CO₂ Adsorption over 3d Transition-Metal Nanoclusters Supported on Pyridinic N₃-Doped Graphene: A DFT Investigation

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Abstract: CO₂ adsorption on bare 3d transition-metal nanoclusters and 3d transition-metal nanoclusters supported on pyridinic N₃-doped graphene (PNG) was investigated by employing the density functional theory. First, the interaction of Co₁₃ and Cu₁₃ with PNG was analyzed by spin densities, interaction energies, charge transfers, and HUMO-LUMO gaps. According to the interaction energies, the Co₁₃ nanocluster was adsorbed more efficiently than Cu₁₃ on the PNG. The charge transfer indicated that the Co₁₃ nanocluster donated more charges to the PNG nanoflake than the Cu₁₃ nanocluster. The HUMO-LUMO gap calculations showed that the PNG improved the chemical reactivity of both Co₁₃ and Cu₁₃ nanoclusters. When the CO₂ was adsorbed on the bare 3d transition-metal nanoclusters and 3d transition-metal nanoclusters supported on the PNG, it experienced a bond elongation and angle bending in both systems. In addition, the charge transfer from the nanoclusters to the CO₂ molecule was observed. This study proved that Co₁₃/PNG and Cu₁₃/PNG composites are adequate candidates for CO₂ adsorption and activation.

Keywords: CO₂ adsorption and activation; HUMO-LUMO gap; charge transfer; stability

1. Introduction

Due to environmental changes such as rising global temperatures, sea levels, and melting of the polar ice caps, concerns are accumulating around the presence of CO₂ in the atmosphere [1]. Furthermore, population growth and rapid industrialization have escalated the release of CO₂ into the atmosphere [2]. In addition, energy requirements for human activities (anthropogenic) have contributed substantially to net CO₂ emissions [3]. In fact, anthropogenic CO₂ emissions have dramatically increased from 27 Gt in 1970 to 49 Gt in 2010 [4]. As a result, many governments have signed the Kyoto Protocol of the United Nations Framework Convention on Climate Change as a precautionary measure to mitigate climate change [5].

Additionally, several technological processes have been implemented to curb CO₂ accumulation by implementing techniques such as the CO₂ capturing and sequestration process [6], CO₂ capturing and utilization processes [7], and CO₂ conversion [8,9]. Yet, the enormous dissociation energy of CO₂ resulting from its molecular stability limits the feasibility of the latter process [10]. Moreover, challenges in developing suitable catalysts in terms of efficiency and selectivity still stand unresolved [11]. That notwithstanding, strides in this area continually seek to find more efficient catalysts that diminish process energy requirements and show high selectivity and stability to CO₂ reduction reactions.
In this regard, a wide variety of catalysts have been studied: primarily, current studies have been centered on nanoclusters, since they exhibit superior catalytic activity with respect to bulk materials handling, enabled by their specific surface area, electronic, optical, magnetic, and mechanical properties, which are strongly associated with their shape, size, and composition [12]. Thus, 3d transition-metal nanoclusters have gained considerable attention since they have demonstrated remarkable performance in CO₂ reduction. For instance, the removal and conversion of CO₂ into liquid fuels using amorphous Cu nanoparticles showed an excellent catalytic activity and selectivity [13]. In another study, Li and colleagues studied the CO₂ reduction over Ni-based electrocatalysts with sizes ranging from a few atoms to over 100 nm. Their results imply that CO₂ reduction and selectivity performance vary according to the size of Ni nanoparticles [14]. Furthermore, another study used Co nanoparticles ranging from 10 to 50 nm prepared for CO₂ methanation and ethanol reforming, demonstrating the nanoparticles’ significant activity in the process [15].

Though the catalytic activities of nanoclusters are acclaimed, they tend to agglomerate, resulting in a decline in activity and stability [16–18]. Therefore, addressing this issue requires the use of high-surface-area nanomaterials to anchor nanoparticles to promote stability and activation. One of the most eminent nanomaterials in this respect is graphene which exhibits high mechanical, thermal, and electrical properties [19–21]. Nonetheless, graphene often necessitates modifications such as doping, functionalization, or the presence of defects on its surface. These adjustments are intended to overcome the low chemical activity of graphene [21,22]. Among the different modifications made to graphene, the pyridinic N₃-doped graphene (PNG) has acquired great importance since it substantially modifies the structural and electronic properties of the pristine graphene. Furthermore, studies based on density functional theory (DFT) have proved that the stability and reactivity of metal nanoclusters were enhanced using PNG layers as support [23–25].

Moreover, using 3d transition-metal nanoclusters supported on PNG for CO₂ reduction has been studied experimentally. For example, Dongare and collaborators investigated electrochemical CO₂ reduction using N-doped graphene-supported Cu nanoparticles. The presence of pyridinic, pyrrolic, and graphitic N were confirmed using X-ray photoelectron spectroscopy (XPS). Furthermore, the high PNG content signified good selectivity toward CO₂ reduction. In the end, the N-doped graphene/Cu nanoparticles composite enhanced the activity and selectivity in CO₂ reduction [26]. Likewise, the incorporation of MnO nanoparticles into an N-doped graphene aerogel for CO₂-to-CO electrochemical reduction was studied. According to XPS spectra, it was found that the primary N species was the pyridinic type. Their results suggest that CO₂-to-CO electrochemical reduction was enhanced by the synergistic effect of the MnO nanoparticles and the N-doped aerogels [27]. Thus, these studies emphasize the central role of N-doped graphene in CO₂ reduction. However, there are no theoretical studies that analyze the effect of the PNG support on the stability and catalytic activity of 3d transition-metal clusters toward CO₂ at the molecular level. Therefore, in this work, CO₂ adsorption and activation on bare 3d transition-metal nanoclusters and 3d transition-metal supported nanoclusters were investigated using DFT calculations, since their adsorption and activation on surfaces are key steps in the CO₂ conversion reaction [28]. To analyze the CO₂ interaction on both bare nanoclusters and nanoclusters supported on PNG, the CO₂ adsorption energy, CO₂ bond elongation, CO₂ bending angle, and charge transfer are calculated since these are indicators of effective CO₂ dissociation [29–32].

2. Materials and Methods

To obtain the most stable CO₂ adsorption on both the bare nanoclusters and nanoclusters supported on PNG graphene, nine initial structures were considered. All initial structures were optimized using the auxiliary density functional theory (ADFT) method implemented in the deMon2k 4.3.8 software [33]. The ADFT is a reliable and efficient alternative to the conventional DFT approach that allows calculations of large complex systems with less computational effort. The revised Perdew–Burke–Ernzerhof (revPBE)
functional was used as the exchange–correlation functional [34]. For the Co, H, C, O, and N atoms, a double-zeta valence plus polarization basis set optimized for generalized gradient approximation (GGA) functionals (DZVP-GGA) was employed [35], and a triple-zeta valence plus polarization basis set optimized for GGA functionals (TZVP-GGA) was used for the Cu atoms [35]. The most stable structures obtained with the ADFT method were reoptimized with the conventional DFT method using the Orca 5.0 software [36]. All DFT calculations were performed using revPBE [34]. The Ahlrichs basis set def2-SVP was used for the C, N, O, and H atoms, and def2-TZVP was used for the Co and Cu atoms [37]. The energy change = 5 × 10⁻⁶ Eh, max. gradient = 3 × 10⁻⁴ Eh/Bohr, RMS gradient = 1 × 10⁻⁴ Eh/Bohr, max. displacement = 4 × 10⁻³ Bohr, and RMS displacement = 2 × 10⁻³ Bohr were the convergence criteria used for geometry optimization.

The icosahedral Co₁₃ and Cu₁₃ nanoclusters (Figure 1a) and the graphene model (Figure 1b) used in this work are reported in Figure 1.

![Figure 1.](image.png)

The CO₂ adsorption energies (E_{ads}) on isolated nanoclusters and nanoclusters supported on PNG were calculated using the basis set superposition error (BSSE) [38]. Moreover, the atom-pairwise (atom-triplewise) dispersion (D3) correction was used for the RevPBE functional using optimized parameters by Grimme et al. [39]. Finally, to analyze the molecular interactions of the Co₁₃ and Cu₁₃ nanoclusters supported on PNG and the CO₂ adsorption over bare nanoclusters and nanoclusters supported on PNG, the quantum theory of atoms in molecules implemented in the Multiwfn program was used [40].

