



Article Selective Hydrogenation of Acetylene Catalysed by a B₁₂N₁₂ Cluster Doped with a Single Nickel Atom: A DFT Study

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Abstract: To obtain a catalyst based on a non-precious metal that can replace traditional palladium-based selective catalysts of acetylene hydrogenation, the catalytic performances of two different configurations of a $B_{12}N_{12}$ cluster doped with a single nickel atom were studied by a density functional theory computational approach. After analysing the effect that the adsorption of reactants onto the clusters has on the reaction path, we determined the lowest energy path for the acetylene double hydrogenation. Comparing the acetylene hydrogenation activities and ethylene product selectivities of the $B_{11}N_{12}N_{11}$ and $B_{12}N_{11}N_{11}N_{12}$ which have different doping sites, we determined the activities of these two catalysts to be similar to each other; however, the $B_{11}N_{12}N_{11}$ cluster was calculated to have higher selectivity for ethylene as a product. This difference may be related to the moderate adsorption of hydrogen and acetylene on the $B_{11}N_{12}N_{12}N_{11}N_{12}N_{12}N_{11}N_{12}N_{12}N_{11}N_{12}N_{$

Keywords: selective hydrogenation; B₁₂N₁₂; DFT; non-precious metal

1. Introduction

Currently, the selective hydrogenation of acetylene to produce ethylene is still mainly realised through use of catalysts comprising palladium or other precious metals as the active material [1–4], in the presence of a carrier and a small amount of inhibitor such as Zn [5], Ag [6], Cu [7] and Si [8]. Palladium-based catalysts are favoured by researchers as a result of their high acetylene hydrogenation activity and their selectivity for ethylene as product [2,9]. On the other hand, palladium is an expensive heavy metal that is quite harmful to the environment [10,11]. Therefore, it is imperative to improve the efficiency and accessibility of the described reaction by finding selective acetylene hydrogenation catalysts of increased activity and decreased cost and environmental impact.

In 2011, Zhang et al. were the first to propose the concept of single-atom catalyst (SAC) [12], which has attracted much research attention, because SACs greatly improve the utilisation rate of the catalysts' active components. SACs have special geometric and electronic characteristics through the coordination of the active centre of a single metal atom and the carrier material, and thus show a completely different catalytic ability than alloys and the pure metal [13]. A series of palladium-based acetylene selective hydrogenation SACs have been introduced, leading researchers to achieve a significant improvement in the catalytic performance [14–17]. The transition metal nickel can also catalyse the hydrogenation of acetylene to ethylene. However, pure metallic nickel displays poor catalytic selectivity, so, in the presence of nickel-based catalysts, the described hydrogenation reaction needs to be conducted at high temperature [18–20]. We thus tried to design a nickel-based selective acetylene hydrogenation SAC of improved efficacy with respect to the known ones. In such SAC, nickel is

the active centre, and Ni atoms at high dispersion are used to dope the catalyst support surface, which is characterised by high surface area, based on the assumption that such a feature may improve the catalyst's activity and selectivity [21].

Since the successful synthesis of the smallest boron nitride fullerene $B_{12}N_{12}$ cluster in 1998 [22], numerous studies have been conducted focusing on this material. Strout's research proved the structure of the $B_{12}N_{12}$ cluster to be very stable [23]. Oku et al. performed molecular orbital calculations to demonstrate the possibility of hydrogen storage in boron nitride clusters [24–26]. Kuo et al. modified the $B_{12}N_{12}$ cluster by incorporating a carbon atom within it to improve this boron nitride fullerene's hydrogen storage performance [27]. The results of Ayub et al.'s research indicate that hydrogen adsorption on the surface of Ni-modified $B_{12}N_{12}$ (Ni-BN) nanoclusters significantly increased with respect to their unmodified counterparts [28]. Therefore, we turned our attention to boron nitride fullerene $B_{12}N_{12}$. Previously, our group has reported that a Pd-doped BN nanocluster can be used as a selective catalyst for acetylene hydrogenation [17].

In the present study, a $B_{12}N_{12}$ cluster is combined with the transition metal nickel as part of the effort to develop an effective and selective catalyst for the hydrogenation of acetylene. Notably, the coordination of B or N atoms has been shown to enhance the ethylene product selectivity of metallic nickel catalysts, and the BN fullerene carrier has been observed to help improve the utilisation of metal atoms to 100%, while preventing excessive adsorption of hydrogen and acetylene onto the catalyst, thus ensuring the catalyst's selectivity. This study has certain reference value in the search for non-precious metals catalysts that may replace traditional palladium-based catalysts of the selective hydrogenation of acetylene to ethylene.

