Reaction mechanism on Ni-C₂-NS single-atom catalysis for the efficient CO₂ reduction reaction

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ABSTRACT
Ni-based single-atom catalysis (Ni-SAC) has been experimentally reported with superior performance in reducing CO₂ to CO. However, due to the ambiguities in its structures, the active sites of Ni-SAC that are responsible for superior performance have not yet been resolved. This work investigates the CO₂ reduction reaction (CO₂RR) mechanism on Ni-SAC by carrying out quantum mechanics (QM) simulation to consider both solvation effects. After exploring multiple possible combinations of N, S, and C, we distinguish a Ni-SAC site with two C, one S, and one N, representing the best performance. The predicted formation energy is closely consistent with experimental onset potential. Our prediction also suggests further improvement by finely tuning the electronics state of metal sites by changing the SAC support.

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Introduction

CO₂, one of most notorious greenhouse gases, is one of the main causes of the increase of global average temperature, climate change, ocean acidification, and extreme weather. Since the industrial revolution, accelerated consumption of fossil fuels has resulted in excessive emission and accumulation of CO₂ in the atmosphere. In 2017, the global average concentration of carbon dioxide in the environment reached 405 ppm [1–3], and it would be reaching 600 ppm by the end of the century [4–6]. This will cause severe damage to the sustainable development of the earth’s ecological environment. So, how to efficiently reduce the content of carbon dioxide in the atmosphere and effectively utilize it has become an important research topic [7–9]. Different approaches have been proposed to address the CO₂ issue, such as increasing the efficiency of fossil fuel combustion, enhancing the physical capture and storage of carbon dioxide, and enhancing the conversion of carbon dioxide to valuable chemicals [10,11]. Among these solutions, electrochemical reduction of carbon dioxide is an effective and proven technology. It’s reducing carbon dioxide emissions and providing sustainable energy for society [12–14].

People widely study the electrocatalytic carbon dioxide reduction reaction (CO₂RR) due to electrocatalysis is a mature technology, and the reaction environment is mild and controllable. Carbon dioxide can be converted into different organic products through multi-electron transfer, such as carbon monoxide, methane, formic acid, and ethylene. Electrocatalysts are one of the crucial factors for determining the type of product. For example, gold (Au) and silver (Ag) can convert CO₂ to CO, HCOOH is the main product on tin and bismuth catalysts, copper is the only catalyst that can obtain multi-carbon products [15–19]. In recent years, with the development of two-dimensional materials, carbon-based single-atom catalysts (SAC) formed by combining transition metals and graphene have great potential in CO₂RR. Some SAC shows better selectivity and improved catalytic efficiency [20–22]. For example, a single atom catalyst that Ni-atom bonded with three or four nitrogen atoms (Ni-SAC) has high selectivity for carbon monoxide. The Faraday efficiency is close to that of gold. It has a very high carbon dioxide reduction activity [22–26].

Ni atoms can combine with three or four nitrogen atoms, and the environment of center metal atoms greatly influences CO₂RR. Wang et al. and Li et al. study the reaction energy and the intermediates of the structure that is Ni with different combinations of carbon and nitrogen atoms and find that the energy barrier of the intermediate *COOH (the key intermediate of CO₂R) increase with more nitrogen atoms combines with Ni, but the desorption of CO become much more accessible [27,28]. Zhao et al. used the solvation model to study nickel catalysts with different coordination further. They found that the structure with only one nitrogen and three carbon atoms coordination showed the highest activity and selectivity [29]. Yang et al. synthesized SAC catalyst with S atom doping, Ni-N₃S, which further improved the selectivity (FE > 97%) of CO₂ reduced to CO. But their DFT results show that the formation energy of *COOH is very high (at least higher than 1.7 eV) indicated that the site was not active [30].

