BNPd single-atom catalysts for selective hydrogenation of acetylene to ethylene: a density functional theory study

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The mechanisms of selective hydrogenation of acetylene to ethylene on B11N12Pd single-atom catalyst were investigated through the density functional theory by using the 6-31++G** basis set. We studied the adsorption characteristics of H2 and C2H2, and simulated the reaction mechanism. We discovered that H2 underwent absolute dissociative chemisorption on single-atom Pd, forming the B11N12Pd(2H) dihydride complex, and then the hydrogenation reaction with C2H2 proceeded. The hydrogenation reaction of acetylene on the B11N12Pd complex complies with the Horiuti–Polanyi mechanism, and the energy barrier was as low as 26.55 kcal mol⁻¹. Meanwhile, it also has a higher selectivity than many bimetallic alloy single-atom catalysts.

1. Introduction

Ethylene is an important polymerization monomer and industrial reaction intermediate, and it is predominantly produced by the pyrolysis of hydrocarbons. The thermal cracking production process always contains on the order of 1% of acetylene; however, ethylene used in the production of polymers needs to contain less than a few parts per million of acetylene in order not to affect the polymerization process [1,2]. The most suitable way to remove a small amount of acetylene in ethylene is to catalyse the hydrogenation of acetylene to produce ethylene.

Pd catalysts have a good conversion rate for hydrogenation reactions and are used as a catalyst for the selective hydrogenation reaction [3–5]. However, the high price assumes far-reaching significance for the research and development of catalysts with high reactivity and selectivity [6,7]. The main reason for the
poor selectivity is the comparable desorption and hydrogenation energy barrier of ethylene on the metal active sites [8]. The selectivity of the Pd catalysts can be improved by modifying with promoters, but this often adds some harmful metal or organic ligands [9–12]. Bimetallic alloys have been extensively explored as an alternative to Pd catalysts [13–17]. But, this technique is limited by the electronic properties of the two metals that are easily separated and inactivated at high temperatures. In order to improve the stability of bimetallic alloys, it is a useful measure to alloy the metal with another metal to form an alloyed single-atom catalyst (SAC) [18,19]. A growing number of reports suggest that Pd atom isolation is beneficial to the selectivity [20–22]. Meanwhile, Zhang and colleagues demonstrated that maximum reduction of the metal particles can not only improve the utilization of metal atoms, but also enhance the catalytic efficiency and selectivity [23,24]. Some of the literature suggests that the selectivity of IB metal alloyed Pd SACs to ethylene might be affected by electron transfer between the IB metal and Pd atom, through DFT calculation [5,25,26]. Lu and colleagues proved that Pd1/C3N4 SAC can enhance both selectivity and coking-resistance for acetylene hydrogenation [27]. This encouraged us to explore single-atom catalysts for hydrogenation of acetylene. In order to obtain a stable single-atom catalyst, we chose a B12N12 nanocage as the support and inserted Pd into the B12N12 framework.

Since Kroto and colleagues discovered C60 in 1985, many researchers have further explored fullerene and related materials [28]. As the analogues of carbon fullerenes, boron nitride (BN) nanocage clusters have been successfully synthesized [29–31], Oku and colleagues successfully synthesized the B12N12 cage and revealed that its four- and six-membered BN rings satisfy the isolated tetragonal rule [30,32]. Among these doped fullerenes, the B12N12 cage is considered to be the smallest stable cage [30,31,33]. Researchers mainly explored these clusters as catalysts on their application as hydrogen-storage materials [34–37]. In this work, a doped B12N12 cage as a B12N11Pd SAC was used as a catalyst for selective hydrogenation of acetylene to ethylene for the first time.

We use density functional theory (DFT) to study the adsorption of H2 and C2H2 on B12N11Pd SAC. The results show that a Pd single atom can effectively dissociate an H2 molecule, which is consistent with the demonstration of Sykes and co-workers [19,38,39]. From the selectivity formula, we conclude that the selectivity of the B11N12Pd SAC is higher than that of the majority of the bimetallic alloy single-atom catalysts [16,17,26]. Our work indicated that the B11N12Pd SAC might be a promising candidate for selective hydrogenation reactions.

