Enhancement in hydrogen molecule adsorption on B$_{12}$N$_{12}$ nano-cluster by decoration of nickel

Ali Shokuhi Rad [a,*], Khurshid Ayub [b]

[a] Department of Chemical Engineering, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran
[b] Department of Chemistry, COMSATS Institute of Information Technology, University Road, Tobe Camp, 22060 Abbottabad, Pakistan

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ABSTRACT

We present here results from detailed investigation on the adsorption property of H$_2$ on the surface of B$_{12}$N$_{12}$ (BN) and Ni-decorated B$_{12}$N$_{12}$ (Ni-BN) nano-clusters through density functional theory (DFT) methods. First, the adsorption of Ni on BN nano-cage resulted in optimization of two distinct geometries (P1 and P2) differing in orientation of nickel on the surface of the nano-cage. The binding properties have been calculated and analyzed theoretically for both geometries of Ni-BN (P1 and P2) in terms of binding energies, band structures, total density of states, and natural bond orbital (NBO) charges. The nickel binds more strongly to BN nano-cage in P1 compared to P2, as revealed from energetic and electronic properties. Hydrogen adsorption has also been studied on Ni-BN (both P1 and P2), and compared with that of bare BN nano-cage. H$_2$ adsorption capacity for nickel decorated BN nano-cage (Ni-BN) is considerably enhanced while there is very low adsorption capacity for pristine BN. Although, decoration of Ni in P1 geometry releases slightly higher energy (~444 kJ/mol versus ~399 kJ/mol for P2), the latter is better adsorbent for H$_2$ molecule. H$_2$ adsorption on Ni-BN in P2 geometry is more exothermic (~144 kJ/mol versus ~108 kJ/mol for position P1). The band gap of Ni-BN nano-cages increases upon interaction with hydrogen, and the effect is more pronounced for P2 geometry compared to P1. Incorporation of Ni enhances the H$_2$ adsorption capacity of BN cluster, significantly.

Introduction

Adsorption of H$_2$ on transition metals such as Pt and Ni is a fundamental aspect of numerous chemical processes. For instance, hydrogenation, de-hydrogenation and hydrogenolysis are a few key reactions in chemical industries involving interaction of H$_2$ with metallic surfaces. Majority of the above-mentioned reactions generally happen on the surface of heterogeneous transition metal catalysts [1–3], and depend on the adsorption behavior of H$_2$ molecule on metallic surface. Moreover, H$_2$ interaction with transition metals is imperative to phenomena such as H$_2$ storage and its purification [4,5].

Sub-surface hydrogen has been shown to play dominant role in some chemical reactions, particularly hydrogenation reactions on nickel and on palladium nanoparticles [6–10]. Therefore, a deep understanding of hydrogen interaction with transition metals is very important for different applications. The interaction of H$_2$ with different surfaces of Pd [11], Ru [12],

* Corresponding author. Fax: +98 11132367735.
E-mail addresses: a.shokuhi@gmail.com, a.shokuhi@qaemiau.ac.ir (A.S. Rad).

Fe [13], Pt [14], and Ni [15,16] are already reported in the literature. Moreover, several metallic hydrides have also been studied for hydrogenation reaction. Applications of metal hydrides for hydrogen-storage are excellently presented in a review article by Sakintuna et al. [17]. In another report, Kalamse et al. [18] studied the interaction of H_2 with C_2H_2Ni, C_2H_4Ni complex and also with their dimer using density functional method.

Experimentally, Shivram and Phillips [19,20] have investigated the interaction of hydrogen molecule with Ti doped ethylene and benzene complexes via nano-gravimetry method. Generally, these studies are restricted on dissociation and adsorption of H_2 on mentioned surfaces. Ferrin et al. [21] performed a comprehensive study on interaction of hydrogen with different facets of seventeen transition metals. Yarovsky and his co-worker also reported the adsorption properties of H_2 on Al_{13} cluster. They concluded that this cluster can be used for H_2 storage [22]. Jagiello et al. [23] used DFT calculation to investigate the potential of porous carbons for H_2 adsorption.

Discovery of carbon nanotubes by Ijimia brought a quick development in the field of nano-scale carbon materials [24]. Besides applications of carbon nano-tube and fullerene C60 in advanced materials, extensive research have been carried out to synthesize spherical or tubular fullerenes of diverse non-carbon inorganic materials. For example boron nitride (BN) [25], and silica [26]and aluminum nitride (AlN) [27] and co-axial cubic AlN–BN composite nanotubes [28] are a few examples in this regard.

