CO₂ Adsorption on PtCu Sub-Nanoclusters Deposited on Pyridinic N-Doped Graphene: A DFT Investigation

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Abstract: To reduce the CO₂ concentration in the atmosphere, its conversion to different value-added chemicals plays a very important role. Nevertheless, the stable nature of this molecule limits its conversion. Therefore, the design of highly efficient and selective catalysts for the conversion of CO₂ to value-added chemicals is required. Hence, in this work, the CO₂ adsorption on Pt₄ₓCu₄₋ₓ (x = 0–4) sub-nanoclusters deposited on pyridinic N-doped graphene (PNG) was studied using the density functional theory. First, the stability of Pt₄ₓCu₄₋ₓ (x = 0–4) sub-nanoclusters supported on PNG was analyzed. Subsequently, the CO₂ adsorption on Pt₄ₓCu₄₋ₓ (x = 0–4) sub-nanoclusters deposited on PNG was computed. According to the binding energies of the Pt₄ₓCu₄₋ₓ (x = 0–4) sub-nanoclusters on PNG, it was observed that PNG is a good material to stabilize the Pt₄ₓCu₄₋ₓ (x = 0–4) sub-nanoclusters. In addition, charge transfer occurred from Pt₄ₓCu₄₋ₓ (x = 0–4) sub-nanoclusters supported on PNG to the CO₂ molecule. These results proved that Pt₄ₓCu₄₋ₓ (x = 0–4) sub-nanoclusters supported on PNG are adequate candidates for CO₂ adsorption and activation.

Keywords: CO₂ adsorption; adsorption energy; charge transfer; stability

1. Introduction

Due to human activity associated with the usage of fossil fuels and industrialization, the concentration of CO₂ in the atmosphere has increased considerably. It is causing environmental problems such as the greenhouse effect, global warming, and climate change among others [1–3]. Therefore, in order to reduce the CO₂ concentration in the atmosphere, various investigations and technologies are being developed such as the CO₂ sequestration process [4,5], and CO₂ conversion into different value-added chemicals is another strategy widely used [6–8]. Nevertheless, the stable nature of the CO₂ molecule limits its conversion [9,10]. Therefore, the design of highly efficient and selective catalysts for the conversion of CO₂ into value-added chemicals is required.
Currently, many catalysts have been designed for CO$_2$ conversion into value-added chemical products, among them the transition metal nanoparticles-based catalysts can be highlighted [11,12]. However, more recently, it has been documented that alloy catalysts have more outstanding catalytic activities than monometallic nanoparticles for CO$_2$ conversion [13,14]. Among the different bimetallic catalysts studied, PtCu nanoparticles have become very important because they present good catalytic properties for the CO$_2$ conversion [15–17]. For example, Cu–Pt alloy nanocubes with a relatively broad range of composition ratios were synthesized and evaluated for CO$_2$ electroreduction reaction [15]. It was found that the Cu–Pt alloys exhibit compositional-dependent activities towards CO$_2$ electroreduction. In another study, Cu–Pt nanocrystals with different amounts of Cu and Pt were prepared and evaluated for CO$_2$ electroreduction reaction [16]. Guo and coworkers highlighted the importance of the compositional effect of Cu–Pt nanocrystals on their catalytical activities in what CO$_2$ electroreduction is concerned. In addition, it was demonstrated that the Cu–Pt (3:1) nanocrystals exhibited the highest activity and faradaic efficiency in the CO$_2$ electroreduction reaction among all the as-prepared Cu–Pt samples. Recently, a density functional theory (DFT) study of CO$_2$ adsorption on Cu$_{4-x}$Pt$_x$ (x = 0–4) clusters was performed [18]. It was computed that the gas phase linear CO$_2$ molecule was deformed upon adsorption, with its bend angle varying from about 134° to 145°, which could favor the CO$_2$ dissociation. It can be inferred from these studies that Cu–Pt alloys are good candidates for the conversion of CO$_2$ to value-added products.

