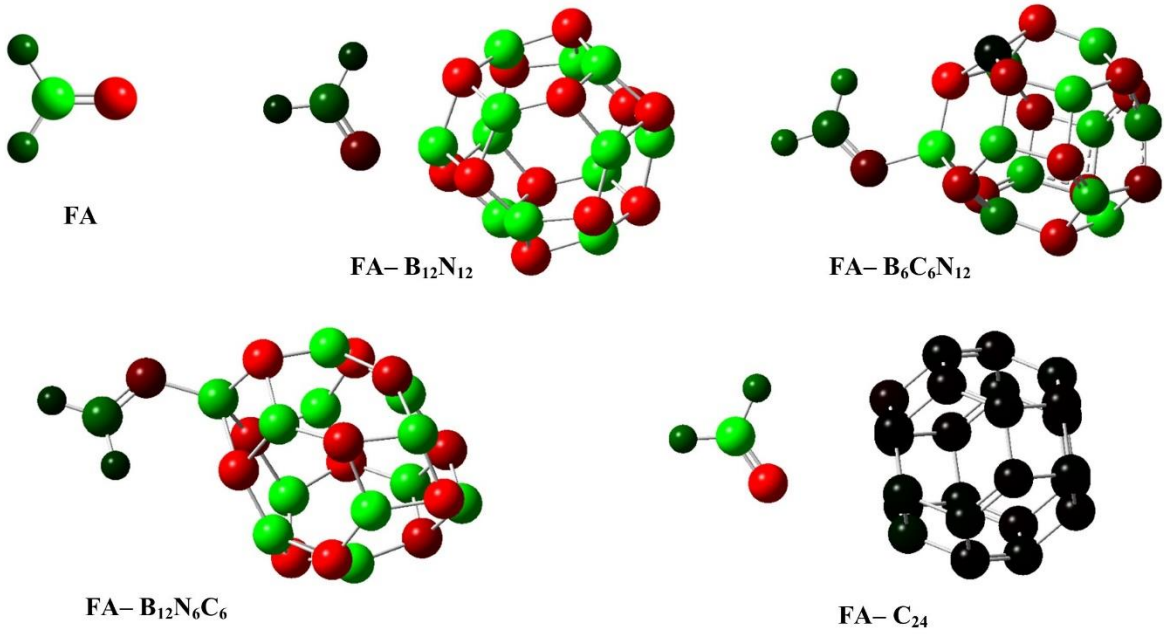

Figure 3. NBO Charge Distribution of Complexes

The calculated adsorption energy results show that interactions have higher tendency to solely molecule, thus in turn after adsorption energies decrease. The lowest adsorption energy belongs to FA-$B_{12}N_6C_6$ complex with a value of -29.63 kcalmol^{-1}. This result suggests the suitability of using $B_{12}N_6C_6$ nanocage for FA adsorption purpose. In contrast the studied nanocages for C_{24} the obtained adsorption energy is the lowest one, -3.34 kcalmol^{-1}. It is also found that the adsorption of FA molecule onto the $B_6N_6C_{12}$, $B_{12}N_6C_6$ have exothermic nature. ΔG value of the FA adsorption onto the $B_{12}N_6C_6$ nanocage also has the lowest value (-17.50 kcalmol^{-1}). The order of change of free energies is FA-$B_{12}N_6C_6$ < FA- $B_6N_6C_{12}$ < FA- $B_{12}N_{12}$ < FA- C_{24}. In contrast to other studied adsorption process, the adsorption of FA molecule onto the C_{24} nanocage has not a spontaneous character with a ΔG value of 5.56 kcalmol^{-1}. The obtained result is also in harmony with the long interaction bond length between FA and C_{24} nanocage. The interaction of FA molecule and boron and nitrogen containing nanocages have spontaneous nature. This implies that modifying C_{24} nanocage can boost the properties of nanomaterial in the favor of desired for efficient adsorption.