These nano-clusters are subject of several recent investigations [29–31] because these clusters with closed electronic shells are extremely stable and potentially important building blocks for advanced materials. Based on different theoretical studies on $(XY)n$ clusters, the fullerene-like cages $X_{12}Y_{12}(X = B, Al, Ga, and Y = N, P, As)$ are known as the most stable clusters [32,33]. Jensen and Toftlund [34] investigated various geometries of $B_{12}N_{12}$ using ab-initio calculation, and they concluded that $B_{12}N_{12}$ cluster is characterized by superior stability compared to analogous C24. $B_{12}N_{12}$ cluster was synthesized by Oku et al. [35], and detected by laser desorption time-of-flight mass spectrometry. These nano-structures are excellent adsorbent and sensor for a variety of molecules.

In our recent research [36], we have investigated the adsorption of guanine molecule on the surface of four nano-cages through DFT calculations. We found that despite $Al_{12}N_{12}$ has the highest adsorption energy; $B_{12}N_{12}$ and $B_{12}P_{12}$ show more changes in electronic property upon adsorption of guanine. Spherical non-carbon nano-cages can also be used for hydrogen storage. For example, Guo et al. have found that a hydrogen molecule interacts with AlN cages with considerable adsorption energy [37]. The capability of AlN nano-structures to store hydrogen has also been studied by Wang et al. [38].

In the recent past, numerous theoretical reports have appeared on metal decorated or doped nanostructures [39–44], besides pure nanostructures. We have reported the adsorption of nickel on the surface of $Al_{12}P_{12}$ [45]. We found that there are four possible sites for decoration of nickel atom. Moreover, it was found that doping of transition metal increases the hydrogen storage potential of clusters [46]. In

particular Ti, V, Ni, and Pd were extensively utilized in the hydrogenation reaction. Moreover, Pd/AlN/SiC, Pd/AlN/SiO$_2$ and PdeNi/AlN/n Sinano-composites have also been used for hydrogen storage and hydrogen sensing [47–49].

Zhang et al. [50] investigated the feasibility of bare and Ni decorated $Al_{12}N_{12}$ cages for hydrogen storage. They found that at $Al_{12}N_{12}$ cage, each Al atom is able to adsorb one H_2 in molecular form, while in the Ni decorated $Al_{12}N_{12}$ cage, the most stable site for Ni atom has been found to adsorb up to three hydrogen molecules.

In the current study, we examine the adsorption of H_2 on the surface of BN and Ni-BN nano-cages. First, we explore the geometric and electronic properties of BN surfaces upon decoration of Ni by examining binding energies, the charge transfer, density of states, dipole moments and adsorption geometries for each position. Then, the relaxed Ni-BN clusters are theoretically investigated for H_2 adsorption. Moreover we also discuss the dissociative or non-dissociative adsorption on the surface of BN and Ni-BN nano-cages. This is the first systematic DFT study of hydrogen adsorption on BN nano-cages.

Computational methods

All calculations were performed using Gaussian 09 suite of program [51] using DFT at B3LYP/6-31G (d,p) functional/basis set. Geometry optimization, density of states (DOS), charge transfer, the molecular electrostatic potential (MEP), and HOMO–LUMO distribution were performed to investigate the adsorption phenomena. B3LYP is a well-known, accurate and frequently used functional for nanostructures like $X_{12}Y_{12}$ [34,44,52]. We have searched on the influence of Ni-decorating on the electronic properties of BN cluster. A number of possible orientation are considered for decoration of Ni on BN nano-cage but all input geometries resulted in optimization of two structures namely P1 and P2 (vide infra). The adsorption energy of Ni on the BN in both positions is calculated by:

$$E_{ad} = E_{Ni-BN} - (E_{BN} + E_{Ni}) \qquad (1)$$

where E_{Ni-BN} is the total (electronic) energy of BN interacting with the Ni and E_{BN} is total energy of an isolated BN, and E_{Ni} is the total electronic energy of an isolated Ni. The interaction energy of H_2 with isolated BN and Ni-BN is calculated by:

$$E_{int (BN)} = E_{H_2-BN} - (E_{BN} + E_{H_2}) \qquad (2)$$

$$E_{int (Ni-BN)} = E_{H_2-Ni-BN} - (E_{Ni-BN} + E_{H_2}) \qquad (3)$$

Where $E_{int(BN)}$ and $E_{int(Ni-BN)}$ correspond to interaction energy of H_2 with BN and Ni-BN, E_{H_2-BN} and $E_{H_2-Ni-BN}$ are total electronic energies of BN and Ni-BN interacting with the H_2, and E_{H_2} is the total energy of an isolated H_2.

Parr et al. [53] mentioned the electrophilicity concept for the first time in 1999. Chemical potential (μ) is defined as [54]:

$$\mu = -1/2 \times (E_{HOMO} + E_{LUMO}) \qquad (4)$$

where E_{HOMO} and E_{LUMO} are the energies of HOMO and LUMO, respectively. Moreover, hardness (η) could be considered using the Koopmans' theorem [54] as: