

Article

First-Principles Investigation of the Stability and CH₄ Activation Capability of Defective h-BN

ChuanYe Xiong ^{1,2} and Jin Tang ^{2,3,*}¹ Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA² Department of Chemistry, University of California, Riverside, CA 92521, USA³ Department of Physiology, University of Texas Southwestern Medical Center, Dallas, TX 75390, USA

* Correspondence: jin.tang@utsouthwestern.edu

Abstract

Hexagonal boron nitride (h-BN) has been widely applied in catalysis. Nevertheless, most research has focused on using h-BN as a substrate to anchor active transition metals, without probing the intrinsic activity of h-BN vacancies. In this work, we investigated the stability and catalytic activity of different h-BN vacancies. We found that B-terminated vacancies are more likely to be exposed under static conditions. The N_v, BN₂, and BN₃ vacancies show intermediate reaction energies for CH₄ activation. Although the B–N pair over the BN₂ vacancy model has the lowest barrier for CH₄ activation, the negative reaction energy could lead to a high potential for surface poisoning. Interestingly, the unsaturated B–B pair over N_v is a promising site for C–H bond activation. Further COHP analysis implies that the high C–H bond homolytic cleavage activity of the B–B pair arises from its relatively weak interaction, which can promote H insertion.

Keywords: h-BN; CH₄ activation; vacancy; DFT; COHP

1. Introduction

Since their first successful synthesis by Balmain in 1842 [1], boron nitride materials have gradually been brought to the attention of the public. Boron nitride materials exist primarily in three crystalline forms: the hexagonal, cubic, and wurtzite forms [2]. Among these, hexagonal boron nitride (h-BN) is the most stable form under normal conditions [2]. Additionally, with the flourishing research on two-dimensional materials [3–5], h-BN has been extensively studied in recent decades [6]. Like graphene, hexagonal boron nitride (h-BN) possesses a layered structure characterized by sp²-hybridized B–N covalent bonds, which grant h-BN excellent thermal conductivity along the layers. Moreover, h-BN exhibits remarkable thermal stability, remaining stable at temperatures up to 1000 °C [7]. Such high stability makes h-BN a promising candidate for catalytic applications.

Pristine boron nitride (BN) is chemically inert owing to its high stability. A common strategy for functionalizing h-BN involves creating vacancy sites on its surface [8–10]. Dr. Jin's group fabricated defective h-BN via energetic electron irradiation, and by combining high-resolution transmission electron microscopy (HRTEM) with exit-wave (EW) reconstruction, they successfully resolved the N-edge vacancy sites [11]. In contrast to Prof. Jin's finding, Ovidiu Cretu's group observed the B-terminated vacancy on h-BN at a high temperature by high-resolution electron energy loss spectroscopy (EELS) mapping [12]. As for the catalytic application of h-BN, researchers have used the vacancy sites as the anchoring points for the active phase for the CO oxidation reaction [13,14] or



Received: 29 January 2026

Revised: 7 March 2026

Accepted: 20 March 2026

Published: 2 April 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

synthesized h-BN coating Pt/Al₂O₃ core-shell structures. The vacancy over the h-BN can selectively allow small reactant molecules to pass through [15]. In addition, numerous computational studies have been carried out to probe the reaction over single-atom-doped BN [16–20]. All these studies focus on the auxiliary role of BN vacancy for chemical reactions while seldom discussing the catalytic effect of the vacancies themselves. Previous studies have demonstrated that defect-regulated B–N frustrated Lewis pair (FLP) sites in h-BN can activate small molecules such as H₂ via heterolytic bond cleavage [21]. However, whether h-BN vacancy can promote methane C–H bond activation through alternative mechanisms remains largely unexplored. In this work, we reveal that unsaturated B–B pairs exposed at B-terminated vacancies can activate methane via a homolytic C–H cleavage mechanism, which is fundamentally different from the previously reported FLP-type activation pathways.

Herein, this study focuses on both N-terminated vacancy (V_c) and B-terminated vacancy in h-BN. A series of h-BN vacancies with different sizes were constructed, including the mono N vacancy (N_v), mono B vacancy (B_v), BN V_c , BN₂ V_c , BN₃ V_c , NB₂ V_c , NB₃ V_c and B₃N₃ V_c , which are shown in Figure 1. Among these vacancy structures, the BN, BN₂, BN₃, and B₃N₃ vacancies have been investigated in a previous study [21] for hydrogenation reactions using a 6 × 6 lateral unit cell, which differs from the computational model employed in this work. The stability of these vacancies was first analyzed, then we utilized CH₄ activation as the probe reaction to investigate the activity of different vacancies. The homolytic activation and heterolytic activation were both studied in different terminations followed by a deeper analysis of the electronic effect.

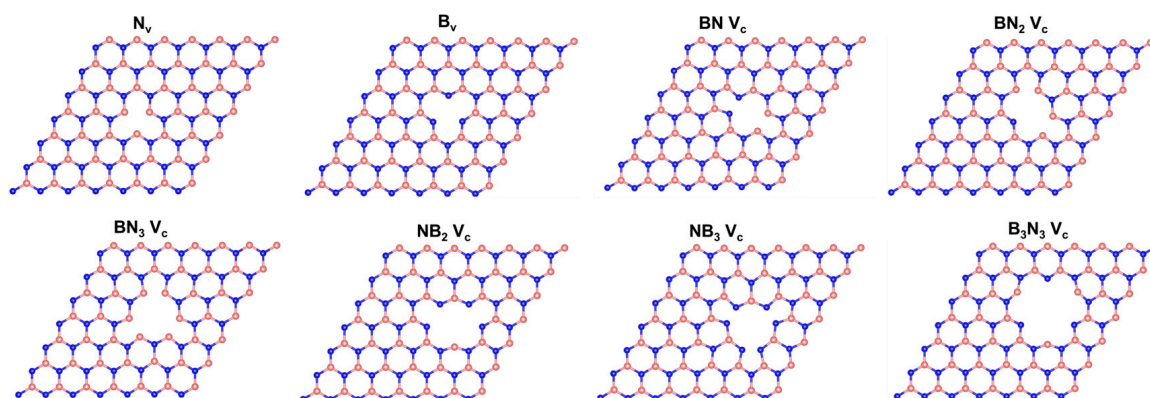


Figure 1. Atomic structures of different h-BN vacancy configurations: mono N_v , mono B_v , BN, BN₂, BN₃, NB₂, NB₃ and B₃N₃ vacancies. Blue and pink spheres represent nitrogen and boron atoms, respectively.

