

Article

Computational Screening of N-Doped Graphene-Supported Cu-Sc Nanoclusters for CO₂ Capture

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Abstract

Converting carbon dioxide (CO₂) into value-added chemicals and/or capturing it before emission are complementary strategies to mitigate rising atmospheric CO₂ levels. Copper-based materials are widely investigated for CO₂ conversion because Cu can bind and electronically activate CO₂ and related intermediates. In this computational research, an evaluation of CO₂ activation in Cu_xSc_y nanoclusters (Cu₃Sc, Cu₂Sc₂, and CuSc₃) anchored on a graphene bilayer doped with three nitrogen atoms (graphene-3N) was performed using conformational screening and thermochemical adsorption analysis at 298.15, 300, and 400 K. Initially, the Cu₃Sc, Cu₂Sc₂, and CuSc₃ nanoclusters were optimized and characterized (relative energy, multiplicity, and electronic characteristics), and the support model (graphene-3N bilayer) was validated by comparing free geometry with partially restricted geometry, corroborating minima through vibrational analysis. Subsequently, CO₂ adsorption/activation on Cu_xSc_y@graphene-3N was evaluated, and ΔH and ΔG values were calculated. Ultimately, based on the ΔG(T) values, the Sabatier regimes were established, where it was observed that Cu₃Sc exhibits moderate exergonic adsorption (ΔG = −76.07, −67.31, and −58.92 kJ·mol^{−1} at 298.15, 350, and 400 K). In contrast, Cu₂Sc₂ exhibits intense adsorption (−165.02, −156.36, and −148.04 kJ·mol^{−1}), and CuSc₃ results in practically irreversible fixation (−293.98, −287.32, and −279.09 kJ·mol^{−1}), giving priority to Cu₃Sc as the most optimal cluster in terms of activation-regeneration.

Keywords: activation; adsorption; CO₂; nanoclusters; copper; scandium; Cu₃Sc; Cu₂Sc₂; CuSc₃; graphene



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1. Introduction

The constant increase in atmospheric carbon dioxide (CO₂) is a key driver of global warming [1–3]. In this context, simply collecting CO₂ is not enough unless a process is implemented to convert it into valuable products [4–6]. However, such conversion is restricted by the remarkable thermodynamic stability of CO₂ and its low intrinsic reactivity [7–9].

From a molecular perspective, the main obstacle lies in the activation of CO₂: the transformation of a linear molecule (O–C–O ≈ 180°) to an adsorbed state that is polarized and curved, which involves the weakening of C–O bonds and the transfer of charge to antibonding orbitals [10–12]. If this phase is not managed correctly, the transformation can become energy-intensive or lose selectivity for alternative routes [13–15]. In electrochemical

systems, this manifests as competition with hydrogen evolution (HER) and as the limitation of faradaic efficiencies directed towards the desired products [16–18].

Consequently, catalysts are essential for mitigating the energy penalty associated with activation and stabilizing key intermediates [10–12]. In the field of metals, copper has been extensively studied for its ability to bind carbon species and facilitate multiple carbon dioxide conversion pathways [19–22]. However, this “multi-path” characteristic tends to compromise selectivity, as minimal fluctuations in the active site (coordination, effective oxidation state, microenvironment) alter the product map.

Two approaches have been identified that are particularly effective in modifying the interaction between CO₂ and the active site: (i) nanostructuring and (ii) bimetalization [23,24]. In nanoclusters, low-coordination sites, such as edges and vertices, are prevalent. This characteristic alters the electronic density of the environment, which, in turn, can promote both CO₂ adsorption and activation by facilitating charge transfer and causing geometric distortion in the adsorbed molecule. The addition of a second metal also makes it possible to alter the electronic arrangement at the site (ligand effect), the local geometry (ensemble effect), and the bond strength of the adsorbed species [25].

Within this context, Cu–Sc systems are conceptually interesting, as they integrate a metal with adaptable surface chemistry (Cu) with a more oxophilic element with Lewis’s acid characteristics (Sc). The latter can polarize CO₂ through preferential coordination to oxygen. However, this feature poses a design risk: if adsorption is too strong, CO₂ becomes excessively stabilized, potentially clogging the active site [22]. From the perspective of catalysis, this can be summarized in a fundamental principle: to achieve optimal performance, it is essential to reach a Sabatier-type equilibrium, in which the interaction is intense enough to facilitate activation but not so rigid as to prevent regeneration [26].

Furthermore, under pragmatic conditions, the nanocluster’s function is supported. The support does not simply act as a “spectator”; it regulates dispersion, sintering, charge transfer, and the structure of the active site. Two-dimensional materials, such as graphene, are essential for their stability, large surface area, and ability to modulate local electronic properties through defects and doping. Specifically, nitrogen-doped graphene provides stronger anchoring sites and an electronic environment that promotes charge transfer to adsorbed species, including carbon monoxide [27].

Despite progress, a methodological limitation persists in the CO₂ literature on nanoclusters: adsorption energies are often addressed without explicitly integrating (a) the entropic contribution that becomes critical with increasing temperature, and (b) the sensitivity of the system to spin multiplicity, particularly when the energy separations between states are small. In nanoclusters, these two dimensions have the capacity to alter the stability hierarchy and, therefore, the reading of “optimal candidate” when changing from ΔE to $\Delta G(T)$.

Based on the above, this study presents a DFT analysis of Cu₃Sc, Cu₂Sc₂, and CuSc₃ nanoclusters anchored to graphene-3N to establish thermodynamic and electronic criteria for CO₂ activation with site-regeneration potential. Initially, relative stability is based on, and relevant electronic components are defined, accounting for multiplicity. Subsequently, CO₂ adsorption is quantified using ΔH and ΔG measurements at 298.15, 350, and 400 K. The adsorption regimes are then classified. A Sabatier rule is proposed to prioritize Cu: Sc compositions that achieve effective activation without compromising reversibility.

2. Materials and Methods

2.1. Computational Methodology and Thermodynamic Analysis

All calculations related to the electronic structure were performed using Density Functional Theory (DFT) with ORCA v6.1.0 software [28]. The r²SCAN-3c method was used

to jointly characterize the geometries, interaction energies, and vibrational contributions in extended cluster-type systems [29]. This scheme combines the functional meta-GGA r^2 SCAN, the def2-mTZVP basis set, the D4 dispersion correction, and the geometrical counterpoise (gCP) correction to reduce the basis-set overlap error. A uniform protocol was applied in all cases, facilitating direct comparisons between metal compositions and different doping types.

Thermodynamic analyses were performed at 298.15 K, 350 K, and 400 K, using a uniform calculation protocol for all species, including surfaces, gas-phase molecules, and adsorbed complexes.

2.2. Cu–Sc Nanocluster Models

A study was conducted on bimetallic nanoclusters composed of four atoms, considering three different compositions: Cu_3Sc , Cu_2Sc_2 , and CuSc_3 . For each composition, representative initial geometries, such as triangular, pyramidal, and quasi-planar arrangements, were subjected to a thorough optimization process (Figure 1). Given that in small clusters multiplicity can significantly influence stability, an evaluation of multiple spin states was carried out for each system.

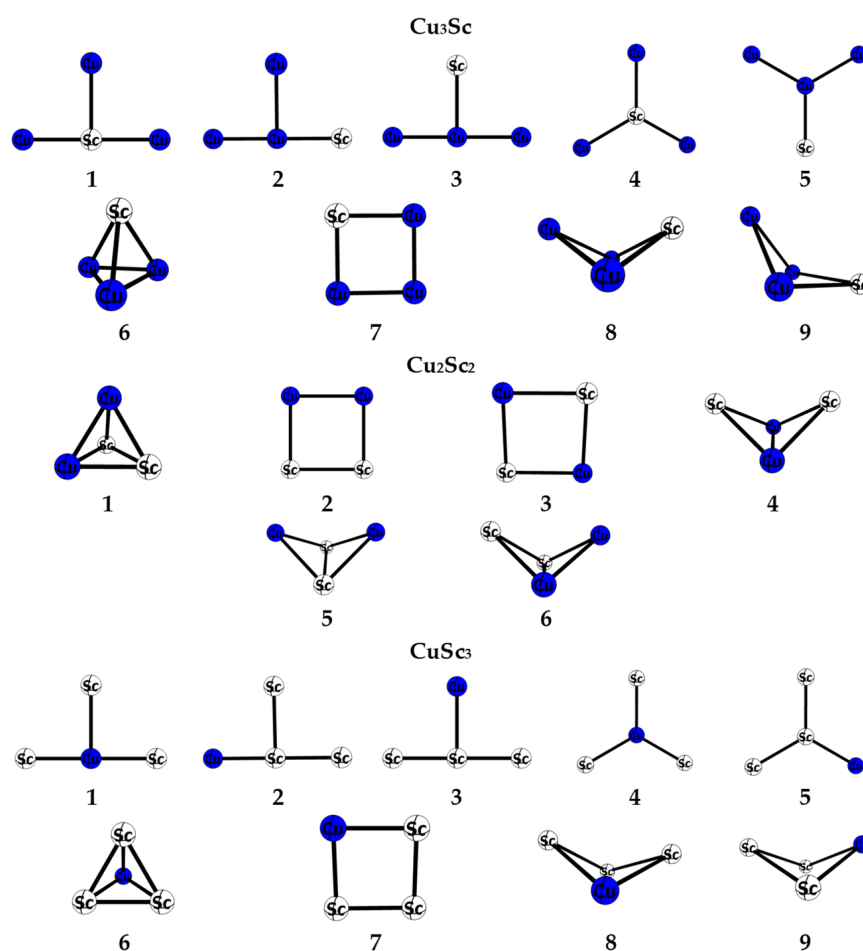


Figure 1. Candidate structural isomers of the tetraatomic clusters Cu_3Sc , Cu_2Sc_2 , and CuSc_3 (2D and 3D forms) generated prior to DFT optimization. The numbers label distinct initial isomeric configurations within each stoichiometric composition and do not imply energetic ordering. Blue and white spheres represent Cu and Sc atoms, respectively.