3. Results
3.1. Properties of Co₁₃, Cu₁₃, Co₁₃/PNG, and Cu₁₃/PNG

First, comparison of the spin multiplicities of bare nanoclusters and nanoclusters supported on the PNG was made. The Co₁₃ and Cu₁₃ nanoclusters possess spin multiplicity values of 32 and 6, respectively, which agree with previous results reported for the Co₁₃ [41] and Cu₁₃ [42] nanoclusters. The optimized Co₁₃ and Cu₁₃ nanoclusters supported on PNG are illustrated in Figure 2. When the Co₁₃ and Cu₁₃ nanoclusters are supported on PNG, a decrement in spin multiplicity was observed in the supported nanoclusters compared to the bare nanoclusters. The Co₁₃/PNG composite ended with a spin multiplicity value of 27, whereas the Cu₁₃/PNG composite was singlet. The spin multiplicity diminution observed in both systems is ascribed to the stabilizing effect of the PNG. This is also consistent with data reported in literature. For instance, for the Pd- and Pt-based nanoclusters supported on the PNG nanoflake, the latter lead to a magnetic-moment decrement in most of the systems; such behavior was associated with the charge transferred from the nanoclusters to the PNG nanoflake [23,24].

Spin densities, interaction energies (E_{int}), and charge transfers were calculated to better understand the interaction between the nanoclusters and PNG support. In Figure 3 the spin density of the Co₁₃ nanocluster supported on the PNG is illustrated, since it is an open-shell
system, and the spin density of the Co$_{13}$ nanocluster is also computed for comparison. As can be seen in Figure 3a, for the Co nanocluster, there is a homogeneous spin density distribution over the Co atoms. When the Co nanocluster is supported on the PNG, the spin density is distributed mostly on the Co atoms and little on the N atoms (Figure 3b).

![Figure 2. Top and side views of the most stable interaction of (a) Co$_{13}$ and (b) Cu$_{13}$ nanocluster deposited on pyridinic N$_3$-doped graphene. Green, orange, black, white, and blue spheres represent Co, Cu, C, H, and N atoms, respectively.](image)

![Figure 3. Spin density distributions of the systems: (a) Co$_{13}$ nanocluster and (b) Co$_{13}$/PNG composite.](image)

The $E_{\text{int}}$ calculated for the Co$_{13}$ and Cu$_{13}$ nanoclusters supported on PNG are $-5.69$ eV and $-4.72$ eV, respectively. It should be noted that both values are substantially higher than those reported in previous findings for the Co$_{13}$ [43,44] and Cu$_{13}$ [45,46] nanoclusters supported on pristine graphene. Therefore, PNG has a more substantial stabilizing effect over the Co$_{13}$ and Cu$_{13}$ nanoclusters compared to pristine graphene. The interaction between the Co$_{13}$ and Cu$_{13}$ nanoclusters with PNG was further investigated by Bader charge transfer. The charge transfer between the Co$_{13}$ and Cu$_{13}$ nanoclusters and the PNG is reported in Table 1. The results suggest that both nanoclusters yielded charge to the PNG since both ended with a total positive charge. The large electronegativity of N and the electronegativity difference of Co and Cu atoms are the principal driving force for the charge transfer. Furthermore, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap was computed for the bare Co$_{13}$ and Cu$_{13}$ nanoclusters and the Co$_{13}$/PNG and Cu$_{13}$/PNG composites, Table 1. The Co$_{13}$ and Cu$_{13}$ nanoclusters show HOMO-LUMO gaps of 0.52 and 0.67 eV, respectively, which imply that the Co$_{13}$ can be more reactive than the Cu$_{13}$ nanocluster as it has been documented.
that a low HOMO-LUMO gap is associated with high chemical reactivity [45,47,48]. The HOMO-LUMO gaps of the Co13/PNG (0.26 eV) and Cu13/PNG (0.21 eV) were lower than that for the bare nanoclusters. Therefore, it is assumed that the presence of the PNG increased the chemical reactivity of the nanoclusters.