2. Results and Discussion

2.1. Structure Optimisation of the Reactants

In Figure 1 are reported the results of the optimisation calculations performed on all reactants and catalysts. The "undoped" $B_{12}N_{12}$ fullerene is characterised by a Th-symmetrical structure with both B and N atoms. The value of Mulliken charge for the B atom is 0.57 and for the N atom is -0.57. As can be evinced from Figure 1a and Table S1, the $B_{12}N_{12}$ cluster consists of four- and six-membered rings. Two kinds of B-N bonds are present: the length of the B-N bond within the four-membered ring is 1.487 Å, whereas that within the six-membered ring is 1.439 Å. Following the introduction of a Ni atom in the $B_{12}N_{12}$ cluster, two different configurations are obtained, depending on which element is replaced by Ni: the $B_{11}N_{12}N_1$ cluster (Figure 1b) and the $B_{12}N_{11}N_1$ cluster (Figure 1c).



Figure 1. The optimised structures of undoped $B_{12}N_{12}$ cluster (**a**), $B_{11}N_{12}Ni$ (**b**) and $B_{12}N_{11}Ni$ (**c**). H atom is white; B atom is pink; C atom is grey; N atom is mazarine; Ni atom is blue.

In the $B_{11}N_{12}N_{$

significantly outward as shown in Figure 1b and Table S2. In the $B_{11}N_{12}N_1$ cluster, the value of the Mulliken charge is -0.43 for N(1) and -0.34 for N(2) as a result of a charge transfer from the N atoms to the Ni centre.

In the $B_{12}N_{11}Ni$ cluster, the lengths of the bonds linking the metal centre to the two adjacent boron atoms B(1) and B(2) are 1.960 Å and 1.977 Å, respectively; these bonds are thus longer than the Ni-N bonds in $B_{11}N_{12}Ni$, and the relevant bond angle measures 92.01°. The Ni atom is more convex outward as shown in Figure 1c and Table S3. In the $B_{12}N_{11}Ni$ cluster, the value of the Mulliken charge is 1.26 for B(1) and 1.12 for B(2), as a result of a charge transfer from the B atoms to the Ni atom.

To render more intuitive the charge distribution in the BN fullerene before and after its doping with Ni, we analysed the molecular electrostatic potential of the $B_{12}N_{12}$, $B_{11}N_{12}N_{11}$ and $B_{12}N_{11}N_{11}$ clusters on the molecular van der Waals surface (electron density: 0.001). In the structures reported in Figure 2, the more intense the blue colour, the more positive the charge, and the more intense the red colour, the more negative the charge. As can be evinced from the mentioned Figure 2a, in undoped BN fullerene, the B atoms are positively charged and the N atoms are negatively charged. In Figure 2b, the electrostatic potential minimum is -0.95 eV above N(2) and the maximum is 2.23 eV above the Ni atom. In Figure 2c, the electrostatic potential minimum is -0.79 eV above N(1) and the maximum is 2.08 eV above the Ni atom. In the $B_{11}N_{12}N_{1}$ and $B_{12}N_{11}N_{1}$ clusters, the Ni atom is highest electropositive, so it has the potential to act as a nucleophilic reaction site, and the N atoms around the metal centre exhibit stronger electronegativity than their counterparts in undoped BN fullerene, which may in turn favour electrophilic reactions.



Figure 2. The molecular electrostatic potential of the $B_{12}N_{12}$ (**a**), $B_{11}N_{12}Ni$ (**b**) and $B_{12}N_{11}Ni$ (**c**) clusters on the molecular van der Waals surface (electron density: 0.001, energies in a.u.).

To deepen understanding of the characteristic of the BN fullerene before and after its doping with Ni, we performed the frontier molecular orbital analysis on the $B_{12}N_{12}$, $B_{11}N_{12}N_{13}$ and $B_{12}N_{11}N_{13}$ cluster. The energies of the frontier orbitals are listed in Table 1. The value of the LUMO – HOMO energy gap of the $B_{12}N_{12}$ cluster is 6.72 eV, which is consistent with that reported in the literature [29]. Furthermore, the energy of the HOMO of each of the two BN clusters doped with the nickel atom is higher than that of the HOMO of the undoped cluster and the energy of the LUMO of each of the two BN clusters doped with the nickel atom is lower than that of the LUMO of the undoped cluster. The lower the energy of LUMO, the more conducive to the filling of electrons, and the higher the energy level of HOMO, the more conducive to the loss of electrons. Therefore, the energy gap between HOMO and LUMO is reduced as a result of the doping process, the change that favours in the next adsorption of the reactants, thus promoting the catalytic reaction activity.

Table 1. The orbital energies on the HOMO and LUMO of $B_{12}N_{12}$, $B_{11}N_{12}N_1$ and $B_{12}N_{11}N_1$, and their energy gaps (energies in eV).