The final configuration of each assignment was determined based on the optimized minimum electronic energy. In the thermochemical study, which varies with temperature,

comparisons were made using the Gibbs free energy, $G(T)$, because the electronic energy of a specific optimized structure remains constant regardless of temperature.

2.3. Construction of Support Models

A finite graphene bilayer model was used to capture the localized chemistry of the active site without the cost of periodic supercells. Pure graphene was used as a reference for structural and electronic properties. To create anchoring sites, a cavity (an extended vacancy defect) was introduced in the center, and the model's edges were filled with hydrogen atoms to prevent spurious radicals. Three carbon atoms were replaced with nitrogen in the defect environment to create the graphene-3N system, thereby regulating the local electron density and improving the anchoring affinity of the metal cluster.

2.4. Thermochemistry and Boltzmann Populations

Harmonic vibrational calculations were used to characterize the optimized structures, confirm that they were minimal (i.e., without imaginary frequencies), and obtain thermochemical corrections. Gibbs free energies and enthalpies were recorded at 298.15, 350, and 400 K (1 atm) using the standard translational-rotational-vibrational partition model. The Boltzmann distribution was used to calculate the relative population of each isomer within the same multiplicity to assess thermal accessibility to nearby minima.

2.5. CO₂ Adsorption

The structures of the complexes were developed by placing a CO₂ molecule in chemically feasible arrangements around the active center (a nanocluster adsorbed on graphene-3N) and then optimized at the same theoretical level. The thermochemical magnitudes of adsorption were calculated, using enthalpy, the entropic term ($-T\Delta S$), and Gibbs free energy as relevant functions. To do this, the difference between the thermodynamic function of the adsorbed complex and the sum of the contributions of the support, the cluster, and CO₂ in the isolated phase was used. This methodology allows explicit separation of the entropic contribution and examination of how spontaneity varies with temperature, distinguishing moderate interactions that may be reversible from deeper fixations, which are associated with a high risk of active-site blocking and loss of regenerability.

All energy parameters associated with adsorption were calculated assuming CO₂(g) at 1 atm under standard ideal-gas conditions. Thermal and zero-point energy (ZPE) corrections were applied consistently, using harmonic frequencies for both isolated species and the adsorbed complex.

2.6. Electronic Analysis

The energy of the frontier orbitals (E_{HOMO} , E_{LUMO}) and the difference $\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ were used to evaluate the electronic modulation of the support. These quantities were used to calculate global reactivity descriptors: hardness $\eta = \Delta E_{\text{gap}}/2$, chemical potential $\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2$, and electrophilicity index $\omega = \mu^2/(2\eta)$. They were used to compare the relative electronic stability and charge transfer propensity between cavity graphene and graphene-3N. Qualitative inspection of the densities and orbitals was performed on the final geometries to rationalize the polarization and activation of CO₂ in the adsorbed complex.

3. Results

3.1. Analysis of the Structure, Stability, and Electronic Characteristics of Cu–Sc Clusters

Figure 2 illustrates the structures and associated energies of the lowest-energy isomers corresponding to the Cu₄–nScn tetrahedral clusters (with n varying from 0 to 4).

Considering that at 298.15 K the thermal energy is expressed as $k_B T \approx 0.025$ eV (where k_B is Boltzmann's constant), it can be reasonably assumed that several isomers could be present in significant quantities at room temperature if their relative energies are less than approximately 0.25 eV [22].

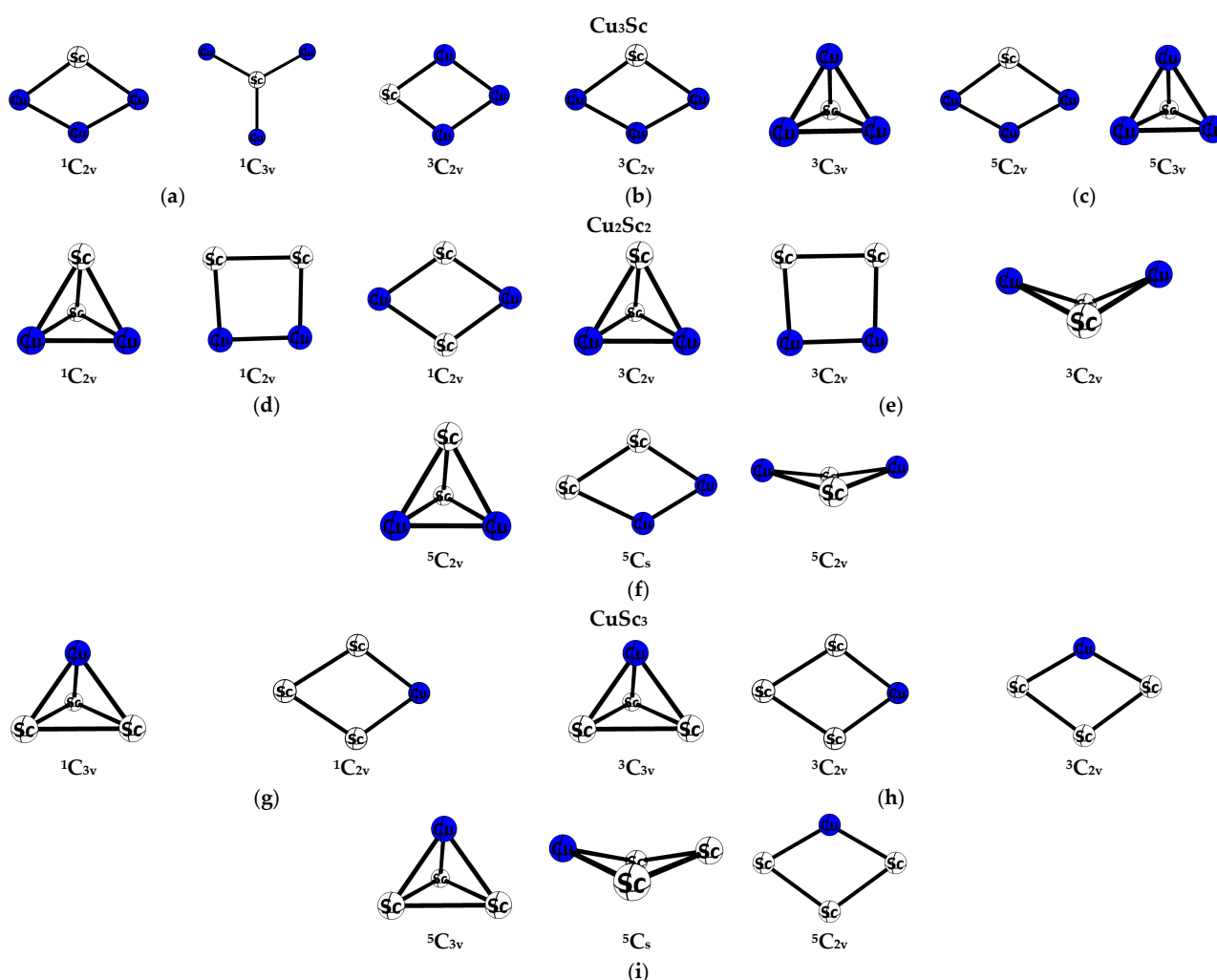


Figure 2. Lowest-energy isomers of four-atom $\text{Cu}_4\text{—Sc}_n$ clusters, where n ranges from 0 to 4: (a) Cu_3Sc singlet; (b) Cu_3Sc triplet; (c) Cu_3Sc quintet; (d) Cu_2Sc_2 singlet; (e) Cu_2Sc_2 triplet; (f) Cu_2Sc_2 quintet; (g) CuSc_3 singlet; (h) CuSc_3 triplet; (i) CuSc_3 quintet. Blue and white spheres represent copper and scandium atoms, respectively.

Figure 2 presents a summary of the optimized geometries (DFT) corresponding to all the isomers analyzed for each of the compositions, covering a total of nine configurations for Cu_3Sc , six for Cu_2Sc_2 , and nine for CuSc_3 (Figure 1). In each situation, the spin multiplicity is clearly specified, whether singlet, triplet, or quintet, as well as the point symmetry related to the most significant conformation. Based on this structure, Figure 3 shows the associated relative energies (E_r) to determine the order of stability and indicate which isomers are thermodynamically accessible under environmental conditions.

