Nitrogen-monovacancy (V_N) Hexagonal Boron Nitride 2D Monolayer Material as an Efficient Electrocatalyst for CO₂ Reduction Reaction

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Abstract

The conversion of waste carbon dioxide (CO₂) gas into valuable products and fuels through an electrocatalytic CO₂ reduction reaction (CO₂RR) is a promising approach. The sluggish kinetics of the CO₂RR require the development of novel strategies for electrocatalyst design. Two-dimensional (2D) materials emerge as promising candidates for CO₂RR due to their distinctive electronic and structural properties. This study follows the first principles based DFT-D method to examine the electrocatalytic competences of the defective twodimensional boron nitride monolayer (d-BN) material towards CO₂RR. Introducing a particular defect with nitrogen vacancies in the 2D single layer pristine hexagonal boron nitride (V_N_d-BN) can efficiently activate the CO₂ molecules for hydrogenation by reducing the electronic band gap of the pristine hBN from 6.23 eV to 3.0 eV. Therefore, V_N_d-BN material can act as a large band gap semiconductor. Our findings demonstrate that the defective regions in the 2D monolayer V_N_d-BN serve as active sites (Boron) for both the adsorption and activation of CO₂. The subsequent hydrogenation steps occur sequentially once the CO₂ molecule is adsorbed on the catalytic surface. Our results indicate that the OCHO* path is the most favorable for CH₄ production. Hence, the 2D monolayer V_N _d-BN material holds a great promise as a cost-effective catalyst for CO₂RR, and it presents a viable alternative to expensive platinum (Pt) catalysts.

Introduction

The rapid growth of industrialization leads to technological advancements in our daily lives, but it also raises significant environmental concerns, primarily due to the increasing pollution levels. The primary source of this increasing pollution level is the combustion of fossil fuels, which alternatively intensifies the CO₂ emissions into our environment and subsequent climate change.^{1–3} Various strategies have been developed to control the unnecessary production of CO₂ emissions, such as minimizing fossil fuel usage by adopting alternate renewable energy sources. An electrochemical CO₂RR is considered one of the most promising techniques for transforming CO₂ into valuable products such as methanol (CH₃OH), methane (CH₄), and formic acid (HCOOH) under room temperature and ambient pressure conditions.^{4–7} This significant step towards this endeavor for electrochemical conversion of CO₂ into valuable products attracts the scientific community for future challenges. Integrating electrochemical CO₂RR into renewable energy sources holds the promise of establishing a carbon-neutral energy cycle.

Over the past decades, researchers have extensively explored photochemical, thermochemical, and electrochemical methods for CO₂ reduction.^{8–12} Thermochemical conversion, which relies on high temperatures, pressures, and equivalent amounts of hydrogen as a reducing agent, makes it impractical for large-scale applications due to energy constraints.^{7,12} In the photochemical processes, a few catalysts have shown some activity in CO₂RR, but their selectivity and production rates are prohibitively low from an economic perspective.^{8,10} In contrast, electrochemical CO₂RR holds various advantages.^{11,13–15} One of the advantages is that it can perform under ambient conditions, and we can precisely control the rate of reaction by adjusting the external bias. Also, the products are generated at the different electrochemical CO₂RR a sustainable option. However, several challenges remain in the field of electrochemical CO₂RR, including high overpotential, low selectivity, and low yields resulting from the thermodynamical stability of CO₂. Furthermore, the use of CO₂

electrocatalysis is limited due to the excessive costs and inaccessibility of novel metal catalysts such as Pt, Au, and Pd.¹⁷ Many efforts have been made to develop novel, feasible, and efficient electrocatalytic materials that can accomplish high rates of CO₂RR with low overpotential as one of the solutions to these issues. Numerous 2D nanosheets can show promise for the reduction of CO₂, depending on the preferred reaction products such as CO, HCOOH, CH₃OH, and CH₄.

The research on 2D nanosheets following the discovery of graphene has expanded significantly over the past decade, and various 2D materials have been identified, such as covalent organic frameworks, chalcogenides, oxides, nitrides, halides, carbides, hydrides, hydroxides, phosphonates, phosphates, metals, and elements from groups IV and V.¹⁸ These 2D materials can exhibit insulating, semiconducting, and metallic properties. Notably, when multi-layered materials are reduced into a monolayer, they exhibit enhanced and novel electronic characteristics due to quantum confinement. Additionally, 2D materials offer a high specific surface area due to their reduced dimensionality. Different methods, such as doping, intercalation, alloying, and chemical functionalization, help us tune the physicochemical properties of 2D materials.¹⁸ These strategies enhance the opportunities to design nanosheets for catalysis as well as energy applications. Catalysis of the 2D nanosheets has gained considerable attention due to their distinctive structural and electronic properties.¹⁹ These ultrathin nanosheets possess exposed surface atoms on both sides and can escape the lattice to create vacancy-type defects. The presence of vacancy defects in nanosheets can result in the reduction of the coordination number of surface atoms, ultimately boosting catalytic performance. Also, the increment in low-coordinated surface sites enhances the chemisorption of reactants. Controlling vacancy defects can help us to modify the catalytic activities and the corresponding electronic structure. Moreover, the atomic sites present at the low coordinated edges of nanosheets exhibit intriguing catalytic properties.

The remarkable properties of 2D materials (especially hexagonal boron nitride (hBN)) have gained significant attention in various scientific fields. For example, the 2D material hBN has numerous applications, such as biomedical devices, power devices, fuel cells, dielectric tunnelling, stretchable optoelectronic devices, and electrocatalytic water splitting.^{20–24} The geometrical structure of hBN closely resembles graphite. A monolayer of hBN can be simulated by substituting all the carbon atoms present in graphene with boron (B) and nitrogen (N) atoms.²⁵ The alternating B/N atoms are covalently bound into a hexagonal layer, and weak van

der Waals forces hold these layers together. Unlike graphite, hBN exhibits a distinct interlayer stacking pattern where B atoms align directly below or above the N atoms in adjacent layers. This configuration indicates the polar nature of B-N bonds due to the distinct electronegativity of B and N atoms, inducing a partial ionic character within these covalent bonds.²⁶ Due to the higher electronegativity of the N atoms, the electron pairs in sp²-hybridized B–N σ bonds are confined to the N atoms. The pristine hBN exhibits exceptional stability, a flat surface, and insulating behavior with a relatively wide bandgap ranging from 3.60 eV to 7.0 eV, depending on the use of experimental methods.^{27–30} This wide bandgap of the material is a challenge for utilizing hBN-based materials as efficient electrocatalysts for the CO₂RR.