2. Results and Discussion

2.1. Formation Energy of Different h-BN Vacancies

The stability of the active site is of vital importance for a catalyst. Therefore, we first investigated the normalized formation energy based on the number of atoms removed from the surface. As shown in Figure 2, the mono B/N vacancy normalized formation energies are larger than those of the larger vacancies. In the B-rich condition, the mono N vacancy forms more easily, while in the N-rich condition, the mono B vacancy forms more easily. Interestingly, we also observe a general trend that with the increase in the vacancy size (number of atoms removed), the normalized formation energy decreases. Also, the formation energy of the BN₂ vacancy is lower than that of the NB₂ vacancy in both the B-rich condition and N-rich condition, although they have the same vacancy size. The same is true of the comparison between the BN₃ and NB₃ vacancy. For both B-rich and N-rich scenarios, the BN₃ vacancy formation energies are always lower than those

of the NB_3 vacancy. This phenomenon suggests that for a medium-sized vacancy, the B edge is thermodynamically favorable as both BN_2 and BN_3 have more B termination than N termination (Figure 1). As for the mono vacancy, the B_v formation energy is only slightly lower than N_v in N-rich conditions. This finding also implies that the B-terminated vacancies tend to be exposed. The phenomenon is consistent with previous computational results showing that N_v forms slightly more easily [22] and that triangle-shaped BN_3 vacancies have been directly observed using high-resolution STEM-EELS experiments [12].

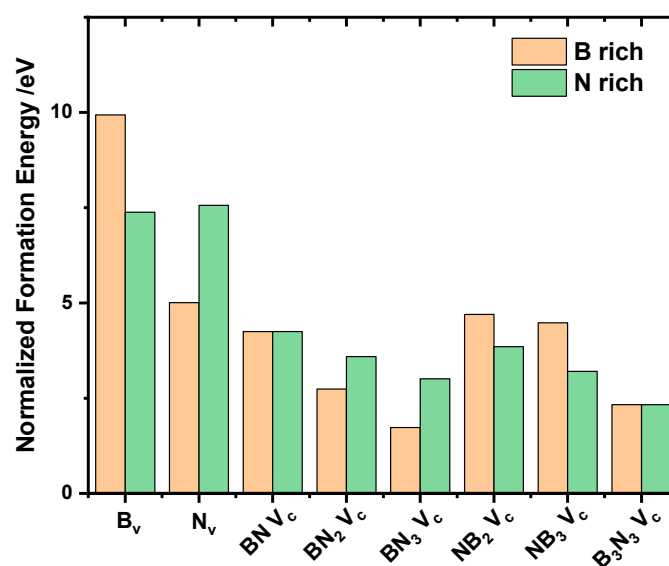


Figure 2. Normalized formation energies of different h-BN vacancy structures under B-rich and N-rich conditions. Orange and green bars represent B-rich and N-rich conditions, respectively.

For the B-rich vacancies, both N_v and $\text{BN}_2 v$ exhibit a total magnetic moment of $1 \mu\text{B}$. As shown in Table S1, the magnetic moments remain essentially unchanged upon adsorption of CH_3 and H species, indicating that the spin state of the defective surface is preserved during the CH_4 activation process. Furthermore, calculations with constrained total magnetic moments were performed to examine alternative spin configurations. As shown in Table S2, the lowest-energy configurations correspond to magnetic moments of $1 \mu\text{B}$ for N_v and $\text{BN}_2 v$ and $0 \mu\text{B}$ for $\text{BN}_3 v$, confirming that the spin states used in the reaction pathway calculations correspond to the most stable magnetic configurations.

2.2. Activity of h-BN Vacancies

In recent years, a number of researchers have used H binding strength as a quick descriptor for screening catalytic surface activity in various reactions such as CH_4 activation [23], HER [24] and HOR [25] reactions. Therefore, we applied the H_2 dissociation energy as the descriptor for screening the activity of the B/N termination in the defective h-BN. As we can see in Figure 3, the pristine boron nitride is inert toward H_2 dissociation. As for each defective site, the unsaturated N is always more reactive than unsaturated B. Especially for the BN_2 vacancy, the H_2 dissociation energy on the unsaturated N over the BN_2 vacancy has already reached 3.03 eV , indicating that the unsaturated N site over the BN_2 vacancy is highly active. In the h-BN system, the H_2 dissociation energy exhibits a positive correlation with the activation barrier for methane C–H bond cleavage (Figure S3).

We further examine the CH_4 activation reaction over our defective h-BN models. CH_4 activation [26,27] is an endothermic reaction, and activating light alkanes has been a critical challenge over recent decades [28]. We also calculated the physical adsorption energies of CH_4 on both defective and pristine h-BN surfaces, as shown in Figure S2. The adsorption energies range from 0 to approximately -0.15 eV , indicating weak physical

adsorption. These results suggest that CH_4 can readily approach the surface prior to C–H bond activation without being strongly bound. The thermodynamic screening of the first C–H bond activation step was performed prior to the transition-state search. An intermediate reaction energy (ΔE) is considered desirable, because a highly positive ΔE would make the reaction thermodynamically unfavorable, whereas an excessively negative ΔE would lead to overly stable final states that may hinder subsequent reaction steps. Multiple possible final-state configurations were examined for each BN vacancy model. In Figure 4, the optimized structures of the final states for CH_4 activation on various h-BN vacancies are displayed, highlighting the different adsorption configurations of the CH_3 and H fragments. For the N_v and B_v , the final states correspond to CH_3 and H fragments bound to the B-terminated and N-terminated sites, respectively. For the BN and B_3N_3 vacancies, four configurations were considered: (i) both CH_3 and H adsorbed on B sites; (ii) both fragments on N sites; (iii) CH_3 on N and H on B; and (iv) CH_3 on B and H on N. For the BN_2 vacancy, which exposes four unsaturated B atoms and one unsaturated N atom, four configurations were evaluated: (i) CH_3 and H adsorbed on adjacent B–B sites; (ii) CH_3 on N and H on B; (iii) CH_3 on B and H on N; and (iv) CH_3 and H adsorbed on non-adjacent B atoms. For the BN_3 vacancy, which has purely B-terminated edges, two configurations were considered: (i) adsorption of CH_3 and H on adjacent B–B sites and (ii) adsorption on non-adjacent B atoms. For the NB_2 vacancy, three configurations were examined: (i) both CH_3 and H adsorbed on N sites; (ii) CH_3 on N and H on B; and (iii) CH_3 on B and H on N. Finally, for the NB_3 vacancy, the configuration with CH_3 and H adsorbed on an adjacent N–N pair was considered.

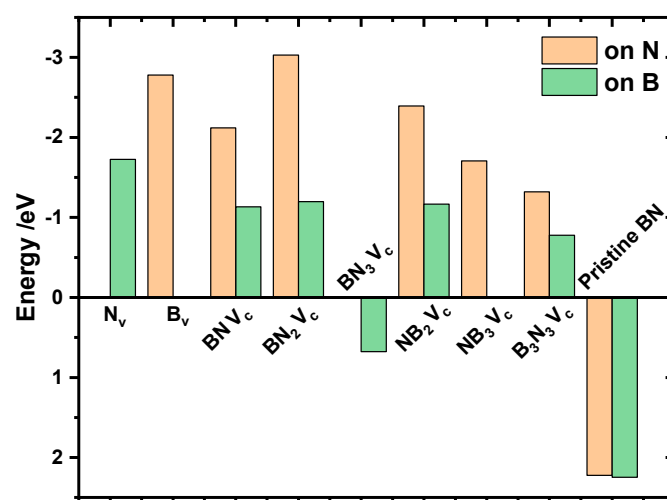


Figure 3. H_2 dissociation energies at various defective h-BN vacancy sites and pristine BN. Orange and green bars represent H_2 dissociation occurring on surface unsaturated N and B sites, respectively.

