

Investigation of Hydrogen Cyanide and Ethanol Adsorption on Aluminum-doped BNNT to Produce 1,3-Oxazole: A DFT Approach

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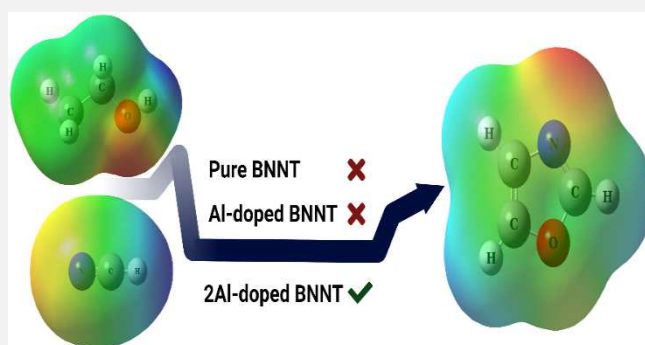


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ABSTRACT

1,3-Oxazole is an essential compound in drug products with many uses. This compound can be produced by the reaction of hydrogen cyanide and ethanol. An expensive toxic metal is commonly used as a catalyst to trigger this reaction. As a result, introducing an inexpensive and metal-free catalyst for this reaction may be helpful. To this end, we studied the boron nitride nanotube with its characteristic properties. The surface activity of the boron nitride nanotube was improved by substituting one boron atom with an aluminum atom for this reaction. In the present work, we examined the possible interactions between the hydrogen cyanide and ethanol molecules on the surface of the aluminum-doped boron nitride nanotube. We explored the electrostatic potential surfaces to predict possible interactions and surface activities. In addition, the thermodynamic parameters have been calculated for the adsorption processes. The calculated thermodynamic parameters show that the adsorption of these molecules on the aluminum-doped boron nitride nanotube is exothermic and thermodynamically favored.



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Keywords: Hydrogen cyanide, ethanol, oxazole, boron nitride nanotube, aluminum-doped

1. Introduction

The heterocyclic compounds with branched conjugated systems including oxazole, thiazole, or pyrazole moieties have shown themselves as powerful scaffolds in drug design [1-3]. 1,3-Oxazole plays a vital role in the manufacture of various biologically active drugs such as brain-derived neurotrophic factor inducers [4], analgesic, trypanocidal activity, antimetabolic agents with pro-apoptotic activity [5], antibacterial and antituberculosis properties [6], antifungal activity, anti-inflammatory [7], antidepressant [8], antimicrobial, antidiabetic and antiobesity [9,10], antiviral, and analgesic effect. Thus, 1,3-Oxazole could be considered as a perspective moiety in the design and further synthesis of novel biologically active agents that exert anticancer activity [11-13].

In many studies, 1,3-Oxazole was produced by nitriles and alcohols [14]. Hydrogen cyanide as a simple nitrile and ethanol as simple alcohol are used to produce 1,3-Oxazole [14]. Due to the thermodynamic stability and kinetically inertness of HCN, there is a need for a catalyst in 1,3-Oxazole production, and for this reaction, metal-based catalysts are common. As metal-based catalysts are expensive and toxic [15], researchers metal-free catalysts for this reaction.

Recently, researchers have used nanostructure materials as metal-free catalysts for many reactions [16-19]. The nanostructure materials have the high surface-to-volume ratio characteristic and have a suitable performance as a catalyst. The boron nitride nanotube exhibited excellent catalytic activity in many studies. However, we need to substitute a boron or nitride atom with heteroatom to improve the surface activity of the nanotube, by modifying the electronic structure. In this study, we explored the adsorption of hydrogen cyanide and ethanol on the boron nitride nanotube theoretically to take 1,3-Oxazole. The pure and Al-doped boron nitride nanotubes were investigated as the adsorption surface in this work. After studying the possible adsorptions of hydrogen cyanide and ethanol on the

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boron nitride nanotube, the possible interactions for the reaction process have been examined. The main aim of this work is to study and suggest a surface for the reaction of hydrogen cyanide and ethanol to take 1,3-Oxazole.