### Table 1. Charge transfers and HOMO-LOMO gaps for Co13, Cu13, Co13/PNG, and Cu13/PNG. The positive values indicate charge transfers from the nanoclusters to the PNG structure.

| Systems     | HOMO-LOMO Gap (eV) | Charge Transfer (e) |
|-------------|--------------------|---------------------|
| Co13        | 0.52               | -                   |
| Cu13        | 0.67               | -                   |
| Co13/PNG    | 0.26               | +1.40               |
| Cu13/PNG    | 0.21               | +0.78               |

#### 3.2. CO2 Adsorption on Co13 and Cu13 Nanoclusters

Several modes of CO2 adsorption on both the bare nanoclusters and nanoclusters supported on PNG were investigated. First, the CO2 molecule was placed over different facets of the Co13 and Cu13 nanoclusters to identify the most optimal adsorption modes. Due to the high symmetry of the icosahedral Co13 and Cu13 nanoclusters, only nine adsorption modes were considered (Figure 4). Specific parameters were considered to evaluate the CO2 adsorption on the Co13 and Cu13 nanoclusters, such as the E_ads, the average bond length, the bending angle of the CO2 molecule, and the charge transfer from the nanoclusters to the CO2 molecule. These parameters were calculated over the most stable structures of CO2 adsorption on nanoclusters and nanoclusters supported on PNG.

![Figure 4. CO2 adsorption modes on nanoclusters.](image)

The most stable model of CO2 adsorption on the Co13 and Cu13 nanocluster is depicted in Figures 5a and 5b, respectively. The results show that CO2 bends when it is adsorbed on the Co13 and Cu13 nanoclusters. Although the CO2 interaction on the Co13 nanocluster is consistent with the findings of other works [30], the interaction of CO2 and Cu13 differs from the one reported in previous studies, because it was reported that CO2 remained linear once adsorbed and only interacted with one Cu atom [30]. However, this distinct interaction might be attributed to the fact that they used nonicosahedral Cu13 nanoclusters.
was adsorbed on Co\textsubscript{13}. Concerning the average bond length and bending angle of the CO\textsubscript{2} molecule (Figure 6). Moreover, the CO\textsubscript{2} values reported in earlier findings. In fact, Ocampo-Restrepo did not report this kind of modification in either the average bond length or bending angle of the CO\textsubscript{2} molecule [30].

Figure 5. CO\textsubscript{2} adsorbed on (a) Co\textsubscript{13} and (b) Cu\textsubscript{13} nanoclusters. The average bond length (Å) and angle bending (°) of CO\textsubscript{2} molecule is depicted. Green, orange, black, and red spheres represent Co, Cu, C, and O atoms, respectively.

To estimate the interaction between the CO\textsubscript{2} molecule and the 3d transition-metal nanoclusters, the E\textsubscript{ads} were calculated. In the case of the CO\textsubscript{2} adsorbed on the Co\textsubscript{13} nanocluster, the E\textsubscript{ads} was −0.94 eV. This value is like those reported in the literature [30,49]. The E\textsubscript{ads} calculated for CO\textsubscript{2} on the Cu\textsubscript{13} nanocluster was −0.18 eV, which agrees with the data reported in literature [30,49]. In addition, an average bond elongation of the CO\textsubscript{2} was observed when it was adsorbed on the Co\textsubscript{13} nanocluster. Regarding the bending angle, there was a pronounced curving with a reduction of 23.94% with respect to the isolated CO\textsubscript{2} molecule. These parameters are comparable to those reported in previous works [30]. Concerning the average bond length and bending angle of the CO\textsubscript{2} molecule adsorbed on the Cu\textsubscript{13} nanocluster. As in the CO\textsubscript{2} adsorbed on the Co\textsubscript{13} nanocluster, an average bond elongation was observed. On the other hand, the bending angle underwent a considerable contraction of 28.34%. Nevertheless, these parameters do not concur with the values reported in earlier findings. In fact, Ocampo-Restrepo did not report this kind of modification in either the average bond length or bending angle of the CO\textsubscript{2} molecule [30].