However, it is well known that metallic nanoparticles tend to agglomerate due to their high surface energies, which in turn involves the coarsening of larger particles from those of smaller size [19,20]. Therefore, to overcome the agglomeration problems, it is necessary to disperse or support these nanoparticles on materials with high surface area. To this end, graphene is considered a good support material due to its high specific surface area, excellent electrical conductivity, and resistance to corrosion [21,22], however, this material has a limited chemical reactivity [23]. Consequently, various approaches have been implemented to improve its activity, e.g., functionalization and doping among others [24–26]. Specifically, among the different dopants used to modify graphene reactivity, pyridinic-type N doping can be highlighted because it enhances both the stability and reactivity of metallic nanoparticles [27,28]. Nowadays, there is a sizeable number of theoretical studies that analyze the stability and reactivity of metal nanoparticles supported on pyridinic N-doped graphene (PNG) [29–31]. These studies show the potential of PNG to improve not only the stability, but also the reactivity of metal nanoparticles for different applications [29–31].

According to the literature, the reactivity and stability of Pt$_{4-x}$Cu$_x$ (x = 0–4) clusters supported on PNG substrate was investigated using the DFT [32]. It was demonstrated that Pt–Cu nanoparticles supported on PNG are good candidates to adsorb the glyphosate molecule and PNG stabilized the Pt–Cu nanoparticles as well [32]. However, to the best of our knowledge, there are no theoretical studies on CO$_2$ adsorption on Pt–Cu clusters supported on PNG using the DFT calculations. Therefore, in this work, the CO$_2$ adsorption on Pt–Cu sub-nanoclusters deposited on PNG was studied using the DFT calculations. In order to achieve this goal, the most stable interaction between the Pt$_{4-x}$Cu$_x$ (x = 0–4) sub-nanoclusters and the PNG was investigated. Furthermore, DFT calculations were used to bring light into the CO$_2$ adsorption on Pt$_{4-x}$Cu$_x$ (x = 0–4) sub-nanoclusters deposited on PNG.

2. Computational Methodology

All calculations were carried out within the DFT implemented in the ORCA 5.0.0 package [33]. All the electronic structure calculations were addressed through the revised Perdew–Burke–Ernzerhof exchange correlation functional (revPBE) [34]. For the C, H, N, and O atoms, the Ahlrichs basis sets def2-SVP were used for the calculations and def2-TZVP for the Cu atoms [35], whereas the Pt ones were treated using the basis set LANL2DZ for effective core potentials [36]. The convergence tolerances for geometry optimization were energy
change = 5 × 10^{-6} \text{Eh}, \text{max. gradient} = 3 \times 10^{-4} \text{Eh/Bohr}, \text{rms gradient} = 1 \times 10^{-4} \text{Eh/Bohr}, \text{max. displacement} = 4 \times 10^{-3} \text{Bohr}, \text{and rms displacement} = 2 \times 10^{-3} \text{Bohr}.

To investigate the stability of Pt_{4-x}Cu_x (x = 0–4) sub-nanoclusters on PNG, the most stable structures for the Pt_{4-x}Cu_x (x = 0–4) sub-nanoclusters were obtained from a previous study [18]. However, it is worth highlighting that these structures were reoptimized employing the methodology used in this study, which are depicted in Figure 1.

![Figure 1. Structures and spin multiplicity (M) of Pt_{4-x}Cu_x (x = 0–4) sub-nanoclusters. (a) Pt_4, (b) Pt_3Cu, (c) Pt_2Cu_2, (d) PtCu_3, and (e) Cu_4.](image)

The pyridinic-type N doping can be located anywhere on the graphene (e.g., edge or center). Here, we used graphene as the support material, therefore, the doping was localized in the center of the graphene. In this case, different numbers of nitrogen atoms (e.g., 1, 2, or 3) can be used. In this work, we used pyridinic-type doping with three N atoms, as it has been a widely used structure [29–31,37]. In this sense, circumcoronene (C_{54}H_{18}) was used as model of graphene. To obtain the PNG structure, a C atom was removed from the center of the graphene to create a vacancy, then the hanging C atoms were replaced by N ones, as shown in Figure 2.