2. Calculation method and models

All density functional calculations were executed using the GAUSSIAN09 program package [40]. The hybrid density functionals of Lee, Yang and Parr (B3LYP) with the 6-31++G** basis set were applied for all structures. The nonlocal correlation functional of B3LYP [41] with the 6-31++G** basis set was used for H, C, B and N atoms, and the B3LYP functional was combined with the LANL2DZ basis set for the Pd atoms. No symmetry constraints were imposed on the geometry optimization. All relative energies in this study were zero-point-energy. All stationary points were characterized as the minima (no imaginary frequency) or transition state (TS; one imaginary frequency) by Hessian calculation. Intrinsic reaction coordinate (IRC) calculations [42,43] were performed to determine if each TS links the correct product with the reactant. Transition-state structures were characterized using frequency calculations and by analysing the vibrational modes. In all instances, only one imaginary frequency corresponding with the reaction coordinate was obtained.

An essential reference point for this calculation is the adsorption energy for C2H2 and H2 absorbed on the B11N12Pd nanocage. In this paper, we used the following definitions for adsorption energy. When H2 or C2H2 is absorbed on B11N12Pd-SAC, the adsorption energy calculated was defined by the following equation.

\[ E = E_{\text{total}} - E_{\text{B11N12Pd}} - E_{\text{H2/C2H2}}. \]  

(2.1)

When H2 is absorbed on BNPd-C2H2, the adsorption energy is calculated as the following equation:

\[ E = E_{\text{total}} - E_{\text{B11N12Pd-C2H2}} - E_{\text{H2}}. \]  

(2.2)

When C2H2 is absorbed on HCl, the adsorption energy is calculated as the following equation:

\[ E = E_{\text{total}} - E_{\text{B11N12Pd-H2}} - E_{\text{C2H2}}. \]  

(2.3)
When $H_2$ and $C_2H_2$ are co-absorbed on $B_{11}N_{12}Pd$ SAC, the co-adsorption energy is calculated as the following equation.

$$E = E_{total} - E_{B_{11}N_{12}Pd} - E_{C_2H_2} - E_{H_2}, \quad (2.4)$$

$E_{total}$ is the total energy of the absorption system; $E_{B_{11}N_{12}Pd}$ is the energy of the $B_{11}N_{12}Pd$ SAC. $E_{H_2/C_2H_2}$ is the energy of $H_2$ or $C_2H_2$. $E_{B_{11}N_{12}Pd-H_2}$ is the energy of the $C_2H_2$ adsorbed on the BNPd nanocage single-atom catalyst.

3. Results and discussion

3.1. Optimized $B_{11}N_{12}Pd$

The optimized structures of the pristine $B_{12}N_{12}$ and $B_{11}N_{12}Pd$ are depicted in figure 1. As expected, the calculated result shows that the charges uniformly distribute among all B(N) atoms in $B_{12}N_{12}$, with a Mulliken value of 0.57 e for B, and $-0.57$ e for N, which is consistent with previous calculations [36]. While one of the B-N bonds was shared between two six-membered rings with a length of about 1.44 Å, the other was shared between a four- and a six-membered ring with length of 1.48 Å. By substituting one Pd atom for a B site in the $B_{12}N_{12}$ nanocage, the charges redistribute on the $B_{12}N_{12}$ cage, and the electrons are found to accumulate around the Pd atom in $B_{11}N_{12}Pd$. The Mulliken charge for Pd is about 2.22 e, while the charge of the replaced B was 0.57 e, which means that the electron transfer is 1.65 e from the Pd atom to the $B_{11}N_{12}$ nanocage. The Pd-N bond which was shared between the two six-membered rings had a length of about 2.10 Å, while the other was shared between a four- and a six-membered ring with a length of 2.04 Å. The adjacent three N atoms have Mulliken charges of $-0.37$, $-0.37$ and $-0.38$ e. This means that the Pd atom and BN nanocage had a strong interaction.