3.3. CO\textsubscript{2} Adsorption on Co\textsubscript{13} and Cu\textsubscript{13} Nanoclusters Supported on PNG

To investigate the CO\textsubscript{2} adsorption on Co\textsubscript{13}/PNG and Cu\textsubscript{13}/PNG composites, we analyzed various adsorption modes described in the preceding section. Again, the E\textsubscript{ads}, the average bond length, and the bending angle were determined to evaluate the CO\textsubscript{2} adsorption. The most optimal adsorption mode for Co\textsubscript{13}/PNG and Cu\textsubscript{13}/PNG composites is depicted in Figures 6a and 6b, respectively. For both composites, the CO\textsubscript{2} preferred to be adsorbed in a bent way. Subsequently, the E\textsubscript{ads} of CO\textsubscript{2} on the Co\textsubscript{13}/PNG and Cu\textsubscript{13}/PNG composites was calculated. The results showed that the CO\textsubscript{2} adsorbs more intensely on the Co\textsubscript{13}/PNG composite with a value of −0.92 eV, whereas the E\textsubscript{ads} of CO\textsubscript{2} on the Cu\textsubscript{13}/PNG composite was only −0.33 eV. As in the CO\textsubscript{2} adsorbed on bare clusters, an average bond elongation of CO\textsubscript{2} was observed when it was adsorbed on nanoclusters supported on PNG (Figure 6). Moreover, the CO\textsubscript{2} bending angle underwent a considerable contraction when it was adsorbed on Co\textsubscript{13} (24.72%) and Cu\textsubscript{13} (22.83%) supported on PNG.

3.4. Bonding Analysis of the CO\textsubscript{2} Interaction on Nanoclusters and Nanoclusters Supported on PNG

Table 2 shows the CO\textsubscript{2} charge transference when is adsorbed on Co\textsubscript{13}, Cu\textsubscript{13}, Co\textsubscript{13}/PNG, and Cu\textsubscript{13}/PNG. The total charge of the CO\textsubscript{2} molecule resulted in negative values for all systems, which indicates that the CO\textsubscript{2} molecule gained a charge after the adsorption. For instance, the CO\textsubscript{2} adsorption on the Co\textsubscript{13} nanocluster enabled the CO\textsubscript{2} to gain a
charge of $-0.74 \, e$, indicating that the charge is transferred from the nanocluster to the CO$_2$ molecule. It was reported that the transfer plays a significant role in the activation of the CO$_2$ molecule [32,49].

![Figure 6. CO$_2$ adsorption on (a) Co$_{13}$/PNG and (b) Cu$_{13}$/PNG. The bond length (Å) and angle bending (°) of CO$_2$ molecule is depicted. Green, orange, black, white, blue, and red spheres represent Co, Cu, C, H, N, and O atoms, respectively.](image)

**Table 2.** Charge transfer from Co$_{13}$, Cu$_{13}$, Co$_{13}$/PNG, and Cu$_{13}$/PNG to CO$_2$ molecule. The negative values indicate charge transfers from the nanoclusters and nanoclusters/PNG to the CO$_2$ molecule.

| Systems        | Charge Transfer toward CO$_2$ (e) |
|----------------|-----------------------------------|
| Co$_{13}$      | $-0.74$                           |
| Cu$_{13}$      | $-0.78$                           |
| Co$_{13}$/PNG  | $-0.75$                           |
| Cu$_{13}$/PNG  | $-0.67$                           |