	номо	LUMO	ΔEg
$B_{12}N_{12}$	-7.95	-1.24	6.72
B ₁₁ N ₁₂ Ni	-7.08	-5.11	1.97
B ₁₂ N ₁₁ Ni	-5.18	-2.52	2.66

To better understand the molecular orbital energy changes associated with the doping of the $B_{12}N_{12}$ cluster with a Ni atom and the contribution of each component to the total density of states, we plotted the total density of states and the density of partial states of the undoped B₁₂N₁₂, B₁₁N₁₂Ni and B₁₂N₁₁Ni clusters. These plots are reported in Figure 3, where each cluster's frontier orbitals are also indicated. As can be evinced from Figure 3a, the value of LUMO – HOMO gap is large, thus the $B_{12}N_{12}$ cluster displays the features of an insulator. The p orbitals of the N atoms are the main contributors of the HOMO and of the lower energy occupied molecular orbitals; on the other hand, the p orbitals of the B atoms are the main contributors of the LUMO and of the higher energy unoccupied molecular orbitals. The features of the plot reported in Figure 3b suggest that, after replacing a B atom with a Ni atom, a new unoccupied molecular orbital is added in the original forbidden band, and this new orbital becomes the LUMO of the $B_{11}N_{12}Ni$ cluster. Notably, the original HOMO increases in energy and shifts to the right. Therefore, upon doping the B₁₂N₁₂ cluster with a nickel atom to form the $B_{11}N_{12}N_1$ cluster, the LUMO – HOMO energy gap decreases. In the $B_{11}N_{12}N_1$ cluster; moreover, the p orbitals of the N atoms are the main contributors to the HOMO, LUMO and the lower energy occupied molecular orbitals, with the contribution to these orbitals of the Ni atom being negligible. The HOMO and LUMO population maps of the $B_{11}N_{12}Ni$ cluster are also reported in Figure 3b; in this case, the electrons are concentrated from N atoms to around the Ni atom compared to the undoped $B_{12}N_{12}$ cluster (see Figure 3a). As can be evinced from Figure 3c, after replacing an N atom with a Ni atom, a new occupied molecular orbital is added to the original forbidden band, and this new orbital becomes the HOMO of the $B_{12}N_{11}Ni$ cluster. Notably, the energy of the original LUMO decreases and moves to the left. As a result of these changes, the LUMO – HOMO energy gap of the $B_{12}N_{11}N_{11}$ cluster is smaller than that of the $B_{12}N_{12}$ cluster. Additionally, in the $B_{12}N_{11}Ni$ cluster, the p orbitals of the B atoms are the main contributors of the HOMO and of the higher energy unoccupied molecular orbitals; on the other hand, the p orbitals of the N atoms are the main contributors of the lower energy occupied molecular orbitals. The s and p orbitals of the B atoms are major contributors of the LUMO, and the orbitals of the Ni atom make some contribution to the HOMO and LUMO. Based on the HOMO and LUMO population maps of the $B_{12}N_{11}N_1$ cluster, we can infer that electrons accumulate near the Ni atom and the B atoms in the metal centre's immediate vicinity. We speculate that Ni and its surrounding B atoms have strong activity.



Figure 3. The TDOS and PDOS of $B_{12}N_{12}$ (**a**), $B_{11}N_{12}N_{11}$ (**b**) and $B_{12}N_{11}N_{11}$ (**c**) and their calculated HOMO and LUMO.

2.2. Adsorption of C_2H_2 and H_2 onto BN Fullerene or the BN-Ni Cluster

Implementing our computational approach, we obtained the stable adsorption configuration and the value for the adsorption energy of acetylene and hydrogen onto BN fullerene and nickel-doped BN clusters. The stable adsorption configurations are reported in Figure 4, whereas the values for the adsorption energies are reported in Table 2.



Table 2. The adsorption energies of C_2H_2 and H_2 separately adsorb on $B_{12}N_{12}$, $B_{11}N_{12}N_1$ and $B_{12}N_{11}N_1$ (energies in kcal/mol).

Figure 4. The optimised structures of C_2H_2 absorbed on $B_{12}N_{12}$ (**a**), $B_{11}N_{12}Ni$ (**b**) and $B_{12}N_{11}Ni$ (**c**); the optimised structures of H_2 absorbed on $B_{12}N_{12}$ (**d**), $B_{11}N_{12}Ni$ (**e**) and $B_{12}N_{11}Ni$ (**f**). H atom is white; B atom is pink; C atom is grey; N atom is mazarine; Ni atom is blue.

In Figure 4a and Table S4 are depicted the optimised configuration of acetylene adsorbed on the $B_{12}N_{12}$ cluster. According to our data, almost no differences exist between the structures of acetylene and the $B_{12}N_{12}$ clusters before and after adsorption. Acetylene and the cluster are quite far from each other, and the adsorption of acetylene on the cluster is physical in nature, with the value of the adsorption energy calculated to be -2.83 kcal/mol.