Several strategies, such as metal doping, functional group adsorption, and hydrogenation, have been explored to enable effective electronic communication with the hBN surface.^{31,32} Unfortunately, these approaches often lead to structural deformations in the pristine 2D planar geometry of hBN due to a mismatch between the size of the metal atom and the B/N atom. Consequently, these modifications may compromise the desired properties of hBN. The hBN material exhibits considerable potential due to its robust chemical stability, making it a noteworthy material explored across various domains, including nitrogen reduction reaction (NRR), CO₂ reduction reaction, and CO oxidation.^{33–38} Chen et al. explored a number of metalloaded BN, revealing that MoN₃/BN is a standout performer in NRR by strategically replacing a B atom with Mo on hBN.³⁸ Ajayan et al. utilized porous hBN as a substrate, employing a one-step vacuum filtration process to successfully fabricate a monoatomic Ru/hBN catalyst for the CO₂RR.³⁵ Furthermore, the defects induced in hBN significantly reduce the band gap, enhancing electrical conductivity to process electrochemical reactions. In other words, it has been observed that the 2D monolayer hBN, in the presence of vacancy defects, gives rise to semiconducting essence.

The 2D pristine hBN nanomaterial cannot be used effectively as an electrocatalyst for the CO₂RR due to its wide electronic band gap (Eg), showing its electrical insulating behavior. Due to the lack of a sufficient number of active catalytic sites, it hinders the practical use of catalytic reactions. A recent experiments performed by Yu Lei et al. demonstrated various vacancies or defects in the pristine 2D single layer hBN material (noted by d-BN), and they found that the presence of different types of vacancies within d-BN induces substantial changes in its band structure and causes a shift in the Fermi energy (E_F) level.³⁹ Furthermore, spin density calculations and electron spin resonance (ESR) experiments provided a theoretical and experimental confirmation of generating localized free radicals in these vacancies.³⁹ In another study, Katerina L. et al. experimentally showed that the 2D monolayer d-BN with nitrogen defects can activate the CO₂ molecule for hydrogenation, and the d-BN sheet can potentially serve as an active electrocatalyst for CO₂RR.⁴⁰ They found that the d-BN with nitrogen defect catalyzes formic acid and methanol formation at different temperatures.⁴⁰ To support and explain the experimental observation, , we have computationally performed our calculations under standard conditions (T = 298.15 K, p = 1 bar, U = 0 V, and pH = 0).

We have theoretically designed a 3x3 supercell of a 2D pristine hBN sheet and introduced a specific defect in this sheet with a single nitrogen-vacancy (V_N), forming a nitrogen defective 2D monolayer boron nitride material noted by V_N d-BN. After that, we studied the electronic and geometrical properties of this material by employing first-principles based dispersion-corrected density functional theory method (DFT-D). This V_N vacancy defect has rendered V_N d-BN material chemically active. The formation of 2D monolayer V_N d-BN material from the 2D single layer pristine hBN is depicted in Fig. 1. Using the same DFT-D approach, we calculated the electronic properties such as the electronic band structure, total density of states (DOS), electronic band gap (E_g) , and position of the Fermi energy level (E_F) to study the properties of the V_N d-BN material with their CO₂RR mechanism precisely. We also performed electron spin density calculations to locate the presence of unpaired electrons in the system. In our previous work, we found that the calculated electronic band gap of the 2D monolayer pristine hBN was about 6.23 eV, but in our current study, we have found that it is reduced to 3.0 eV after introducing the V_N vacancy defect to the pristine hBN which is consistent with the previous study.⁴¹ This reduction in the band gap indicates a novel strategy to improve the CO₂RR performance of the V_N d-BN material which is well harmonized with the experimental observation.⁴⁰ We investigated the CO₂RR mechanism on the surface of 2D single layer V_N d-BN material. Our research thoroughly examined how CO₂ is converted into various products on the catalytic surface using a first principles-based DFT-D approach which explain the experimental results obtained by Chagoya et al.⁴⁰ We carefully analyzed the adsorption configurations of CO₂ and its intermediates during the CO₂RR process by calculating the changes in Gibbs free energy (ΔG). Our calculations outlined the essential stages of hydrogenating CO₂ into C1 products, such as CO, HCOOH, CH₃OH, and CH₄, indicating that the 2D monolayer V_N d-BN material exhibits higher CO₂RR selectivity towards CH₄ formation. The findings of this study confirm that the 2D monolayer V_N d-BN can efficiently serve as an electrocatalyst for the CO₂RR.



Fig. 1 Equilibrium structures of (a) the pristine 2D monolayer hBN and (b) the 2D monolayer V_N_d -BN materials. (The dotted lines represent the boundary of 3 × 3 supercells.)

Theoretical Methodology and Computational Details

(a) Methodology

We investigated the equilibrium structures and properties of the 2D monolayer V_N d-BN material by employing a periodic hybrid dispersion-corrected first principles-based B3LYP-D3 density functional theory (DFT-D) method. which.⁴²⁻⁴⁵ We performed these calculations by using ab initio based CRYSTAL17 suite code, which employs Gaussian types of atomic basis sets during the computations. It is more efficient than plane wave-based codes for hybrid DFT-D calculations.⁴⁶⁻⁵¹ We used specific Gaussian basis sets with triple-ζ valence and polarization quality (TZVP) for oxygen (O), hydrogen (H), carbon (C), boron (B), and nitrogen (N) atoms in the present investigation. Due to weak van der Waals (vdW) interactions among the atoms within the layers of V_N d-BN nanosheet, we have also considered the significance of vdW dispersion effects. To address long-range vdW interactions, Grimme's 3rd order (-D3) corrections were incorporated in these computations.⁵² The B3LYP-D3 method is helpful in providing reliable and appealing geometries for the monolayer 2D structures because energy and density have the minimum effect of spin contamination in our calculations, where we set the electronic self-consistency scale to 10^{-7} atomic units. Two-dimensional vacuum slabs were constructed for the materials to incorporate the electrostatic potential in the computations. We take energy calculations with respect to the vacuum where the height of the vacuum cell is set at 500 Å. We employed a $4 \times 4 \times 1$ Monkhorst–Pack k-mesh grid where we sampled all integrations of the first Brillouin zone.⁵³ We have set a 10⁻⁷ a.u. threshold for convergence of energy and electron density. We have also used the (VESTA) visualization code for the graphical analysis of all the optimized structures.⁵⁴