The electron localization function (ELF) was used to analyze the type of bond formed by the CO$_2$ interaction on free nanoclusters and nanoclusters supported on PNG. ELF analysis is widely used to understand the nature of chemical bonds, which allows for differentiating covalent bonds and lone pairs (ELF = 1), as well as ionic bonds, hydrogen bonds, and van der Waals interactions (ELF = 0). Figure 7 shows the ELF plots for the CO$_2$ adsorbed on nanoclusters and nanoclusters supported on PNG. As can be observed, the red region between the C atoms and the metal atom has ELF values of 0.8 and 0.9 for the C-Co (Figure 7a) and C-Cu bonds (Figure 7b), respectively. The high ELF value indicates a high charge transfer from the Cu$_{13}$ to the CO$_2$ molecules, in accordance with the total charge calculated (see Table 2). For the CO$_2$ adsorbed on the nanocluster/PNG, the ELF value is $-0.85$ when the CO$_2$ is absorbed on the Co$_{13}$/PNG composite and $-0.8$ when the CO$_2$ is absorbed on the Cu$_{13}$/PNG composite, suggesting a lower charge transfer from the metal cluster to the CO$_2$ molecule (see Figure 7c,d). For the CO$_2$ adsorption on Co$_{13}$ and on Co$_{13}$/PNG, a red region between the C and Co is observed, suggesting a bonding C-Co. Meanwhile, for CO$_2$ on Cu$_{13}$ a uniform red region is observed between C and a Cu. However, when CO$_2$ is adsorbed on Cu$_{13}$/PNG a semicircular region appears between C and two Cu atoms (see Figure 7d), suggesting that C is bonded with two Cu atoms.
Figure 7. Electron localization function contours for: (a) CO$_2$ adsorption on Co$_{13}$, (b) CO$_2$ adsorption on Cu$_{13}$, (c) CO$_2$ adsorption on CO$_{13}$/PNG, and (d) CO$_2$ adsorption on Cu$_{13}$/PNG.

4. Conclusions

The CO$_2$ adsorption on bare 3$d$ transition-metal nanoclusters and 3$d$ transition-metal nanoclusters supported on the PNG was investigated using the ADFT. First, the interaction between Co$_{13}$ and Cu$_{13}$ nanoclusters with PNG was studied by spin densities, interaction energies, charge transfers, and HUMO-LUMO gaps. The results revealed that the PNG enhanced the stability and chemical reactivity of the 3$d$ transition-metal nanoclusters. Subsequently, the CO$_2$ was adsorbed on bare 3$d$ transition-metal nanoclusters, and 3$d$ transition-metal nanoclusters supported PNG. Numerous indicators such as bond elongation, angle bending, and charge transfer were used to characterize the CO$_2$ interaction on these systems. In terms of bond elongation, bare nanoclusters and nanoclusters supported on PNG induced a CO$_2$ bond elongation. In addition, the CO$_2$ molecule experienced a bending angle when it was adsorbed on bare nanoclusters and nanoclusters supported on PNG. Charge transfer analysis revealed that the CO$_2$ gained charge when it was adsorbed on 3$d$ transition-metal nanoclusters and 3$d$ transition-metal nanoclusters supported on PNG nanosheet. Although the nanoclusters and nanoclusters supported on PNG exhibited similar reactivity towards CO$_2$, nanoclusters supported on PNG have the advantage of the support material providing excellent stability to the nanoclusters; therefore, they will not present agglomeration problems.

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27. Wang, M.; Zhang, B.; Ding, J.; Xu, N.; Bernards, M.T.; He, Y.; Shi, Y. Three-Dimensional Nitrogen-Doped Graphene Aerogel-Supported MnO Nanoparticles as Efficient Electrocatalysts for CO₂ Reduction to CO. ACS Sustain. Chem. Eng. 2020, 8, 4983–4994. [CrossRef]

28. Wang, H.; Nie, X.; Guo, X.; Song, C. A computational study of adsorption and activation of CO₂ and H₂ over Fe(0 0 0) surface. J. CO₂ Util. 2016, 15, 107–114. [CrossRef]

29. Dean, J.; Yang, Y.; Austin, N.; Veser, G.; Mpourmpakis, G. Design of Copper-Based Bimetallic Nanoparticles for Carbon Dioxide Adsorption and Activation. ChemSusChem 2018, 11, 1169–1178. [CrossRef]

30. Ocampo-Restrepo, V.K.; Zibordi-Besse, L.; Da Silva, J.L.F. Ab initio investigation of the atomistic descriptors in the activation of small molecules on 3d transition-metal 13-atom clusters: The example of H₂, CO, H₂O, and CO₂. J. Chem. Phys. 2019, 151, 214301. [CrossRef]

31. Pangh, A. Catalytic cleavage of CO₂ on bimetallic Ni₃M (M = Ni, Mo, Sc, and Y) nanoclusters: A DFT study. Catal. Commun. 2020, 149, 106245. [CrossRef]