According to Figure 3 and taking as reference the thermodynamic threshold of 0.25 eV (approximately $24.1 \text{ kJ}\cdot\text{mol}^{-1}$) to evaluate co-population at 298 K, it is evident that Cu–Sc clusters composed of four atoms are not governed by a single isolated energy minimum, but are distributed in a group of low-energy isomers (multiple nearby minima) whose accessibility is also influenced by the spin state. In Cu_3Sc , the singlet isomer 5 ($M = 1$) has the lowest energy configuration, characterized by a quasi-planar rhombohedral geometry,

as shown in the $^1C_{2v}$ motif in Figure 2a. However, this state exhibits a fundamental degeneracy with isomer 6, for which the estimated energy difference is only $\Delta E = 0.03 \text{ kJ}\cdot\text{mol}^{-1}$, a value that falls within the usual numerical uncertainty range of the DFT method at the theoretical level used. Thus, no relevant energy difference is observed between these two isomers, so both are classified in the same low-energy, nearly degenerate category. Additionally, local minima are identified at equally low energies ($\Delta E \approx 0.21 \text{ kJ}\cdot\text{mol}^{-1}$). A second set of isomers is identified in the range of approximately 5.7 to $5.8 \text{ kJ}\cdot\text{mol}^{-1}$, predominantly in the triplet state, which falls within a thermally accessible interval.

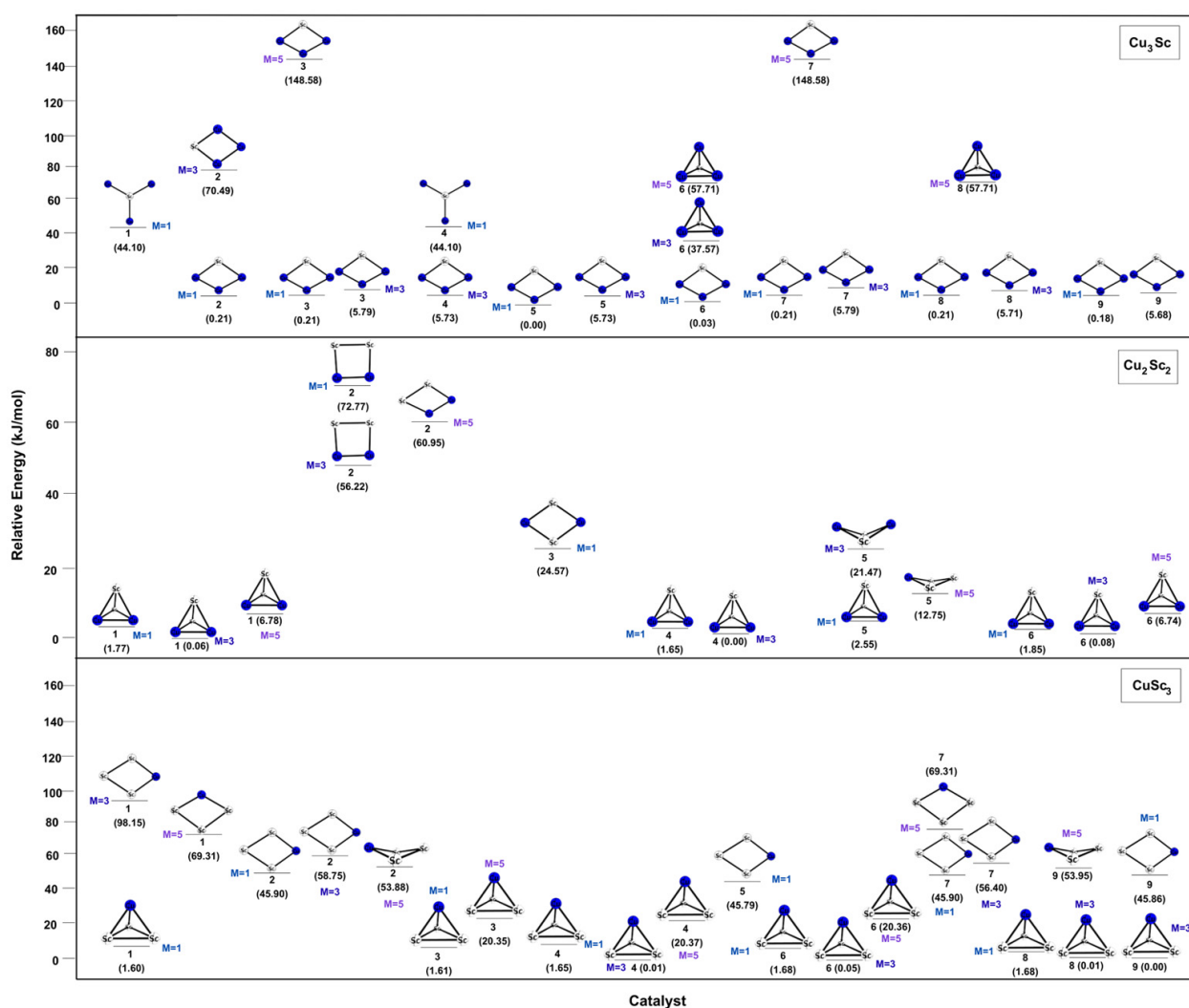


Figure 3. Relative energies (kJ mol^{-1}) and spin multiplicities of the optimized isomers of the four-atom clusters Cu_3Sc , Cu_2Sc_2 , and CuSc_3 . Isomer labels are retained from Figure 1 for identification of the corresponding 2D and 3D geometries within each stoichiometric composition. Blue and white spheres represent Cu and Sc atoms, respectively.

For Cu_2Sc_2 , the ground state is located in the triplet 4 isomer ($M = 3$) ($\Delta E = 0.00 \text{ kJ}\cdot\text{mol}^{-1}$), consistent with a $^3C_{2v}$ motif (Figure 2e), followed by low-energy competitors ($\Delta E \approx 1.06\text{--}2.55 \text{ kJ}\cdot\text{mol}^{-1}$) and other isomers in the range $\sim 6.7\text{--}21.5 \text{ kJ}\cdot\text{mol}^{-1}$, suggesting moderate energy dispersion but still compatible with co-population at 298 K. In CuSc_3 , the global minimum corresponds to the triplet isomer 9 ($M = 3$) ($\Delta E = 0.00 \text{ kJ}\cdot\text{mol}^{-1}$), with nearly degenerate isomers ($\Delta E \approx 0.01\text{--}0.05 \text{ kJ}\cdot\text{mol}^{-1}$) and other low-energy minima at $\sim 1.6\text{--}1.7 \text{ kJ}\cdot\text{mol}^{-1}$, in addition to structures close to $\sim 20.3 \text{ kJ}\cdot\text{mol}^{-1}$.

According to Figure 3, the most thermodynamically stable clusters for each stoichiometry are Cu₃Sc–isomer 5 (*M* = 1), Cu₂Sc₂–isomer 4 (*M* = 3), and CuSc₃–isomer 9 (*M* = 3), which correspond to the global minima. However, the existence of competing isomers with energies below approximately 24 kJ·mol^{−1} (0.25 eV) indicates that, at room temperature, it is more appropriate to describe the population as a set of energetically close states (dependent on multiplicity) rather than a single predominant conformation.

3.2. Thermal Population of Isomers by Boltzmann Distribution

To measure the thermal accessibility of the identified local minima, an estimate of each isomer's relative population was obtained from a Boltzmann distribution. This was done using the relative energies ΔE with respect to the most stable minimum in the analyzed set. The probability P_i related to isomer i was determined as follows:

$$P_i = \frac{e^{\frac{-\Delta E_i}{RT}}}{\sum_j e^{\frac{-\Delta E_j}{RT}}} \quad (1)$$

where R represents the universal gas constant, and T denotes the temperature in absolute terms.

Figure 4a–c indicate that the equilibrium population is not dominated by high-energy states, but is controlled by a limited group of minima with $\Delta E \leq 6$ kJ·mol^{−1}. In contrast, configurations with $\Delta E \geq 35$ –45 kJ·mol^{−1} contribute insignificantly over the temperature range analyzed.

In Cu₃Sc (Figure 4a), the distribution is regulated by the singlet manifold, presenting total fractions of 91.77% at 298.15 K, 88.86% at 350 K, and 86.21% at 400 K (Table S1a, Supplementary Materials). These fractions are distributed relatively evenly among seven low-energy isomers (mainly structures 2, 3, 5, 6, 7, 8, and 9, each with approximately 12–14% representation), suggesting the absence of a dominant conformer under ambient conditions. On the other hand, triplets represent a minor contribution, although increasing with temperature (8.26% → 11.16% → 13.77%), linked to a group of isomers that are around $\Delta E \approx 5.7$ –5.8 kJ·mol^{−1}. In contrast, quintets remain virtually unoccupied due to their greater energy differences, which exceed ~58 kJ·mol^{−1} (Supplementary Materials).

In the case of Cu₂Sc₂ (Figure 4b), a clear concentration of the population was observed in extremely low-energy triplets, with overall contributions of 77.81% at 298.15 K, 74.08% at 350 K, and 70.86% at 400 K (Table S1b, Supplementary Materials). This distribution is dominated by three nearly isoenergetic minima (structures 1, 4, and 6), each with an approximate probability of 23–26%. Singlets show a constant participation (16.17% → 17.20% → 17.83%), distributed among four closely spaced isomers ($\Delta E \approx 1.65$ –2.55 kJ·mol^{−1}). In this system, increasing temperature increases the availability of moderately excited quintets (especially structures 1 and 6). The proportion of these quintets rises from 6.02% to 11.31% when moving from 298.15 to 400 K, which is consistent with the intermediate energy separations ($\Delta E \approx 6.7$ –6.8 kJ·mol^{−1}).