In table 1, we list the HOMO and LUMO distributions and frontier molecular orbital (FMO) energies of the $B_{12}N_{12}$ and $B_{11}N_{12}Pd$ nanocages, respectively. One can see that after Pd doping, the orbital energy of HOMO was reduced, which means the stability of the $B_{11}N_{12}Pd$ SAC is enhanced; the band gap ($\Delta E_g$) between HOMO and LUMO also decreases, which facilitates the interaction between adsorbates and the surfaces.

3.2. Adsorption of reactants

The molecular orbital calculations and electron density analysis can be used to determine the adsorption position of $C_2H_2$ and $H_2$ molecules on $B_{11}N_{12}Pd$ SAC. According to the FMO analysis of the $B_{11}N_{12}Pd$ SAC, the Pd atom may be the only active site (figure 1). In order to fully consider the possible adsorption sites, we put $C_2H_2$ and $H_2$ on different sites both around the Pd atom and the BN nanocage structure, and obtained the most stable adsorption structures, which are shown in figure 2.

Figure 3 shows that an $H_2$ molecule was initially absorbed on the Pd atom of the $B_{11}N_{12}Pd$ SAC with an adsorption of about 6.28 kcal mol$^{-1}$; the length between Pd and $H_2$ was about 1.94 Å, the bond length of $H_2$ was 0.78 Å, and it increased by 0.04 Å compared with the free $H_2$ molecule, indicating that there was interaction between $H_2$ and $B_{11}N_{12}Pd$ SAC. Subsequently, a TS was formed when the $H-H$ bond length was about 1.01 Å, which increased by 0.27 Å compared with the free $H_2$ molecule. From the vibrational analysis, we obtained only one imaginary frequency ($-1426.63$ cm$^{-1}$), as the two H atoms of $H_2$ gradually separate approaching the B and Pd atoms. Then the two H atoms finally settled and formed the $B_{11}N_{12}Pd(2H)$ dihydride complex, with a 2.72 Å distance for $H-H$, and the system gains a stabilization energy of $-18.83$ kcal mol$^{-1}$, indicating $H_2$ absolutely dissociative chemisorption.

To investigate the kinetic issue in the process of the hydrogenation on the $B_{11}N_{12}Pd$ SAC, we calculated the activation barrier for one $H_2$ fully chemisorbed on the $B_{11}N_{12}Pd$ SAC. Figure 3 shows the calculated reaction diagram for the $H_2$ adsorption on $B_{11}N_{12}Pd$ SAC. The corresponding activation barrier (energy difference between TS and initial state (IS)) for the hydrogenation reaction is found to be 12.56 kcal mol$^{-1}$, indicating $H_2$ dissociative chemisorption on the $B_{11}N_{12}Pd$ SAC and the diffusion process of H atoms are facile.

In table 2, the Mulliken charge of absorbed $C_2H_2$ is 0.47 e, indicating that an electron transfer of 0.47 e occurred from $C_2H_2$ to $B_{11}N_{12}Pd$ SAC; the length between Pd and $C_2H_2$ is 2.30 Å, meaning that the $C_2H_2$ molecules were absorbed only on the single Pd atom. The optimal adsorption energy of $C_2H_2$ is $-14.95$ kcal mol$^{-1}$, which can be seen in table 2.
Figure 1. The optimized structures of undoped $\text{B}_2\text{N}_2$ cluster and Pd-doped $\text{B}_1\text{N}_2\text{Pd}$ SAC and the corresponding calculated HOMO and LUMO at B3LYP/6-31++G** level. H, white; B, pink; N, blue; Pd, blue-green.