In Figure 4b and Table S5 are depicted the stable configuration of acetylene adsorbed on the $B_{11}N_{12}Ni$ cluster. In this case, some changes in the configuration of acetylene and the $B_{11}N_{12}Ni$ cluster are observed as a result of the adsorption process. Acetylene is close to the $B_{11}N_{12}Ni$ cluster and is 2.146 Å apart. The C(2) of acetylene and the Ni atom of the cluster are close to each other, and the C=C bond is slightly elongated with respect to 'free' acetylene (to a value of 1.215 Å). Following acetylene adsorption, the Ni atom is relatively more convex, with the length of the Ni–N(2) bond increasing to a value 1.942 Å and that of the Ni–N(3) bond increasing to 1.952 Å. The value of the N(2) –Ni–N(3) bond angle is reduced to 101.8°. Acetylene is physically adsorbed onto the $B_{11}N_{12}Ni$ cluster, with the value for the adsorption energy calculated to be –11.92 kcal/mol. The Mulliken charge for C(1) has a value of –0.094 and for C(2) is –0.160; in this case, the Mulliken charge for Ni has a value of –0.163; consequently, the charge transfer from acetylene to the Ni centre.

In Figure 4c and Table S6 a stable configuration of acetylene adsorbed onto the $B_{12}N_{11}Ni$ cluster is depicted. As can be evinced from this figure, the configurations of acetylene and of the $B_{12}N_{11}Ni$ cluster are significantly different from their "free" counterparts, with acetylene undergoing an obvious deformation as a result of the adsorption process. Acetylene's C(1) is adsorbed onto the Ni atom of the cluster, with a value for the length of the Ni–C(1) bond of 1.894 Å. Acetylene's C(2) is adsorbed onto the B(1) atom of the cluster, and the C(2)–B(1) bond length has a value of 1.857 Å. The C–C bond is elongated to a value of 1.344 Å, and the Ni atom in the $B_{12}N_{11}Ni$ cluster is convex to C(1). Following acetylene adsorption, the length of Ni–B(1) bond increases to 2.399Å and that of the Ni-B(2) bond increases to 2.035Å. Furthermore, the value for the B(1)–Ni–B(2) bond angle decreases to 88.19°. Acetylene is chemisorbed on the $B_{12}N_{11}Ni$ cluster, and the adsorption energy is calculated to have a value of -40.40 kcal/mol. The Mulliken charge for C(2) has a value of -0.061 and that for B(1) is 0.584, as a result of the charge transfer from C(2) to B(1). The Mulliken charge for C(1) has a value of -0.497 and that for the Ni atom is -0.515, with the charge being transferred from the Ni atom to C(1); in this case, the Mulliken charge for B(2) has a value of 0.922, and charge is transferred from B(2) to the Ni atom.

In Figure 4d and Table S7 are depicted the optimised configuration of hydrogen adsorbed on the $B_{12}N_{12}$ cluster. Following this adsorption process, the configurations of hydrogen and cluster remain almost unchanged. Hydrogen and the $B_{12}N_{12}$ cluster are quite far from each other. Hydrogen adsorption on the $B_{12}N_{12}$ cluster is physical in nature, and the adsorption energy is calculated to have a value of -0.05 kcal/mol.

In Figure 4e and Table S8, the stable configuration of hydrogen adsorbed on the $B_{11}N_{12}Ni$ cluster is depicted. As can be evinced from this figure, the configurations of hydrogen and the cluster change significantly following adsorption. Hydrogen is completely dissociated on the $B_{11}N_{12}Ni$ cluster, and the adsorption energy is -1.90 kcal/mol. The distance between the two hydrogen atoms is 2.793 Å. H1 is adsorbed on the N(2) atom, and the length of the H–N bond is 1.019 Å. H(2) is adsorbed on the Ni atom, and the length of the H–Ni bond is 1.409 Å. The Ni atom protrudes away from the N(1) atom, and the value for the N(2)–Ni–N(3) bond angle is reduced to 98.28°. The Mulliken charge for H(2) has a value of 0.137, as a result of the charge transfer from H(2) to the Ni centre. The Mulliken charge for N(1) has a value of -0.834 and that for H(1) is 0.459, with the charge being transferred from H(1) to N(1).

In Figure 4f and Table S9, the stable configuration of hydrogen adsorbed on the $B_{12}N_{11}Ni$ cluster is depicted. As can be evinced from this figure, the configurations of hydrogen and the $B_{12}N_{11}Ni$ cluster change very significantly following adsorption. Hydrogen is completely dissociated on the $B_{12}N_{11}Ni$ cluster, and the adsorption energy is calculated to have a value of -4.28 kcal/mol. The distance between the two H₂-derived hydrogen atoms is 2.379 Å. H(1) is adsorbed on B(1), and the length of the H(1)–B(1) bond is 1.217 Å. H(2) is adsorbed on the Ni atom, and the length of the H(2)–Ni bond is 1.557 Å. The Ni atom protrudes away from B(1), and the value for the N(2)–Ni–N(3) bond angle is reduced to 80.62°. The value of the Mulliken charge for H(2) is -0.089, as a result of the charge transfer from H(2) to the Ni atom. The Mulliken charge for H(1) is 0.079 and that for B(1) is 1.633; in this case, charge is transferred from H(1) to B(1).

2.3. Acetylene Selective Hydrogenation Reaction Mechanism

The addition reaction between acetylene and hydrogen taking place on the catalyst's surface starts with the stable co-adsorption (CO) of the two reactants on the said surface; it then passes through several transition states (TS) and intermediates (IM), to finally yield the reaction product (P).

