Density functional study on the interaction of Graphene-supported Nickel cluster with CO₂ molecule

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Abstract. We try to use small size Ni cluster supported on graphitic material as an alternative for CO₂ hydrogenation catalyst. As an initial step, we study the ability of the supported Ni₄ cluster to interact with CO₂ molecule by means of density functional theory-based calculations. We find that strong CO₂ adsorption can only be formed on top of the Ni₄ cluster site. Due to the strong Ni₄-CO₂ interaction, the CO₂ molecule is always adsorbed with a bidentate adsorption configuration on the Ni₄ cluster. The graphene surface and Ni₄-graphene interface cannot accommodate CO₂ chemisorption due to the weak graphene-CO₂ interaction.

1. Introduction
Research on CO₂ conversion to renewable fuel through hydrogenation reaction has become an attractive project due to its economic potential for industrial feedstock and potential renewable energy sources [1,2]. In spite of its relatively mature and eminent implementation in chemical industries, researchers and practitioners are still in dispute. One of the challenges of this process is to find an optimum catalyst. Using conventional catalyst such as Cu-ZnO/Al₂O₃, CO₂ conversion through hydrogenation reaction needs high pressure and high temperature condition to be enacted [3]. This harsh working condition is needed owing to the high activation energies required by various steps in the CO₂ hydrogenation reaction networks. More efforts are needed to find a better catalyst that can work in a milder working condition.

Nickel (Ni) is a well-known transition metal that has been successfully applied as a catalyst in various chemical reactions [4–6], including CO₂ conversion into diverse hydrocarbons and alcohols. Unfortunately, Ni surface in its pure form is not an appropriate catalyst for CO₂ hydrogenation reaction [7–14]. One of the primary culprits for this phenomenon is the weak interaction between the relatively inert CO₂ molecule and the Ni surface even though the ability of Ni surface to provide H atom through H₂ dissociation is acclaimed [15]. Various attempts have been done to engineer the activity of Ni metals towards CO₂ hydrogenations such as alloying with transition metals [16–19] or using Ni in the form of metal clusters supported on transition metal oxide [20,21]. These strategies have been proven to be able to enhance the interaction of Ni with CO₂ molecule. Unfortunately, the CO₂ conversion rate is still inadequate.
In order to improve the activity of Ni as CO₂ hydrogenation catalyst, we try the possibility of adopting small nickel cluster (Ni₄) supported on graphene (Ni₄/graphene) as a candidate for the catalyst. As an initial step, we study the interaction of Ni₄/graphene with CO₂ molecule using density functional theory-based calculations [22,23]. From our previous study, we know that the use of small cluster configuration can enhance the catalytic activity of Pd metal toward CO₂ hydrogenation reaction quite significantly as compared to the activity of Pd surface [24–26]. Therefore, we expect that the use of small Ni cluster might also produce a similar trend. In recent years, the single atom catalyst (SAC) Ni has gain popularity due to its good performance as a catalyst for CO₂ electroreduction to CO [2,27].

The active site structure of SAC Ni is a graphitic carbon embedded by a Ni-Ni₄ defect. This configuration is actually one of the infamous active site configuration of a pyrolyzed TM/N/C (TM= Mn, Fe, Co, Ni) catalyst which is frequently used as a catalyst for oxygen reduction reaction in acidic and alkaline fuel cells [28–35]. The role of graphitic structure of SAC Ni system towards CO₂ reduction reaction is still unclear. We speculate that the graphitic structure might have some role in catalyzing the CO₂ reduction reaction whose reaction steps are in principle quite similar with the CO₂ hydrogenation reaction. Therefore, we attempt to use graphene as a support material for Ni₄ cluster for this study.

2. Computational Detail

All of the electronic structure calculations are executed using Quantum Espresso package [36] based on spin-polarized density functional theory [22,23]. Generalized gradient approximation using the Perdew-Burke-Ernzerhof (PBE) functional was applied to describe the exchange and correlation effect [37]. Rappe-Rab-Kaxiras ultrasoft pseudopotentials (rkjus) are used to describe the interaction between valence electrons and the ion core.