This work will explore the relationship between the structure of SAC sites and the CO₂R performance. The atomic-based theoretical calculation has the advantage of investigating the reaction mechanism and distinguishing the active sites. The insufficient consideration of the solvation effect might also contribute to the overestimation. The solvation effect has been proved crucial in reliable predictions, which is also very challenging in DFT calculations [31,32]. In this work, the solvation effect and voltage effect are fully considered in the calculation of DFT. To find the definite catalytic site, we studied SAC sites with different sulfur doping through the simulation method. Meanwhile, we try to
answer the questions, such as if the catalytic performance can be improved, what the specific catalytic structure is.

**Method**

All of the calculations were first performed with the Vienna ab initio simulation package (VASP 5.4.4) [33–35], using generalized gradient approximation (GGA-PBE) [36] to describe exchange-correlation energy and the projector augmented wave (PAW) method [37] to account for electron-ion interactions. Meanwhile, van der Waals (vdW) interactions were taken into account using the DFT-D3 method [38–40]. The kinetic energy cut-off for plane wave expansions was set to 480 eV, and the gamma-centered k-mesh sampled the reciprocal space with a grid of $3 \times 3 \times 1$. And using an implicit solvation model makes the calculated reaction conditions closer to the actual situation of the experiment [41]. The implicit solvation model of VASPsol is employed to describe the effect of electrostatics, cavitation, and dispersion on the interaction between a solute and solvent. The relative permittivity of the solvent is 78.4. The debye screening length is 3.0 Å [42,43]. In structure optimizing, the atoms were relaxed until the maximum residual force and energy went below the threshold value of 0.01 eV Å$^{-1}$ and $10^{-6}$ eV. The model is based on Ni-C$_2$N$_2$, in which a sulfur atom is doped to replace any nitrogen atom to form a Ni-C$_2$-NS structure. The PBE-optimized lattice parameter 14.816 Å and the vacuum layers of at least 15 Å, the slab sizes are 6 × 6 or 4 × 4, depending on the number of atoms in simulation for enough computational efficiency. The optimized structures are shown in Figure S1.

The convergence criteria are $10^{-5}$ eV energy differences for solving for local minima (initial states (IS) and final states (FS)) searching transient state (TS). All IS, TS, and FS geometries (atomics coordinates) are converged to within 0.02 eV Å$^{-1}$ for the maximal component of forces and the vacuum level at least up to 20 Å net of the water model. The TS search was conducted by using the climbing image nudged elastic band (CI-NEB) method [44] to generate initial guess geometries, followed by the dimer method [45] to converge to the saddle points.

Zero-point energies (ZPE) and enthalpy and entropy contributions to free energies at room temperature (298.15 K) were calculated from vibrational modes of surface species. Due to the explicit water molecules are not properly constrained by the hydrogen bonding network, and low-frequency modes can cause unphysically large entropy contributions. They were reset to a threshold value of 60 cm$^{-1}$. The Gibbs free energy of each intermediate in CO$_2$R (*COOH, *CO) is given by Equation (1):

$$G_{298.15} = E_{\text{DFT}} + \text{ZPE} - \text{TS}$$

$E_{\text{DFT}}$ is the energy of intermediates in each elementary step during CO$_2$R, and the adsorption entropy $S$ is obtained through frequency calculation and calculated only for the surface adsorbate. For the catalytic activity, the formation energies of critical elementary steps are calculated by Equation (2), Equation (3) under the CHE model (Computational Hydrogen Electrode), which was proposed by Norskov et al. [46].

$$\Delta G_{\text{sol,COOH}}^\text{sol} = G_{\text{sol,COOH}}^\text{sol} - G_{\text{sol,CO}_2}^\text{sol} - \frac{1}{2} G_{\text{H}_2} - G_{\text{sol}}^\text{sol}$$

$$\Delta G_{\text{sol,CO}}^\text{sol} = G_{\text{sol,CO}}^\text{sol} + G_{\text{H}_2O} - G_{\text{sol,COOH}}^\text{sol} - \frac{1}{2} G_{\text{H}_2}$$
**G**\textsuperscript{\texttext{sol}} means the Gibbs free energy is calculated under implicit solvation correction, * means the surface without adsorbate. Equation (2) and equation (3) show the formation energy of the *COOH (potential determined step, PDS) and *CO. For the stability of the Ni atom in Ni-SAC, we calculated the binding energy for the Ni atom in Equation (4).