2.3.1. Effect of Co-Adsorption Structure on Hydrogenation of Acetylene to Ethylene

To study the effect that different co-adsorbed structures have on acetylene hydrogenation, we investigated the mechanism of acetylene hydrogenation under two different co-adsorptions on the surface of the $B_{12}N_{11}Ni$ cluster. In Figure 5a and Tables S10–S16, the configuration changes

associated with each step of reaction pathway for the hydrogenation of acetylene to ethylene taking place on the surface of the $B_{12}N_{11}Ni$ cluster are depicted. In Figure 5b, the energy changes associated with each step of the pathway is reported.



Figure 5. The reaction process and potential energy change for the different reaction pathways R3 of catalytic hydrogenation of acetylene to ethylene on $B_{12}N_{11}Ni$. (a) The structures of calculated hydrogenation reaction diagram for the $B_{12}N_{11}Ni$. (b) The reaction process and potential energy change of catalytic hydrogenation of ethylene to ethylene on the $B_{12}N_{11}Ni$. H atom is white; B atom is pink; C atom is grey; N atom is mazarine; Ni atom is blue.

The reaction pathway starts with co-adsorption configuration CO involving the $B_{12}N_{11}Ni$ cluster; initially, the two carbon atoms of acetylene are adsorbed on the Ni centre and boron atom B(2); on the other hand, dihydrogen is adsorbed around the Ni centre, with the two H atoms partially dissociating from each other. The distance between the two H₂-derived hydrogen atoms is slightly larger than the isolation state. The adsorption energy of the co-adsorbed structure is -42.41 kcal/mol. H(2) vibrates in the C(1) direction, and H(1) vibrates in the B(3) direction to produce the transition state TS1 (characterised by a single imaginary frequency of -1248.70 cm⁻¹), then reaction intermediate IM1 is produced. In it, H(1) has been adsorbed on B(3), H(2) has been added to C(1) and the distance between C(1) and Ni has increased with respect to the case of the co-adsorbed structure CO. Notably, the value for the energy barrier separating TS1 from CO is 6.54 kcal/mol. Next, H(1) attacks C(1) to

produce transition state TS2, the species characterised by a single imaginary frequency $(-356.31 \text{ cm}^{-1})$; notably, the value for the energy barrier separating IM1 from TS2 is 26.07 kcal/mol. Intermediate IM2 is subsequently produced, whereby the CH₃CH group has been adsorbed on the B₁₂N₁₁Ni cluster. Finally, H(3) migrates from C(1) to C(2), and ethylene is produced by way of transition state TS3 (characterised by a single imaginary frequency of -1028.14 cm^{-1}). The process whereby IM2 turns into TS3 is the rate controlling step of the reaction pathway, and the overall pathway's activation energy is calculated as 41.79 kcal/mol.

In another reaction route, the reaction pathway starts with co-adsorption configuration CO2. In Figure 6a and Tables S17–S30 are depicted the configuration changes associated with the various steps of the pathway and the energy changes are reported in Figure 6b. The adsorption energy of CO2 is calculated as -51.87kcal/mol. The two acetylene carbon atoms get adsorbed on the Ni atom, and the two H₂-derived hydrogen atoms completely dissociate and get individually adsorbed onto the two B atoms bound to the nickel centre. Subsequently, the transition state TS1 is produced, which corresponds to the structure characterised by only one imaginary frequency (-1193.64 cm⁻¹). In this structure, the B–H bond is elongated to a value of 1.736 Å, and H(2) attacks C(2) to produce the reaction intermediate IM1, which is characterised by an energy barrier of 19.51 kcal/mol. The H(1) atom, which is bound to B(1), then approaches C(1), and, after passing through the transition state TS2, which is the structure characterised by only one imaginary frequency (-1182.85 cm⁻¹), the intermediate IM2 is produced. The process just described, whereby TS2 turns into IM2, is the rate-determining step in acetylene hydrogenation to ethylene. The energy barrier of the entire reaction is calculated to be 28.17 kcal/mol, whereas the desorption energy of ethylene is 17.15 kcal/mol.

Our data indicate that the activation energy of the second reaction pathway is lower than the first reaction pathway, so the second is the optimal pathway for acetylene hydrogenation to ethylene via catalysis by the $B_{12}N_{11}Ni$ cluster. The starting points of these reaction pathways consist in different co-adsorbed structures. By comparing the data we collected on the two reaction pathways, we determined that the co-adsorbed structures would greatly affect the reaction.

In CO2, hydrogen is completely dissociated, and the H_2 -derived H atoms are adsorbed on the B atoms where the B atoms are nearby both sides of the two acetylenic carbons. The adsorption positions of the hydrogen atoms render favourable these atoms' attack on different carbon atoms. In CO, as acetylene occupies the adsorption site on the catalyst, the two H_2 -derived hydrogen atoms can only be adsorbed around the Ni atom. After H(1) is added to C(1), the vinyl group rotates away from the Ni centre, as a result of an increase in steric hindrance, and H(2) can only be added to the C(1) atom, which is the closest to it, to produce the CH₃CH moiety. For the migration of H atoms between two carbon atoms to take place, an extremely high energy barrier needs to be overcome, which accounts for the higher activation energy of the first pathway. What is why a suitable co-adsorbing structure can facilitate the reaction, and an unsuited co-adsorbing structure can be adverse.