Finally, CuSc₃ (Figure 4c) shows a notable bias toward *M* = 3, with a triplet population of 82.15% at 298.15 K, which decreases to 79.42% at 400 K (Table S1c, Supplementary Materials). This manifold is distributed almost equally among four practically degenerate minima (structures 4, 6, 8, and 9), each with an approximate probability of 19.7–20.7%. Accessible singlets contribute a smaller but significant proportion (17.83–20.35% as the temperature increases), corresponding to isomers with an energy difference (ΔE) of approximately 1.60–1.68 kJ·mol^{−1}. In contrast, quintets are practically irrelevant ($\leq 0.21\%$ at 400 K) due to their activation energy, which is around $\Delta E \approx 20.35$ –20.37 kJ·mol^{−1}.

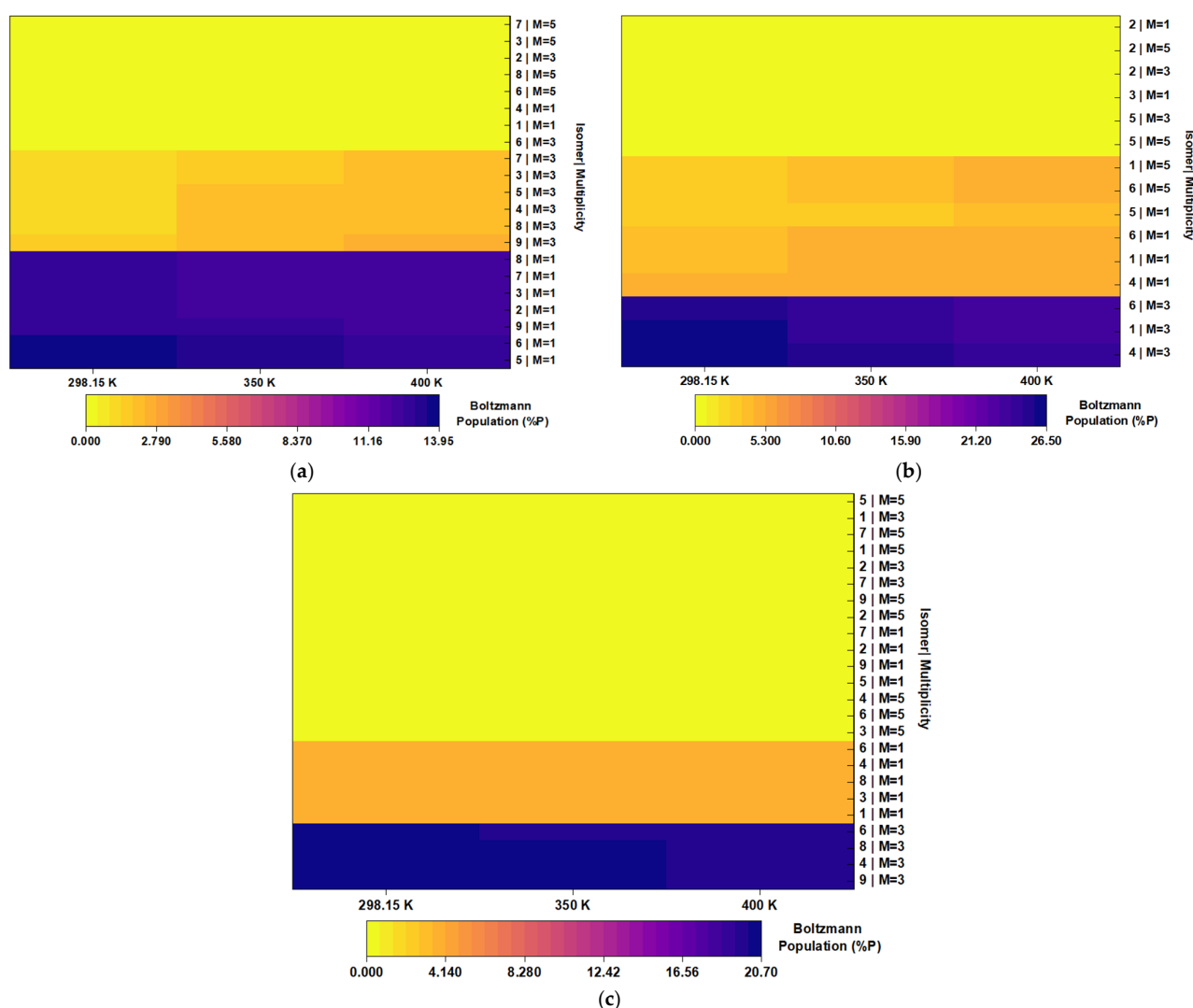


Figure 4. Heat map of the Boltzmann populations of isomers and spin multiplicities for Cu₃Sc (a), Cu₂Sc₂ (b), and CuSc₃ (c) over the 298.15–400 K temperature range.

3.3. Nitrogen-Modified Graphene Surface

To establish a computationally representative and efficient support for anchoring metal nanoclusters and evaluating CO₂ adsorption, two references were taken into account: (i) the graphene bilayer in its pure state (pristine graphene) and (ii) an active surface obtained by doping with three nitrogen atoms (graphene-3N). The structures were refined and validated through vibrational analysis, confirming the presence of absolute minima on the potential energy surface (i.e., the absence of imaginary frequencies). This section analyzes the robustness of the support, the influence of doping on its electronic behavior, and the immediate impact on the initial capture and stabilization of CO₂, assuming the chosen nanocluster is a global minimum.

3.3.1. Stability and Active Surface Area of Modified Graphene

The first criterion for selecting the support was the vibrational validity of the optimized minimum. In constrained models, edge fixing can cause artificial decoupling between the relaxed and rigid zones, generating spurious modes. For this reason, vibrational analysis was used as a criterion to ensure the existence of an absolute minimum.

Computational Cost

To create a protocol that can be replicated, a comparison was made between total geometric optimization strategies (Figure 5a) and partial geometric optimization strategies (Figure 5b), in which peripheral atoms were restricted. Total optimization was considered more advantageous because it reduced processing time and avoided anomalies caused by mechanical constraints in large sheets. Consequently, it was established as the reference scheme for both the support (pristine graphene and graphene-3N) and the adsorbate-support systems. This principle ensures methodological consistency among the bare support, the support containing nanoclusters, and the complex with CO₂, which is essential for comparing relative energies and thermochemical magnitudes under equivalent conditions.

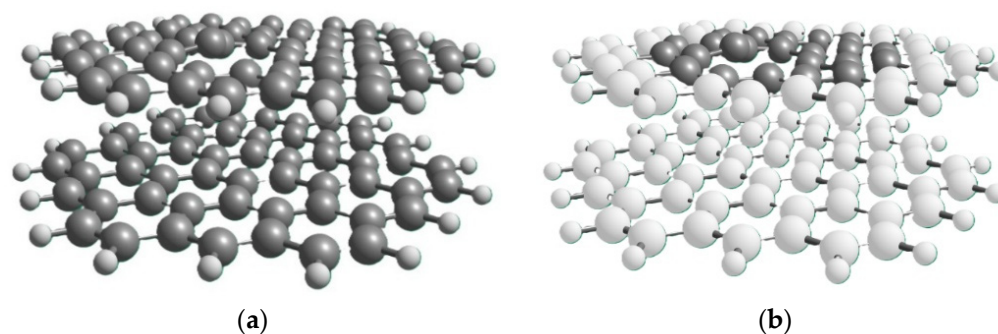


Figure 5. Atomic structure of graphene with vacancies used in the optimization tests: (a) fully unrestricted model, in which all atoms were allowed to relax; (b) partially restricted model, in which dark-gray atoms were allowed to relax whereas light-gray atoms were kept fixed. Carbon and hydrogen atoms are represented according to their relative sizes.

Under the same computational technique, complete and partial optimization strategies were compared methodologically. For both supports, total optimization in this internal test yielded shorter wall-clock times than partial optimization: graphene-3N required 13.48 h compared to 21.68 h, and the double-layer cavity model required 6.52 h compared to 11.92 h (Table 1). Since comprehensive optimization eliminates vibrational artifacts related to geometric limitations and is more convenient within this workflow, it was chosen as the standard protocol.

Table 1. Computing time (h) for geometric optimization of Cavity and Cavity-3N supports under free and restricted schemes.

System	Free	Res
Cavity	6.52	11.92
Cavity-3N	13.48	21.68

3.3.2. Constraint-Release Thermochemistry of Cavity and Cavity-3N Bilayer Supports

Before analyzing CO₂ adsorption, the thermochemical impact was quantified using a bilayer model with partial optimization (restricted model) compared to the fully relaxed model (free model). In the restricted model, the lower layer and the outermost atoms of the upper layer were fixed, while the area adjacent to the cavity was left free. The imposed limitations can give rise to imaginary frequencies that concentrate near edges or fixed atoms, resulting in artifacts inherent to the procedure. Therefore, the data presented in Table 2 do not reflect absolute stability or defect formation energies compared to pure graphene. Instead, Table 2 presents the thermochemistry associated with the release of constraints, which is used as an indicator of the penalty (or stabilization) imposed by the cavity and cavity-3N constrained protocol.

