CO₂ adsorption on graphene supported Ni catalysts

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Abstract. We perform density functional theory (DFT) study of CO₂ adsorption on graphene supported Ni catalyst. We implement ordinary PBE functional as well as van der Waals density functional (vdW-DF) to accommodate weakly interaction between CO₂ and graphene. Based on vDW-DF calculations, we obtained that CO₂ is physisorbed on pristine graphene, in contradiction with PBE results. The adsorption energy further increases when we introduce single Ni adatom and small Ni cluster on graphene. The adsorbed CO₂ bond angle and bond length on graphene with single Ni adatom and cluster are deformed from its gas phase condition, indicating that CO₂ is chemically adsorbed on the decorated graphene area. Our results provide useful insight into appropriate design of graphene supported metal catalysts.

1. Introduction
Continuous rise of carbon dioxide (CO₂) amount in the air has become one of the biggest problem in many countries since it can lead to global warming catastrophe. CO₂ pollutant mainly comes from the combustion of vehicles, industrial activities, forest fire, and others processes. The propitious acts are then necessary to reduce the amount of this greenhouse gas. Carbon capture, storage, or utilization through reduction reaction have been regarded as promising ways to control CO₂ amount [1–4]. Noble metal such as Pt, Au, and Pd are usually involved as a catalyst in those processes [5–7]. However, those noble metals are scarce and quite expensive. The development of cheaper and more effective catalysts is then required to construct large-scale practical application in reducing CO₂ gas pollutant.

Minimizing the size of catalyst particle is one promising solution to promote the catalytic performance and reduce the production cost. Graphene is one of the best support media of nanoparticle catalysts due to its large surface area for chemical reaction [8]. Graphene supported platinum (Pt) and palladium (Pd) clusters have shown preeminent activity for CO oxidation and methanol oxidation [7, 9–11]. Moreover, other transition metal adatoms or dopants, e.g. Au [12], Fe [13], Cu [14], and Al [15] on graphene have also shown promising results in reduction reaction of inert gases.
Among the aforementioned transition metals, nickel (Ni) can be also one of possible metal adatom on graphene which has excellent catalytic activity towards gas adsorption. According to the previous density functional theory (DFT) studies with generalized gradient approximation (GGA) based functionals, Ni adatoms and/or dopants promote the interaction between graphene and CO$_2$ [16,17]. The adsorption of CO$_2$ was then significantly increased on Ni cluster modified graphene surface [18]. However, there are still many obscure aspect in the CO$_2$ interaction on Ni-graphene.

Previous DFT studies utilized standard GGA functionals to elucidate CO$_2$ interaction on Ni-graphene system. This standard functional is known to be inadequate to describe weakly bound systems [19–22]. The description of weakly bound systems can be achieved by introducing van der Waals density functional (vdW-DF) method. In this method, a fully nonlocal correlation energy functional is introduced upon the exchange-correlation energy term [23, 24]. Therefore, in this work, we investigate the CO$_2$ interaction on Ni-graphene surface using van der Waals density functional (vdW-DF) method. We anticipate that the vdW-DF study of this system would give worthwhile insight for further investigation on related CO or CO$_2$ activation on graphene supported nano-particle catalysts.

2. Computational Details
We elucidate the CO$_2$ adsorption on graphene supported single atom and trimer cluster of Ni catalysts by means of vdW-DF method to clarify the effect of local surface geometry. We use one of vdW functionals namely rev-vdW-DF2 functional [21]. As for CO$_2$ on pristine graphene, we also compare our results obtained by vdW with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation incorporated in standard GGA functional [25]. The calculations were carried out by using Vienna Ab-initio Simulation Package (VASP) [26,27]. The core electrons are replaced by the projector augmented wave (PAW) pseudo-potentials with energy cutoff of 520 eV. The convergence criterion of self-consistent calculation is set to 10$^{-5}$ eV. The layer and adsorbates are relaxed until the force drop to 0.005 eV·Å$^{-1}$. In order to avoid the interaction between graphene sheet, we place 25 Å of vacuum layer along the z direction. The Brillouin zone was sampled by 4×4×1 and 3×3×1 $k$-points of Monkhorst-Pack grid for 3×3 and 4×4 graphene unit cells, respectively.

Firstly, we assess the PBE and rev-vdW-DF2 functionals in the CO$_2$ adsorption energy ($E_{ads}$) as a function of molecule-surface distance on pristine graphene sheet. The $E_{ads}$ is defined by

$$E_{ads} = E_{tot} - (E_{gra} + E_{CO2}),$$

where $E_{tot}$, $E_{gra}$, and $E_{CO2}$ represent the total energies of the adsorbed system, an isolated pristine graphene, and an isolated CO$_2$ molecule in gas phase, respectively. Then, we investigate CO$_2$ adsorption on graphene supported single atom and trimer cluster of Ni catalysts. The qualitative adsorption energy of CO$_2$ on Ni/graphene system is evaluated in the same manner of CO$_2$ on pristine graphene. However, we use isolated Ni adatom or cluster on graphene as a reference.

