Density Functional Study on the Formation of Sulfur-doped Configuration on the Active Site of Pyrolyzed Fe/N/C Catalyst

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Abstract. We study the formation of sulphur-doped configuration on the graphitic active site of pyrolyzed Fe/N/C catalyst by means of density functional theory (DFT) calculations. The active site of pyrolyzed Fe/N/C catalyst is modelled by graphitic-FeN₄ structure. The most stable S-doped configuration is found when an S atom is directly bonded to one of N atom of the FeN₄ site. Unfortunately, our calculation results indicate that the formation of S-doped configuration on graphitic FeN₄ structure is energetically unfavourable. The incorporation of S-doping in the graphitic-FeN₄ system induces strong geometrical reconstructions that breaks the planarity of the original structure.

1. Introduction

One of the major obstacle in the commercialization of hydrogen fuel cell-based technology is the intensive usage of scarce platinum (Pt) metal as the main material for cathode catalyst. Platinum metal is used as the cathode catalyst because of its good ability in catalyzing the notoriously slow and complex oxygen reduction reaction (ORR) in the cathode side of hydrogen fuel cell. One of the possible solution for this commercialization problem is by substituting Pt in the cathode of hydrogen fuel cell with a significantly cheaper catalyst. Pyrolyzed Fe/N/C catalyst is a non-precious metal catalyst (NPMC) which is known for having good ORR activity and stability. However, the best ORR activity of this kind of catalyst is still about ~1/13 of the Pt-based catalyst [1-3]. Therefore, we need more efforts to improve the ORR activity of Pyrolyzed Fe/N/C catalyst.

In our previous study, we reported on the effect of interaction between neighboring FeN₄ site with C₂N site of pyrolyzed Fe/N/C catalyst [4]. We found that such interaction improve the ORR activity of the C₂N site. We also tried to doped the graphitic active sites of pyrolyzed Fe/N/C catalyst with a boron (B) atom [5]. We found that the presence of B-doped site next to the FeN₄ site could promote O₂ side-on adsorption configuration on the FeN₄ that significantly facilitates the O-O bond dissociation process [5]. Those studies demonstrate that the interaction among the active sites of pyrolyzed Fe/N/C are very important and should not be neglected.

In recent years, several studies show that ORR activity of some graphitic-based catalysts can be enhanced by incorporating sulphur doping into the catalyst structure [6-9]. This study motivates us to...
introduce S-doped to the active site of pyrolyzed Fe/N/C catalyst, since this catalyst also possess a graphitic structure. The main active site of pyrolyzed Fe/N/C catalyst is the graphitic-FeN$_4$ configuration. We expect that the S-doped site might interact directly with the FeN$_4$ site like the one in the B-doped system [5]. The interaction between FeN$_4$ site with S-doped site might result in the enhancement of the ORR activity of pyrolyzed Fe/N/C catalyst.

As an initial study, we try to simulate the formation of S-doped configuration on graphitic-FeN$_4$ system using density functional theory-based calculations. We look for S-doped configuration that has the smallest formation energy. From this calculation we can obtain insights whether the formation of such S-doped-graphitic-FeN$_4$ configuration is realistic or not.

2. Computational Details
In this work, we investigate the possibility for the formation of S-doped configuration on graphitic-FeN$_4$ system using density functional theory (DFT) calculations [10,11]. Spin-polarized calculations were performed using Quantum-Espresso package [12]. Exchange and correlation effects were incorporated within the generalized gradient approximation, using the Perdew-Burke-Ernzerhof (PBE) functional [13]. Kohn-Sham eigenfunctions were expanded on plane-waves basis sets where the interaction between the valence electrons and ion cores are described by ultrasoft pseudopotentials [14]. Converged results have been achieved by using cutoff energies of 30 Ry on the plane wave and of 360 Ry on the electronic density. The integration in Brillouin-zone is done on 2x2x1 k-points grid sampled by Monkhorst-Pack scheme [15]. All atomic components were fully relaxed with force tolerance of 0.05 eV/Å. The effect of van der Waals interactions is described using the semi-empirical correction scheme of Grimme, DFT-D2 [16]. Calculation for isolated molecule is done at the gamma point in a 30x30x30 Å$^3$ cubic cell.