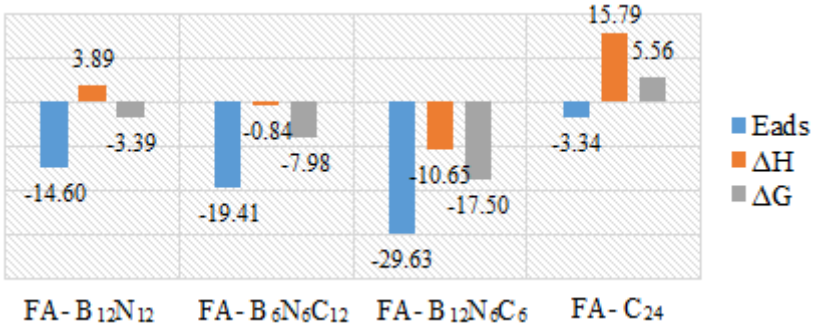

Figure 4. The Changing of Energetic Parameters for Different FA-Nanocage Systems

Investigation of the Electronic Structure Changing

The electronic structure change of nanocages after adsorption of FA is investigated, and results are presented in this part of the study. As, the reactive nature of molecules can be determined by calculating global reactivity indices (Aydogdu & Hatipoglu, 2022b). The calculated global reactivity indices results are listed for before and after adsorption process in Table 1. The changing of ΔE and dipole moment values for adsorption process are also given in Table 2.

It is understood from Table 1 that after occurring of adsorption the energies of frontier molecular orbitals, and the values of global reactivity indices have changed. Hardness value of FA-$B_{12}N_6C_6$ complex decrease to 2.01 eV value.

The changing of electrophilic index and softness values are vice versa. The values of electrophilic index and softness values for FA-$B_{12}N_6C_6$ complex are 4.28, and 0.25 eV respectively. These all mean that the reactivity of the studied nanocages increase after adsorption.

Table 1. Global Reactivity Indices (in eV unit)

	E_{HOMO}	E_{LUMO}	η	μ	ω	S
FA	-9.31	0.23	4.77	-4.54	2.16	0.10
$B_{12}N_{12}$	-9.46	-0.01	4.72	-4.73	2.37	0.11
$B_6N_6C_{12}$	-6.82	-2.30	2.26	-4.56	4.60	0.22
$B_{12}N_6C_6$	-7.45	-2.38	2.53	-4.91	4.76	0.20
C_{24}	-7.49	-0.30	3.59	-3.89	2.11	0.14
FA- $B_{12}N_{12}$	-8.74	-2.20	3.27	-5.47	4.57	0.15
FA- $B_6N_6C_{12}$	-6.09	-2.14	1.98	-4.11	4.28	0.25
FA- $B_{12}N_6C_6$	-6.74	-2.72	2.01	-4.73	5.56	0.25
FA- C_{24}	-7.30	-0.28	3.51	-3.79	2.05	0.14

As seen from the Table 2 that FMO energy difference (ΔE) decreases after adsorption of FA molecule onto the nanocage. The highest decrease of ΔE belongs to FA-$B_{12}N_{12}$ and FA-$B_{12}N_6C_6$ complex systems with the values of % 30.77 and %20.69. Hence, dipole moment values decrease after the interaction of FA molecule and the nanocages. FA-$B_{12}N_6C_6$ complex dipole moment value is the highest one. As a result of changing electronic properties of nanocages after interaction, electrical conductivity increased, and it may lead to generation of an electrical signal. This means that $B_{12}N_{12}$ and $B_{12}N_6C_6$ nanocages can be used as FA sensor.

Table 2. The Calculated Values of FMO Energy Difference (ΔE), and Dipole Moment (D)

	Before			After	
	ΔE (eV)	D (Debye)		ΔE (eV)	D (Debye)
$B_{12}N_{12}$	9.45	0.01	FA- $B_{12}N_{12}$	6.54	7.13
$B_6N_6C_{12}$	4.52	5.08	FA- $B_6N_6C_{12}$	3.96	5.63
$B_{12}N_6C_6$	5.07	0.94	FA- $B_{12}N_6C_6$	4.02	7.36
C_{24}	7.19	0.00	FA- C_{24}	7.02	2.57

Based on the calculated results, the electronic properties of the nanocages change with the occurring of interaction complex structures. As the electronic nature of nanocages differs after adsorption, these nano materials can be used as a sensing material for FA molecule. From all of these results the studied nanocages can be used for sensing and/or removing of FA gas on the environment.

The Effect of the Number of FA on the Adsorption Process

There is also one important thing about adsorption process rather than sensitivity. This is that the nano material should contain large active area. For this reason in this part of the study adsorption efficiency changing of $B_{12}N_6C_6$ with increasing number of FA molecule (n=1-4) is studied. The optimized geometries for the adsorption complexes (2FA-$B_{12}N_6C_6$, 3FA-$B_{12}N_6C_6$, 4FA-$B_{12}N_6C_6$) are illustrated in Figure 5.

As seen from the figure that the distance of oxygen atom of FA and B atom of $B_{12}N_6C_6$ for 2FA-$B_{12}N_6C_6$ complex are 1.54 and 1.52 Å. With the increasing number of FA molecules the same bond length for the newly occurred one gets a larger value. As a conclusion, addition of new adsorbed FA molecule onto the $B_{12}N_6C_6$ alters the molecular geometries of complexes.