(b) CO₂RR mechanism

In the CO₂RR process, electrons move toward the cathode through an external circuit, and each electron, together with a proton, reaches toward the CO₂ molecule and makes a bond with the carbon or oxygen atom, forming various products. These products can be formic acid (HCOOH), carbon monoxide (CO), methanol (CH₃OH), and methane (CH₄), based on the paths followed. The primary two-electron (2e⁻) reduction products in CO₂RR are carbon monoxide (CO) and formic acid (HCOOH), as shown in eqn. (1) and (2). Initially, the hydrogenation of adsorbed CO₂ molecule results in the formation of either COOH* or OCHO*, which can further be reduced to CO* or HCOOH*, respectively. As illustrated in the equations below, the intermediates CO* and HCOOH* can then leave the catalyst surface, and one can get CO and HCOOH molecules as final products, respectively, during CO₂RR. Here "*" represents the active site on the surface of the catalyst.

$$CO_2^* \rightarrow COOH^* \rightarrow CO^* + H_2O \rightarrow CO$$
 (1)

$$CO_2^* \to OCHO^* \to HCOOH^* \to HCOOH$$
 (2)

The further hydrogenation of adsorbed CO* to COH* or CHO* can lead to the generation of CH₃OH and CH₄ molecules as the six-electron or eight-electron reduction products, respectively. To produce a CH₃OH molecule as a final product, eqn. (3) presents the pathway where initially CHO*/COH* reduced to CHOH*, which further reduced to CH₂OH*. Finally, *CH₂OH is reduced to give CH₃OH as the ultimate product.

$$CHO^*/COH^* \to CHOH^* \to CH_2OH^* \to CH_3OH^* \to CH_3OH$$
(3)

$$CHO^*/COH^* \to CHOH^* \to CH^* + H_2O \to CH_2^* \to CH_3^* \to CH_4^* \to CH_4$$
(4)

$$CHO^*/COH^* \to CHOH^* \to CH_2OH^* \to CH_2^* + H_2O \to CH_3^* \to CH_4^* \to CH_4$$
(5)

$$CHO^*/COH^* \to OCH_2^* \to OCH_3^* \to O^* + CH_4 \to OH^* \to H_2O^* \to H_2O$$
(6)

The formation of a CH₄ molecule as a final product can occur through three possible routes, as shown in eqn. (4), (5), and (6). Eqn. (4) involves the initial reduction of CHO* or COH* to CHOH*, followed by hydrogenation to CH* intermediate and H₂O molecule. Subsequently, CH* undergoes further reduction to CH₄ through a series of hydrogenation steps. However, it is important to emphasize that the hydrogenation of CHOH* to the formation of CH* intermediate usually presents a high energy barrier compared to the formation of CH₂OH* and OCH₃* intermediates, which indicates that the path in eqn. (4) is less favorable than that mentioned in eqn. (5) and (6) when the CO₂RR takes place on the catalytic surface. In eqn. (5), the intermediate CHO* or COH* is initially reduced to CHOH*, which further hydrogenates to CH₂OH* and then generates a CH₂* intermediate along with a water molecule. Next, the CH₂* intermediate undergoes hydrogenation to CH₃*, producing CH₄ as a final product which leaves from the catalyst surface. On the other hand, eqn. (6) presents an alternative path where CHO* is reduced to OCH₂* and further undergoes hydrogenation to form an OCH₃* intermediate. The OCH₃* intermediate is further reduced into a CH₄ molecule in the next step, leaving a single oxygen atom (O*) on the catalytic surface. Eventually, the remaining O* on the catalytic surface is reduced to OH*, and at last, during further hydrogenation, an H₂O molecule is produced as a final product.

(c) Thermodynamic analysis and energy calculations

The DFT-D approach was consistently applied throughout the calculations to accurately account for the changes in Gibbs free energy (Δ G) during the CO₂RR process. The catalytic performance of the V_N_d-BN material in the CO₂RR was studied by computing the change in Gibbs free energy (Δ G) for each intermediate species involved in the subject reaction. We use the *Computational Hydrogen Electrode* (CHE) model to determine the values of Δ G of each intermediate species during the CO₂RR process. We performed all of these calculations under standard conditions (T = 298.15 K, p = 1 bar, U = 0 V, and pH = 0). We have followed the method proposed by Nørskov et al., which demonstrated that the chemical potential of 4 sum of both electron and proton (H⁺ + e⁻) can be correlated with the chemical potential of ½ H₂ molecule in the gaseous state utilizing the standard hydrogen electrode.⁵⁵ Here, we use this correlation under standard conditions to calculate the energy change for the hydrogenation in each reaction step of CO₂RR. We calculated the change in adsorption energies (Δ E) by determining the energy difference between the model with the adsorbed species [E_{slab}+adsorbate], the catalytic model V_N d-BN [E_{adsorbent}], and the adsorbate itself [E_{adsorbate}], as given below:

$$\Delta E = E_{slab + adsorbate} - (E_{adsorbent} + E_{adsorbate})$$

The negative value of change in adsorption energy represents the stability of intermediates on the catalytic surface, indicating that the adsorbate is energetically bound to the surface of V_N _d-BN material. Hence, this negative value of change in adsorption energy is favorable for elementary reactions on the surface of V_N _d-BN. Additionally, we computed the changes in Gibbs free energy (ΔG) for each reaction step of the CO₂RR occurring on the surface of V_N _d-BN material using the following equation:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH}$$

Here, ΔE represents the change in adsorption energy, ΔE_{ZPE} represents the zero-point energy, ΔS is the entropy correction (differences between the gas phase and the adsorbed state), and T represents the temperature of the system (we considered here room temperate (T = 298.15 K) for this work). The term ΔG_{pH} represents the Gibbs free energy change resulting from changes in H⁺ concentration in an acidic medium, and for this study, we set a zero value to the term ΔG_{pH} .