2. Computational details

In this work, we investigated the adsorption of hydrogen cyanide and ethanol molecules on the boron nitride nanotube to obtain 1,3-Oxazole. All the calculations have been carried out by using density functional theory (DFT) at the B3LYP/6-31G(d) level of theory [20] performed in the GAMESS program suite [21]. To study the surface activity of boron nitride nanotubes, the pure and aluminum-doped zigzag (6,0) boron nitride nanotubes (BNNT) were used. The end boron and nitrogen atoms of the studied nanotube were saturated by hydrogen atoms. The diameter of the studied nanotube and its number of atoms were in good agreement with the other works in this field [22]. All possible configurations have been probed to understand how the hydrogen cyanide and ethanol molecules have been adsorbed on the studied BNNT to produce 1,3-Oxazole. Electrostatic surface potential (ESP) for pure and Al-doped BNNT, together with hydrogen cyanide and ethanol molecules, were obtained to be able to suggest the possible interactions. Thermodynamic parameters of any interactions have been estimated, by the same level of theory. The net charge transfer (q_{CT}) from the hydrogen cyanide and ethanol molecules to the pure and Al-doped BNNT was calculated using Mulliken population analysis, which is the charge difference between the adsorbed hydrogen cyanide and ethanol molecules.

In this work, the adsorption of hydrogen cyanide and ethanol on every possible site in the center place of pure and Al-doped BNNT has been studied. After characterizing the possible adsorption of both hydrogen cyanide and ethanol molecules on the studied nanotubes, possible reactions to produce the 1,3-Oxazole were studied. In the following subsection, all the adsorption processes. To study the reaction of hydrogen cyanide and ethanol on BNNT as a catalyst needs one or both hydrogen cyanide and ethanol molecules to be adsorbed on the surface of the catalyst. Therefore, we studied the possible adsorptions. To that end, we first looked at the ESP of the hydrogen cyanide and ethanol molecules and the pure and Al-doped BNNT. Many studies use ESP to predict the possible interactions between the structures [23].

As can be seen from **Figure 1A**, from a potential point of view, the ESP for the HCN in the region around the N atom is negative and the region around the H atom is positive. The ESP for the ethanol (**Figure 1B**) shows that the potential around O atoms is strongly negative and around the H atom bonded to the O atom is positive slightly. On the other hand, as shown in **Figure 1C**, the potential around the B and N atoms in the center of BNNT is about neutral. For the Al-doped BNNT, the potential around the B and N atoms is like the BNNT, and around the Al atom, it is strongly positive (see **Figure 1C**). So, the adsorption between the opposite potential sites of the studied structures should occur. We studied every possible adsorption for the correctness of the previous sentence. Nevertheless, sometimes the adsorption between structures with the same potential may also happen. Hence, to explore possible adsorptions first, the interaction of HCN and ethanol molecules with the BNNT has been investigated, separately.

The HCN molecule was set upright on the carbon atom and the center of a honeycomb of BNNT from the N atom and H atom, individually. In this work, the adsorption of hydrogen cyanide and ethanol on every possible site in the center place of pure and Al-doped BNNT has been studied. After characterizing the possible adsorption of both hydrogen cyanide and ethanol molecules on the studied nanotubes, possible reactions to produce the 1,3-Oxazole were studied. In the following subsection, all the adsorption processes. To study the reaction of hydrogen cyanide and ethanol on BNNT as a catalyst needs one or both hydrogen cyanide and ethanol molecules to be adsorbed on the surface of the catalyst. So, we studied the possible adsorptions. For this, we first looked at the ESP of the hydrogen cyanide and ethanol molecules and the pure and Al-doped BNNT. Many studies use ESP to predict the possible interactions between the structures [23].

As illustrated in **Figure 1A**, from a potential point of view, the ESP for the HCN in the region around the N atom is negative and the region around the H atom is positive. The ESP for the ethanol (**Figure 1B**) shows that the potential around O atoms is strongly negative and around the H atom bonded to O atom is positive slightly. On the other hand, as shown in **Figure 1C**, the potential around the B and N atoms in the center of BNNT is about neutral. For the Al-doped BNNT, the potential around the B and N atoms is like the BNNT, and around the Al atom, it is strongly positive (see **Figure 1C**). So, the adsorption between the opposite potential sites of the studied structures should occur. We studied every possible adsorption for the correctness of the previous sentence. However, sometimes the adsorption between structures with the same potential may also happen. As a result, for a study about

possible adsorptions, first, the interaction of HCN and ethanol molecules with the BNNT has been probed, separately. The HCN molecule was set upright on the carbon atom and the center of a honeycomb of BNNT from the N atom and H atom, individually.