2.3.2. Effect of Different Ni-Doped Catalysts on the Acetylene Hydrogenation Activity

To compare the effect that different Ni doping sites on the $B_{12}N_{12}$ clusters have on the acetylene hydrogenation activity, we also explored the mechanism of acetylene hydrogenation to ethylene on the $B_{11}N_{12}Ni$ cluster. In Figure 7a and Tables S31–S42 are depicted the configuration changes associated with the various steps of the optimal pathway on the $B_{11}N_{12}Ni$ cluster and the energy changes are reported in Figure 7b. Herein, acetylene is adsorbed around the Ni atom, and the two H₂-derived hydrogen atoms are completely dissociated, with each of them adsorbed on either the Ni atom or one of the nitrogen atoms bound to the metal centre. The value for the co-adsorption energy is calculated to be -17.60 kcal/mol. The only imaginary frequency of the first transition state TS1 is -237.87 cm⁻¹. In this state, H(1) attacks C(1) to produce the intermediate IM1, whose formation is characterised by an energy barrier of 2.13 kcal/mol. H(2), which is attached to N(1), then attacks C(2), and, after passing through transition state TS2 characterised by a single imaginary frequency of -1890.66 cm⁻¹, the intermediate IM2 is produced. The process whereby TS2 is transformed into IM2 is

the rate determining step in the hydrogenation of acetylene to ethylene; the energy barrier of reaction pathway is calculated to be 26.54 kcal/mol, whereas the desorption energy of ethylene is 9.75 kcal/mol.



Figure 6. (a) The structures of calculated hydrogenation reaction diagram for the $B_{12}N_{11}N_i$. (b) The reaction process and potential energy change of catalytic hydrogenation of ethylene to ethane on the $B_{12}N_{11}N_i$. H atom is white; B atom is pink; C atom is grey; N atom is mazarine; Ni atom is blue.



Figure 7. (a) The structures of calculated hydrogenation reaction diagram for the $B_{11}N_{12}N_{11}$. (b) The reaction process and potential energy change of catalytic hydrogenation of ethylene to ethane on the $B_{12}N_{11}N_{11}$. H atom is white; B atom is pink; C atom is grey; N atom is mazarine; Ni atom is blue.

Our data indicate that the activation energy on the $B_{11}N_{12}Ni$ cluster is lower than the $B_{12}N_{11}Ni$ cluster, so the hydrogenation of acetylene to ethylene on $B_{11}N_{12}Ni$ clusters has better reaction activity. This shows that compared with the structure in which nickel is coordinated with three boron atoms, nickel is more active in coordination with three nitrogen atoms. Similarly, the desorption energy of ethylene on the $B_{11}N_{12}Ni$ cluster is lower than the $B_{12}N_{11}Ni$ cluster. It demonstrates that ethylene is more easily desorbed from the $B_{11}N_{12}Ni$ cluster, thereby reducing the possibility of deep hydrogenation. We surmise that the $B_{11}N_{12}Ni$ cluster is more ethylene-selective than the $B_{12}N_{11}Ni$ cluster.

2.3.3. Selectivity of Acetylene Hydrogenation to Ethylene

For the purpose of determining whether the $B_{11}N_{12}N_i$ and $B_{12}N_{11}N_i$ clusters have ethylene selectivity, deep hydrogenation was continued to produce ethane after getting ethylene and compared its activation energy with that of ethylene.

In Figure 7, we hydrogenated intermediate IM2 further, so as to produce intermediate IM3, which is characterised by ethylene and hydrogen co-adsorbed on the $B_{11}N_{12}Ni$ cluster. In this intermediate, hydrogen is completely dissociated: H(5) is adsorbed on Ni and H(6) is adsorbed on N(3); the distance between Ni and N(3) has increased from 1.952 Å to 3.099 Å with respect to IM2. After transition state TS3, which is characterised by having only one imaginary frequency of -185.86 cm^{-1} , is produced, H(5) is added to C(1) to produce intermediate IM4. At this time, the distance between H(6) and C(2) is large. Following the ensuing formation of transition state TS4 (characterised a single imaginary frequency of -428.73 cm^{-1}), H(6) rotates in the C(2) direction so that intermediate IM5 forms, wherein Ni and N(3) are close in space to each other. After the ensuing formation of transition state TS5, which is characterised by a single imaginary frequency of -1535.98 cm^{-1} , H(6) is added to C(2) to form ethane. The energy required for the described process to take place is calculated to be 34.04 kcal/mol, and this process is the rate-controlling step in the generation of ethane. As the activation energy required to form ethane is greater than that required for ethylene production (26.54 kcal/mol), the hydrogenation of acetylene occurring on the $B_{11}N_{12}Ni$ cluster is a selective process, with ethylene being the favoured product, with a calculated value for the selectivity of 24.29.