Results and discussions

To investigate the CO_2RR mechanism, we computationally designed a 3x3 supercell of a 2D monolayer pristine hBN sheet containing totally number of nine B atoms and nine N atoms. The, we introduced a single nitrogen-vacancy defect (V_N) in this 2D monolayer pristine hBN sheet to form a 2D monolayer V_N d-BN material. The equilibrium structures of both the 2D pristine hBN and V_N d-BN materials are shown in Fig. 1a and 1b, respectively. In our recent previous work, we already discussed both the structural and electronic properties of the pristine 2D monolayer hBN material in detail.⁴¹ Recent studies have demonstrated that introducing vacancy defects modifies the physiochemical and electronic structure of materials, improving electrocatalytic performance through defect engineering.³⁹⁻⁴¹ The catalytic activity of the d-BN depends on the distribution and position of defects within the structure. It is already experimentally and theoretically confirmed by ESR and spin density calculations that these defects generate localized free radicals.³⁹ We studied the structural and electronic properties of the 2D monolayer V_N_d-BN material to analyze the electrocatalytic performance towards the CO₂RR. The electronic properties, i.e., electronic band structure and total density of states of the 2D monolayer V_N_d-BN material are shown in Fig. 7a. Our current DFT-D analysis indicates the values of lattice constants calculated to be a = 7.285 Å, b = 7.438 Å along with the interfacial angles $\alpha = \beta = 90^{\circ}$ and $\gamma = 119.32^{\circ}$ with the P1 symmetry. The V_N d-BN sheet exhibits an electronic band gap of 3.0 eV, which results in a large band gap semiconductor material. The reduced electronic bandgap of V_N d-BN material raises the electron concentration and improves the conductivity to perform CO₂RR. It may be helpful to facilitate the electron transfer toward reactants in CO₂RR processes. It offers a novel strategy for effectively utilizing the V_N d-BN material to perform the CO₂RR. Consequently, we expect this 2D monolayer V_N_d-BN material to demonstrate an improved electrocatalytic activity for CO₂RR.

The vibrational stability of a system is a crucial aspect determining its overall stability, especially in relaxed configurations. Raman spectroscopy provides valuable insight into the vibrational modes of molecules of materials, offering a detailed picture of their structural dynamics. Under the DFT-D approaches, we use the B3LYP-D3 method implemented in the CRYSTAL17 suite code to simulate the Raman spectrum, which helps us to study the stability of a system, Raman active frequencies, and amplitudes of vibrational modes under various conditions. For these calculations, we have used a set of 4 x 4 x 1 Monkhorst-Pack k-point grids. We have performed the harmonic vibrational analysis with thermochemistry at room temperature (T = 298.15 K) to check the thermal stability of the system. This harmonic vibrational analysis of the equilibrium structure of both the 2D monolayer pristine hBN and V_N_d-BN materials help to study Raman spectra. Fig. 2 shows the simulated Raman spectrum for both (a) hBN and (b) V_N d-BN materials. In the simulated Raman spectrum of the pristine 2D single layer hBN, two distinct peaks are observed at wavenumbers 877.77 cm⁻¹ and 1372.35 cm⁻¹, obtained by the DFT-D method. We have also identified two intense peaks for the simulated Raman spectrum of the 2D single layer V_N d-BN material. One of these peaks corresponds to a vibrational mode (v_1) occurring at a wavenumber of 1422.21 cm⁻¹, considered as a reference with 100% intensity. The second vibrational mode (v_2) appears at 1338.39 cm⁻¹ and exhibits approximately 98% of the intensity of the highest Raman active vibrational mode v_1 . We have also observed other vibrations to the left of this intense peak, but their intensity is less than the v_1 vibrational mode. The range of these vibrations is around 50–80% of the intensity of the v_1 mode. The Raman active spectrum spread from 100 to 1550 cm⁻¹ in this case. However, all other vibrations are comparatively less intense, falling below 50% of the intensity of v_1 .



10

Fig. 2 Simulated Raman spectra of the (a) pristine 2D monolayer hBN and (b) 2D monolayer V_N_d -BN materials are shown here.

After determining the stable configuration, electronic structure, geometry, and electronic properties of the V_N d-BN material, we have explored how effective this V_N d-BN material is as an electrocatalyst for CO₂RR. The primary objective of this work is to examine the potential of this V_N d-BN sheet as an efficient electrocatalytic material for the CO₂RR. In this study, we have explored various possible reaction pathways and primary reduction products involved in the CO₂RR utilizing the periodic 2D slab structure of the V_N_d-BN material, which is based on the computational hydrogen electrode (CHE). The complete CO₂RR process includes multiple reaction steps with various intermediates. By studying numerous adsorption sites, we have identified the most stable adsorption structures of the reaction intermediates. In our analysis, we have only focused on the formation of single-carbon intermediates and products such as HCOOH, CO, CH₃OH, and CH₄. Here, by following an experimental work by Katerina L. et al., we have excluded all other possibilities of the formation of multi-carbon compounds.⁴⁰ The main objective of the present theoretical work is to explain the experimental observation performed by Katerina L. et al.⁴⁰ During each hydrogenation step, several CO₂RR routes can exist where the H can adsorb on the C or O atom. In this present study, we have discussed the most favorable reaction path of CO₂RR towards various intermediates and products in detail. We have calculated the change in Gibbs free energies for all considered paths, helping us to understand the complete reduction process and determine the optimal path and final achievable products on the surface of the V_N d-BN electrocatalyst.

The adsorption of linear CO₂ molecules is challenging because CO₂ is fully oxidized and thermodynamically stable. So, in most of the cases, it cannot be absorbed effectively and spontaneously on the catalytic surface. Therefore, we have considered the adsorption and activation of CO₂ molecules on the surface of the catalysts as the first step of CO₂RR. Usually, this process requires electron injection into the antibonding $2\pi_u$ orbitals of the CO₂ molecule. Therefore, the 2D monolayer V_N_d-BN can capture the CO₂ molecule effectively due to its large number of exposed active sites with the improved electron transfer capacity due to free radicals. In the most stable adsorption configuration of the CO₂ molecule, one of the oxygen and carbon atoms are bonded with two active sites (Boron), as shown in Fig. 3a. When CO₂* interacts with the V_N_d-BN material at its surface, the C-O bond length significantly increases from 1.160 Å to 1.292 Å obtained by the DFT-D method. After the adsorption of CO₂* onto the V_N_d-BN surface, the equilibrium bond lengths for B-C, B-O, and C-O are found to be 1.591 Å, 1.392 Å, and 1.292 Å, respectively, as reported in Table 1. Now, the linear structure of the CO₂ molecule transforms to a V-shape structure with an angle of 120.29°. This transformation indicates that the V_N_d-BN material effectively activates the CO₂ molecule. The value of ΔG during this reaction step is approximately -0.92 eV, as reported in Table 2, indicating an exothermic nature of the reaction and, hence, thermodynamically favorable. Therefore, the negative value of change in Gibbs free energy of adsorption of CO₂* favors the stability of the reaction on the catalytic surface. The optimized lattice parameters, space group symmetry, electronic band gap, and average bond lengths for the CO₂ adsorption on the surface of the 2D monolayer V_N_d-BN material under equilibrium conditions are presented in Table 1.