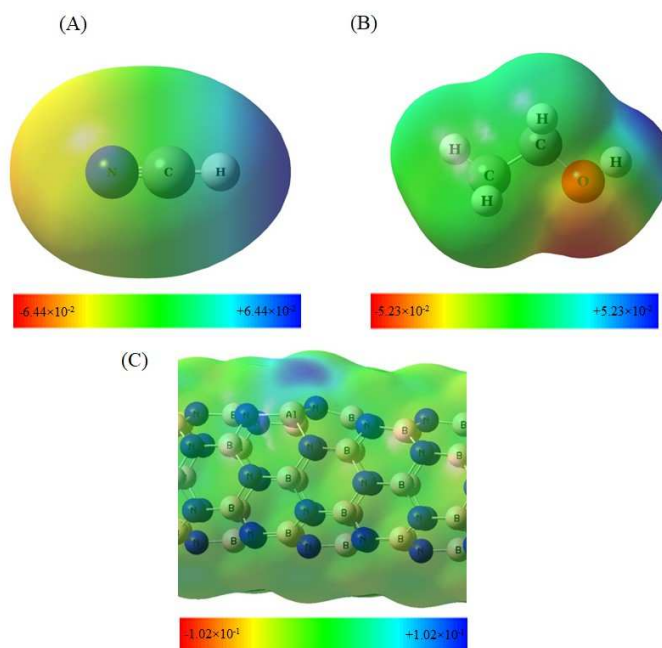


Figure 1. Electrostatic surface potential for (A) hydrogen cyanide, (B) ethanol, and (C) Al-doped BNNT.

For these configurations, adsorption did not occur, neither from the N atom nor from the H atom. Consequently, ethanol was the other molecule we would like to study its possible interactions with BNNT. To inspect the ethanol molecule adsorption on BNNT, it was set upright on B and N atoms and the center of a honeycomb from three sides (O atom, H atom bonded to O, H atom bonded to C). There was no adsorption between the ethanol molecule and the BNNT for the said positions.

As mentioned earlier, no suitable adsorption happened for the HCN and ethanol molecules on BNNT as a catalyst to occur reaction between them. So, to improve the BNNT surface activity, one of the boron atoms of BNNT was replaced by an aluminum atom, and we named it Al-doped BNNT. For this nanotube, the possible adsorption was studied, too. First step; the HCN molecule was set upright on the Al atom from the N and H atom sides. The only adsorption occurred between the N atom of the HCN and the doped Al atom. The calculated adsorption energy for this process is $-25.08 \text{ kcal.mol}^{-1}$ (see **Table 1**), and it shows, that this adsorption process is exothermic. To continue, for the reaction of HCN and ethanol, there were two possible ways. For the first way, the ethanol molecule is closed to the adsorbed HCN, and then the reaction between them was inspected for the second way, the ethanol molecule was adsorbed on BNNT, and then the reaction with HCN was studied. For the first way, the ethanol molecule from the O atom closed to H, C, and N atoms of the adsorbed HCN, and the possible adsorptions were studied.

There was no interaction between the mentioned studied configurations to use as a first intermediate for the study of one reaction pathway. For the second way, the configuration that the HCN molecule has been adsorbed on the Al-doped BNNT, the possible adsorption of the ethanol molecule was studied. Some of the configurations for the studied adsorptions are shown in **Figure 2** which the B series are the configurations after energy optimization. The ethanol molecule was set upright on the B and N atoms and the center of the honeycomb from the three mentioned sides. There was no adsorption between the ethanol molecule and the BNNT for the said positions. Second step; the ethanol molecule was set upright on the Al atom from the O atom and the H atom bonded to the O atom, and the H atoms bonded to the C atom sides. The only adsorption occurred between the O atom of the ethanol and the doped Al atom (configuration 7B). The obtained adsorption energy for this configuration is $-9.62 \text{ kcal.mol}^{-1}$ (see **Table 1**). This adsorption process is exothermic and thermodynamically

avored. Then we studied the closing of the HCN molecule to the adsorbed ethanol from N and H atoms to investigate the reaction between them. There was no interaction between the corresponding sides for this configuration, either. Additionally, we studied the adsorption of the HCN molecule from N and H atoms on B and N atoms and also the center of one of the honeycombs of Al-doped BNNT. Nonetheless, there was no adsorption between the mentioned sides of HCN and the Al-doped BNNT for the said positions. Accordingly, this time the study of the reaction of HCN with ethanol molecule on the surface is impossible, too. The calculated thermodynamic parameters for the two configurations that HCN or ethanol molecules adsorbed on Al-doped BNNT are listed in **Table 1**.