Table 1. The orbital energies for the HOMO and LUMO of $\text{H}_2$, $\text{C}_2\text{H}_2$, $\text{B}_2\text{N}_2$, and $\text{B}_1\text{N}_2\text{Pd}$ SAC, and their energy gaps ($\Delta E$) between $\text{H}_2$, $\text{C}_2\text{H}_2$ and $\text{B}_2\text{N}_2$/B$_{\text{n}}$N$_2$Pd. Energies are in eV.

|          | HOMO  | LUMO  | $\Delta E_e$ (H$_2 \rightarrow$ BN) | $\Delta E_e$ (BN $\rightarrow$ H$_2$) | $\Delta E_e$ (C$_2$H$_2 \rightarrow$ BN) | $\Delta E_e$ (BN $\rightarrow$ C$_2$H$_2$) |
|----------|-------|-------|-------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| $\text{H}_2$ | 11.83 | 0.53  |                                     |                                      |                                      |                                      |
| $\text{C}_2\text{H}_2$ | -8.08 | 0.11  |                                     |                                      |                                      |                                      |
| $\text{B}_2\text{N}_2$ | 7.95  | -1.24 | 6.72                                 | -10.59                              | -6.85                                | -8.06                                |
| $\text{B}_1\text{N}_2\text{Pd}$ | -6.64 | -4.33 | 2.31                                 | -7.50                               | -3.75                                | -6.75                                |

3.3. Mechanisms of selective hydrogenation of acetylene to ethylene by $\text{B}_1\text{N}_2\text{Pd}$ single-atom catalyst

3.3.1. $\text{C}_2\text{H}_2$ adsorbed onto the $\text{B}_1\text{N}_2\text{Pd}(2\text{H})$ dihydride complex

As shown in figure 4 (R1), the $\text{B}_1\text{N}_2\text{Pd}(2\text{H})$ dihydride complex adsorbed by the $\text{C}_2\text{H}_2$ is a little different from that on the bare $\text{B}_1\text{N}_2\text{Pd}$ SAC. Simultaneously, the binding sites of H atoms on $\text{B}_1\text{N}_2\text{Pd}(2\text{H})$ dihydride complex are practically unchanged. When $\text{C}_2\text{H}_2$ is adsorbed on $\text{B}_1\text{N}_2\text{Pd}(2\text{H})$ dihydride complex as equation (2.3), the adsorption energy is calculated to be $-11.98 \text{ kcal mol}^{-1}$, indicating that the complex has a high adsorption to $\text{C}_2\text{H}_2$. The most stable adsorption energies of $\text{H}_2$ and $\text{C}_2\text{H}_2$ on the $\text{B}_1\text{N}_2\text{Pd}$ SAC are $-17.23$ and $-14.95 \text{ kcal mol}^{-1}$, respectively, as shown in equation (2.1). As in equation (2.4), the co-adsorption of $\text{H}_2$ and $\text{C}_2\text{H}_2$ on the $\text{B}_1\text{N}_2\text{Pd}$ SAC is $-29.22 \text{ kcal mol}^{-1}$, which is less than the sum of the individual $\text{C}_2\text{H}_2$ and $\text{H}_2$ adsorption energies ($-32.18 \text{ kcal mol}^{-1}$). This indicates that there is an interaction between $\text{H}_2$ and $\text{C}_2\text{H}_2$, and the adsorption of the two H atoms does not change obviously when the two adsorbates occur simultaneously on the $\text{B}_1\text{N}_2\text{Pd}$ SAC. The results show that this interaction does not affect the mechanism of the reaction.

As figure 4 shows, the complex of acetylene (R1) is formed by the adsorption of the acetylene molecule on $\text{B}_1\text{N}_2\text{Pd}(2\text{H})$. Both of the reactants were absorbed on the single Pd atom, which can
Figure 2. The stable structures of H₂ and C₃H₂ absorbed on B₁₁N₁₂Pd SAC. H, white; B, pink; N, blue; Pd, blue-green.

Figure 3. Calculated hydrogenation reaction diagram for the B₁₁N₁₂Pd SAC. The schematic diagrams of initial (IS), transition (TS) and final (FS) states are illustrated by side views. H, white; B, pink; N, blue; Pd, blue-green.