The adsorption energies for 2FA-$B_{12}N_6C_6$, 3FA-$B_{12}N_6C_6$, 4FA-$B_{12}N_6C_6$ are calculated as -26.20, -65.83, and -71.32 $kcalmol^{-1}$ respectively. It is understood from the adsorption energies that with the increasing of FA molecules, adsorption becomes easier. The calculated values of FMO energy difference for complexes are 3.82, 3,50, and 3.72

eV. These values are lower the obtained value for one FA adsorbed nanocage complex's value (4.02 eV). All these mean that adsorption of more FA molecule onto the $B_{12}N_6C_6$ nanocage has higher tendency than one FA molecule.

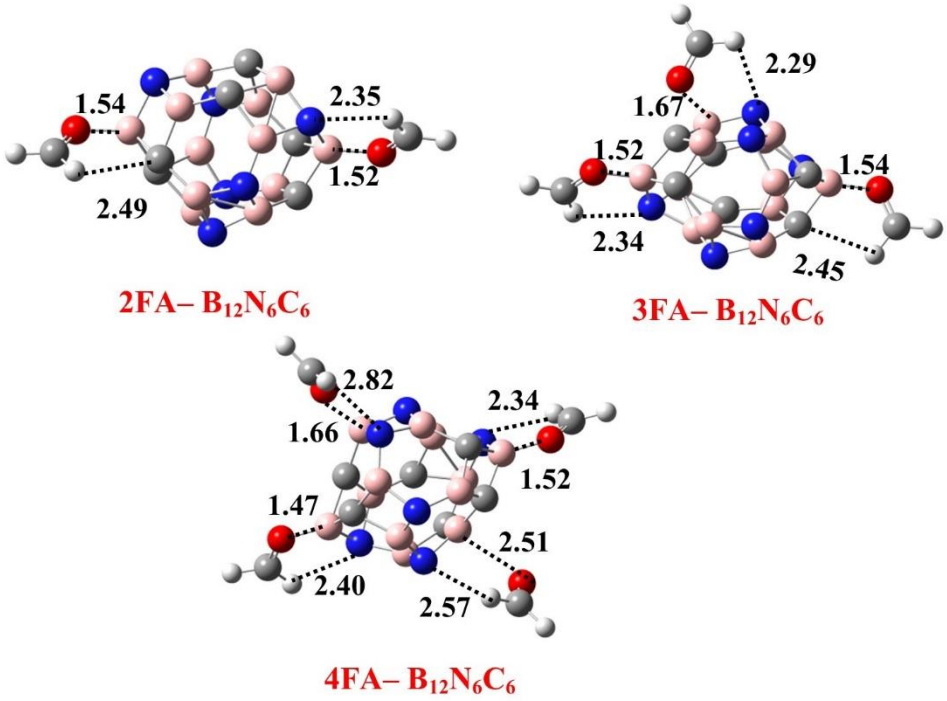

Figure 5 The Molecular Geometries for Different Numbers of FA Molecules (N=1-4) and Nanocages

CONCLUSIONS

Formaldehyde (FA) is threat to human health with its toxic character, so sensing and /or removing it from environment is necessary. In this study the adsorption nature of FA molecule onto the $B_{12}N_{12}$, $B_6N_6C_{12}$, $B_{12}N_6C_6$, and C_{24} nanocages have studied by M06-2X method. According the obtained results FA adsorption onto the nanocages have negative adsorption energies. The highest E_{ads} value belongs to FA- $B_{12}N_6C_6$ nanocage structure with a value of -29.63 kcalmol^{-1}. As well as occurring this structure has the highest spontaneous character. However, the interaction of FA molecule with C_{24} nanocage is not spontaneously occur. Nonetheless, doping of C_{24} nanocage with different number of boron and nitrogen atom is necessary to make nanocage sensitive to FA. It is understood that the reactive nature of nanocages increases after the interaction. Besides, the effect of increasing number of FA molecules on the adsorption is also investigated. It is found that up to four FA molecules adsorption spontaneously occurs. To sum up, depending on all the calculated results $B_{12}N_6C_6$ nanocage may be utilized for removing and/or sensing formaldehyde in the environment. The obtained results may be used for new nano materials development.

Artificial Intelligence Contribution Statement

This manuscript was entirely written, edited, analyzed, and prepared without the assistance of any artificial intelligence tools. All content, including text, data analysis, and figures, was solely generated by the author.

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