Materials Chemistry and Physics 194 (2017) 337–344

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Adsorption properties of acetylene and ethylene molecules onto pristine and nickel-decorated $Al_{12}N_{12}$ nanoclusters

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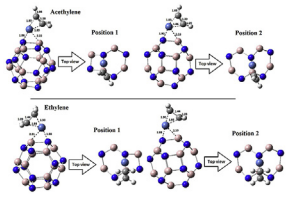
HIGHLIGHTS

- B3LYP and WB97XD functionals were used to investigate the adsorption of ethylene and acetylene.
- Ni-decorated $Al_{12}N_{12}$ shows much higher adsorption property than pristine $Al_{12}N_{12}$ for ethylene and acetylene adsorption.
- Pristine $Al_{12}N_{12}$ is p-type semiconductor while Ni-decorated $Al_{12}N_{12}$ is n-type semiconductor.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 December 2016
Received in revised form
17 February 2017
Accepted 1 April 2017
Available online 3 April 2017

Keywords:
$Al_{12}N_{12}$
Nickel
C_2H_2
C_2H_4
Nanocluster
Fullerene-like cage

ABSTRACT

We present here theoretical results on adsorption of two important industrial gases (C_2H_2 and C_2H_4) on free $Al_{12}N_{12}$ and Ni-decorated $Al_{12}N_{12}$ fullerene-like nanoclusters. Binding energies have been calculated with B3LYP and wB97XD methods of density functional theory. The binding energies were corrected for the basis set superposition error (BSSE) for 6-31G (d,p) basis set. Despite both molecules could be adsorbed on the surface of free $Al_{12}N_{12}$ with moderate binding energies of ~ −37 (BSSE corrected: −25.7) kJ/mole for ethylene and ~−58 (BSSE corrected: 44.6) kJ/mole for acetylene, based on wb97xd functional, however much strong interaction is achieved for Ni-decorated nano-cages over pure $Al_{12}N_{12}$. Adsorption energy of acetylene varies depending on the position of nickel decoration whereas the adsorption of ethylene is independent of the position of nickel decoration. The adsorption energies for acetylene and ethylene on $Al_{12}N_{12}$ nano-cage range from −294 to −410 (−202.1 to −281.3, BSSE corrected) kJ/mol. Along with high values of adsorption energy for Ni-decorated $Al_{12}N_{12}$ nano-cage, we found relatively low interaction distance, and high orbital hybridization upon adsorption of mentioned molecules on the surface Ni-AlN. Results of charge analyses show that upon adsorption of these molecules on free $Al_{12}N_{12}$, it acts as p-type semiconductor which interestingly, changes to n-type semiconductor when nickel is decorated on its surface.

1. Introduction

Nanostructures are appealing adsorbent for a variety of molecule due to their unique electronic properties and high ratio of surface to volume [1]. Discovery of carbon nano-tube has triggered the research on utilizing these nano-structures materials (graphene and its family) for sensor applications [2–9]. The key point of all

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http://dx.doi.org/10.1016/j.matchemphys.2017.04.002
0254-0584/

these studies is increase in the electrical conductivity of graphene on electrochemical sensing of analytes. With the passage of time, metal and non-metal hybrid materials have appeared in the literature as sensor for various analytes. These hybrid materials are particularly appealing due to their high electrophilicity. These materials could be in different shapes, including sheet-like [10,11] and fullerene-like [12].

Group III-V $X_{12}Y_{12}$ semiconductors are excellent sensors because of their excellent physical as well as chemical properties [13–20]. Many reports exist in the literature where adsorption of a variety of molecules is studied on the surface of $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$, and $B_{12}P_{12}$ fullerene-like semiconductors [15–18]. Between diverse semiconductors, $Al_{12}N_{12}$ is of exceptional interest because of its low electron attraction and exclusive thermo physical properties [21]. Wu et al. demonstrated that the $Al_{12}N_{12}$ nanocluster is energetically the most stable cluster among the different types of (AlN)n clusters [22]. We became interested in exploring the sensing properties of $Al_{12}N_{12}$ nano-cage for acetylene and ethylene molecules.

Adsorption of acetylene (C_2H_2) and ethylene (C_2H_4) at different surfaces is the subject of many experimental and theoretical studies [23–27]. Transition metals of the VIII group are brilliant catalysts for reactions involving unsaturated hydrocarbons [23] which clearly reflect that they are also good adsorbent for these molecules. For this reason, it could be interesting to explore the interaction of lightweight hydrocarbons such as C_2H_2 and C_2H_4 on appropriate surfaces containing transition metals [23–27]. In this regard [27], recently, we have investigated adsorption property of these two molecules on the surface of Pt-decorated graphene. We demonstrated that this modified graphene surface is excellent adsorbent for acetylene and ethylene whereas very weak adsorption is shown by pristine graphene.