![Figure 2. Pyridinic N_3-doped graphene structure.](image)

The binding energies (E_b) between the Pt_{4-x}Cu_x (x = 0–4) sub-nanoclusters and the PNG were calculated as follows:

\[
E_b = E_{\text{sub-nanocluster/PNG}} - (E_{\text{sub-nanocluster}} + E_{\text{PNG}})
\]

where \(E_{\text{sub-nanocluster/PNG}}\), \(E_{\text{sub-nanocluster}}\), and \(E_{\text{PNG}}\) are the energies of the Pt_{4-x}Cu_x (x = 0–4) sub-nanoclusters deposited on PNG, Pt_{4-x}Cu_x (x = 0–4) sub-nanoclusters, and the PNG structure, respectively.

The adsorption energies (E_ads) of CO_{2} on Pt_{4-x}Cu_x (x = 0–4) sub-nanoclusters deposited on PNG were obtained as:

\[
E_{\text{ads}} = E_{\text{sub-nanocluster/PNG+CO}_2} - (E_{\text{sub-nanocluster/PNG}} + E_{\text{CO}_2})
\]
where $E_{\text{sub−nanocluster/PNG+CO}_2}$ is the energy of CO$_2$ adsorbed on Pt$_{4-x}$Cu$_x$ (x = 0–4) sub-nanoclusters deposited on PNG, while $E_{\text{sub−nanocluster/PNG}}$ and $E_{\text{CO}_2}$ are the energies as a single point calculation of the free-standing Pt$_{4-x}$Cu$_x$ (x = 0–4) sub-nanoclusters supported on PNG and the CO$_2$ molecule from the optimized structure of the Pt$_{4-x}$Cu$_x$ (x = 0–4)/PNG+CO$_2$ composite, respectively.

To analyze the molecular interactions of the sub-nanoclusters supported on PNG and the CO$_2$ adsorption over Pt$_{4-x}$Cu$_x$ (x = 0–4) sub-nanoclusters deposited on PNG, the Quantum Theory of Atoms in Molecules (QTAIM) developed by Bader was employed for the charge transfer analyses; to this end, the Multiwfn program was used [38].

3. Results
3.1. Stability of Pt$_{4-x}$Cu$_x$ (x = 0–4) Sub-Nanoclusters on PNG

The most stable interaction between Pt$_{4-x}$Cu$_x$ (n = 0–4) sub-nanoclusters and PNG was determined using several configurations. Figures 3 and 4 illustrate the most stable interactions between the Pt$_{4-x}$Cu$_x$ (n = 0–4) sub-clusters and PNG. It was found that the most stable interaction between the Pt$_4$ sub-cluster and the PNG was with a Pt atom trapped in the vacancy of the PNG, which is consistent with a previous study reported in literature [39]. It is also investigated that the most stable interaction between the Pt$_3$Cu sub-nanocluster and PNG is with a Pt atom trapped in the vacancy of the PNG. For the case of Pt$_3$Cu$_2$ sub-nanocluster deposited on PNG, two isoenergetic structures were found as the most stable structures, see Figure 3c,d. In the first structure, the interaction occurred with two Cu atoms joined with PNG, where one of the atoms is anchored in the vacancy, while in another structure located at only 0.05 eV above the most stable structure, the interaction is with one atom of Cu and one of Pt, in this case the Cu atom is anchored into the vacancy.