To compare the effect that different Ni doping sites on the $B_{12}N_{12}$ clusters have on the ethylene selectivity of the acetylene hydrogenation, we also explored the mechanism of acetylene hydrogenation to ethane after the formation of ethylene on the $B_{12}N_{11}N_1$ cluster. As can be inferred from the data reported in Figure 6, intermediate IM2 is further hydrogenated to form intermediate IM3. In this intermediate, dihydrogen has dissociated completely, and the two resulting hydrogen atoms are adsorbed on different boron atoms located in the vicinity of the nickel centre. Ethylene, at this stage, is not obviously deformed and adsorbed on the top of the Ni atom. The distance between Ni and B(2) increases with respect to the IM2 case to 2.026 Å. After the transition state TS3, which is characterised by a single imaginary frequency of -154.31 cm⁻¹, is produced, the C–C bond of ethylene increases in length, and C(1) approaches B(2), leading to the formation of intermediate IM4. The ensuing formation of intermediate IM5 is achieved by the preliminary formation of transition state TS4 (characterised by a single imaginary frequency of -1151.81 cm⁻¹), whereby H(5) is added to ethylic carbon C(2). Notably, in IM5 C(2) rotates away from the N atom. This rotation may be due to the increase in steric hindrance associated with the attachment of three hydrogen atoms to C(2). After transition state TS5, characterised by a single imaginary frequency of -302.29 cm⁻¹, has been produced, H(6) migrates from B(1) to the vicinity of B(2), the atom to which the ethyl group is attached, and the intermediate IM6 is produced. The energy required for this process to occur is calculated to be 34.65 kcal/mol, and this process is the rate-limiting step in ethane formation. Then transition state TS6 (characterised by a single imaginary frequency of -1063.04 cm⁻¹) is produced, and finally H(6) is added to C(1) to form ethane. As the activation energy required for ethane formation is greater than that required for ethylene formation (28.17 kcal/mol), the acetylene hydrogenation reaction taking place on the $B_{12}N_{11}N_{11}$ cluster is selective for ethylene as the product and the value for the selectivity of ethylene 17.49.

3. Computational Methods

In the present study, the Gaussian 09 software package was used [30], and all calculations were processed implementing the B3LYP hybrid density functional method [31–35]. The 6-31+G(d,p) basis set [36,37] was used for the B, C, N and H atoms, and the LANL2DZ base group [38–40] was used for the Ni atom. The counterpoise method was used to correct the base set superposition error [41]. The long-range dispersion correction was performed by the Grimme empirical dispersion correction method (DFT-D3) [42]. Frequency calculations were implemented to optimise the structures of the catalysts, reactants, intermediates, transition states and product in the absence of symmetry

constraints. Notably, the transition state is the only species characterised by only one imaginary frequency. At the same time, intrinsic reaction coordinate calculations were performed in order to verify whether the transition state can be connected to the two intermediates in the reaction pathway [43,44]. All the energies involved in the calculation are taken as the zero-point corrected electronic energies, taking the Basis Set Superposition Error into consideration. Wave function analysis was performed using the Multiwfn program [45,46]. The possible reactive sites, adsorption configurations and charge changes of the reactants were explored through analysis of the frontier molecular orbitals, density of states, molecular electrostatic potentials and atomic charges of BNNi clusters.

The adsorption energy (E_{ad}) was calculated employing Equation (1):

$$E_{ad} = E_{adsorption \ state} - (E_{hydrogen/acetylene} + E_{catalyst}), \tag{1}$$

The value of the catalyst's selectivity can be obtained employing Equation (2):

Selectivity =
$$E_{\text{ethane barrier}} - E_{\text{ethylene desorption}}$$
 (2)

4. Conclusions

The results of our investigation indicate that the acetylene hydrogenation reactions catalysed by the above mentioned single-nickel-doped clusters conform to the Horiuti–Polanyi mechanism [47]. The activity of the $B_{11}N_{12}Ni$ and $B_{12}N_{11}Ni$ clusters differs by only 1.63 kcal/mol, but the $B_{11}N_{12}Ni$ cluster is expected to display higher ethylene product selectivity than the $B_{12}N_{11}Ni$ cluster. This difference may be the result of the moderate degree of acetylene and hydrogen adsorption on the $B_{11}N_{12}Ni$ cluster based on the Sabatier Principle, a different scenario to those of the undoped $B_{12}N_{12}$ and the $B_{12}N_{11}Ni$ clusters. The low intensity of the described interaction is beneficial to the progress of the hydrogenation reaction, and it does not cause ethylene desorption to become difficult. Compared with the catalytic systems investigated in previously published studies, whose results are reported in Table 3 [17,48–50], the $B_{11}N_{12}Ni$ cluster has moderate acetylene hydrogenation activity and increased ethylene selectivity. In particular, the hydrogenation activity of the $B_{11}N_{12}Ni$ cluster is almost equivalent to that of the $B_{11}N_{12}Pd$ cluster with similar structure, but the ethylene selectivity is much better. The $B_{11}N_{12}Ni$ cluster has certain development prospects in catalytic the selective hydrogenation of acetylene by non-precious metals.