In the present research, we demonstrate adsorption of C_2H_2 and C_2H_4 on the surface of pristine and nickel-decorated fullerene-like $Al_{12}N_{12}$ by using density functional theory (DFT). To the best of our knowledge, there is no report in the literature on the adsorption of these molecules on nickel decorated nano-cages. We analyzed all possible relaxed structures of adsorbed C_2H_2 and C_2H_4 on above-mentioned surfaces. We present the results on adsorption through values of binding energy, the net amount of charge transfer, HOMO as well as LUMO distribution of all free- and complexed form of $Al_{12}N_{12}$ nano-cage.

2. Method of calculations

Because of limited surface area of $Al_{12}N_{12}$ nanocluster, one may use isolated nanocluster rather than periodical border conditions for its calculation [28], so we consider isolated systems for all optimizations and calculations used in this study.

To determine the geometries of adsorbed C_2H_2 and C_2H_4 on pristine and Ni-decorated $Al_{12}N_{12}$, we used DFT method using B3LYP (and wb97xd) with 6-31G (d,p) basis set as implemented in Gaussian 09 suite of program [29]. A number of possible orientations of acetylene and ethylene on the surfaces of AlN and Ni@AlN are considered. The geometries were optimized without any symmetry constraints. The optimized geometries are perturbed by manually displacing the analyte and allowing it to relax again. The B3LYP is well known and appropriate for nanocluster calculations [17,18]. Moreover, It has been formerly proven that B3LYP/6-31G(d,p) is an optimal level of theory to achieve reliable and accurate results at minimum cost [30]. During all optimizations, the global charge of systems was neutral.

Since dispersion forces may have important role for above-mentioned systems, therefore, accurate estimation of binding energies is calculated with dispersion corrected functional. For this aim, the adsorption energy has been investigated using long range corrected meta-hybrid functional (wB97XD) [31].

The net charge transfer upon complexation of C_2H_2 and C_2H_4 molecules with pristine and decorated $Al_{12}N_{12}$ was calculated using natural bond orbital (NBO) from the differences in their charge concentrations before and after adsorption.

Binding energies are calculated according to the following equations:

$$E_b \text{ (for AlN)} = E_{(X-ALN)} - E_{AlN} - E_X \quad (1)$$

$$E_b \text{ (for Ni} - \text{decorated AlN)} = E_{(X-NiALN)} - E_{NiAlN} - E_X \quad (2)$$

Where E_{AlN} and E_{NiAlN} correspond to total energies of free $Al_{12}N_{12}$ and Ni-decorated $Al_{12}N_{12}$, respectively. $E_{(X\text{-}ALN)}$ is the energy of complexed form of $Al_{12}N_{12}$, $E_{(X\text{-}NiALN)}$ is the energy of complexed form of Ni-decorated $Al_{12}N_{12}$, E_x is the energy of free acetylene or ethylene. Calculations involving interacting molecules are susceptible to basis set superposition error. In these complexes, each molecule utilizes functions from the neighboring molecules which effectively increases the basis set. Therefore, it becomes necessary to correct for these errors. Besides using infinite basis set, BSSE is an effective approach to eliminate the error. All calculations in this study are BSSE corrected. Counter poise method corrects this energy as shown in Equation (3).

$$\Delta E_{b,\,CP} = \Delta E_b - E_{BSSE} \quad (3)$$

Where $\Delta E_{b,\,CP}$ and E_{BSSE} are counterpoise corrected energy and the energy of basis set superposition error, respectively.

The electrophilicity concept was stated by Parr et al. [32]. Chemical potential (μ) is defined based the subsequent equation [33]:

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

where E_{HOMO} is the energy of HOMO and E_{LUMO} is the energy of LUMO. In addition, hardness (η) can be calculated using the Koopmans' theorem [33] as:

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (5)$$

Softness (S) [33] and electrophilicity (ω) [33] are defined as the subsequent equations, respectively.

$$S = 1/(2\eta) \quad (6)$$

$$\omega = \mu^2/2\eta \quad (7)$$

3. Results and discussion

We have shown recently that nickel adsorbs on the surface of AlN nano-cage in four distinct geometries (P1-P4) [20]. These geometries differ in orientation of nickel on the nano-cage. The highest binding energies of nickel on AlN nano-cage are observed for P1 and P2 geometries (113.6 and 113.7 kcal mol-1 for P1 and P2, respectively). P1 and P2 geometries refer to Ni@b64 and Ni@b66, respectively. Ni@b64 is the geometry where nickel is adsorbed on a bond shared between four and six membered ring. Similarly, Ni@b66 is the adsorption of nickel on a bond shared between two six membered ring. The other orientations (P3 and P4) are thermodynamically less stable than P2 by 3.5 and 27.0 kcal mol^{-1}. P3 and P4 correspond to the adsorption of nickel at the center of four and six membered ring, respectively. P1 and P2 geometries of