The value of cutoff for plane-wave and electronic density are 30 Ry and 360 Ry, respectively. The Brillouin zone sampling for the calculation of the isolated nickel cluster and CO₂ molecule are simulated using gamma point, while the calculation for the rest is carried out using 2 x 2 x 1 k-points. The energy and optimized geometry of an isolated Ni₄ cluster and an isolated CO₂ molecule are computed in a 30 Å x 30 Å x 30 Å unit cell.

In this study, we focus on two issues: (1) Ni₄ adsorption on a 5x5 graphene sheet and (2) CO₂ adsorption on the Ni₄/graphene. Small Ni₄ cluster is used as a Ni₄ model because this is the minimum Ni₄ cluster size that can accommodate simultaneous co-adsorption of a CO₂ molecule and an H atom on the cluster. The co-adsorption state of CO₂ and H is important for continuing the hydrogenation reaction. Graphene sheet with 5x5 size is chosen because it can provide large enough space to support the Ni₄ cluster while minimizing its interactions with other Ni₄ clusters on the adjacent unit cells. The supercell size has been conformed to the size of the modeled graphene cell size to preserve the periodicity in xy-direction. In z-direction, we considered a vacuum space of 15 Å to minimize the interaction between repeated surfaces.

We perform geometry optimizations without any constraint to study the adsorption of Ni₄ cluster on graphene and CO₂ molecule on Ni₄/graphene. The energy of several possible adsorption sites and adsorption conformations are tested and compared to get the most stable adsorption configuration. We check three possible areas for CO₂ adsorption sites on Ni₄/graphene: (1) on the Ni₄ cluster, (2) on the graphene sheet, and (3) on the interface between Ni₄ and graphene sheet.

The adsorption energies ($E_{ad}$) of the adsorbate are evaluated using this following formula:

$$E_{ad} = E_{tot} - (E_{surf} + E_{mol})$$

where $E_{tot}$ represents value of total energy of whole catalysis system after adsorption, $E_{surf}$ corresponds to total energy of clean surface (graphene surface for the case of Ni₄ adsorption on graphene and Ni₄/graphene for the case of CO₂ adsorption) and $E_{mol}$ is the total energy of the adsorbed molecule (Ni₄ cluster for the case of Ni₄ adsorption on graphene and CO₂ molecule for the case of CO₂ adsorption on Ni₄/graphene). Charge population on individual atoms are calculated using Bader charge analysis [38].
3. Results and Discussion

3.1 Adsorption of Ni₄ cluster on graphene
First, we discuss about the feasibility of Ni₄ cluster adsorption on graphene sheet. We find that the Ni₄ cluster can be strongly adsorbed on the graphene with adsorption energy of -2.39 eV and average adsorption distance of 2.086 Å. The Ni₄ cluster maintained its tetrahedron conformation after adsorption. This adsorption causes some slight elongations in the average Ni-Ni bond distance of the Ni₄ cluster. The accommodate this adsorption, the Ni-Ni bond is elongated from 2.286 Å to 2.311 Å. Bader charge analysis shows that the graphene surface receives about 0.76e from the Ni₄ cluster. This indicates strong interaction between Ni₄ cluster and graphene surface, consistent with the values of Ni₄ adsorption energy. The structure of isolated Ni₄ cluster and its adsorption on graphene surface is shown in figure 1.

![Figure 1](image)

**(a)** Optimized structure of isolated Ni₄ cluster and its adsorption on graphene surface.

3.2 CO₂ Adsorption
Important geometrical and energetical results for CO₂ adsorption on the Ni₄/Graphene are presented in Table 1, Table 2 and figure 2. As mentioned in Section 2, we try to adsorb the CO₂ molecule on three general sites: (1) on the Ni₄ cluster, (2) Ni₄-graphene interface and (3) graphene surface.