provide an excellent condition for heterogeneous catalytic reactions. R₁ passes through a small energy barrier to obtain TS₁. From the vibrational analysis of TS₁, we obtained only one imaginary frequency (−645.43 cm⁻¹), which was associated with the stretching motion of the H atom adjacent to the Pd atom. We can deduce that the H atom adjacent to Pd is active in TS₁. IRC calculation testified that TS₁ connected the co-adsorption and IMS₁ and showed that no further intermediates are involved in the reaction. Then the H atom that is linked to the Pd atom approaches to form a vinyl-B₁₁N₁₂Pd(H) intermediate (IMS₁); the length of C=C double bonds is 1.34 Å, which is close to the C=C bond length of free C₂H₄. The H atom which is linked with the N atom has a nearly neutral charge, which denotes the weak binding of intermediates. The IMS₁ through a 26.22 kcal mol⁻¹ energy can proceed to the TS₂; from the vibrational analysis of TS₂, we obtained only one imaginary frequency (−1041.20 cm⁻¹), which was associated with the stretching motion of the H atom linked to the B atom. IMS₂ approaches the vinyl-B₁₁N₁₂Pd and
Figure 4. The reaction process and potential energy change for the different reaction pathways R1 (left) and R2 (right) of catalytic hydrogenation of acetylene to ethylene on the B11N12Pd SAC. The schematic diagrams of co-adsorption (R), transition (TS), intermediate (IMS) and final (FS) states are illustrated by side views. H, white; B, pink; N, blue; Pd, blue-green; C, grey.

Table 2. The optimal adsorption energies and Mulliken charge of H2, C2H2, C2H4, C2H6 separately absorbed on B11N12Pd SAC. H + H represents the H2 dissociative adsorption on B11N12Pd SAC. Energies are in kcal mol\(^{-1}\); Mulliken charges are in e.

|  | energies | Mulliken charge |
|---|---|---|
| H2 | −3.32 | 0.24 |
| H + H | −18.83 | 0.45 |
| C2H2 | −14.95 | 0.47 |
| C2H4 | −16.55 | 0.26 |
| C2H6 | −2.41 | −0.02 |

Table 3. Comparison of the energy barriers for the desorption energy of ethylene (E_{ad}), desorption barriers of ethylene (E_{ad}), and the difference between desorption and hydrogenation barrier of ethylene (∆E_\text{a}) with different catalysts. Energies are in kcal mol\(^{-1}\).

|  | E_{ad} | E_{ad} | ∆E_\text{a} | reference |
|---|---|---|---|---|
| B11N12Pd | 29.35 | −16.55 | 12.8 | this work |
| Au-Ni(111) | 13.84 | −6.23 | 7.61 | 16 |
| Cu-Ni(111) | 16.6 | −14.07 | 2.54 | 16 |
| Ag-Cu(111) | 15.91 | −6.46 | 9.45 | 17 |
| Pd-Cu(000) | 17.29 | −11.07 | 6.22 | 17 |
| PdGa | 21.22 | −11.99 | 9.23 | 23 |
forms an ethane molecule on the B$_{11}$N$_{12}$Pd SAC. Then C$_2$H$_4$ is desorbed and achieves the final state (FS); the C$_2$H$_4$ only needs 16.55 kcal mol$^{-1}$ energy to move away, and the low desorption energy can ensure the selectivity of ethylene.

From the energy diagrams of the R1, the step from IMS1 to TS2 is the rate-limiting step. We calculated the activation energy of hydrogenation of acetylene to ethylene action as 26.22 kcal mol$^{-1}$ (the activation energy is the biggest energy difference in the energy diagram, as shown in figure 4), which is similar to the Pd$_5$ cluster (the lowest activation energy is 25.72 kcal mol$^{-1}$) [44]. This indicates that the B$_{11}$N$_{12}$Pd SAC has a similar activation energy for hydrogenation of acetylene to ethylene; moreover, it can make full use of the noble metal and decrease the price of the catalyst.