Fig. 3 Adsorption of CO_2 molecule and formation of COOH* and OCHO* intermediates on the surface of V_N _d-BN material with the optimized structures of (a) CO_2^* , (b) COOH*, and (c) OCHO*.

After the successful adsorption of the CO_2 molecule, the first stage of hydrogenation of the adsorbed CO_2 molecule can take place either on the C or O site, resulting in the formation of a stable carboxyl group (COOH) or formate group (OCHO) intermediates, respectively. Fig. 3 shows the optimized structures of both the COOH and OCHO intermediates formed during the CO_2RR on the surface of V_N _dBN material. The initial hydrogenation step is crucial in determining the overall reaction path of CO_2RR . In this study, we have extensively examined paths of both the COOH and OCHO intermediates formic acid (HCOOH), methanol (CH₃OH), and methane (CH₄). The potential energy surface diagram (as depicted in Fig. 6) i.e., reaction pathway shows the relative Gibbs free energies for both the considered paths of CO₂RR on the surfaces of the 2D V_N _d-BN material. It also shows the formation of different intermediates and products with C1 species according to the number of hydrogenation steps for both CO₂RR paths.

CO₂RR through the COOH path

The formation of COOH* on the surface of V_N d-BN material occurred through the first hydrogenation step at the O site of the adsorbed V-shaped CO₂ molecule as depicted in Figure 3a. Fig. 4 shows the equilibrium structures of all these intermediates of the COOH path with their corresponding values of ΔG . The hydrogenation at the O site does not significantly change the CO₂ hydrogenation structure. During this hydrogenation step, the B-O bond splits, and a new O-H bond is formed on the catalytic surface, forming a COOH* intermediate, as shown in Fig. 3b and 4a. In this elementary reaction step, we observed a ΔG value of -0.5 eV for the COOH* formation on the surface of the 2D monolayer V_N d-BN material. The negative value of ΔG indicates that the reaction step is exothermic and spontaneous. In the second hydrogenation step, the hydrogen can bond with a C or O atom of the COOH* intermediate. If the hydrogen bonds with the oxygen atom located distantly from the surface, it produces an H₂O molecule, which leaves the catalytic surface, and only CO* remains on the surface of V_N d-BN material, as shown in Fig. 4c. In this step, we observed a value of ΔG around -1.67 eV. The higher negative value of ΔG indicates that hydrogen can strongly bind to the surface of V_N d-BN material, making the desorption step difficult. On the other hand, if hydrogen bonds with the carbon atom, it leads to the formation of HCOOH* intermediate on the surface of V_N d-BN material, as depicted in Fig. 4b. This reaction step shows a positive value of ΔG around 1.87 eV. This higher positive value of ΔG signifies a weak hydrogen binding on the surface of V_N d-BN material, which will create difficulty in adsorption. The negative value of ΔG for CO^{*} formation confirmed the exothermic nature of the reaction, so it occurs spontaneously on the surface of V_N d-BN material. In contrast, the positive value of ΔG for HCOOH* formation indicates the endothermic nature of the reaction, so we require energy for hydrogenation on the catalytic surface. Here, we consider the CO* formation due to its negative value of ΔG for further hydrogenation. The CO* intermediate plays a crucial role in the CO₂RR as its ability to adsorb on a catalyst strongly influences whether CO becomes the primary

product or undergoes additional hydrogenation. If the value of ΔG for forming the CO* is small, it will desorb as a CO molecule from the catalytic surface as the final product. However, if the value of ΔG for forming the CO* on the surface of V_N_d-BN material is moderate, it will more favorably generate final products containing more than two electrons, such as CH₃OH and CH₄. Here, the value of ΔG is around -1.67 eV, indicating that CO* hydrogenates in further reaction steps to produce CH₃OH or CH₄ as a final product.

In the third hydrogenation step, the adsorbed CO* molecule undergoes further hydrogenation to yield COH* and CHO* rather than undergoing desorption. On the V_N_d-BN surface, the value of ΔG required for CO* hydrogenation to form CHO* intermediate is 1.98 eV, as shown in Fig. 4d. In contrast, the value of ΔG required for CO* hydrogenation to form COH* intermediate is 4.32 eV, as shown in Fig. 4e. The positive value of ΔG for both cases indicate the endothermic nature of the reaction, so we require energy for further hydrogenate the CO* intermediate on the surface of the 2D single layer V_N_d-BN material. This higher positive value of ΔG signifies a weak hydrogen binding on the surface of V_N_d-BN material, which will create difficulty in adsorption. Therefore, the higher positive value of ΔG hinders the further hydrogenation of CO* intermediate. It leads to a thermodynamically unfavorable reaction as a higher applied potential will be required to generate CHO* and COH* intermediate along the COOH path.



Fig. 4 Formation of HCOOH*, CO*, CHO*, and COH* intermediates on the surface of the 2D monolayer V_N _d-BN material with the equilibrium structures of (a) COOH*, (b) HCOOH*, (c) CO*, (d) CHO*, and (e) COH*.

CO₂RR through the OCHO path

Now, we initiate the CO₂RR using an activated CO₂ molecule on the surface of the V_N d-BN material for the OCHO path. Fig. 5 shows the equilibrium structures and values of ΔG for possible intermediates of the OCHO path during the CO₂RR process. The first hydrogenation step occurs at the C site of adsorbed CO₂ molecules and splits the C-B bond. Then hydrogen and the carbon atom form a C-H bond, resulting in the formation of an OCHO* intermediate, as shown in Fig. 5b. In this hydrogenation step, we observed a value of ΔG around -1.44 eV for OCHO* intermediate formation, as reported in Table 2. The negative values of ΔG indicate that the reaction step is exothermic and spontaneous. It is important to note here that the value of ΔG for OCHO* formation ($\Delta G = -1.44 \text{ eV}$) is higher than the value of ΔG for COOH* formation ($\Delta G = -0.50 \text{ eV}$), so the formation of OCHO* intermediate is considered thermodynamically more favorable. Also, the higher energy released during OCHO* formation indicates the effective activation of the CO₂ molecule on the surface of the 2D monolayer V_N_d-BN material. Therefore, we considered the formation of OCHO* intermediate on the surface of V_N d-BN material as a primary product for further reduction. The second hydrogenation step occurs at the distantly located O site on the surface of the OCHO* intermediate. This hydrogenation step results in the formation of an OCHOH* intermediate on the catalytic surface, as shown in Fig. 5c. The calculated value of ΔG for this reaction step is 1.80 eV, as reported in Table 2. The positive values of ΔG indicate the endothermic nature of the reaction, so we require energy to hydrogenate the OCHOH* intermediate further on the surface of the V_N d-BN material. So, this positive change in the value of ΔG provides some resistance to further hydrogenation on the catalytic surface. Still, this path is more favorable than the previously discussed COOH path. Therefore, we consider the formation of an OCHOH* intermediate for further reduction on the surface of the V_N d-BN material.