In Figure 5, the calculated reaction energies for CH_4 C–H bond cleavage for different h-BN vacancies are summarized. The unsaturated N sites exhibit very strong reactivity toward CH_3 and H adsorption, resulting in highly negative reaction energies. In contrast, the B sites are less reactive, and the reaction energies become more positive when both CH_3 and H fragments bind to B atoms. In addition, the CH_3 radical preferentially adsorbs at B sites, whereas the H atom is more favorably stabilized at N sites. By screening all vacancy models, we find that the N_v and BN_2 vacancies exhibit intermediate reaction energies for C–H bond activation (between 0 and -2 eV), which are considered favorable for catalytic reactions. We also observe that for the BN_3 vacancy, although the distant B–B pair cannot stabilize the final state of CH_3 and H adsorption, the adjacent B–B pair can still stabilize the dissociation products. Therefore, the BN_3 vacancy was also included in the

subsequent transition-state barrier calculations. The B_3N_3 vacancy exposes three boron and three nitrogen atoms, creating multiple potential active sites for methane activation. As shown in Figure 5, CH_4 dissociation on N-exposed sites of the B_3N_3 vacancy exhibits highly exothermic reaction energies. Although such strong exothermicity suggests that methane activation can occur readily, the excessively strong binding of reaction intermediates may hinder product desorption and limit catalytic turnover. Therefore, compared with smaller vacancies, the B_3N_3 vacancy is less favorable for efficient methane activation due to the overbinding of intermediates.

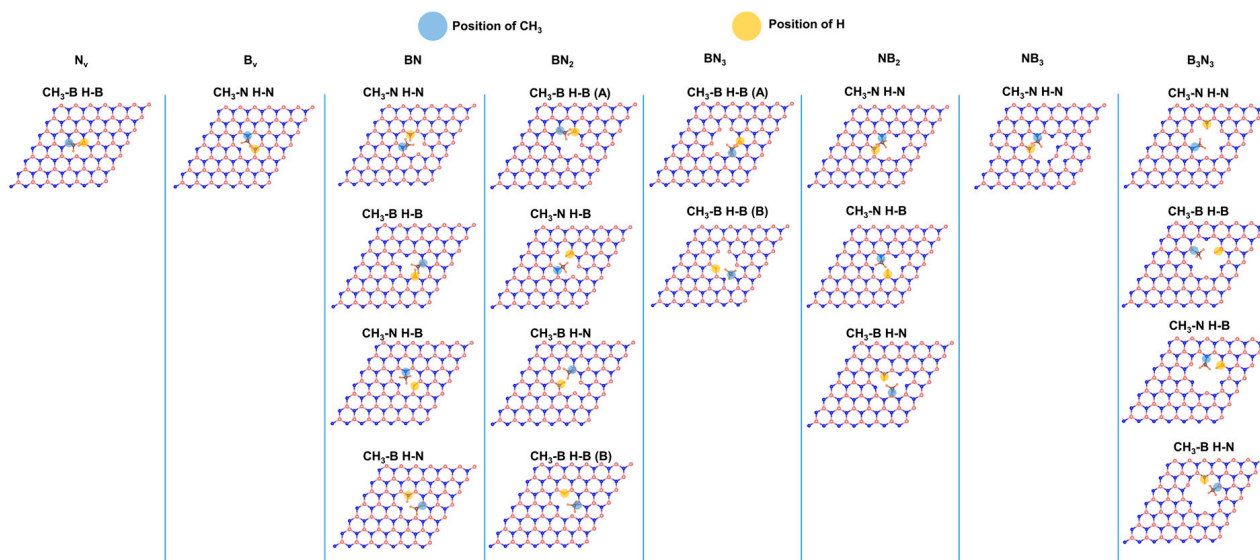


Figure 4. Optimized structures of the final states for CH_4 activation at different h-BN vacancy sites. The dissociated CH_3 fragment is marked in blue, while the dissociated H fragment is highlighted in yellow.

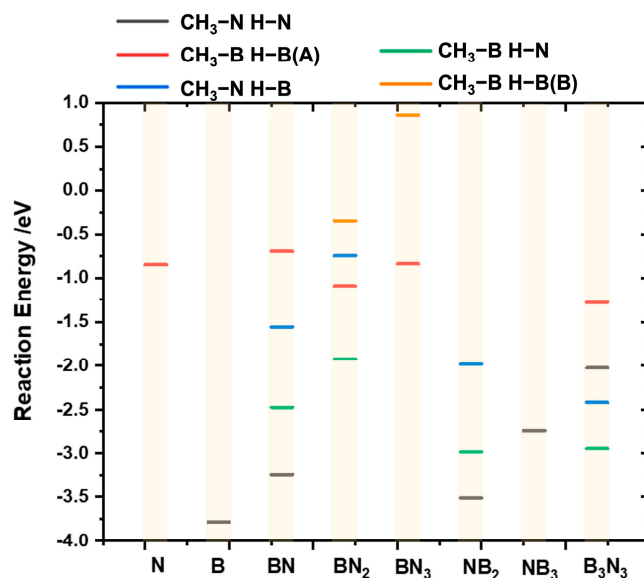


Figure 5. Calculated reaction energies for CH_4 C-H bond cleavage for different h-BN vacancy defects, including mono N_v , mono B_v , BN , BN_2 , BN_3 , NB_2 , NB_3 , and B_3N_3 vacancies.

As for the N_v and BN_3 vacancies (Figure 6), owing to their pure B termination, they can activate CH_4 by homolytic cleavage on the adjacent B-B pair. As for the BN_2 V_c , it can activate CH_4 by homolysis on its unsaturated B-N pair or heterolysis on its unsaturated B-B pair. Owing to the very negative reaction energy of CH_4 heterolysis activation over

$\text{BN}_2 \text{V}_\text{C}$, the barrier is as low as 0.50 eV (Figure 7), which is much lower than the homolysis over the adjacent B–B pair of the N_V , $\text{BN}_2 \text{V}_\text{C}$ and $\text{BN}_3 \text{V}_\text{C}$. The high activity of the B–N pair over the BN_2 vacancy can be attributed to the frustrated Lewis acid–base pair, which is commonly active for the C–H bond activation reaction [29,30]. However, the reaction energy is still as negative as -1.92 eV, which has the tendency to poison the surface. Interestingly, we found that the adjacent unsaturated B–B pair over N_V , $\text{BN}_2 \text{V}_\text{C}$ and $\text{BN}_3 \text{V}_\text{C}$ can activate the C–H bond by homolytic cleavage. Moreover, the reaction energy of homolytic cleavage is between -0.5 eV and -1 eV, which is a promising value for C–H activation, especially the B–B pair over N_V ; the C–H activation barrier is only 1.07 eV, making it an excellent active site for C–H bond cleavage. The calculated activation barriers for CH_4 dissociation at the defective h-BN sites are 0.50 eV for the B–N pair in $\text{BN}_2 \text{V}_\text{C}$ and 1.07 eV for the B–B pair in N_V . These values are comparable to those reported for precious metal catalysts, such as Pt [31] (~ 1.15 eV) and Ru [32] (~ 0.4 – 0.7 eV). This comparison highlights the remarkable catalytic potential of defective h-BN for methane activation, even in the absence of metal components. Such metal-free catalytic activity could significantly reduce reliance on expensive noble metals, lowering catalytic costs while offering promising opportunities for alkane activation and subsequent transformation.