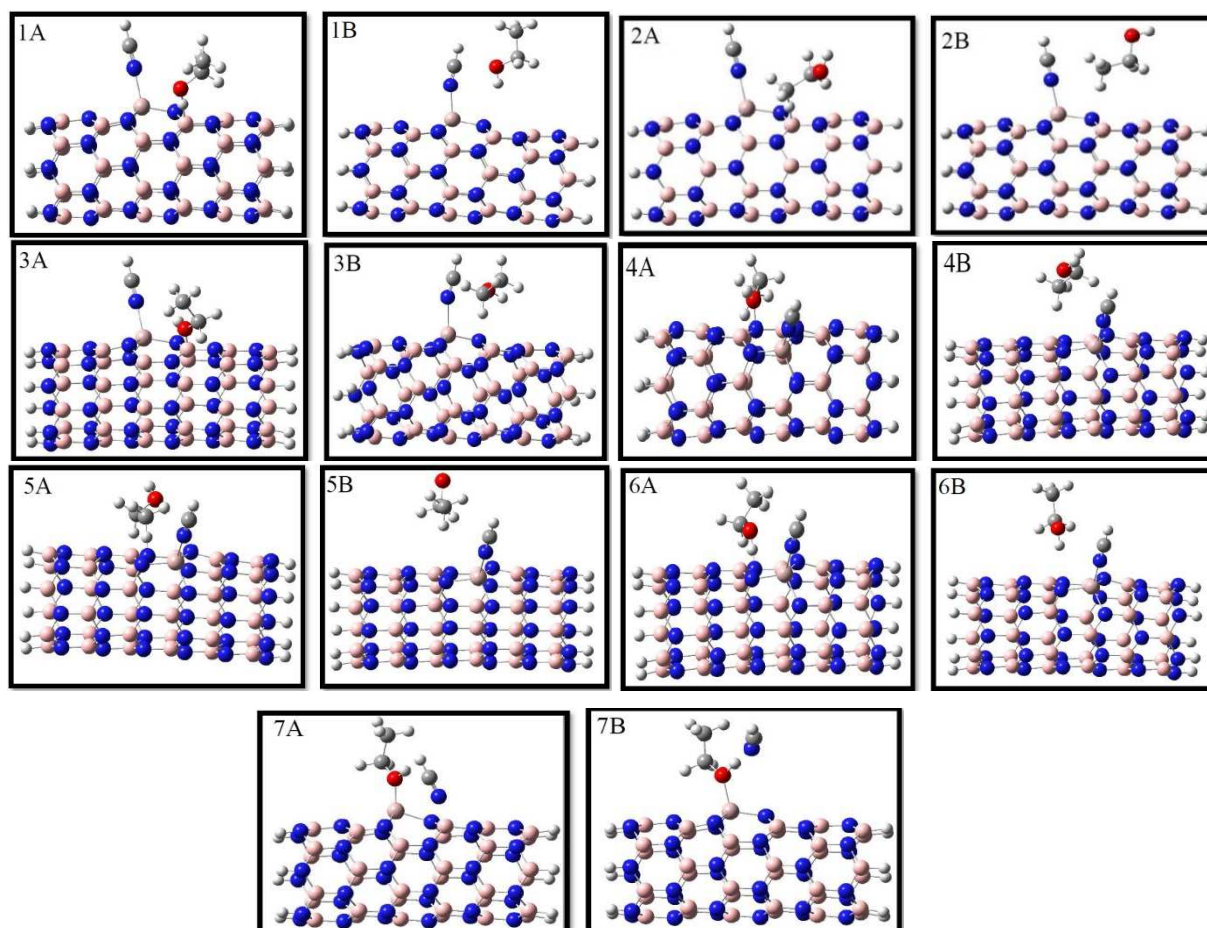


Figure 2. Configurations of some of the possible interactions (A) series are before optimization and (B) series are after optimization.

Table 1. The adsorption energy, changes of Gibbs free energy (ΔG_{298}), and q_{CT} for Al-doped BNNT with adsorbed HCN, or ethanol.