3.3.2. Vinylidene adsorbed onto the B$_{11}$N$_{12}$Pd(2H) dihydride complex

As figure 4 (R2) shows, there is another pathway from vinylidene (C=CH$_2$) to C$_2$H$_4$, in which the H atom adsorbed on the Pd atom of R2 can move to the vinylidene to form ethenyl-B$_{11}$N$_{12}$Pd(H), with only 4.16 kcal mol$^{-1}$ difference of free energies. Then the remaining H atom which linked to the B atom of IMS1 is transferred to the ethenyl group to obtain ethenylidene via TS2, whose free energy is −36.96 kcal/mol. In the complicated pathways of acetylene hydrogenation, ethenylidene can obtain the C$_2$H$_4$ by proton translocation (TS3). The free energies of the TS for the IMS2 and IMS3 are −39.12 kcal mol$^{-1}$. The final step was the C$_2$H$_4$ molecule desorption from the B$_{11}$N$_{12}$Pd, and the desorption energy was 16.55 kcal mol$^{-1}$. From the vibrational analysis of the TS, we obtained only one imaginary frequency for each TS (−1099.77, −1167.07, −923.56 cm$^{-1}$). To gain a better understanding of the reaction, series IRC calculation testified that the TS connected the co-adsorption and IMS, and showed that no further intermediates are involved in the reaction.

From the potential energy change of catalytic hydrogenation of acetylene to ethylene in figure 4 (R2), the activation energy is 39.12 kcal mol$^{-1}$, and the rate-controlling step is also from IMS2 to TS3. Considering the complex hydrogenation pathways, it is found that the semi-hydrogenation of acetylene on the B$_{11}$N$_{12}$Pd cluster is easy to achieve.

3.3.3. H$_2$ adsorbed onto the B$_{11}$N$_{12}$Pd–C$_2$H$_2$ complex

We also investigated the non-Horiuti–Polanyi mechanism of selective hydrogenation of acetylene on the B$_{11}$N$_{12}$Pd, as shown in the electronic supplementary material, figure S1–S3; the activation energy of hydrogenation of acetylene to ethylene action is 57.79, 53.26 and 55.84 kcal mol$^{-1}$. This means that selective hydrogenation of acetylene on the B$_{11}$N$_{12}$Pd complies with the Horiuti–Polanyi mechanism. Therefore, the lowest activation energy of hydrogenation of acetylene to ethylene is 26.22 kcal mol$^{-1}$.

3.3.4. C$_2$H$_4$ adsorbed onto the B$_{11}$N$_{12}$Pd(2H) dihydride complex

In order to clearly research the selectivity of the catalyst, we studied the reaction of ethylene to produce ethane. As figure 5 shows, C$_2$H$_4$ was first adsorbed onto the B$_{11}$N$_{12}$Pd(2H) dihydride complex to form the co-adsorption configuration (R3); according to equation (2.3) the adsorption energy is −12.67 kcal mol$^{-1}$, indicating that the complex also has a high adsorption to C$_2$H$_4$ compared with C$_2$H$_2$. R3 passes through a small energy barrier to obtain TS1. From the vibrational analysis of TS1, we obtained only one imaginary frequency (−639.02 cm$^{-1}$), which was associated with the stretching motion of the H atom that is linked to the Pd atom. We can observe that the H atom adjacent to Pd is active in TS1. Then the H atom approaches to form an ethyl-B$_{11}$N$_{12}$Pd(H) intermediate (IMS1); the length of C=C double bonds of C$_2$H$_4$ is 1.37 Å, which is raised 0.03 Å compared with the TS1. The IMS1 through a 29.35 kcal mol$^{-1}$ energy can proceed to the TS2. IRC calculation testified that TS1 connected the co-adsorption and IMS1 and showed that no further intermediates are involved in the reaction. The length of C=C double bonds is 1.34 Å, which is close to the C≡C bond length of free C$_2$H$_4$. The H atom which is linked to the N atom has a nearly neutral charge, which denotes the weak binding of intermediates. The IMS1 through a 26.22 kcal mol$^{-1}$ energy can proceed to the TS2; from the vibrational analysis of TS2, we obtained only one imaginary frequency (−1597.33 cm$^{-1}$), which was associated with the stretching motion of the H atom linked to the B atom. IMS2 approaches the vinyl-B$_{11}$N$_{12}$Pd and forms an ethane molecule on the B$_{11}$N$_{12}$Pd SAC. Then C$_2$H$_6$ is desorbed and the FS is obtained; the dissociation energy of C$_2$H$_6$ is about 2.83 kcal mol$^{-1}$.