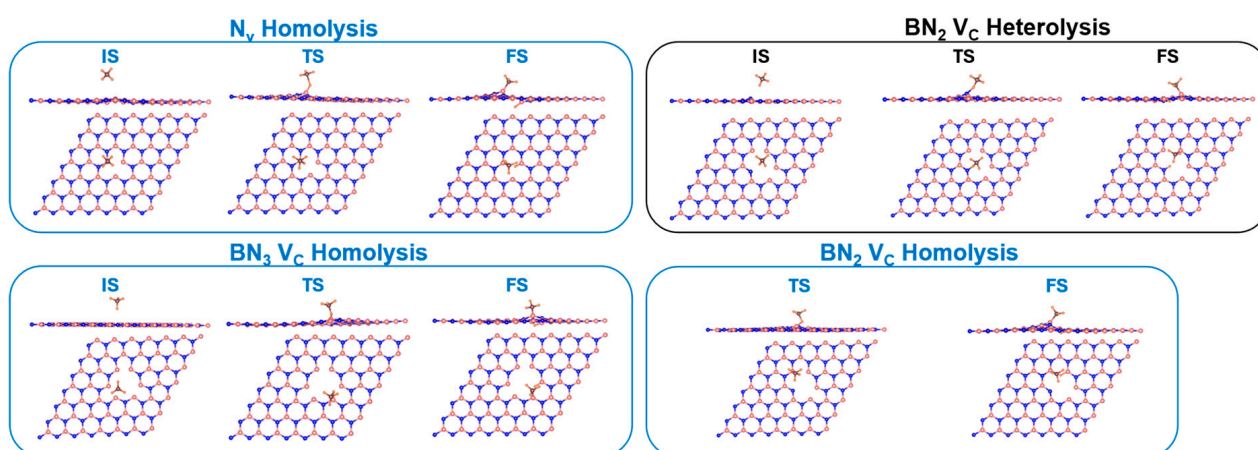


Figure 6. Optimized structures along the CH_4 activation pathways at N_V , $\text{BN}_2 \text{V}_\text{C}$, and $\text{BN}_3 \text{V}_\text{C}$ sites, including the initial state (IS), transition state (TS), and final state (FS) for both homolytic and heterolytic C–H bond cleavage.

2.3. Intrinsic Nature of the Unsaturated B–B Pair

To gain deeper insight into the role of the unsaturated B–B pair, we further examined the structures of the original vacancy surfaces and the transition states of CH_4 homolytic cleavage on these vacancies. As shown in Figure 8, the B–B distance on the pristine N_V vacancy is 2.27 Å, which is significantly longer than those in the BN_2 (2.01 Å) and BN_3 (1.97 Å) vacancies. A similar trend is observed in the transition states for CH_4 dissociation. The B–B distance in the transition state on the N_V vacancy (2.65 Å) remains larger than that on the BN_2 (2.42 Å) and BN_3 (2.19 Å) vacancies. The larger separation between the unsaturated B atoms facilitates the insertion of hydrogen during the C–H bond cleavage process, which contributes to the lower activation barrier observed on the N_V vacancy. Furthermore, the B–H bond length in the transition state on the N_V vacancy (1.28 Å) is shorter than those on BN_2 (1.35 Å) and BN_3 (1.31 Å) vacancies. This indicates a stronger interaction between hydrogen and the unsaturated boron sites on the N_V vacancy. This observation is consistent with the more negative H_2 dissociation energy on the unsaturated B sites of N_V compared with those of BN_2 and BN_3 vacancies, as shown in Figure 3.

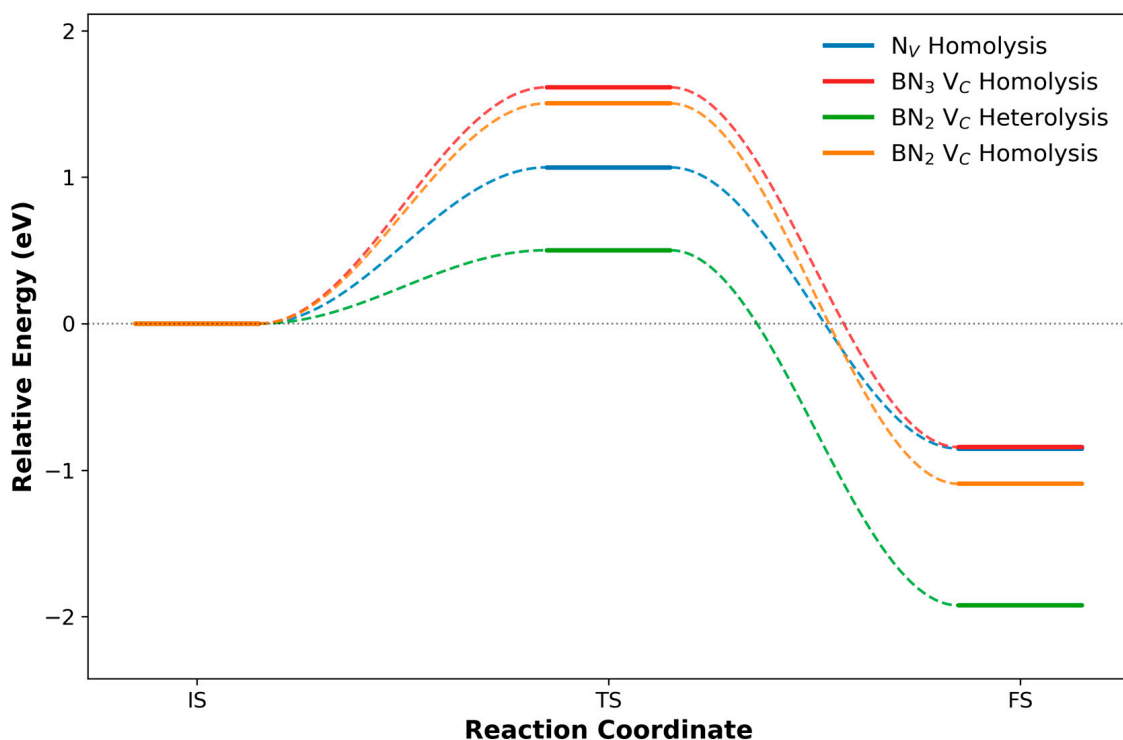


Figure 7. Reaction energy profiles for CH_4 cleavage at N_v , $\text{BN}_2 \text{V}_c$, and $\text{BN}_3 \text{V}_c$ sites. The energy changes along the reaction coordinate from the initial state (IS) through the transition state (TS) to the final state (FS) are shown for both homolytic and heterolytic C–H bond cleavage pathways.