Table 2. Thermochemical comparison of the cavity and cavity-3N bilayer supports (same level of theory and standard state).

System	T (K)	ΔH (kJ/mol)	ΔS Correction (kJ/(mol))	ΔG (kJ/mol)
Cavity	298.15	−40.51	1.64	−38.87
	350	−40.63	1.86	−38.76
	400	−40.73	2.10	−38.63
Cavity-3N	298.15	−5.48	1.47	−4.01
	350	−5.49	1.73	−3.76
	400	−5.51	1.97	−3.55

To this end, Table 2 shows the thermochemistry of constraint release (relaxation), as defined in the following computational cycle.

Restricted double-layer support → Free bilaminar support (completely relaxed) and calculated at each temperature by:

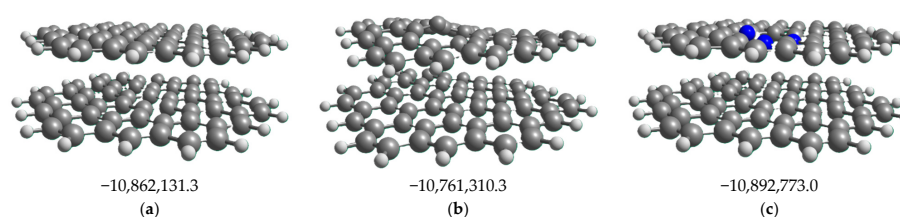
$$\Delta X_{\text{relax}}(T) = X_{\text{free}}(T) - X_{\text{restricted}}(T) \text{ with } X \in \{H, G\} \quad (2)$$

where H is the enthalpy, and G is the Gibbs free energy. To eliminate any ambiguity related to units and symbols, the concept of entropy is presented as an energy contribution:

$$-T\Delta S_{\text{relax}}(T) = \Delta G_{\text{relax}}(T) - \Delta H_{\text{relax}}(T) \quad (3)$$

Table 2 indicates that the nature of the support used significantly influences this variation in thermochemistry. In the case of the undoped cavity, both ΔH_{relax} and ΔG_{relax} have negative values. They are greater in magnitude, with ΔH_{relax} in the approximate range of −40.5 to −40.7 kJ·mol^{−1} and ΔG_{relax} between −38.9 and −38.6 kJ·mol^{−1} at temperatures of 298.15 to 400 K. On the other hand, for cavity-3N, these values are also negative, although significantly lower, with ΔH_{relax} ranging from −5.48 to −5.51 kJ·mol^{−1}, and ΔG_{relax} varying from −4.01 to −3.55 kJ·mol^{−1}. In the two systems analyzed, the variation in ΔH_{relax} with respect to temperature is minimal. At the same time, the modification of ΔG_{relax} within the range examined is fundamentally related to the increase in the entropic component ($-T\Delta S_{\text{relax}}$).

Figure 6 shows a qualitative comparison of the electronic energies of pure graphene, the cavity, and graphene-3N. Although numerical values are presented, these systems are not isostechiometric. Therefore, their total electronic energies cannot be directly compared to measure their relative stability. In this context, the image is used only to show the basic energy differences between the three support models.

**Figure 6.** Electronic energies (kJ/mol) of the support: pristine graphene (a), cavity (b), and graphene-3N (c). The blue and gray spheres represent nitrogen and carbon atoms, respectively.

3.3.3. Analysis of Stability and Reactivity Based on Global Descriptors

After determining the thermochemical preference of the N-doped support compared to the undoped cavity, we analyzed how doping affects the electronic structure and, therefore,

the support's ability to transfer charge. The frontier orbitals (Figure 7) indicate direct control of the HOMO–LUMO separation (ΔE): the cavity has an intermediate value (0.872 eV), whereas 3N doping significantly increases this separation (1.581 eV), indicating a support less prone to charge redistribution or electronic excitations.

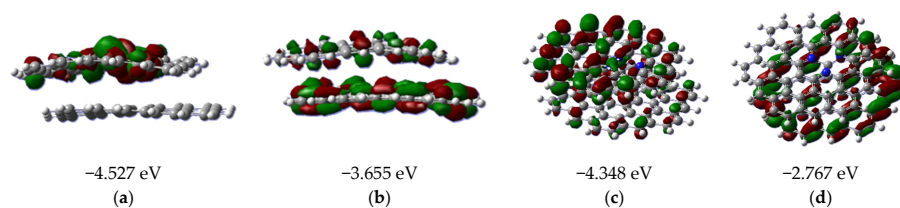


Figure 7. HOMO energy for the cavity (a), LUMO energy for the cavity (b), HOMO energy for graphene-3N (c), LUMO energy for graphene-3N (d), and the band gap (ΔE_{gap}). Red and green isosurfaces denote opposite orbital phases. Gray, blue, and white spheres represent C, N, and H atoms, respectively.

This trend is consistently reflected in the global descriptors (Table 3). Graphene-3N has the highest hardness ($\eta = 0.791$ eV) and the lowest electrophilicity ($\omega = 7.99$ eV), making it the most stable support at the electronic level (with lower polarizability and a lower tendency to accept charge). The undoped cavity exhibits an intermediate regime in η and ΔE ($\Delta E = 0.872$ eV; $\eta = 0.436$ eV), but retains a more negative chemical potential ($\mu = -4.0915$ eV), consistent with greater relative electronic availability compared to doped surfaces.

Table 3. Global descriptors (η , μ , ω) of the support for cavity and graphene-3N.

System	ΔE (eV)	η (eV)	μ (eV)	ω (eV)
Cavity	0.872	0.436	−4.0915	19.16
Cavity-3N	1.581	0.791	−3.5578	7.99

Finally, MEPs (maps of electrostatic potential) corroborate these spatial disparities: the areas surrounding the defect exhibit electrostatic gradients that regulate initial contact with polar and electrophilic species. In this section, to highlight the electronic diversity induced by doping, the MEP is used as a visual aid (Figure 8).

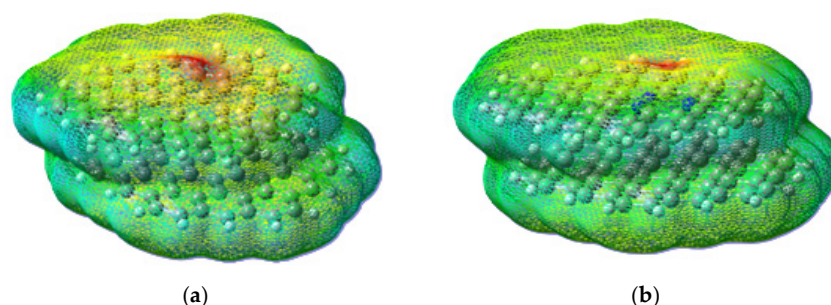


Figure 8. Representation of the MEP of graphene with cavity (a) and nitrogen-modified graphene (b) in a range between -0.05 (red) and 0.05 (blue) in atomic units. The color scale ranges from -0.05 a.u. (red, more negative potential) to $+0.05$ a.u. (blue, more positive potential), with intermediate colors representing intermediate potential values.

Global Descriptors of Reactivity of Adsorbed Complexes $\text{Cu}_x\text{Sc}_y@3\text{N-Graphene}$

The global reactivity descriptors for the fully adsorbed complexes ($\text{Cu}_x\text{Sc}_y@3\text{N-graphene}$) were evaluated to represent the species directly involved in CO_2 adsorption. As

shown in Table 4, Cu₃Sc@3N-graphene and Cu₂Sc₂@3N-graphene have smaller HOMO–LUMO gaps ($\Delta E = 0.219$ and 0.231 eV, respectively) and lower hardness values ($\eta = 0.109$ and 0.115 eV) compared to CuSc₃@3N-graphene ($\Delta E = 0.518$ eV; $\eta = 0.259$ eV). This suggests that the electronic structures of the former are softer and more prone to electronic reorganization in the adsorbed state.

Table 4. Global descriptors (η , μ , ω) for Cu_xSc_y@3N-graphene systems.

System	ΔE (eV)	η (eV)	μ (eV)	ω (eV)
Cu ₃ Sc@3N-graphene	0.518	0.259	−3.041	1.198
Cu ₂ Sc ₂ @3N-graphene	0.231	0.115	−2.936	0.498
CuSc ₃ @3N-graphene	0.219	0.109	−3.028	0.502

The chemical potential values are relatively similar, ranging between $\mu = -3.028$ and -3.041 eV. In contrast, the electrophilicity index shows a more notable difference, with a higher value for CuSc₃@3N-graphene, which is $\omega = 1.198$ eV, compared to Cu₃Sc@3N-graphene, which has $\omega = 0.502$ eV, and Cu₂Sc₂@3N-graphene, with $\omega = 0.498$ eV.

3.4. Nanocluster Adsorption and CO₂ Adsorption in Graphene-3N-Nanocluster Complex

With the graphene-3N support validated, the global minimum nanocluster was selected as a representative active site, and CO₂ adsorption on the graphene-3N/nanocluster complex was evaluated. Table 5 summarizes the adsorption thermodynamics at 298.15, 350, and 400 K (ΔH , $-T\Delta S$, and ΔG), while Figure 9 shows the optimized geometries (initial and final configurations).