In the third hydrogenation step, the hydrogen combines with the distantly located oxygen atom of the O-H site in the OCHOH* intermediate, and the H₂O molecule is desorbed from the catalytic surface. Here, only CHO* remains on the surface of V_N _d-BN material, as shown in Fig. 5d. The calculated value for ΔG is -0.55 eV for CHO* intermediate formation,

as reported in Table 2. The negative value of ΔG indicates the exothermic nature of this reaction step. So, it spontaneously occurs on the catalytic surface. It is important to note that the OCHO path is more favorable than the COOH path here, but at the end of both reaction paths, we get CHO* as a common reaction intermediate. In the fourth hydrogenation step, the hydrogenation of CHO* can lead to the formation of CHOH* and OCH₂* intermediates. Now, if the hydrogen atom bonded to the C site on the surface of the CHO*, it forms an OCH₂* intermediate. But if a hydrogen atom bonded to the O site on the surface of the CHO* intermediate is calculated to be 1.21 eV, while the value of ΔG for the OCH₂* intermediate formation is calculated to be 1.21 eV, while the value of ΔG for the OCH₂* intermediate formation is around 0.11 eV obtained by the DFT-D method. Here, the change in Gibbs free energies for both the reaction steps is positive, which shows the endothermic nature of the reaction steps of these intermediate states. However, the value of ΔG for the OCH₂* formation is much less than that for the HCOH* formation, so we consider the formation of the OCH₂* intermediate on the surface of V_N_d-BN for further reduction. The equilibrium structure of OCH₂* intermediate on the surface of the 2D monolayer V_N_d-BN material is depicted in Fig. 5e.



Fig. 5 Adsorption of CO₂ molecule and formation of various intermediates on the surface of 2D monolayer V_N _d-BN material with the equilibrium structures of (a) CO₂*, (b) OCHO*, (c) OCHOH*, (d) CHO*, (e) OCH₂*, (f) OCH₃*, (g) O*, and (h) OH*.

In the fifth hydrogenation step, the intermediate OCH_2^* undergoes further hydrogenation, where a hydrogen atom is adsorbed at the C site to form the OCH_3^* reaction intermediate. Fig. 5f shows the equilibrium structure of the OCH_3^* intermediate on the surface of the 2D monolayer V_N_d -BN material. The calculated value of ΔG for the OCH_3^* intermediate formation on the catalytic surface is about -1.13 eV, as reported in Table 2. The negative value of ΔG indicates the exothermic nature of the reaction, which spontaneously occurs on the catalytic surface. In the sixth step, the OCH_3^* intermediate can undergo hydrogenation on the surface of the V_N_d -BN material with two possibilities. The first possibility is where hydrogen gets bonded at the O site of the OCH_3^* intermediate, which leads to the formation of a CH₃OH molecule. This CH₃OH molecule gets desorbed from the surface of the V_N_d -BN material as a final product. The second possibility is the desorption of a CH₄ molecule from the catalytic surface. Now, only a single oxygen atom remains to produce an H_2O molecule as a final product after two more successive hydrogenation steps. The hydrogenation of the OCH₃* intermediate to form CH₃OH* is accompanied by a value of ΔG around 1.37 eV. In comparison, the formation of the O* intermediate with desorption of the CH₄ molecule has a change in Gibbs free energy around 0.40 eV, as reported in Table 2. The value of ΔG for both steps is positive, which shows the endothermic nature of both reaction steps. The formation of an O* intermediate is more favorable than the desorption of a CH₃OH molecule due to a comparatively smaller value of ΔG . Hence, we consider an O* intermediate with the desorption of a CH₄ molecule on the catalytic surface for further reduction. The optimized structure of O* intermediate on the surface of the 2D monolayer V_N_d-BN material is shown in Fig. 5g.

The intermediate O* undergoes further hydrogenation in the seventh step, where hydrogen bonds with the remaining oxygen on the catalytic surface to form the OH* intermediate, as shown in Fig. 5h. The value of ΔG for this reaction step is around -1.37 eV, as reported in table 2. The negative value of ΔG for OH* formation confirmed the exothermic nature of the reaction, so it occurs spontaneously on the catalytic surface. The remaining OH* intermediate bonded with hydrogen in the last hydrogenation step, forming an H₂O molecule that desorbed from the catalytic surface for the next cycle. The value of ΔG for this hydrogenation step is around 2.18 eV, as reported in Table 2. So, the hydrogenation of OH* is the highly endothermic reaction step and is also considered a rate-limiting step of CO₂RR. The formation of H₂O from the OH* intermediate serves as a crucial step that contributes to the overall reaction and plays a pivotal role in facilitating subsequent cycles of the reaction. The value of change in Gibbs free energy for H₂O formation on the catalytic surface is highly positive, but still, it is a crucial reaction step because it provides an active catalytic surface for the next cycle of CO₂RR. The formation of H₂O at the end of the reaction cycle restores the active sites on the catalytic surface, preparing it for initiating further CO₂RR cycles. The formation of H₂O may create a thermodynamic barrier, but it is a crucial intermediate in restoring the catalyst surface. Therefore, it draws our attention to its importance in sustaining and enhancing the efficiency of CO₂RR processes.

The potential energy surface (PES) diagram illustrates the energetics of the CO_2RR mechanism on the surface of V_N d-BN material. We present the two prominent paths in the

PES diagram by studying all possible routes. The first is the COOH* path, represented by red color, and the second is the OCHO* path, represented by blue color in the PES diagram, as shown in Fig. 6. Both pathways represent a series of intermediate steps leading to the final product. We can easily understand which path is more thermodynamically favorable by analyzing the relative Gibbs free energies along these CO₂RR pathways. The PES diagram shows which path is more accessible and gives essential information about how likely it will happen. This analysis showed us that the OCHO* path exhibits more favorable than the COOH* path. This conclusion results from observing the change in Gibbs free energy for the formation of each reaction intermediate along both paths. Consequently, the OCHO* path emerges as the preferred route for the CO₂RR process on the surface of the 2D monolayer V_N d-BN material. Various factors, such as the specific electronic and structural properties of the 2D monolayer V_N d-BN material, favorably influence the adsorption and activation of CO₂ molecules and intermediates along the OCHO* path. Thoroughly analyzing the PES diagram with the react pathways offers valuable insights into how the CO₂RR process happens on the surface of V_N d-BN material. It highlights the importance of the OCHO* path in reacting toward favorable results which is accord with the experimental observation performed by Katerina et al.⁴⁰



Reaction Pathway

Fig. 6 Relative Gibbs free energy diagram for the CO_2RR on the surface of the 2D monolayer V_N_d -BN material.