![Figure 3](attachment:image.png)  
Figure 3. Top and side views of the most stable configurations of the adsorption of Pt$_{4-x}$Cu$_x$ (x = 0–2) sub-nanoclusters on PNG. (a) Pt$_4$/PNG, (b) Pt$_3$Cu/PNG, and (c,d) Pt$_2$Cu$_2$/PNG. Note that (d) is a quasi-degenerated state of the Pt$_2$Cu$_2$/PNG system with a difference in energy of 0.05 eV.
For PtCu3 sub-nanoclusters supported on PNG, two isoenergetic configurations were also computed as the most stable structures, see Figure 4a,b. In the case of the most stable interaction, it is observed that the interaction between the PtCu3 sub-nanoclusters and PNG occurred with three Cu atoms (Figure 4a), while in another structure, the interaction between the sub-nanocluster and the PNG occurred via two Cu atoms, see Figure 4b. Finally, for Cu4 sub-nanocluster deposited on PNG, two Cu atoms interacted with the PNG. In addition, the Eb between the Pt4-xCu3 (x = 0–4) sub-nanoclusters and the PNG were calculated, see Table 1. It is observed that Eb are substantially higher than those reported in previous findings for Pt-based sub-nanoclusters supported on pristine graphene [40,41]. Therefore, it can be inferred that PNG is a good support material for Pt-based nanoclusters. In addition, the calculated Eb between the Pt4 and the PNG is −3.61 eV, which is similar to that reported in the literature with a value of −4.40 eV [39].

Table 1. Binding energies (E_b) and charge transfer between the Pt4-xCu3 (x = 0–4) sub-nanoclusters and the PNG.

| System          | E_b (eV) | QTAIM Charge (e) |
|-----------------|---------|------------------|
| Pt4/PNG         | −3.61   | 0.23             |
| Pt3Cu/PNG       | −3.01   | 0.26             |
| Pt3Cu2/PNG      | −2.65   | 0.52             |
| PtCu3/PNG       | −3.26   | 0.69             |
| Cu4/PNG         | −2.44   | 0.37             |

The interaction between the Pt4-xCu3 (x = 0–4) sub-nanoclusters and PNG was further investigated by the QTAIM charge transfer, see Table 1. The results suggest that Pt4-xCu3 (x = 0–4) sub-nanoclusters transfer charge to the PNG structure since these ended with a total positive charge, which can be attributed to the large electronegativity of the N atoms. Furthermore, it is observed that as the content of Cu in the sub-nanoclusters increases, the charge transfer from sub-nanoclusters to the PNG tends to increase as well, which can be attributed to the low electronegativity of the Cu atoms.

3.2. \( \text{CO}_2 \) Adsorption on Pt4-xCu3 (x = 0–4) Sub-Nanoclusters Deposited on PNG

To analyze the adsorption and activation of the \( \text{CO}_2 \) molecule on the Pt4-xCu3 (x = 0–4) sub-nanoclusters deposited on PNG, the \( \text{CO}_2 \) adsorption energy, \( \text{CO}_2 \) bond elongation, \( \text{CO}_2 \) bending angle, and charge transfer from sub-nanoclusters supported PNG to \( \text{CO}_2 \) were used as indicators of an effective \( \text{CO}_2 \) dissociation process [42,43]. To obtain the most stable interaction between the \( \text{CO}_2 \) and sub-nanoclusters supported PNG, several modes (e.g., top, bridge, and hollow) of \( \text{CO}_2 \) adsorption on sub-nanoclusters supported...
on PNG were investigated. In Figure 5, the most stable CO₂ adsorption on the Pt₄₋ₓCuₓ (x = 0–4) sub-nanoclusters supported on the PNG is reported. The results show that the CO₂ molecule is deformed when it is adsorbed on the Pt₄₋ₓCuₓ (x = 0–4) sub-nanoclusters supported on PNG (Figure 5), giving way to a bending angle from 135.86° up to 141.25°, see Table 2. Similar results were obtained when the CO₂ molecule was adsorbed on Cu₄₋ₓPtₓ (x = 0–4) clusters [18]. In addition, it can be observed that the CO₂ is adsorbed side-on type on Pt₄₋ₓCuₓ (x = 1–4)/PNG composites, whereas for the Pt₄/PNG composite the CO₂ molecule is bonded with a Pt atom. The type of CO₂ adsorption on Pt₄₋ₓCuₓ (x = 0–4) sub-nanoclusters deposited on PNG is reported. The results show that the CO₂ molecule is deformed when it is adsorbed on Pt₄₋ₓCuₓ (x = 0–4) sub-nanoclusters supported on PNG: (a) Pt₄, (b) Pt₃Cu, (c) Pt₂Cu₂, (d) PtCu₃, and (e) Cu₄.