Table 5. Thermodynamic data of the CO₂ adsorption process in the graphene-3N-cluster complex (Cu₃Sc, Cu₂Sc₂, and CuSc₃) at various temperatures.

System	T (K)	ΔH_{ads} (kJ·mol ^{−1})	$-T\Delta S_{\text{ads}}$ (kJ·mol ^{−1})	ΔG_{ads} (kJ·mol ^{−1})
Cu ₃ Sc@3N-graphene	298.15	−124.76	+48.69	−76.07
	350	−124.26	+56.95	−67.31
	400	−123.75	+64.83	−58.92
Cu ₂ Sc ₂ @3N-graphene	298.15	−213.29	+48.27	−165.02
	350	−212.78	+56.42	−156.36
	400	−212.22	+64.18	−148.04
CuSc ₃ @3N-graphene	298.15	−343.23	+49.25	−293.98
	350	−344.76	+57.43	−287.32
	400	−344.21	+65.13	−279.09

To prevent redundancy and simplify direct comparison between Cu_xSc_y compositions, the thermochemical parameters of CO₂ adsorption are briefly presented through the adsorption magnitudes (ΔH_{ads} , $-T\Delta S_{\text{ads}}$, and ΔG_{ads}) at temperatures of 298.15, 350, and 400 K, which are defined as follows:

$$\Delta X_{\text{ads}} = X(\text{graphene-3N}/\text{cluster} + \text{CO}_2) - X(\text{graphene-3N}/\text{cluster}) - X(\text{CO}_2) \quad (4)$$

$$X \in \{\Delta H, -T\Delta S, \Delta G\}$$

Table 5 shows a clear trend: the adsorption strength increases with the addition of Sc, following the order Cu₃Sc < Cu₂Sc₂ < CuSc₃ in terms of ΔH_{ads} and ΔG_{ads} . In all three scenarios, ΔH_{ads} is very negative and largely independent of temperature (fluctuations are less than 1 kJ·mol^{−1}), indicating that enthalpic contributions from chemical interactions at the active site predominate in CO₂ stabilization. In contrast, the entropic term ($-T\Delta S_{\text{ads}}$)

increases with T (from approximately 49 to 65 $\text{kJ}\cdot\text{mol}^{-1}$), making ΔG_{ads} less negative with temperature: between 298 and 400 K, ΔG_{ads} becomes less harmful. However, it remains exergonic throughout the range.

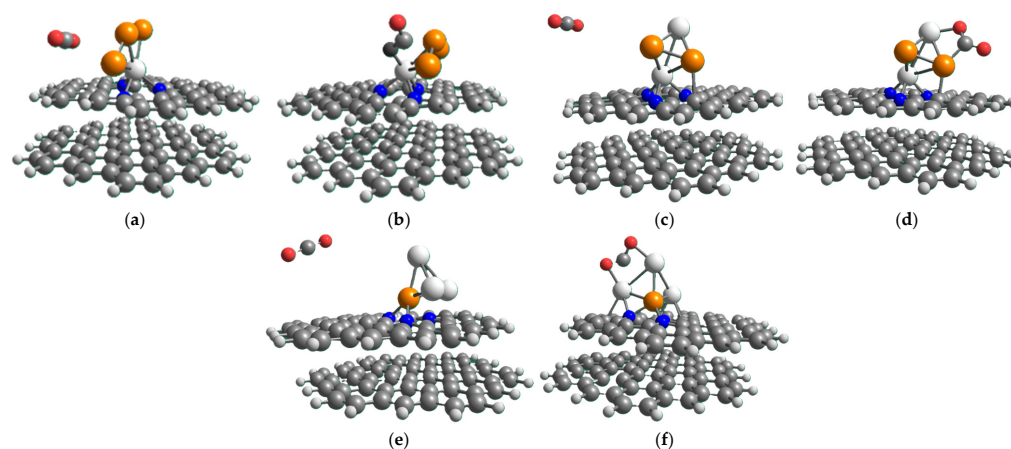


Figure 9. CO_2 adsorption on graphene-3N/global-minimum nanocluster: initial and final geometries. Reaction scheme for a CO_2 molecule interacting with the nitrogen-doped graphene surface and the Cu_3Sc cluster (**a,b**); reaction scheme for a CO_2 molecule interacting with the nitrogen-doped graphene surface and the Cu_2Sc_2 cluster (**c,d**); reaction scheme for a CO_2 molecule interacting with the nitrogen-doped graphene surface and the CuSc_3 cluster (**e,f**). Gray, blue, orange, white, red, and light-gray spheres represent C, N, Cu, Sc, O, and H atoms, respectively.

According to a Sabatier-style interpretation, the values of ΔG_{ads} suggest that the three Cu–Sc compositions span different ranges of CO_2 adsorption strength. However, all are in the exergonic zone (indicating a robust bond). Within this framework, Cu_3Sc ($\Delta G_{\text{ads}} \approx -76$ to $-59 \text{ kJ}\cdot\text{mol}^{-1}$) is the composition that exhibits the lowest adsorption strength compared to the rest of the analyzed series ($\text{Cu}_3\text{Sc} < \text{Cu}_2\text{Sc}_2 < \text{CuSc}_3$). Cu_2Sc_2 ($\Delta G_{\text{ads}} \approx -165$ to $-148 \text{ kJ}\cdot\text{mol}^{-1}$) and, in particular, CuSc_3 ($\Delta G_{\text{ads}} \approx -294$ to $-279 \text{ kJ}\cdot\text{mol}^{-1}$) show increasing thermodynamic stabilization of the CO_2 adsorption state, which translates into a notable inclination towards its retention (Figure 10).

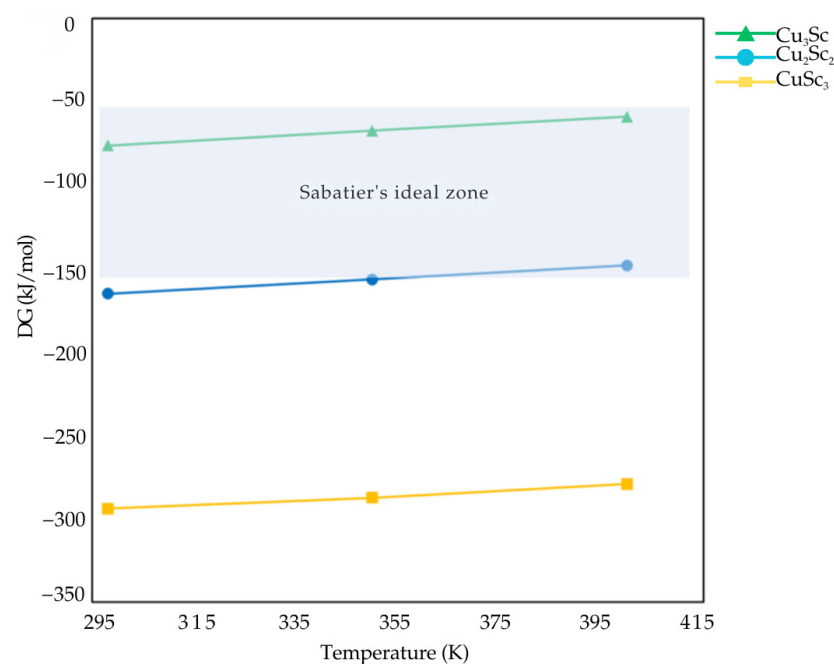


Figure 10. Gibbs free energy trend (ΔG) vs. Cluster composition in the graphene-3N complex.

3.5. Activation of CO₂ Adsorbed on Cu_xSc_y@3N-Graphene: Geometric Descriptors, Charge Transfer, and QTAIM Topological Validation

In Figure 11 and Table 6, CO₂ activation after adsorption on Cu_xSc_y@graphene-3N is evaluated using geometric descriptors such as the ∠O–C–O angle and C–O bond lengths, as well as electronic descriptors including the net charge acquired by CO₂, $\Delta Q(\text{CO}_2) = q(\text{C}) + q(\text{O1}) + q(\text{O2})$, derived from Hirshfeld analysis.