3. Results and Discussion
3.1. CO$_2$ on pristine graphene
We have investigated CO$_2$ adsorption on pristine graphene using PBE and rev-vdW-DF2 functionals. As shown in figure 1, we have checked the adsorption geometry of CO$_2$ on three different sites and two different orientations. The adsorption energies curve is shown in figure 2. The two functionals give quite different behavior of CO$_2$ adsorption on graphene. Ordinary PBE shows almost repulsive interaction, while rev-vdW-DF2 produces good adsorption energy curve with a clear equilibrium distance (~3.20 Å). The calculated $E_{ads}$ by rev-vdW-DF2 are quite
Figure 1. Top view of CO$_2$ adsorption on bridge, hollow, and top sites of pristine graphene sheet.

similar for all possible configurations in figure 1 (0.15 ± 0.02 eV), indicating that CO$_2$ molecule is physisorbed on graphene sheet. The physisorbed geometry of CO$_2$ molecule on pristine graphene is similar with its gas phase, 180° of O−C−O bond angle and 1.18 Å of C−O bond length. Our calculated $E_{\text{ads}}$ is reasonably in good agreement with previous experimental investigation of CO$_2$ on pristine graphene sheet [28]. Based on our calculation results, vdW functional is clearly important to describe the interaction of inert molecule such CO$_2$ on graphene sheet.

Figure 2. Adsorption energy curve of CO$_2$ on pristine graphene sheet as a function of molecule-surface distance.

3.2. CO$_2$ on graphene supported single Ni adatom
In the prior discussion, we have shown that rev-vdW-DF2 produces reliable adsorption energy curve of CO$_2$ on pristine graphene which is compatible with the general notion of atomic and/or molecular adsorption on surfaces. Thus, in the next case, we will only focus our calculations
using rev-vdW-DF2 functional. To investigate CO$_2$ interaction on graphene supported single Ni adatom, we firstly check the stability of Ni adsorption on pristine graphene sheet. We compared two possible adsorption sites, namely the hollow site of six-member ring of graphene and bridge site of two carbon atoms in graphene sheet. It turns out that the interaction energy of Ni adatom is $\sim 0.20$ eV more stable on the hollow site than that of bridge site, which is in good agreement with previous experimental observation [29,30].

We then investigate CO$_2$ adsorption on graphene supported Ni adatom. Figure 3 shows that CO$_2$ molecule is chemically adsorbed on the surface with calculated $E_{\text{ads}}$ of 1.34 eV. The calculated $E_{\text{ads}}$ is much higher than that on pristine graphene sheet. Furthermore, the geometry of adsorbed CO$_2$ on this system is completely different from its on pristine graphene. The adsorbed CO$_2$ bond angle is deformed to 149° and one of its C−O bond length is elongated up to 1.26 Å. In the optimized geometry (figure 3), we notice that Ni atom stays near the bridge site after CO$_2$ adsorption. The presence of single Ni adatom may disrupt the inertness of potential surface of pristine graphene sheet. Thus, it can provide active site to adsorb CO$_2$ molecule.

![Optimized CO$_2$ adsorption geometry on graphene supported Ni adatom. Blue, yellow, and red spheres correspond to Nickel, Carbon, and Oxygen atoms, respectively.](image)

**Figure 3.** Optimized CO$_2$ adsorption geometry on graphene supported Ni adatom. Blue, yellow, and red spheres correspond to Nickel, Carbon, and Oxygen atoms, respectively.

3.3. CO$_2$ on graphene supported Ni cluster

Finally, we discuss the CO$_2$ adsorption on graphene supported Ni cluster. Here, we consider small cluster which consists of three Ni adatoms (trimer). Figure 4 shows two possible geometry configurations of Ni trimer on graphene sheet. First, all three Ni atoms attach to bridge site and the other configuration has three Ni atoms on hollow site of graphene six-member ring. We obtained that the formation energy of Ni trimer on bridge site is 0.57 eV more stable than that on hollow site. Thus, we consider CO$_2$ adsorption on this stable configuration.

We obtained two most stable configurations of CO$_2$ adsorption on graphene supported Ni trimer (figure 5). First, CO$_2$ is attached on the bridge site of Ni cluster with $E_{\text{ads}}$ of 1.86 eV (figure 5a). The second one is attached on the hollow site of Ni cluster with $E_{\text{ads}}$ of 2.19 eV (figure 5b). The results clearly show that the presence of Ni cluster enhance the catalytic activity of graphene sheet. On cluster system, the bond angle of adsorbed CO$_2$ is deformed to 130°, indicating strong interaction between Ni cluster and CO$_2$. The calculated bond angle is comparable with previous study of Ni cluster on monovacancy graphene sheet [18]. Moreover, its C−O bond length is a bit longer than that on single Ni adatom case. The presence of Ni adatom/cluster obviously enhances the catalytic activity of graphene sheet.
4. Conclusions

The adsorption of CO$_2$ graphene supported single Ni adatom and Ni cluster has been studied by means of vDW-DF. The considered functionals produce different behaviors in describing the adsorption properties. The rev-vdW-DF2 functional gives reasonable potential energy curve of CO$_2$ adsorption on pristine graphene, while ordinary PBE shows almost repulsive interaction between CO$_2$ and graphene. The presence of single Ni adatom and cluster enhances the adsorption of CO$_2$ on graphene sheet. The adsorption energy of CO$_2$ on graphene supported single Ni adatom is almost ten times higher than that on pristine graphene sheet, indicating...
that Ni adatom produce significant catalytic activity on inert graphene sheet. The deformation of CO\(_2\) bond angle and bond length on graphene supported single Ni adatom and cluster are convincingly shown the strong hibridization between CO\(_2\) and Ni atoms. Our results may provide useful insight into the mechanism of CO\(_2\) adsorption on graphene supported Ni adatoms/dopant and further study in heterogeneous catalysis of CO\(_2\) activation/reduction.

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