Table 1 Equilibrium structural parameters, lattice constants, and electronic band gap (E_g) parameters of various systems of the CO₂RR.

Reaction	Lattice	Interfacial	Space	Electronic	Average bond distance (in Å)				
intermediate	parameters	angles in	group &	band gap					
	(Å)	degree	symmetry	(E _g in eV)	B-C	B-O	С-О	С-Н	0-Н
CO ₂ *	a = 7.509,	$\alpha = \beta = 90$	P1	0	1.591	1.392	1.292	-	-
	b = 7.540	$\gamma = 120.480$							
OCHO*	a = 7.215,	$\alpha = \beta = 90$	P1	5.30	-	1.417	1.281	1.096	-
	b = 7.472	$\gamma = 118.882$							
OCHOH*	a = 7.209,	$\alpha = \beta = 90$	P1	0	-	1.382	1.374	1.091	0.971
	b = 7.476	$\gamma = 118.879$							
CHO*	a = 7.259,	$\alpha = \beta = 90$	P1	0	1.604	-	1.228	1.113	-
	b = 7.474	$\gamma = 119.041$							
OCH ₂ *	a =7.361,	$\alpha = \beta = 90$	P1	0	1.576	1.559	1.470	1.089	-

	b = 7.549	$\gamma = 119.192$							
OCH3*	a = 7.497,	$\alpha = \beta = 90$	P1	0	-	1.390	1.417	1.092	-
	b = 7.497	$\gamma = 120.000$							
O*	a = 7.209,	$\alpha = \beta = 90$	P1	1.68	-	1.360	-	-	-
	b = 7.483	$\gamma = 118.796$							
OH*	a = 7.497,	$\alpha = \beta = 90$	P1	0	-	1.396	-	-	0.968
	b = 7.497	$\gamma = 120.000$							

Table 2 Change in Gibbs free energy (ΔG in eV) and relative Gibbs free energy of all the intermediates during the CO₂RR performed on the surface of the 2D monolayer V_N_d-BN material is reported here.

Various CO ₂ RR Steps	$\Delta \mathbf{G} (\mathbf{eV})$	Relative free energy (eV)
$V_{N_d}-BN^* \rightarrow CO_2^*$	-0.93	-0.93
$CO_2^* \rightarrow OCHO^*$	-1.44	-2.37
$OCHO^* \rightarrow OCHOH^*$	1.80	-0.57
$OCHOH^* \rightarrow CHO^* + H_2O$	-0.55	-1.12
$CHO^* \rightarrow OCH_2^*$	0.11	-1.01
$OCH_2^* \rightarrow OCH_3^*$	-1.13	-2.14
$OCH_3^* \rightarrow O^* + CH_4$	0.40	-1.74
$O^* \rightarrow OH^*$	-1.37	-3.11
$OH^* \rightarrow V_N_d-BN^*+H_2O$	2.14	-0.97



Fig. 7 Schematic illustration of the electronic band structures and total density of states of the 2D monolayer V_N_d -BN material and all the reaction intermediates along the OCHO path during CO₂RR process are plotted here: (a) V_N_d -BN, (b) CO₂*, (c) OCHO*, (d) OCHOH*, (e) CHO*, (f) OCH₂*, (g) OCH₃*, (h) O*, and (i) OH*

In our investigation of the CO₂RR mechanism on the surface of the 2D monolayer V_N_dBN material, we employed the DFT-D method to explore the electronic properties to understand the catalytic activity of the material. Specifically, we focused on the band structure, electronic band gap (Eg), Fermi energy (EF) level, and total density of states (DOS) for the V_N_d -BN material and each reaction intermediate along the OCHO path during CO₂RR. The band structure analysis helps us understand the electronic behavior of a material, highlighting its potential for catalytic activity. Meanwhile, the DOS calculations provide detailed information on the density of electronic states, helping us to observe the availability and distribution of electronic states. To precisely represent the electronic structure, we selected the k-vector path along the highly symmetric directions, named $\Gamma-M-M-\Gamma$, within the first Brillouin zone for band structure plots. Using the band structure calculations, we have plotted eight electronic energy bands. Four out of these eight energy bands lying above the Fermi energy (EF) level are named conduction bands, whereas the remaining four lying below the

Fermi energy level are named valence bands. The Fermi energy (E_F) level is represented by the dotted blue line in the computed band structures and DOS calculations as depicted in Figure 7a-I for all the reaction intermediates involved in the subject reaction along with the 2D monolayer V_N _dBN material. We have computed the value of Fermi energy level (E_F) at -3.39 eV in the electronic band structures and total DOS of the 2D monolayer V_N _d-BN material, as shown in Fig. 7a. We observed a tiny fraction of electron density in the total DOS calculations just below the Fermi energy level.

In the electronic band structure calculations, during the initial hydrogenation step, where the CO₂ molecule adsorbs on the surface of the V_N_d-BN material, the Fermi energy (E_F) level shifts toward the conduction band. Eventually, one of the electronic energy bands belonging to the conduction bands crosses the Fermi energy (E_F) level, indicating a conductive nature of CO₂*. The DOS calculations reveal a substantial electron density of states around the Fermi level (E_F), which also confirms the conductive nature of CO₂* reaction intermediate formed during the CO₂RR, as shown in Fig. 7b. This characteristic promotes electron propagation during the reaction, and it helps to improve the efficiency of the CO₂RR mechanism. This conductive nature is observed consistently in the further hydrogenation steps involving OCHOH*, CHO*, OCH2*, OCH3*, and OH* on the surface of the 2D monolayer V_N_d-BN material, as shown in Fig. 7d, 7e, 7f, 7g, and 7i, respectively. We observe similar trends in the electronic band structure calculations of these intermediate states, where one of the electronic energy bands of the valence bands shifts towards the Fermi energy level and crosses it, confirming the conductive nature of these intermediates. We also calculated the total DOS for these intermediates and observed the electron density around the Fermi energy level, which also indicates the conductive nature of these intermediates. We also computed the electronic band structure and total DOS of the remaining intermediates formed during the CO₂RR. The electronic band structure calculations of the reaction intermediates OCHO* and O* reaction steps reveal the presence of an energy bandgap in these systems, as shown in Fig. 7c and 7h, respectively. In the DOS calculations, we observed a small fraction of electron density just below the Fermi energy level for these systems. Fig. 7a-i shows the electronic band structure and total DOS of the 2D monolayer $V_{\rm N}\sp{d-BN}$ material along all the reaction intermediates involved in the subject reaction. Fig. 6 illustrates the PES diagram, in which we present the relative Gibbs free energies of the two prominent reaction pathways (COOH and OCHO) of the CO₂RR mechanism on the surface of the 2D monolayer V_N d-BN material. Table 1 provides a detailed comparison of various reaction intermediates throughout the