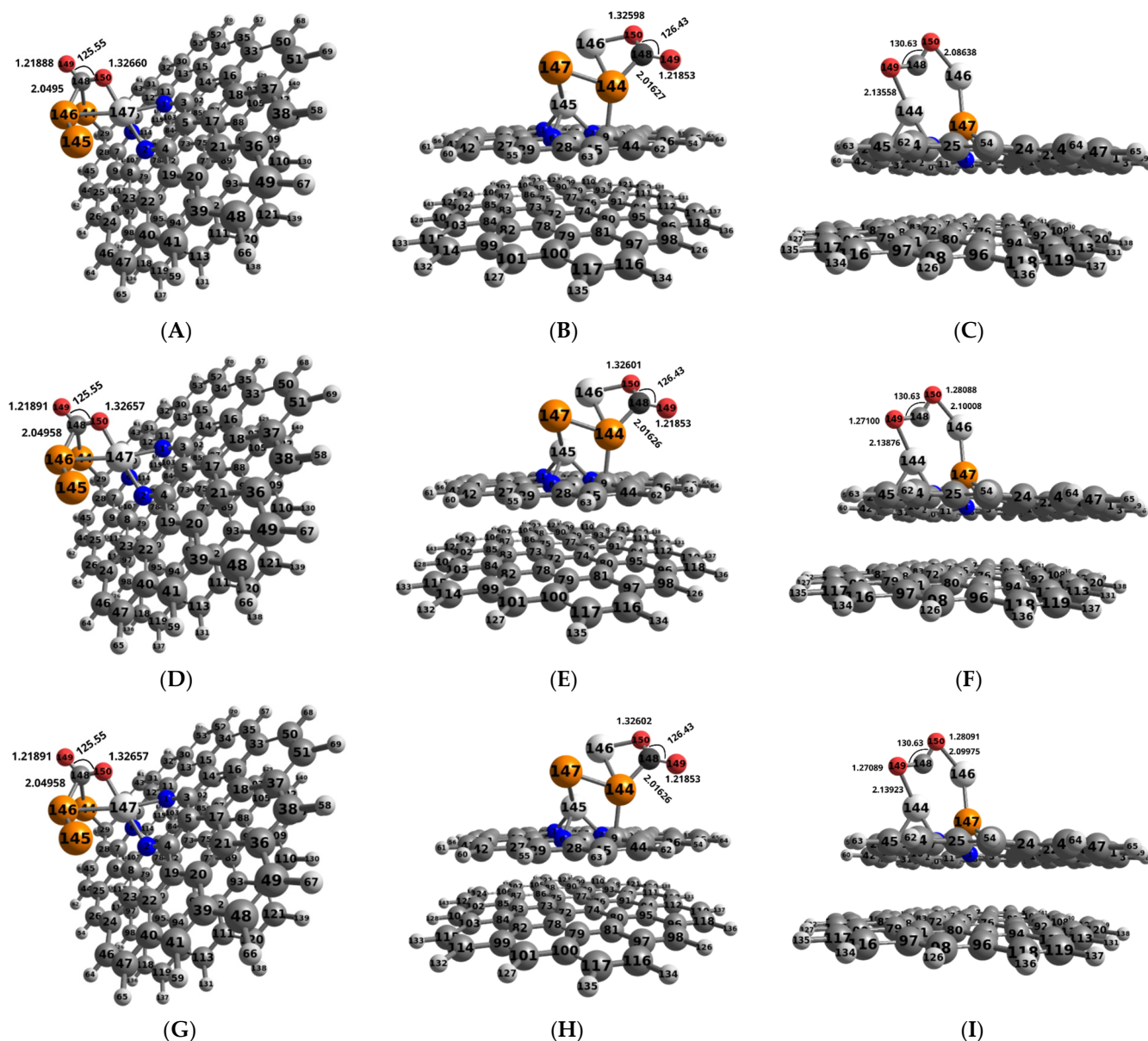


Figure 11. Optimized CO₂ adsorption geometries on Cu₃Sc anchored on NGE, showing bond lengths (Å) and O–C–O angles (°): 298.15 K (A) and (D–G) at 350 and 400 K; Optimized CO₂ adsorption geometries on Cu₂Sc₂ anchored on NGE, showing bond lengths (Å) and O–C–O angles (°): 298.15 K (B) and (E–H) at 350 and 400 K; Optimized CO₂ adsorption geometries in CuSc₃ anchored on NGE, showing bond lengths (Å) and O–C–O angles (°): 298.15 K (C) and (F–I) at 350 and 400 K. Gray, blue, orange, white, red, and light-gray spheres represent C, N, Cu, Sc, O, and H atoms, respectively.

CO₂ in its gaseous state has a linear geometry, with an O–C–O angle of 180° and a distance between the carbon and oxygen atoms of approximately 1.18 Å. Unlike non-adsorbed complexes, all adsorbed complexes show a notable loss of linearity ($\angle\text{O–C–O} \approx 125.55\text{--}130.63^\circ$), as well as a clear elongation of the C–O bond

($d(\text{C-O}) \approx 1.218\text{--}1.326$ Å for Cu_3Sc and Cu_2Sc_2 ; $1.270\text{--}1.282$ Å for CuSc_3). A significant charge accumulation is also observed in the CO_2 fragment ($\Delta Q(\text{CO}_2) \approx -0.449$ e for Cu_3Sc , -0.316 e for Cu_2Sc_2 , and between -0.412 and -0.425 e for CuSc_3), suggesting that this is a chemisorbed or activated CO_2 state, as opposed to weak physisorption (Table 6; Figure 11).

Table 6. Geometric and load transfer metrics (Hirshfeld) of CO_2 adsorbed on $\text{Cu}_x\text{Sc}_y\text{@graphene-3N}$ at different temperatures: atomic charges (e), angle $\angle\text{O-C-O}$ ($^\circ$), lengths C–O (Å), and key metal– CO_2 distance (M–C/M–O, Å).

System	T (K)	$q(\text{C}_{\text{CO}_2})$ (e)	$q(\text{O1}_{\text{CO}_2})$ (e)	$q(\text{O2}_{\text{CO}_2})$ (e)	$\Delta Q(\text{CO}_2)$ Hirshfeld (e)	$\angle\text{O-C-O}$ ($^\circ$)	$d(\text{C-O1})$ (Å)	$d(\text{C-O2})$ (Å)	$d(\text{M-C})/d(\text{M-O})$ (Å)
$\text{Cu}_3\text{Sc@3N-graphene} + \text{CO}_2$	298.15	0.0704	−0.3161	−0.2037	−0.4494	125.55	1.2188	1.3266	2.0495
	350	0.0704	−0.3161	−0.2036	−0.4493	125.55	1.2189	1.3266	2.0495
	400	0.0704	−0.3161	−0.2036	−0.4493	125.55	1.2189	1.3266	2.0495
$\text{Cu}_2\text{Sc}_2\text{@3N-graphene} + \text{CO}_2$	298.15	0.0368	−0.3682	0.0154	−0.3160	126.43	1.2185	1.3259	2.0163
	350	0.0368	−0.3681	0.0151	−0.3162	126.43	1.2185	1.3260	2.0163
	400	0.0367	−0.3681	0.0152	−0.3162	126.43	1.2185	1.3260	2.0163
$\text{CuSc}_3\text{@3N-graphene} + \text{CO}_2$	298.15	−0.7226	0.0196	0.2909	−0.4120	130.63	1.2702	1.2817	2.1356
	350	−0.5867	0.0145	0.1477	−0.4245	130.63	1.2710	1.2808	2.1388
	400	−0.5860	0.0140	0.1478	−0.4242	130.63	1.2709	1.2809	2.1392

Of all the systems analyzed, $\text{Cu}_3\text{Sc@graphene-3N}$ stands out for its remarkable charge transfer and evident bond asymmetry (one C–O bond considerably longer than the other), suggesting a more polarized adsorption mechanism. In contrast, $\text{CuSc}_3\text{@graphene-3N}$ exhibits a less pronounced activation signature, with a more balanced C–O elongation and a wider crucial metal– CO_2 distance. It is important to note that the activation metrics show remarkable insensitivity to temperature within the range of 298 to 400 K. Variations in $\angle\text{O-C-O}$ and $\Delta Q(\text{CO}_2)$ are minimal, and bond distances change only marginally. This indicates that both the adsorption geometry and activation state remain stable over the analyzed temperature range.

After determining, through geometric descriptors such as the angle $\angle\text{O-C-O}$ and the distance $d(\text{C-O})$, as well as the charge $\Delta Q(\text{CO}_2)$ according to Hirshfeld, that the adsorbed CO_2 exhibits a state similar to “activated chemisorption” in $\text{Cu}_x\text{Sc}_y\text{@graphene-3N}$, a QTAIM topological analysis (AIM) topological analysis was performed (Figure 12). The purpose of this analysis was to validate the assignment based on electron density and to enable the identification of subtle differences among the compositions.

Figure 12 illustrates the bond paths and bond critical points (BCPs) related to the interaction between CO_2 and the cluster in $\text{Cu}_3\text{Sc@3N-graphene} + \text{CO}_2$ (A), $\text{Cu}_2\text{Sc}_2\text{@3N-graphene} + \text{CO}_2$ (B), and $\text{CuSc}_3\text{@3N-graphene} + \text{CO}_2$ (C). In the first two systems, inter-fragment connectivity between the adsorbate and the metal center is observed, providing direct topological evidence of the specific CO_2 –metal interaction. This is consistent with the activated character that had previously been inferred from the deformation of CO_2 , the elongation of C–O bonds, and the net charge accumulation on the CO_2 fragment.

The QTAIM descriptors presented in Table 7 support this interpretation. In the first two complexes, the Laplacian of the density at the relevant charge critical points (BCPs) is positive ($\nabla^2\rho_{\text{C}} > 0$). On the other hand, the total energy density is negative ($H < 0$), and the ratio $|V|/G$ is just above unity, with an approximate value of $|V|/G \approx 1.24\text{--}1.25$. This pattern is distinguished by coordinative or polarized interactions of the “closed-shell” type, which make a significant stabilizing contribution due to partial sharing of electron density. This is consistent with chemisorption in metal– CO_2 systems, where activation manifests as a combination of electronic polarization and structural reorganization of the adsorbate.