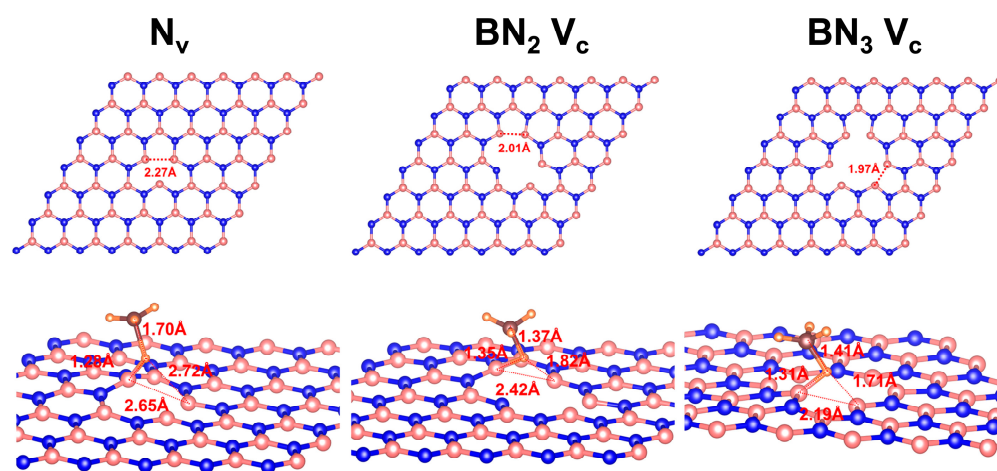


Figure 8. Optimized structures of the clean vacancy surfaces (**top**) for N_v , $\text{BN}_2 \text{V}_c$, and $\text{BN}_3 \text{V}_c$ sites and the corresponding transition-state structures for CH_4 homolytic C–H bond cleavage (**bottom**).

To further understand the electronic interaction between the unsaturated B–B pairs, crystal orbital Hamilton population (COHP) analysis was performed. COHP analysis decomposes the bonding and antibonding contributions between specific atomic pairs, where bonding states stabilize the interaction and antibonding states weaken it. As shown by the $-\text{COHP}$ curves in Figure 9, both the $\text{BN}_2 \text{V}_c$ and $\text{BN}_3 \text{V}_c$ sites exhibit pronounced bonding peaks below the Fermi level. These occupied bonding states indicate stronger B–B interactions in these vacancy configurations, which could make structural rearrangement during hydrogen insertion less favorable.

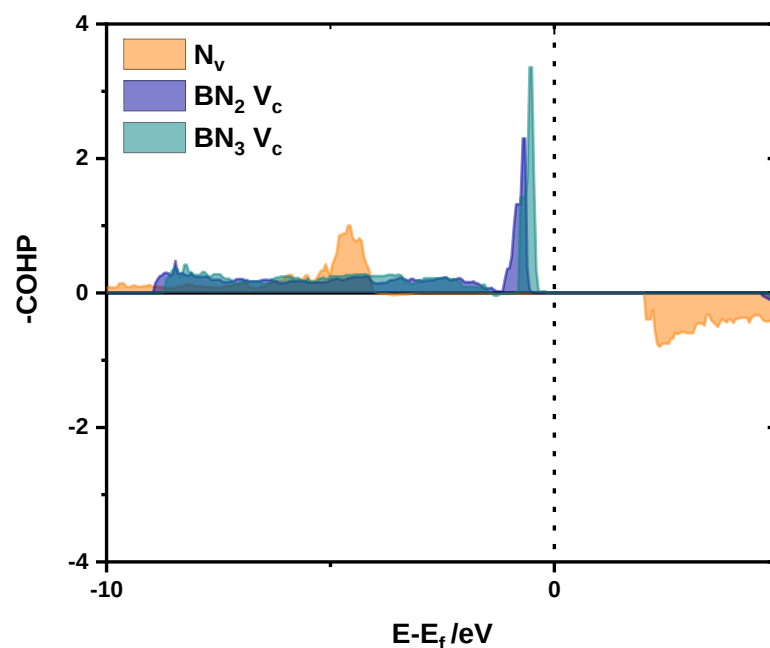


Figure 9. COHP analysis for the B–B interaction at the N_v , $BN_2 V_c$, and $BN_3 V_c$ sites.

The integrated COHP (ICOHP) values further quantify the interaction strength between the B atoms. More negative ICOHP values correspond to stronger bonding interactions between atom pairs. As listed in Table 1, the ICOHP value of the B–B pair in the N_v vacancy is less negative than those of the $BN_2 V_c$ and $BN_3 V_c$ sites, indicating relatively weaker B–B interactions in the N_v configuration. Combined with the larger B–B distance observed in the N_v vacancy (Figure 8), this weaker interaction may facilitate structural flexibility during methane activation. These results suggest that the unsaturated B–B pair on the N_v vacancy provides a more favorable geometric and electronic environment for CH_4 activation.

Table 1. ICOHP value over N_v , $BN_2 V_c$, and $BN_3 V_c$.

Vacancy	ICOHP
N_v	−1.03
$BN_2 V_c$	−2.30
$BN_3 V_c$	−2.47

To further examine the electronic redistribution during the reaction, charge density difference analysis and Bader charge calculations were also performed. As shown in Figure 10, during the homolytic activation of CH_4 on the N_v vacancy, both boron atoms of the unsaturated B–B pair exhibit electron depletion after adsorption of the CH_3 and H radicals. In contrast, for the heterolytic activation on the $BN_2 V_c$ vacancy with an unsaturated B–N pair, electron accumulation occurs at the nitrogen atom bonded to hydrogen, while the boron atom interacting with the CH_3 fragment shows electron depletion. In addition, the CH_3 fragment consistently gains electron density, as indicated by the yellow regions in the charge density difference maps, while electron depletion is observed around the vacancy region. These results indicate significant charge redistribution during CH_4 activation and provide additional electronic evidence supporting the proposed homolytic and heterolytic activation mechanisms.