| Sites               | E_{ads} (eV) | Ni-C (Å) | Ni-O (Å) | C-O_{bond} (Å) | C-O_{free} (Å) | O-C-O (°) | Ni-Ni (Å) | Ni-C (Å) |
|---------------------|--------------|----------|----------|----------------|----------------|-----------|-----------|----------|
| Ni₄ cluster         | -0.94        | 1.814    | 1.931    | 1.264          | 1.232          | 136.93    | 2.453     | 2.059    |
| Ni₄-graphene interface | -0.64       | 1.907    | 1.991    | 1.251          | 1.205          | 146.86    | 2.341     | 2.088    |
| Graphene            | -0.29        | 2.326    | 2.403    | 1.18           | 1.167          | 178.52    | 2.314     | 2.098    |
| Isolated CO₂        | -0.29        | 1.171    | 1.171    |                |                |           |           |          |

**Table 1.** Results of CO₂ adsorption in the most stable sites on Ni₄/graphene

| Systems                          | ΔQ^{Ni}_{ads} (e) | ΔQ^{CO₂} (e) |
|----------------------------------|------------------|--------------|
| Ni₄ adsorption on Graphene       | -0.76            |              |
| CO₂ adsorption on Ni₄ cluster site | -1.25           | 0.66         |
| CO₂ adsorption on Ni₄-graphene interface | -1.10           | 0.49         |
| CO₂ adsorption on Graphene       | -0.82            | 0.04         |

**Table 2.** Charge transfer (ΔQ) after adsorption
Figure 2. Optimized geometries for CO$_2$ adsorption on (a) Ni$_4$ cluster, (b) Ni$_4$-graphene and (c) graphene surface.

For the case of adsorption on the Ni$_4$ cluster, we try various adsorption sites and conformations of CO$_2$ molecule on the Ni$_4$ site of Ni$_4$/graphene system. We find that the most stable CO$_2$ adsorption configuration is achieved when the CO$_2$ molecule is directly adsorbed on the surface of Ni$_4$ cluster with a bidentate adsorption configuration with CO2 adsorption energy of -0.94 eV (see Fig. 2a). The C atom and one of the O atom of CO$_2$ molecule make direct contact with Ni$_4$ cluster and form C-Ni and O-Ni bonds. The linear O-C-O angle of CO$_2$ molecule is bended to 136.93° and the average Ni-Ni bond of Ni$_4$ cluster is also elongated from 2.311 Å to 2.453 Å. This situation indicates a strong surface-adsorbate interaction which is consistent with the value of CO$_2$ adsorption energy. The bending of O-C-O linear angle is caused by the large electron transfer (0.66e) from the Ni$_4$/graphene surface to the adsorbed CO$_2$ molecule. These extra charges occupy the antibonding orbital of CO$_2$ molecule and makes the internal repulsion among O-C-O atoms become stronger. The CO$_2$ molecule has to break its linear structure to minimize this repulsion. This mechanism results in a CO$_2$ bidentate adsorption configuration. This mechanism is similar with the case of CO$_2$ bidentate adsorption on Pd$_x$ cluster [24–26]. The formation of CO$_2$ bidentate adsorption configuration on the Ni$_4$ cluster might facilitate the first CO$_2$ hydrogenation step to produce HCOO or HOCO as in the Pd$_x$ cluster case [25,26].

For the second case, we find that the molecule actually cannot be adsorbed on the interface of Ni$_4$/graphene. Instead, the CO$_2$ molecule moves to Ni$_4$ site and forms a bidentate adsorption configuration (see Fig. 2b). However, this adsorption configuration is energetically less favorable than the most stable adsorption configuration on the first case. This situation is indicated by a weaker CO$_2$ adsorption energy (-0.64 eV), a larger CO$_2$ adsorption distance (C-CO$_2$-Ni$_4$ 1.907 Å), and a smaller charge transferred to the adsorbed CO$_2$ (0.49 e).

For the case of CO$_2$ adsorption on graphene surface, we find that the CO$_2$ molecule can only be adsorbed physically on the surface. This physisorption state is characterized by a weak adsorption energy (-0.29 eV), a large CO$_2$ adsorption distance (C-CO$_2$-Ni$_4$ 2.236 Å), a very small charge transfer to adsorbed CO$_2$ (0.04e). The small value of charge transfer indicates the absence of orbital overlaps between CO$_2$ molecular orbitals and graphene surface states. This suggests that the interaction between CO$_2$ molecule and graphene surface is indeed very weak.