Catalyst	E _{ethylene barrier}	Selectivity	B ₁₂ N ₁₁ Ni
B ₁₁ N ₁₂ Ni	26.54	24.29	This work
B ₁₂ N ₁₁ Ni	28.17	17.49	This work
Ni ₃ Sn	42.43	12.91	[29]
Ni ₃ Sn ₃	12.22	3.23	[29]
NiGa(111)	24.44	14.53	[30]
Ni ₆	22.60	15.35	[31]
$B_{11}N_{12}Pd$	26.55	12.80	[12]

Table 3. Comparison of the energy barriers for the desorption energy of ethylene and the selectivity with different catalysts (energies in kcal/mol).

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/1/115/s1, Table S1. The Cartesian coordinates of B12N12 cluster, Table S2. The Cartesian coordinates of B11N12Ni cluster, Table S3. The Cartesian coordinates of B12N11Ni cluster, Table S4. The Cartesian coordinates of acetylene adsorption on B12N12 cluster, Table S5. The Cartesian coordinates of acetylene adsorption on B11N12Ni cluster, Table S6. The Cartesian coordinates of acetylene adsorption on B12N12 cluster, Table S6. The Cartesian coordinates of acetylene adsorption on B12N12Ni cluster, Table S6. The Cartesian coordinates of acetylene adsorption on B12N11Ni cluster, Table S6. The Cartesian coordinates of hydrogen adsorption on B12N12 cluster, Table S8. The Cartesian coordinates of hydrogen adsorption on B12N11Ni cluster, Table S9. The Cartesian coordinates of hydrogen adsorption on B12N11Ni cluster, Table S9. The Cartesian coordinates of hydrogen adsorption on B12N11Ni cluster, Table S9. The Cartesian coordinates of hydrogen adsorption on B12N11Ni cluster, Table S9. The Cartesian coordinates of hydrogen adsorption on B12N11Ni cluster, Table S9. The Cartesian coordinates of hydrogen adsorption on B12N11Ni cluster, Table S10. The Cartesian coordinates of CO on B12N11Ni cluster, Table S11. The Cartesian coordinates of TS1 on B12N11Ni cluster, Table S12. The Cartesian coordinates of IM1 on B12N11Ni cluster, Table S13. The Cartesian

coordinates of TS2 on B12N11Ni cluster, Table S14. The Cartesian coordinates of IM2 on B12N11Ni cluster, Table S15. The Cartesian coordinates of TS3 on B12N11Ni cluster, Table S16. The Cartesian coordinates of IM3 on B12N11Ni cluster, Table S17. The Cartesian coordinates of CO2 on B12N11Ni cluster, Table S18. The Cartesian coordinates of TS1 on B12N11Ni cluster, Table S19. The Cartesian coordinates of IM1 on B12N11Ni cluster, Table S20. The Cartesian coordinates of TS2 on B12N11Ni cluster, Table S21. The Cartesian coordinates of IM2 on B12N11Ni cluster, Table S22. The Cartesian coordinates of IM3 on B12N11Ni cluster, Table S23. The Cartesian coordinates of TS3 on B12N11Ni cluster, Table S24. The Cartesian coordinates of IM4 on B12N11Ni cluster, Table S25. The Cartesian coordinates of TS4 on B12N11Ni cluster, Table S26. The Cartesian coordinates of IM5 on B12N11Ni cluster, Table S27. The Cartesian coordinates of TS5 on B12N11Ni cluster, Table S28. The Cartesian coordinates of IM6 on B12N11Ni cluster, Table S29. The Cartesian coordinates of TS6 on B12N11Ni cluster, Table S30. The Cartesian coordinates of IM7 on B12N11Ni cluster, Table S31. The Cartesian coordinates of CO on B11N12Ni cluster, Table S32. The Cartesian coordinates of TS1 on B11N12Ni cluster, Table S33. The Cartesian coordinates of IM1 on B11N12Ni cluster, Table S34. The Cartesian coordinates of TS2 on B11N12Ni cluster, Table S35. The Cartesian coordinates of IM2 on B11N12Ni cluster, Table S36. The Cartesian coordinates of IM3 on B11N12Ni cluster, Table S37. The Cartesian coordinates of TS3 on B11N12Ni cluster, Table S38. The Cartesian coordinates of IM4 on B11N12Ni cluster, Table S39. The Cartesian coordinates of TS4 on B11N12Ni cluster, Table S40. The Cartesian coordinates of IM5 on B11N12Ni cluster, Table S41. The Cartesian coordinates of TS5 on B11N12Ni cluster, Table S42. The Cartesian coordinates of IM6 on B11N12Ni cluster.

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