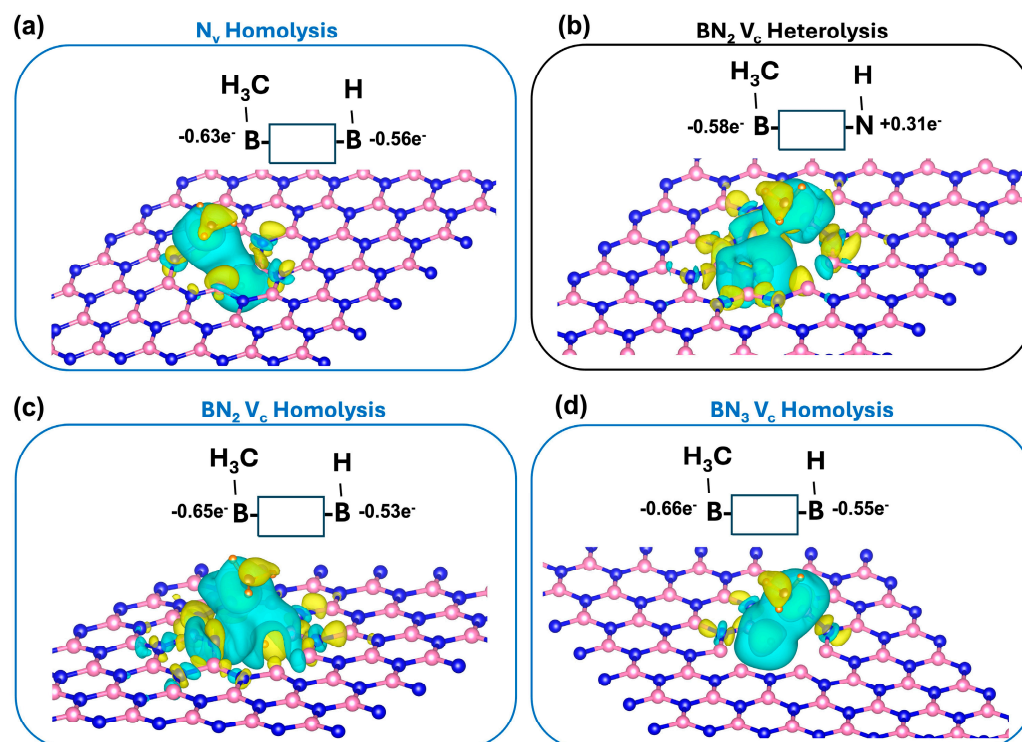


Figure 10. Charge density difference maps with corresponding Bader charge variations relative to the clean defective surface for CH₄ activation on h-BN vacancies: (a) homolytic C–H cleavage on the N_v; (b) heterolytic C–H cleavage on the BN₂ V_c; (c) homolytic C–H cleavage on the BN₂ V_c; and (d) homolytic C–H cleavage on the BN₃ V_c. Cyan and yellow regions represent electron depletion and electron accumulation, respectively.

3. Computational Methods

Spin-polarized calculations were carried out using the Vienna Ab initio Simulation Package (VASP) version 5.4.4 [33]. In terms of the exchange-correlation functional, Perdew, Burke, and Ernzerhof (PBE) [34] were utilized with the projector augmented wave potentials [35]. For the Van der Waals correction, D3 method [36] was used. A $1 \times 1 \times 1$ k-point mesh sampling was chosen for the 7×7 h-BN lateral unit cell with a vacuum layer of ~ 20 Å. For single-point calculations, a $5 \times 5 \times 1$ k-point grid was adopted. To verify the reliability of our computational setup, a k-point convergence test was performed for the pristine 7×7 h-BN supercell (Figure S1). The total energy differences are negligible (<0.01 eV) upon increasing the k-point density, indicating that $1 \times 1 \times 1$ k-point sampling is sufficient for structural optimization, while a $5 \times 5 \times 1$ mesh provides well-converged electronic properties. Although the GGA functional is known to underestimate the band gap [37], the purpose of this test is to assess numerical convergence rather than to reproduce the experimental band gap value.

The transition states were located by the climbing-image nudged elastic band method (CI-NEB) [38]. The convergence criterion was set as 0.05 eV/Å for structural optimization and transition-state searches. The vibrational frequencies of the transition states are shown in Tables S3–S6. The presence of one large imaginary frequency confirms that the structures correspond to transition states.

The normalized vacancy formation energy (vacancy formation energy per missing atom) is calculated as follows in Equation (1) and the chemical potentials of boron (μ_B) and nitrogen (μ_N) are constrained by the stability condition of pristine h-BN, as expressed in Equation (2):

$$E_f^* = (E_{BN\text{ defect}} - n_{B\text{ defect}}\mu_B - n_{N\text{ defect}}\mu_N) / N \quad (1)$$

$$E_{\text{pristine BN}} = n_B \text{ pristine} \mu_B + n_N \text{ pristine} \mu_N \quad (2)$$

Experimentally, the relative concentration of active boron and nitrogen species can be tuned during h-BN growth by adjusting the precursor feeding rate, temperature, and carrier gas composition [39], thereby enabling B-rich or N-rich environments. Under B-rich conditions, the chemical potential of boron is referenced to bulk boron, i.e., $\mu_B = E_{\text{bulk B}}$. Under N-rich conditions, the chemical potential of nitrogen is referenced to nitrogen gas, i.e., $\mu_N = \frac{1}{2} E_{N_2}$. The remaining chemical potential in each case is determined from the constraint given in Equation (2).

Crystal Orbital Hamiltonian Population (COHP) analysis [40] was performed by the Local Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER 3.2.0) program [41,42].

4. Conclusions

The stability and catalytic activity of various h-BN vacancies were systematically investigated. The calculations show that B-terminated vacancies, particularly the BN_2 and BN_3 vacancies, are thermodynamically more stable than their N-terminated counterparts under both B-rich and N-rich conditions, suggesting that B-terminated vacancies are more likely to be exposed on defective h-BN surfaces. Regarding methane activation, the B–N pair over the BN_2 vacancy exhibits very high reactivity toward C–H bond cleavage; however, the excessively exothermic reaction energy indicates strong binding of intermediates, which may lead to surface poisoning and limit catalytic turnover. In contrast, the unsaturated B–B pair exposed at the N_v provides a more balanced reaction energetics with a moderate reaction energy and a relatively low activation barrier for CH_4 activation.