In general, we find that the most feasible adsorption site for CO$_2$ on Ni$_4$/graphene is only on Ni$_4$ cluster site. This situation is different with the case of CO$_2$ adsorption on Ni cluster supported on metal-oxide system where the most stable adsorption site is on the Ni cluster-metal-oxide interface [20,21]. Therefore, the main active site for CO$_2$ hydrogenation on the Ni$_4$/graphene system most likely will only occur on top of the Ni$_4$ cluster.
4. Summary
We study the adsorption of CO$_2$ on Ni$_4$ cluster supported on graphene. We find that strong CO$_2$ adsorption can only be formed on top of the Ni$_4$ cluster site. Due to the strong Ni$_4$-CO$_2$ interaction, the CO$_2$ molecule is always adsorbed with a bidentate adsorption configuration on the Ni$_4$ cluster. The graphene surface and Ni$_4$-graphene interface cannot accommodate CO$_2$ chemisorption due to the weak graphene-CO$_2$ interaction. We expect that only Ni$_4$ cluster site will act as the active site for CO$_2$ hydrogenation on Ni$_4$/graphene system since strong CO$_2$ adsorption can only occur on this particular site.

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References
[1] Xiaoding X and Moulijn J A 1996 Mitigation of CO2 by chemical conversion: Plausible chemical reactions and promising products Energy and Fuels 10 305–25
[2] Cheng Y, Yang S, Jiang S P and Wang S 2019 Supported Single Atoms as New Class of Catalysts for Electrochemical Reduction of Carbon Dioxide Small Methods 3 1800440
[3] Waugh K C 1992 Methanol Synthesis Catal. Today 15 51–75
[4] Agusta M K, Saputro A G, Ihsan A Z, Krishna R, Fathurrahman F, Dipojono H K and Diño W A 2019 Coadsorption of hydrazine (N2H4) and OH on NiZn surface: a DFT-based study Surf. Sci. 121505
[5] Agusta M K, Purwoko P H, Saputro A G, Fathurrahman F, Dipojono H K and Diño W A 2017 Conformational effects on hydrazine and OH coadsorption on Ni(111): A first-principles investigation Surf. Sci. 664 185–93
[6] Zhang J, Wang Y, Dong H and Zhou X 2019 Theoretical investigation of loading Ni clusters on the A-Ga 2 O 3 surfaces for photocatalytic hydrogen evolution J. Energy Chem. 30 8–18
[7] Peng G, Sibener S J, Schatz G C and Mavrikakis M 2012 CO 2 hydrogenation to formic acid on Ni(110) Surf. Sci. 606 1050–5
[8] Catapan R C, Oliveira A A M, Chen Y and Vlachos D G 2012 DFT study of the water-gas shift reaction and coke formation on Ni(111) and Ni(211) surfaces J. Phys. Chem. C 116 20281–91
[9] Vesselli E, Rizzi M, de Rogatis L, Ding X, Baraldi A, Comelli G, Savio L, Vattuone L, Rocca M, Fornasiero P, Baldereschi A and Peressi M 2010 Hydrogen-assisted transformation of CO 2 on nickel: The role of formate and carbon monoxide J. Phys. Chem. Lett. 1 402–6
[10] Vesselli E, De Rogatis L, Ding X, Baraldi A, Savio L, Vattuone L, Rocca M, Fornasiero P, Peressi M, Baldereschi A, Rosei R and Comelli G 2008 Carbon dioxide hydrogenation on Ni(110) J. Am. Chem. Soc. 130 11417–22
[11] Ding X, De Rogatis L, Vesselli E, Baraldi A, Comelli G, Rosei R, Savio L, Vattuone L, Rocca M, Fornasiero P, Ancilotto F, Baldereschi A and Peressi M 2007 Interaction of carbon dioxide with Ni(110): A combined experimental and theoretical study Phys. Rev. B - Condens. Matter Mater. Phys. 76 1–12