\[
\text{BE}(\text{Ni}) = E_{(\text{Ni}-\text{C}_2-\text{NS})} - E_{\text{C}_2-\text{NS}}(\text{energy without center Ni atoms)} - E_{(\text{Ni})}(\text{energy of a single Ni atom})
\]

In Equation (4), \(E_{(\text{Ni}-\text{C}_2-\text{NS})}\) is the total energy for the surface \(E_{\text{C}_2-\text{NS}}\) is the surface energy without center Ni atoms. \(E_{(\text{Ni})}\) is the energy of a single Ni atom.

**Result and discussion**

**Advantage of implicit solvation**

In the experimental research of Yang et al., they show Ni-atom is the main catalytic atoms and three steps that can take place on Ni-SAC: (1) \(* + \text{CO}_2 + \text{H}^+ + e^- \rightarrow \text{COOH}\), referred to as the *COOH formation step; (2) \(*\text{COOH} + \text{H}^+ + e^- \rightarrow \text{COOH}\), referred to as the *CO formation step; and (3) \(*\text{CO} \rightarrow * + \text{CO}\), referred to as the CO desorption step. The first two steps are electrochemical, while the last is a thermal step. However, the formation energy of *COOH obtained by their vacuum calculation is very high, indicating that CO2R is difficult to occur.

Considering the implicit solvation correction, we repeat the reaction mechanism of CO2R on the two structures of Ni-N4 and Ni-N3-S in Yang’s work. The optimized geometries of the reactive intermediates are shown Figure 1(a–h), and the free energy profile is in Figure 1(i). According to the DFT results, the implicit solvation correction can better describe the whole reaction process. Firstly, implicit solvation correction significantly reduces the formation energy of the PDS, *COOH on both active sites (at least reduce 0.25 eV). Secondly, the result shows the desorption energy of CO on Ni-N3-S reduces by 0.168 eV, which indicates that CO is easier to desorb. However, the formation energy of *COOH remained high under the solvation model, each of the active sites at least higher than 1.5 eV. This indicates that reducing carbon dioxide to carbon monoxide is difficult to occur at these two catalytic sites, which is not consistent with the observed phenomenon. Therefore, we believe that Ni-N3-S is unlikely to be the active site in sulfur-doped Ni-SAC.

![Figure 1](image-url)

Figure 1. a) and b) are the top view of the Ni-N4 catalyze site, c) and d) are the side view of the Ni-N4 catalyze site. e) and f) are the top view of the Ni-N3-S catalyze site, g) and h) are the side view of the Ni-N3-S catalyze site. The grey, red, yellow, white, and light blue atoms represent C, O, S, H, and Ni. i) is the CO2 to CO reaction on the N3-S (blue line) and N4 (black line) site. The red line and pink data indicate the structure under the solvation model on Ni-N4 and Ni-C3-S site.
Therefore, we first searched for possible sites of sulfur-doped Ni-SAC. As shown in Figure S6, the formation energy of *COOH is the PDS, which is 0.717 eV on Ni-N2-S2 and 1.257 eV on Ni-N2-S3. Instead, the PDS on Ni-C2-NS is only 0.461 eV. Thus, one S already reaches the best performance, while adding more S has no further improvements. Meanwhile, more S severely worsen the stability as shown in Table S1. Depending on two references, one is the formation of *COOH, which is the PDS of the whole reaction process and refers to the overpotential of the entire reaction process. The other is the desorption energy of CO. Combined with these two points, we screened out the catalytic sites of different combinations of carbon and nitrogen atoms connected to nickel. The calculated *COOH formation energy and CO desorption energy is shown in Figure 2(a), and the optimized geometries are shown in Figure 2(b–g). It can be seen from Figure 2(a) that nitrogen and sulfur atoms have a significant influence on the whole catalytic reaction. According to Ni-N4 and Ni-N3-S, the doping of sulfur atoms dramatically reduces the formation energy of *COOH. The doping of nitrogen atoms promotes the formation of *COOH through the reaction at the two catalytic sites of Ni-C3-S and Ni-C2-NS, which is also conducive to the desorption of CO. In the whole reaction, the formation energy of PDS in Ni-C2-NS is the lowest, which is most conducive to the reaction. Therefore, the DFT calculation indicates that Ni-C2-NS is a possible catalytic site.