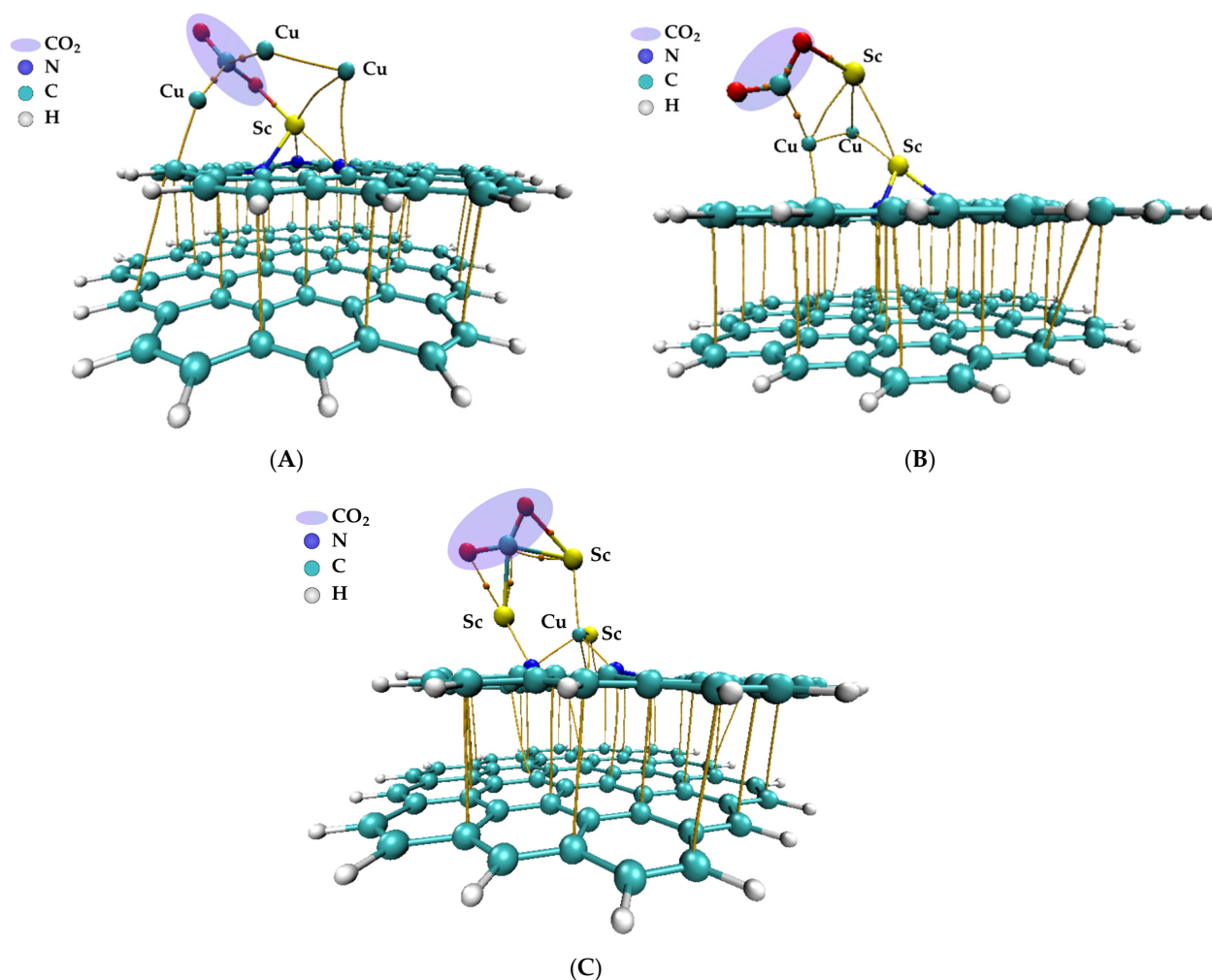


Figure 12. QTAIM topology of the $\text{CO}_2\text{-Cu}_x\text{Sc}_y\text{@graphene-3N}$ system: bond paths and bond critical points (BCPs) that show CO_2 –metal interaction and electronic connectivity in (A) $\text{Cu}_3\text{Sc@graphene-3N} + \text{CO}_2$; (B) $\text{Cu}_2\text{Sc}_2\text{@graphene-3N} + \text{CO}_2$, and (C) $\text{CuSc}_3\text{@3N-graphene} + \text{CO}_2$.

Table 7. Integrated QTAIM descriptors of the set of BCPs associated with CO_2 adsorption on $\text{Cu}_x\text{Sc}_y\text{@graphene-3N}$: electron density (ρ_c), Laplacian ($\nabla^2\rho_c$), total energy density (H), potential (V), kinetic (G), and ratio $|V|/G$.

System	ρ_c	$\nabla^2\rho_c$	H	V	G	$ V /G$
$\text{Cu}_3\text{Sc@3N-graphene} + \text{CO}_2$	2.45×10^{-1}	6.97×10^{-1}	-5.84×10^{-2}	-2.91×10^{-1}	2.33×10^{-1}	1.25
$\text{Cu}_2\text{Sc}_2\text{@3N-graphene} + \text{CO}_2$	2.00×10^{-1}	6.43×10^{-1}	-5.10×10^{-2}	-2.63×10^{-1}	2.12×10^{-1}	1.24
$\text{CuSc}_3\text{@3N-graphene} + \text{CO}_2$	2.71×10^{-1}	1.18	-1.68×10^{-2}	-3.28×10^{-1}	3.11×10^{-1}	1.05

The comparative analysis of the compositions also reveals a pattern that is consistently aligned with the previous $\Delta Q(\text{CO}_2)$ results. In the $\text{Cu}_3\text{Sc@3N-graphene} + \text{CO}_2$ system, integrated electron density values are observed that are slightly higher in the relevant BCPs ($\rho_c = 2.45 \times 10^{-1}$), as well as more pronounced local stabilization ($H = -5.84 \times 10^{-2}$) compared to $\text{Cu}_2\text{Sc}_2\text{@3N-graphene} + \text{CO}_2$, which has $\rho_c = 2.00 \times 10^{-1}$ and $H = -5.10 \times 10^{-2}$. On the other hand, the $|V|/G$ ratio remains practically constant (1.25 vs. 1.24). This pattern indicates that, in an N-doped support environment, both systems exhibit a similar interaction. However, Cu_3Sc shows a slightly more pronounced intensity and polarization of the CO_2 –cluster interaction, consistent with the greater net charge transfer to CO_2 evident in the Hirshfeld analysis.

4. Discussion

The gas-phase screening procedure developed by Szalay et al. represents a significant milestone in identifying Cu_3X motifs with the potential to interact with/activate CO_2 , including Cu_3Sc as a promising composition. In this context, our research does not seek to present Cu_3Sc as a “new” compositional discovery, but rather to verify and expand this active motif in a context closer to a supported material. In this context, the behavior of the cluster is no longer governed exclusively by its intrinsic composition, but also by the cluster-support coupling.

The main contribution of this research lies in the explicit integration of Cu–Sc synergy with nitrogen-doped graphene. The N-doped support does not serve as an inert surface: it provides more robust anchoring sites, alters the local electronic distribution, and can stabilize cluster geometries/electronic states that differ from those favored in the gas phase. Therefore, the adsorption thermodynamics and signals linked to activation (CO_2 geometric changes and charge transfer) should be interpreted as emergent properties of the $\text{Cu}_x\text{Sc}_y\text{@graphene-N}$ system, rather than attributes of the individual nanocluster. This perspective facilitates the analysis of two aspects that gas-phase screening does not capture: (i) how anchoring at N-sites restructures the hierarchy of isomers/states (including spin sensitivity) and (ii) how the support modulates the balance between adsorbate stabilization and effective adsorption strength under supported material conditions. Consequently, although the general trend aligns with that of Szalay et al., the added value of this study is to quantify and rationalize the impact of the functionalized support, thereby establishing a design framework based on the cooperative cluster–graphene–N interaction rather than on the metal composition itself.

5. Conclusions

In conclusion, Cu_xSc_y stoichiometry and graphene–3N support engineering jointly control CO_2 adhesion strength and electronic access. N doping expands the HOMO–LUMO gap to $\Delta E = 1.58$ eV (compared to 0.87 eV in the cavity), increases the hardness ($\eta = 0.79$ eV), and decreases the electrophilicity ($\omega = 7.99$ eV), which stabilizes the support and concentrates the activation in the nanocluster. Cu_3Sc , among the series evaluated, shows the best compromise for operating in a catalytic cycle: moderate exergonic adsorption ($\Delta G_{\text{ads}} = -76.07, -67.31, \text{ and } -58.92 \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15, 350, and 400 K) with an entropic penalty that increases and reduces spontaneity without completely suppressing it. On the other hand, the increase in Sc leads to overbonding: Cu_2Sc_2 and CuSc_3 cause the adsorption well ($\Delta G_{\text{ads}} = -165.02 \rightarrow -148.04$ and $-293.98 \rightarrow -279.09 \text{ kJ}\cdot\text{mol}^{-1}$) to deepen, which is beneficial for activation/capture but also increases the likelihood that the active site is blocked and reduces regenerability. Therefore, to balance CO_2 activation and desorption under working conditions, the rational design of Cu–Sc sites on graphene–N should aim to maintain $|\Delta G_{\text{ads}}| \sim 60\text{--}80 \text{ kJ}\cdot\text{mol}^{-1}$ as the operating range.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su18073497/s1>, Table S1a. Cu_3Sc ; Table S1b. Cu_2Sc_2 ; Table S1c. CuSc_3 .

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