Interestingly, while B–N pairs behave as frustrated Lewis pairs that activate molecules through heterolytic pathways, our results demonstrate that unsaturated B–B pairs provide a distinct catalytic motif that promotes homolytic methane activation. COHP analysis further reveals that the relatively weak electronic interaction between the two B atoms facilitates hydrogen insertion during C–H bond cleavage. These findings reveal a novel promising catalytic principle for defective h-BN surfaces, where B-terminated vacancies containing unsaturated B–B pairs can act as active centers for metal-free methane activation. This work provides mechanistic insight into the intrinsic catalytic role of h-BN vacancies and highlights their potential for metal-free alkane activation and conversion. Also, it should be noted that the present study focuses on the elementary C–H bond activation step. A comprehensive catalytic evaluation, including catalyst regeneration, possible surface poisoning by intermediates, competitive adsorption, and subsequent reaction pathways, would require the construction of a full reaction network and microkinetic analysis, which will be explored in future work.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16040321/s1>, Figure S1: K-point convergence test for the pristine 7×7 h-BN supercell; Figure S2: Calculated CH_4 adsorption energies on various h-BN vacancies and pristine h-BN; Figure S3: Correlation between the H_2 dissociation Energy and methane C–H bond activation barrier; Table S1: VASP-calculated magnetic moments (MAGMOM) of the defective h-BN surfaces with and without adsorbates; Table S2: VASP-calculated relative energies (eV) of the final states for CH_4 dissociation forming surface $CH_3\cdot$ and $H\cdot$ species on N_v , $BN_2 V_c$, and $BN_3 V_c$ defects under different total magnetic moments (NUPDOWN values); Table S3: Calculated vibrational frequencies (cm^{-1}) for the transition state of CH_4 homolytic C–H bond activation on the N_v ; Table S4: Calculated vibrational frequencies (cm^{-1}) for the transition state of CH_4 homolytic C–H bond activation on the $BN_2 V_c$; Table S5: Calculated vibrational frequencies (cm^{-1}) for the

transition state of CH₄ heterolytic C–H bond activation on the BN₂ V_C; Table S6: Calculated vibrational frequencies (cm^{−1}) for the transition state of CH₄ homolytic C–H bond activation on the BN₃ V_C.

Author Contributions: Conceptualization, C.X. and J.T.; methodology, C.X.; software, C.X.; validation, C.X. and J.T.; formal analysis, C.X.; investigation, C.X.; resources, C.X.; data curation, C.X.; writing—original draft preparation, C.X.; writing—review and editing, J.T.; visualization, C.X.; supervision, J.T.; project administration, J.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data will be made available upon reasonable request.

Acknowledgments: The authors sincerely acknowledge the computing resources provided by Southern Methodist University O'Donnell Data Science and Research Computing Institute (ODSRCI) and the University of California, Riverside High-Performance Computing Center (HPCC). This article is based on material previously presented in Chapter 4 of the author's doctoral dissertation: Xiong, C. Novel Single-Atom Catalysts (SACs) Design Based on First Principles; Ph.D. Dissertation, UC Riverside, 2024 [43]. Portions of the text and figures have been reproduced or adapted with permission.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Balmain, W.H. Bemerkungen Über Die Bildung von Verbindungen Des Bors Und Siliciums Mit Stickstoff Und Gewissen Metallen. *J. Für Prakt. Chem.* **1842**, *27*, 422–430. [\[CrossRef\]](#)
- Weng, Q.; Wang, X.; Wang, X.; Bando, Y.; Golberg, D. Functionalized Hexagonal Boron Nitride Nanomaterials: Emerging Properties and Applications. *Chem. Soc. Rev.* **2016**, *45*, 3989–4012. [\[CrossRef\]](#) [\[PubMed\]](#)
- Yu, S.; Wu, X.; Wang, Y.; Guo, X.; Tong, L. 2D Materials for Optical Modulation: Challenges and Opportunities. *Adv. Mater.* **2017**, *29*, 1606128. [\[CrossRef\]](#) [\[PubMed\]](#)
- Luo, B.; Liu, G.; Wang, L. Recent Advances in 2D Materials for Photocatalysis. *Nanoscale* **2016**, *8*, 6904–6920. [\[CrossRef\]](#)
- Kobernik, T.N.; Kartsev, A.I. Gas Adsorption on the Co₂Te₃ Monolayer: Density Functional Theory Study. *J. Phys. Chem. Lett.* **2024**, *15*, 12151–12155. [\[CrossRef\]](#)
- Pakdel, A.; Bando, Y.; Golberg, D. Nano Boron Nitride Flatland. *Chem. Soc. Rev.* **2014**, *43*, 934–959. [\[CrossRef\]](#)
- Kostoglou, N.; Polychronopoulou, K.; Rebholz, C. Thermal and Chemical Stability of Hexagonal Boron Nitride (h-BN) Nanoplatelets. *Vacuum* **2015**, *112*, 42–45. [\[CrossRef\]](#)
- Lin, Y.; Williams, T.V.; Cao, W.; Elsayed-Ali, H.E.; Connell, J.W. Defect Functionalization of Hexagonal Boron Nitride Nanosheets. *J. Phys. Chem. C* **2010**, *114*, 17434–17439. [\[CrossRef\]](#)
- Beheshtian, J.; Peyghan, A.A.; Bagheri, Z. Functionalization of BN Nanosheet with N₂H₄ May Be Feasible in the Presence of Stone–Wales Defect. *Struct. Chem.* **2013**, *24*, 1565–1570. [\[CrossRef\]](#)
- Tissen, M.; Kushchuk, L.I.; Bagzhanov, D.; Vasenko, A.S.; Pashkovskaia, V.D.; Lvov, B.G.; Vasilyev, D.; Kartsev, A. Impact of Vacancies on 2D Transition Metal Trichlorides TMCl₃ (TM = V, Ni, and Mo) Electric and Magnetic Characteristics. *J. Phys. Chem. Lett.* **2026**, *17*, 466–475. [\[CrossRef\]](#)
- Jin, C.; Lin, F.; Suenaga, K.; Iijima, S. Fabrication of a Freestanding Boron Nitride Single Layer and Its Defect Assignments. *Phys. Rev. Lett.* **2009**, *102*, 195505. [\[CrossRef\]](#) [\[PubMed\]](#)
- Cretu, O.; Lin, Y.-C.; Koshino, M.; Tizei, L.H.G.; Liu, Z.; Suenaga, K. Structure and Local Chemical Properties of Boron-Terminated Tetravacancies in Hexagonal Boron Nitride. *Phys. Rev. Lett.* **2015**, *114*, 075502. [\[CrossRef\]](#) [\[PubMed\]](#)
- Li, L.; Liu, X.; He, H.; Zhang, N.; Liu, Z.; Zhang, G. A Novel Two-Dimensional MgO-h-BN Nanomaterial Supported Pd Catalyst for CO Oxidation Reaction. *Catal. Today* **2019**, *332*, 214–221. [\[CrossRef\]](#)
- Zhu, W.; Wu, Z.; Foo, G.S.; Gao, X.; Zhou, M.; Liu, B.; Veith, G.M.; Wu, P.; Browning, K.L.; Lee, H.N.; et al. Taming Interfacial Electronic Properties of Platinum Nanoparticles on Vacancy-Abundant Boron Nitride Nanosheets for Enhanced Catalysis. *Nat. Commun.* **2017**, *8*, 15291. [\[CrossRef\]](#)
- Bi, W.; Hu, Y.; Li, W.; Jiang, H.; Li, C. Construction of Nanoreactors Combining Two-Dimensional Hexagonal Boron Nitride (h-BN) Coating with Pt/Al₂O₃ Catalyst toward Efficient Catalysis for CO Oxidation. *Ind. Eng. Chem. Res.* **2018**, *57*, 13353–13361. [\[CrossRef\]](#)