**CO2R on Ni-C2-NS**

The DFT calculation in vacuum indicates that CO2 is weakly physisorbed, which can not explain the experimentally observed chemisorbed CO2. With consideration of applied voltage and solvation, we find the chemisorbed CO2 on Ni-C2-NS from DFT calculations. The free energy profile of CO2 reduction on Ni-C2-NS site is shown in Figure 3(a). The DFT calculation indicates that there exists the *COO intermediate in CO2R in the *COOH formation step, which can divide into two steps: (1) *e− + CO2 → *COO−, *e− is one election on the surface. This step refers to the chemisorbed CO2 on the one negative charge surface with implicit solvation correction. The optimized geometries are
shown in Figure 3(b). CO$_2$ was from the physical adsorption change to chemical adsorption due to the bond for linear CO$_2$ was bend and the angle of bonding up to 142.08°. The distance for Ni to CO$_2$ decreases 1.13 Å from physisorbed CO$_2$ (3.283 Å) to chemisorbed CO$_2$ (2.105 Å). The geometries are shown in Figure S2. The barrier for this process only 0.516 eV. (2) *COO$^-$ + H$^+$ + e$^-$ → *COOH$^-$, this is the *COOH formation step. This process was in acid condition. As shown in Figure S3, four H$_2$O atoms and one H$_3$O$^+$ were added. The hydrogen which in H$_3$O$^+$ transfer to *COO to form *COOH indirectly. The barrier in this step is 0.376 eV. In the last step, the hydrogen from H$_3$O$^+$ direct transfer to COOH to form CO and H$_2$O.

**Stability of Ni-C$_2$-NS active site**

In electrochemical reactions, the stability of a single atom catalyst is essential because it can lead to the destruction of the active site after many cycles. In the Ni-C$_2$-NS catalyst, Ni is the main active site as indicated from the PDOS shown in Figure 4(a). The binding energy of Ni with the surrounding atoms is −3.54 eV, which is higher than that of Ni in Ni-N$_4$ (shown in Figure S4). This indicates that Ni atoms are relatively stable in catalysis. In Figure 4(b), Ni in the Ni-C$_2$-NS catalyst shows a stronger interaction with the...
surrounding atoms due to the high peak overlap of Ni bonding atoms compare with Ni-N_3-S (PDOS in Figure S5), which also proved the stability of the Ni site.

**The application of M_x-C2-NS catalytic sites**

To expand its application, we have calculated the CO_2R of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Mo, Pd, Rh, Ru, Au, Ir, Pt, W transition metal atoms at this site. There are two important factors: the *COOH formation and the other is the desorption of *CO. As shown in Figure 5, Ti and Cd metal represents improved performance because the *COOH formation energy is lower and *CO desorption is easier than those of Ni.
energy of $^1$COOH. Still, they have a high CO desorption energy (higher than 1.02 eV). This type of catalyst is likely to get depth products in CO$_2$RR, such as HCOOH.

**Conclusion**

In this work, we studied the catalytic reaction of CO$_2$ on sulfur-doped SAC using the DFT method. Solvation is fully considered in our calculation. Our calculation method can completely repeat the results of explicit water molecule calculation, verifying the reliability of our theoretical calculation. We scanned for a variety of possible SAC sites. Different from previous studies, we found that Ni-C$_2$-NS was the active site. The onset potential predicted by theoretical calculation was 0.67 eV, which was highly consistent with the experimental results. Our work provides a theoretical basis for designing better catalyst structures in the future.

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**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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