Configuration	E_{ads} (kcal/mol)	ΔG_{298} (kcal/mol)	E_{gap} (eV)	q_{CT} (e)
Al-doped BNNT+HCN	-25.08	-10.38	3.76	-0.17
Al-doped BNNT+Ethanol	-9.62	-4.83	5.18	-0.15

Total electronic density of states (DOS) for the pure, Al-doped BNNT, with and without HCN and ethanol molecules has been calculated in this work. The DOS plots for nanotubes with and without HCN and ethanol molecules are plotted in **Figure 3**, for the briefness. The HOMO–LUMO gap (E_{gap}) for nanotubes with the studied molecules is displayed in **Table 1**. It is well known that the electrical conductance of a material is related to its E_{gap} value and changing the values of E_{gap} leads to an effect on electric conductivity and so on sensitivity. As can

be seen from **Figure 3**, the calculated DOS plots for the pure, Al-doped BNNT show the E_{gap} value is 4.56 and 5.07 eV, respectively. By adsorption of the HCN or ethanol molecules on the Al-doped BNNT it changes to 3.76 and 5.18 eV, respectively. So adsorption of these molecules on mentioned nanotube could change the E_{gap} . So, Al-doped BNNT has a surface activity for these adsorptions.

The activity of the surface was improved by substituting one boron atom with the aluminum atom and thus, the adsorption problem of hydrogen cyanide and ethanol molecules was resolved. But the reaction happens between the two adsorbed molecules on the catalyst surface, and it needs to adsorb each other. Since the adsorption of the individual hydrogen cyanide and ethanol on the doped aluminum is exothermic, and thermodynamically favored, hydrogen cyanide and ethanol should adsorb on two doped aluminums on the surface. Thus, the two-time aluminum-doped boron nitride nanotube may be a suitable catalyst for producing the 1,3-Oxazole at room temperature with or without using any palpable energy.

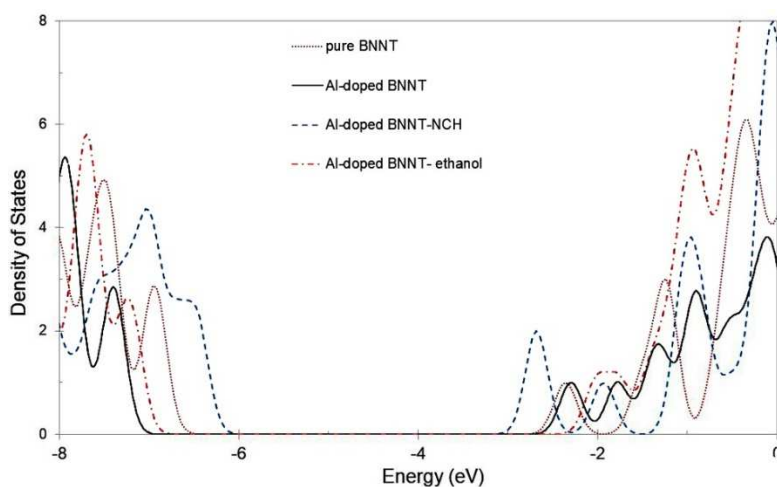


Figure 3. The DOS of pure BNNT, Al-doped BNNT, Al-doped BNNT/NCH, and Al-doped BNNT/ethanol.

3. Conclusion

In the present work, we focused on the free metal catalysts to produce the 1,3-Oxazole from hydrogen cyanide and ethanol. We have studied boron nitride nanotubes for their characteristic properties as catalysts. Pure boron nitride nanotube has not acted as a suitable catalyst in the first step for adsorption. As a result, we improved its activities by substituting one boron atom with the aluminum atom. The adsorption problem of hydrogen cyanide and ethanol has been resolved by an aluminum-doped boron nitride nanotube. But the two molecules need to adsorb each other on the catalyst surface so that reaction happens between them. As the adsorption of the individual of hydrogen cyanide and ethanol on the doped aluminum is exothermic and thermodynamically favored, so, hydrogen cyanide and ethanol should adsorb on two doped aluminum on the surface. Hence, the two-time aluminum-doped boron nitride nanotube may be a suitable catalyst for producing the 1,3-Oxazole at room temperature with or without using any palpable energy.

Authors' contributions

All authors contributed to data analysis, drafting and revising of the paper and agreed to be responsible for all the aspects of this work.

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Declaration of competing interest

The authors declare no competing interest.

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Data availability

Data will be made available on request.

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