16. Xiong, C.; Dai, S.; Wu, Z.; Jiang, D. Single Atoms Anchored in Hexagonal Boron Nitride for Propane Dehydrogenation from First Principles. *ChemCatChem* **2022**, *14*, e202200133. [\[CrossRef\]](#)
17. Zhao, J.; Chen, Z. Single Mo Atom Supported on Defective Boron Nitride Monolayer as an Efficient Electrocatalyst for Nitrogen Fixation: A Computational Study. *J. Am. Chem. Soc.* **2017**, *139*, 12480–12487. [\[CrossRef\]](#)
18. Sredojević, D.N.; Belić, M.R.; Šljivančanin, Ž. Hydrogen Evolution Reaction over Single-Atom Catalysts Based on Metal Adatoms at Defected Graphene and h-BN. *J. Phys. Chem. C* **2020**, *124*, 16860–16867. [\[CrossRef\]](#)
19. Gao, M.; Lyalin, A.; Taketsugu, T. Catalytic Activity of Au and Au₂ on the h-BN Surface: Adsorption and Activation of O₂. *J. Phys. Chem. C* **2012**, *116*, 9054–9062. [\[CrossRef\]](#)
20. Datta, J.; Majumder, C. Stabilizing Co, Ni and Cu on the h-BN Surface: Using O–O Bond Activation to Probe Their Performance as Single Atom Catalyst. *Catal. Today* **2021**, *370*, 75–82. [\[CrossRef\]](#)
21. Chen, H.; Xiong, C.; Moon, J.; Ivanov, A.S.; Lin, W.; Wang, T.; Fu, J.; Jiang, D.; Wu, Z.; Yang, Z.; et al. Defect-Regulated Frustrated-Lewis-Pair Behavior of Boron Nitride in Ambient Pressure Hydrogen Activation. *J. Am. Chem. Soc.* **2022**, *144*, 10688–10693. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Fartab, D.S.; Kordbacheh, A.A. Lithium Doping and Vacancy Effects on the Structural, Electronic and Magnetic Properties of Hexagonal Boron Nitride Sheet: A First-Principles Calculation. *Superlattices Microstruct.* **2018**, *118*, 185–195. [\[CrossRef\]](#)
23. Latimer, A.A.; Kulkarni, A.R.; Aljama, H.; Montoya, J.H.; Yoo, J.S.; Tsai, C.; Abild-Pedersen, F.; Studt, F.; Nørskov, J.K. Understanding Trends in C–H Bond Activation in Heterogeneous Catalysis. *Nat. Mater.* **2017**, *16*, 225–229. [\[CrossRef\]](#)
24. Dubouis, N.; Grimaud, A. The Hydrogen Evolution Reaction: From Material to Interfacial Descriptors. *Chem. Sci.* **2019**, *10*, 9165–9181. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Zheng, J.; Nash, J.; Xu, B.; Yan, Y. Perspective—Towards Establishing Apparent Hydrogen Binding Energy as the Descriptor for Hydrogen Oxidation/Evolution Reactions. *J. Electrochem. Soc.* **2018**, *165*, H27. [\[CrossRef\]](#)
26. Taifan, W.; Baltrusaitis, J. CH₄ Conversion to Value Added Products: Potential, Limitations and Extensions of a Single Step Heterogeneous Catalysis. *Appl. Catal. B Environ.* **2016**, *198*, 525–547. [\[CrossRef\]](#)
27. Nkinahamira, F.; Yang, R.; Zhu, R.; Zhang, J.; Ren, Z.; Sun, S.; Xiong, H.; Zeng, Z. Current Progress on Methods and Technologies for Catalytic Methane Activation at Low Temperatures. *Adv. Sci.* **2023**, *10*, 2204566. [\[CrossRef\]](#)
28. Sattler, J.J.H.B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B.M. Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides. *Chem. Rev.* **2014**, *114*, 10613–10653. [\[CrossRef\]](#)
29. Wischert, R.; Copéret, C.; Delbecq, F.; Sautet, P. Optimal Water Coverage on Alumina: A Key to Generate Lewis Acid–Base Pairs That Are Reactive Towards the C–H Bond Activation of Methane. *Angew. Chem. Int. Ed.* **2011**, *50*, 3202–3205. [\[CrossRef\]](#)
30. Stephan, D.W.; Liu, L.L. Radicals Derived from Lewis Acid/Base Pairs. *Chem. Soc. Rev.* **2019**, *48*, 3454–3463. [\[CrossRef\]](#)
31. Psogianakakis, G.; St-Amant, A.; Ternan, M. Methane Oxidation Mechanism on Pt(111): A Cluster Model DFT Study. *J. Phys. Chem. B* **2006**, *110*, 24593–24605. [\[CrossRef\]](#)
32. Kokalj, A.; Bonini, N.; Sbraccia, C.; de Gironcoli, S.; Baroni, S. Engineering the Reactivity of Metal Catalysts: A Model Study of Methane Dehydrogenation on Rh(111). *J. Am. Chem. Soc.* **2004**, *126*, 16732–16733. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186. [\[CrossRef\]](#)
34. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Blöchl, P.E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953–17979. [\[CrossRef\]](#)
36. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104. [\[CrossRef\]](#)
37. Xiao, H.; Tahir-Kheli, J.; Goddard, W.A.I. Accurate Band Gaps for Semiconductors from Density Functional Theory. *J. Phys. Chem. Lett.* **2011**, *2*, 212–217. [\[CrossRef\]](#)
38. Henkelman, G.; Uberuaga, B.P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, *113*, 9901–9904. [\[CrossRef\]](#)
39. Stehle, Y.; Meyer, H.M.I.; Unocic, R.R.; Kidder, M.; Polizos, G.; Datskos, P.G.; Jackson, R.; Smirnov, S.N.; Vlassioulis, I.V. Synthesis of Hexagonal Boron Nitride Monolayer: Control of Nucleation and Crystal Morphology. *Chem. Mater.* **2015**, *27*, 8041–8047. [\[CrossRef\]](#)
40. Steinberg, S.; Dronskowski, R. The Crystal Orbital Hamilton Population (COHP) Method as a Tool to Visualize and Analyze Chemical Bonding in Intermetallic Compounds. *Crystals* **2018**, *8*, 225. [\[CrossRef\]](#)
41. Maintz, S.; Deringer, V.L.; Tchougréeff, A.L.; Dronskowski, R. LOBSTER: A Tool to Extract Chemical Bonding from Plane-Wave Based DFT. *J. Comput. Chem.* **2016**, *37*, 1030–1035. [\[CrossRef\]](#)

42. Dronskowski, R.; Bloechl, P.E. Crystal Orbital Hamilton Populations (COHP): Energy-Resolved Visualization of Chemical Bonding in Solids Based on Density-Functional Calculations. *J. Phys. Chem.* **1993**, *97*, 8617–8624. [[CrossRef](#)]
43. Xiong, C. Novel Single-Atom Catalysts (SACs) Design Based on First Principles. Ph.D. Thesis, University of California, Riverside, CA, USA, 2024.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.