We use graphitic FeN$_4$ configuration to represent the main active site structure of pyrolyzes Fe/N/C catalyst. This active site configuration is known to be stable and active toward O$_2$ molecule. We use a layer of 6x6 graphene which is embedded with a FeN4 site as the supercell model. We add vacuum region of 15 Å in the direction perpendicular to the surface to prevent the interaction between neighboring layers due to periodic boundary condition.

![Figure 1](image.png)

Figure 1. Model for S-doped graphitic FeN$_4$ surface. The position of some S-doped sites those have relatively low total energies (as compared to all possible C-substituted sites) are labeled by S1-S7.

To model the S-doped configuration, we substitute a C atom in the unit cell with an S atom. We compare the relative energies of several possible S-doped locations (the doping position is labeled by S1-S7 in Fig. 1) in order to find the most stable S-doped configuration. To get further insight about the stability of the S-doped configuration, we calculate the formation energy of the system using the following formula:

$$E_{\text{formation}} = E_{\text{structure}} - (n_c \mu_c + n_{Fe} \mu_{Fe} + 4n_N \mu_N + \mu_S).$$
The negative value of $E_{\text{Formation}}$ indicates that the proposed configuration might be formed in real experiment while positive value suggests that the formation of the structure is going to be difficult. $E_{\text{Structure}}$ is the total calculated energy of the system. $n_c$ is the number of C atoms in the unit cell. $\mu_C$ is the chemical potential of C atom defined as energy per C atom in a perfect graphene. $\mu_{\text{Fe}}$ is the chemical potential of Fe according to the energy per Fe atom in bcc iron. $\mu_N$ is the chemical potential of N atom which is taken from half of total energy of an isolated N$_2$ molecule. $\mu_S$ is the chemical potential of S atom defined as energy per S atom in a bulk sulphur crystal.

### 3. Results and Discussion

The calculated formation energies for S-doped configuration are presented in Table 1. These seven S-doped configurations have the lowest total energies as compared to the other possible S-doped configurations (not shown in the Fig. 1). From these data, we can see that the formation energies of S-doped configurations are quite high. The large positive value indicates that the formation of S-doped configuration on graphitic-FeN$_4$ structure is energetically infeasible.

**Table 1.** Calculated formation energies of S-doped configurations in Fig. 1.

| S-doped Location | $E_{\text{Formation}}$ (eV) |
|------------------|------------------------------|
| S1               | 3.78                         |
| S2               | 3.81                         |
| S3               | 3.77                         |
| S4               | 3.80                         |
| S5               | 3.27                         |
| S6               | 3.80                         |
| S7               | 3.50                         |

![Figure 2](image1.png)

**Figure 2.** The most stable configuration of S-doped configuration on graphitic FeN$_4$ structure. Top-view (a) and side-view (b).

The most stable S-doped configuration (the lowest formation energy: S7) is shown in Fig. 2. The S atom is directly bonded with an N atom of the FeN$_4$ site. The incorporation of S atom in the graphitic FeN$_4$ structure distorts the planarity of the initial structure quite significantly. The distortion occurs not only in the most stable structure but also in all S-doped configurations. Such geometrical distortion contributes to the increase of the total energy of the system which of course also lowering the stability of the system. The condition is very similar with the one in S-doped graphene [7]. Moreover, the formation energy on S-doped site in a perfect graphene sheet is also quite high. Therefore, the interaction of S atom with the FeN4 site like in our system does not significantly modify the nature of S-doped configuration in graphitic structure.
4. Summary
We report on a theoretical study of formation of S-doped configuration on graphitic-FeN\textsubscript{4} system using density functional theory-based calculations. The most stable S-doped configuration is found when an S atom is directly bonded to one of N atom of the FeN\textsubscript{4} site. Unfortunately, we find that the formation of S-doped configuration on graphitic FeN\textsubscript{4} structure is energetically very unfavorable. The incorporation of S-doping in the graphitic-FeN\textsubscript{4} system induces a distortion that breaks the planarity of the original structure. This distortion reduces the stability of the system.

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