Figure 5. Top and side views of the most stable CO₂ adsorption sites on the sub-nanoclusters supported on the PNG: (a) Pt₄, (b) Pt₃Cu, (c) Pt₂Cu₂, (d) PtCu₃, and (e) Cu₄.
Table 2. Properties of the CO\textsubscript{2} adsorption on the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters supported on PNG.

| System            | $E_{ads}$ (eV) | Charge Transfer Toward CO\textsubscript{2} (e) | Average CO\textsubscript{2} Bond Length (Å) | Bending Angle of CO\textsubscript{2} (°) |
|-------------------|----------------|---------------------------------------------|-------------------------------------------|----------------------------------------|
| CO\textsubscript{2}/Pt\textsubscript{4}/PNG | −1.06 | −0.37                                       | 1.24                                       | 141.25                                 |
| CO\textsubscript{2}/Pt\textsubscript{3}Cu/PNG | −2.21 | −0.42                                       | 1.24                                       | 140.03                                 |
| CO\textsubscript{2}/Pt\textsubscript{2}Cu\textsubscript{2}/PNG | −2.34 | −0.44                                       | 1.25                                       | 139.32                                 |
| CO\textsubscript{2}/PtCu\textsubscript{3}/PNG | −2.48 | −0.46                                       | 1.25                                       | 135.86                                 |
| CO\textsubscript{2}/Cu\textsubscript{4}/PNG | −1.81 | −0.58                                       | 1.24                                       | 138.27                                 |

Finally, Table 2 shows the charge transfer between the CO\textsubscript{2} molecule and the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters supported on the PNG. The total charge of the CO\textsubscript{2} molecule resulted in negative values for all the systems studied, which indicated that the CO\textsubscript{2} molecule gained charge after the adsorption. Furthermore, it is observed that as the Cu content in the sub-nanoclusters increases, the charge transfer from the sub-nanoclusters supported on PNG to CO\textsubscript{2} molecule tends to increase as well, which can be attributed to the low electronegativity of the Cu atoms. Moreover, it is found that the charge transfer plays a significant role in the activation of the CO\textsubscript{2} molecule [42,43].

4. Conclusions

The CO\textsubscript{2} adsorption on the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters deposited on PNG was studied using the density functional theory. To the best of our knowledge, this is the first study on the CO\textsubscript{2} adsorption on the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters supported on PNG. First, the stability of the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters supported on PNG was analyzed. The results revealed that PNG enhanced the stability of the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters. After, the CO\textsubscript{2} adsorption on the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters deposited on PNG was computed. Numerous indicators such as $E_{ads}$, average bond length elongation, angle bending, and charge transfer were used to characterize the CO\textsubscript{2} interaction on the proposed systems. When the CO\textsubscript{2} molecule was adsorbed on the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters supported on the PNG, the CO\textsubscript{2} underwent both bond length elongation and bending angle. In addition, the charge transfer from the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters supported on PNG to the CO\textsubscript{2} molecule was observed. The results obtained with those indicators suggest that the activation of the CO\textsubscript{2} molecule took place. Therefore, the Pt\textsubscript{4-x}Cu\textsubscript{x} (x = 0–4) sub-nanoclusters supported on PNG are suitable candidates for the CO\textsubscript{2} adsorption and activation.

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