From the energy diagrams of R3, the step from IMS1 to TS2 is the rate-limiting step. We calculated the activation energy of hydrogenation of ethylene to ethane action as 29.35 kcal mol$^{-1}$, which is higher
Figure 5. The reaction process and potential energy change of catalytic hydrogenation of ethylene to ethane on the B_{11}N_{12}Pd SAC. The schematic diagrams of co-adsorption (R), transition (TS), intermediate (IMS) and final (FS) states are illustrated by side views. H, white; C, grey; B, pink; N, blue; Pd, blue-green.

than that of the acetylene to ethylene action. This indicates that the B_{11}N_{12}Pd SAC has a high selectivity of acetylene hydrogenation to ethylene.

3.3.5. H_2 adsorbed onto the B_{11}N_{12}Pd–C_2H_4 complex

We also investigated the hydrogenation of ethylene to ethane action onto the B_{11}N_{12}Pd in non-Horiuti–Polanyi mechanism (electronic supplementary material, figure S4); the activation energy is 53.11 kcal mol$^{-1}$. This means that hydrogenation of ethylene onto the B_{11}N_{12}Pd complies with the Horiuti–Polanyi mechanism. Therefore, the lowest activation energy of hydrogenation of acetylene to ethylene is 29.35 kcal mol$^{-1}$. 
3.4. Selectivity of the acetylene hydrogenation to ethylene on B_{11}N_{12}Pd SAC

The factor influencing the selectivity of acetylene hydrogenation to ethylene is considered to be the difference between the desorption barriers and the hydrogenation barrier of ethylene [8,45]; we defined the difference as $\Delta E_a$. The desorption barriers are estimated with the absolute value of the adsorption energies according to the approximation made in previous studies [8,16,46–50]. Namely, we define

$$\Delta E_a = E_a - |E_{ad}|,$$

where $E_a$ and $E_{ad}$ are the hydrogenation and desorption barriers of ethylene, respectively. This equation indicates that the more positive the $\Delta E_a$, the more selective the catalyst will be for the production of ethylene compared with ethane formation. As Table 1 shows, B_{11}N_{12}Pd has a better selectivity than most bimetallic alloys [13,16,17,26].

A high selectivity also can be judged from the following two aspects. One is a low desorption energy of ethylene, which can effectively inhibit the hydrogenation of ethylene to produce ethane. In this work, the desorption energy of ethylene (16.55 kcal mol$^{-1}$) is less than the activation energy of ethylene (29.35 kcal mol$^{-1}$), which can ensure a high selectivity. The other is a high ethylene hydrogenation activation energy. In this work, the acetylene hydrogenation activation energy is 26.55 kcal mol$^{-1}$, which is less than the ethylene hydrogenation activation energy. Therefore, we can draw the conclusion that the B_{11}N_{12}Pd SAC has a high selectivity for the acetylene hydrogenation to ethylene.

4. Conclusion

This work uses DFT to study the catalytic process of selective hydrogenation on B_{11}N_{12}Pd SAC. The results show that a Pd single atom can effectively dissociate an H$_2$ molecule and form the B_{11}N_{12}Pd(2H) dihydride complex, with the hydrogenation of acetylene to ethylene following the Horiiuti–Polanyi mechanism. The activation energy for hydrogenation of acetylene is similar to that with Pd clusters, which is beneficial to reduce the cost of the catalyst. Besides, the low desorption energy of ethylene and high ethylene hydrogenation activation energy can ensure that the B_{11}N_{12}Pd SAC has a high selectivity. From the selectivity formula, we conclude that the selectivity of the B_{11}N_{12}Pd SAC is higher than that of the majority of the binary metal monometallic catalysts. This work provides a theoretical basis for the development of catalysts with novel high catalytic performance and selectivity for hydrogenation.

Data accessibility. All original data can be accessed at the Dryad Digital Repository [51].

Authors’ contributions. L.K. designed and conceived the experiments; W.G. performed the experiments, analysed the data and wrote the paper with the direction from L.K.; all authors participated in the analysis, interpretation and review of the results and provided input in the writing process of the paper. All authors gave final approval for publication.

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