[12] Ding X, Pagan V, Peressi M and Ancilotto F 2007 Modeling adsorption of CO 2 on Ni(110) surface Mater. Sci. Eng. C 27 1355–9
[13] Wang S, Cao D, Li Y, Wang J and Jiao H 2005 Chemisorption of CO 2 on Nickel Surfaces J. Phys. Chem. B 109 18956–63
[14] Remediakis I N, Abild-Pedersen F and Nørskov J K 2004 DFT study of formaldehyde and methanol synthesis from CO and H2 on Ni(111) J. Phys. Chem. B 108 14535–40
[15] Kresse G 2000 Dissociation and sticking of H2 on the Ni(111), (100), and (110) substrate Phys. Rev. B 62 8295–305
[16] Studt F, Sharaftudinov I, Abild-Pedersen F, Elkjær C F, Hummelshoj J S, Dahl S, Chorkendorff I and Nørskov J K 2014 Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol Nat. Chem. 6 320–4
[17] Studt F, Abild-Pedersen F, Wu Q, Jensen A D, Temel B, Grunwaldt J D and Nørskov J K 2012 CO hydrogenation to methanol on Cu-Ni catalysts: Theory and experiment J. Catal. 293 51–60
[18] Maulana A L, Putra R I D, Saputro A G, Agusta M K, Nugraha N and Dipojono H K 2019 DFT and Microkinetic Investigation of Methanol Synthesis via CO2 Hydrogenation on Ni(111)-based Surfaces Phys. Chem. Chem. Phys. 1–11
[19] Nørskov, Saputro A G, Agusta M K, Rusydi F, Maezono R and Dipojono H K 2016 DFT study of the formate formation on Ni(111) surface doped by transition metals [Ni(111)-M; M=Cu, Pd, Pt, Rh]. Journal of Physics: Conference Series vol 739
[20] Carrasco J, Barrio L, Liu P, Rodriguez J A and Ganduglia-Pirovano M V 2013 Theoretical studies of the adsorption of CO and C on Ni(111) and Ni/CeO2(111): Evidence of a strong metal-support interaction J. Phys. Chem. C 117 8241–50
[21] Pan Y X, Liu C J and Ge Q 2010 Effect of surface hydroxyls on selective CO2 hydrogenation over Ni4/γ-Al2O3: A density functional theory study J. Catal. 272 227–34
[22] Hohenberg P and Sham L J 1965 Self-Consistent Equations Including Exchange and Correlation Effects Phys. Rev. 140 A1133–A1138
[23] Saputro A G and Akbar T 2017 Reaksi Hidrogenasi Metoksida Menjadi Metanol pada Klaster Pd 6 Ni 53–7
[24] Saputro A G, Agusta M K, Wungu T D K, Suprijadi, Rusydi F and Dipojono H K 2016 DFT study of adsorption of CO2 on palladium cluster doped by transition metal Journal of Physics: Conference Series vol 739
[25] Zheng T, Jiang K, Ta N, Hu Y, Zeng J, Liu J and Wang H 2019 Large-Scale and Highly Selective CO2 Electrocatalytic Reduction on Nickel Single-Atom Catalyst Joule 3 265–78
[34] Saputro A G, Rusydi F, Kasai H and Dipojono H K 2012 Oxygen reduction reaction on cobalt-(6)pyrrole cluster: Density functional theory study J. Phys. Soc. Japan 81 2–6

[35] Saputro A G and Kasai H 2014 Density functional theory study on the interaction of O2 and H2O2 molecules with the active sites of cobalt-polypyrrole catalyst J. Phys. Soc. Japan 83 1–11

[36] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti G L, Cococcioni M, Dabo I, Dal Corso A, De Gironcoli S, Fabris S, Fratesi G, Gebauer R, Gerstmann U, Gougoussis C, Kokalj A, Lazzeri M, Martin-Samos L, Marzari N, Mauri F, Mazzarello R, Paolini S, Pasquarello A, Paulatto L, Sbraccia C, Scandolo S, Sclauzero G, Seitsonen A P, Smogunov A, Umari P and Wentzcovitch R M 2009 QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials J. Phys. Condens. Matter 21

[37] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8

[38] Bader R F W 1990 Atoms in Molecules (Oxford: Clarendon Press)