 CO_2RR process, including their equilibrium lattice constants, space group symmetry, shift of Fermi energy level, electronic band gap, and average bond lengths. Table 2 presents the change in Gibbs free energy (ΔG) and relative Gibbs free energy for each intermediate involved in the CO_2RR process performed on the surface of the 2D single layer V_N_d-BN material.



Fig. 8 Electron spin density calculations of V_N_d -BN material and all intermediates formed along the OCHO path during the CO₂RR process: (a) V_N_d -BN, (b) CO₂*, (c) OCHO*, (d) OCHOH*, (e) CHO*, (f) OCH₂*, (g) OCH₃*, (h) O* and (i) OH*.

In this study, we also calculated the electron spin densities of the 2D single layer V_N_d -BN material along all the intermediate states formed during the CO₂RR process by using the same DFT-D method, as depicted in Fig. 8. The electron spin densities offer crucial insights into the electronic structure and reactivity of these systems, which are essential for understanding their catalytic activity towards the CO₂RR. The significance of these calculations lies in their ability to elucidate the distribution of unpaired electrons, which directly influences the reactivity of materials. The distribution of electron spin density is crucial to show how the spin polarization is within the molecular orbitals. The analysis of spin densities

unveils distinct patterns of electron localization and delocalization, highlighting the pivotal role of adsorption sites on the surface of V_N d-BN material in modulating electron transfer kinetics. The spin density represents the mismatch between the numbers of spin-up (α) and spin-down (β) electrons employed to estimate the presence of unpaired electrons. Under these conditions of unequal distribution of spin-up and spin-down electrons, spin polarization comes into the picture, which also results in non-zero spin density. The spin density functional theory (SDFT) extends DFT to include magnetic fields alongside scalar external potentials from the nuclei. Two space functions, spin density (s) and electron density (ρ), serve as fundamental variables in SDFT. The spin density reflects interactions among electron spins within a system and plays a crucial role in understanding the magnetic phenomena of the material.⁵⁶ In Fig. 8, the α -spin electrons, i.e., the positive component of the electronic wave function, are represented by the highlighted yellow color, while the β -spin electrons, i.e., the negative component of the electronic wave function, are represented by the sky-blue color. The spin density distribution within a molecule is crucial for understanding the propagation of spin polarization in molecular complexes and crystals. It is helpful to understand various magnetic interactions, which are a function of molecular orientation as well as packing. Hence, we can say that electron density plays a crucial role in electrocatalysis during the CO₂RR to facilitate electron transfer in the reaction mechanism.

Conclusions

In our current work, we have investigated the electrocatalytic activities of the defective 2D monolayer hexagonal boron nitride (d-BN) towards CO_2RR which is consistent with the experimental observation. By introducing a single nitrogen-vacancy (V_N) defect in the pristine 2D monolayer hBN, we have examined the electrocatalytic activity of the 2D single layer V_N_d-BN material towards the CO₂RR. We have simulated the Raman spectroscopy of the V_N_d-BN material to determine its overall stability to perform the CO₂RR. We have followed the DFT-D method to computationally explore the structural and electronic properties of the 2D monolayer V_N_d-BN material as well as for all the intermediate states formed during the CO₂RR. We have calculated the electronic properties of the V_N_d-BN material towards all the intermediate states formed during the CO₂RR. We have calculated the electronic properties of the V_N_d-BN material towards all the intermediate states formed during the CO₂RR. We have calculated the electronic properties of the V_N_d-BN material towards all the possible reaction intermediates formed during the CO₂RR, including its band structure and total DOS at the equilibrium position. The findings of our current work suggest that after the introduction of the V_N defect in the pristine 2D monolayer hBN, the electronic band gap of the

2D monolayer V_N d-BN material is reduced to 3.0 eV. After determining the stable configuration and electronic properties of the V_N d-BN material, we have explored various possible reaction pathways and primary reduction products involved in the CO₂RR. In the present investigation, we have considered a periodic structural slab structure of the V_N d-BN material and CO₂RR process has been investigated based on the computational hydrogen electrode (CHE). We have also calculated the electron spin density of all the systems which helps us to locate the unpaired electrons around the defective reason of the V_N d-BN material. This DFT-D approach was consistently applied throughout the calculations to the precise depth of Gibbs free energy during the CO₂RR process. We have explored the two prominent reaction pathways such as COOH* and OCHO* on the surface of the 2D single layer V_N d-BN material. Both the reaction pathways represent a series of intermediate steps leading to the final product. The results of our analysis showed that the OCHO* path exhibits more favorable than the COOH* path. Also, we found that the 2d monolayer V_N d-BN material is more likely to generate CH₄ as the final product rather than CO, HCOOH, and CH₃OH during the CO₂RR process. The hydrogenation of OH* intermediate is the rate-limiting step. Overall, the V_N d-BN material demonstrates significant activity and selectivity as an electrocatalyst for the reduction of CO₂ to CH₄. Hence, the 2D monolayer V_N d-BN exhibits promising electrocatalytic activity for CO₂RR with substantially improved reaction kinetics.

Conflicts of Interest:

The authors have no additional conflicts of interest.

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Author Contributions:

Dr. Pakhira designed the project, and he conceived the complete idea of this current research project work, Mr. Lokesh Yadav computationally studied the electronic structures and properties of the 2D monolayer hBN and V_N _d-BN materials. Dr. Pakhira and Mr. Lokesh Yadav explored the whole reaction paths, transition states, and reaction barriers. They explained the CO₂RR mechanism by the DFT Quantum Mechanical calculations. Dr. Pakhira and Mr. Lokesh wrote the whole manuscript and prepared all the tables and figures in the manuscript. Dr. Pakhira and Mr. Lokesh interpreted and analyzed the computed results, and Dr. Pakhira supervised the project work.

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