32. Austin, N.; Butina, B.; Mpourmpakis, G. CO₂ activation on bimetallic CuNi nanoparticles. Prog. Nat. Sci. 2016, 26, 487–492. [CrossRef]

33. Geudtner, G.; Calaminici, P.; Carmona-Espíndola, J.; del Campo, J.M.; Domínguez-Soria, V.D.; Moreno, R.F.; Gamboa, G.U.; Goursot, A.; Köster, A.M.; Reveles, J.U.; et al. deMon2k. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 548–555. [CrossRef]

34. Calaminici, P.; Janetzko, F.; Köster, A.M.; Mejía-Olvera, R.; Zuniga-Gutierrez, B. Density functional theory optimized basis sets for gradient corrected functionals: 3d transition metal systems. J. Chem. Phys. 2007, 126, 044108. [CrossRef]

35. Neese, F. Software update: The ORCA program system, version 4.0. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2018, 8, 1–6. [CrossRef]

36. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Phys. Chem. Chem. Phys. 2005, 7, 3297–3305. [CrossRef]

37. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. J. Comput. Chem. 2011, 32, 1456. [CrossRef]

38. Boys, S.F.; Bernardi, F.D. The Calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol. Phys. 1970, 19, 553–566. [CrossRef]

39. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. J. Comput. Chem. 2011, 32, 1456. [CrossRef]

40. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, 580–592. [CrossRef]

41. Wang, Y.; Wang, L.; Ma, S. Role of defects in tuning the adsorption of CO over graphene-supported Co₁₃ cluster. Appl. Surf. Sci. 2019, 481, 1080–1088. [CrossRef]

42. Montejo-Alvaro, F.; Rojas-Chávez, H.; Herrera-Rivera, R.; Mtz-Enríquez, A.; Cruz-Martínez, H.; Medina, D. Investigating the stability of icosahedral Ni₁₃₋ₓCuₓ (x = 1–12) bimetallic nanoclusters supported on defective graphene: Insights from first-principles calculations. Phys. E Low-dimensional Syst.Nanostructures 2019, 118, 113880. [CrossRef]

43. Liu, L.; Su, Y.; Gao, J.; Zhao, J. Electronic and magnetic properties for Co₁₃ clusters deposited on graphene: A first-principles exploration. Phys. E Low-dimensional Syst. Nanostructures 2012, 46, 6–11. [CrossRef]

44. Alonso-Lanza, T.; Ayuela, A.; Aguilera-Granja, F. Chemical Bonding of Transition-Metal Co₁₃ Clusters with Graphene. ChemPhysChem 2015, 16, 3700–3710. [CrossRef]

45. Montejo-Alvaro, F.; Oliva, J.; Zarate, A.; Herrera-Trejo, M.; Hdz-García, H.; Mtz-Enriquez, A. Icosahedral transition metal clusters (M₁₃, M = Fe, Ni, and Cu) adsorbed on graphene quantum dots, a DFT study. Phys. E Low-dimensional Syst. Nanostructures 2019, 110, 52–58. [CrossRef]

46. García-Rodríguez, D.; Mendoza-Huizar, L.; Díaz, C. A DFT study of Cu nanoparticles adsorbed on defective graphene. Appl. Surf. Sci. 2017, 412, 146–151. [CrossRef]

47. Ruiz-Morales, Y. HOMO-LUMO gap as an index of molecular size and structure for polycyclic aromatic hydrocarbons (PAHs) and asphaltenes: A theoretical study. I. J. Phys. Chem. A 2002, 106, 11283–11308. [CrossRef]

48. Caglar, A.; Düzenli, D.; Onal, I.; Tsezvin, I.; Sahin, O.; Kivrak, H. A novel experimental and density functional theory study on palladium and nitrogen doped few layer graphene surface towards glucose adsorption and electrooxidation. J. Phys. Chem. Solids 2020, 150, 109684. [CrossRef]

49. Mendes, P.C.D.; Ocampo-Restrepo, V.K.; Da Silva, J.L.F. Ab initio investigation of quantum size effects on the adsorption of CO₂, CO, H₂O, and H₂ on transition-metal particles. Phys. Chem. Chem. Phys. 2020, 22, 8998–9008. [CrossRef]