Density Functional Theory Calculation of Electronic Structure of Fe-N-C, Fe-O-C, Fe-P-C, Fe-S-C Single-atom Catalysts Systems

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Abstract—Single atom catalysts (SACs) have emerged as a novel class of heterogeneous catalysts which exhibit superior catalytic performance in various reactions, CO oxidation, CO2 conversion, oxygen reduction reaction (ORR), etc. It is challenging to explore electronic structure and catalytic mechanics of SACs when the single metal atom is bonding with different dopants via experimental methods, which influence the catalytic efficiency directly. In this paper, Density Functional Theory (DFT) calculations, an ab initio simulation methods, have been carried out to investigate the properties of Fe-N-C, Fe-O-C, Fe-P-C, and Fe-S-C with oxo or hydroxyl group, four common SACs models. Geometry structure of Fe-N-C, Fe-O-C, Fe-P-C, Fe-S-C, and after each has bonded with oxo or hydroxyl group are studied. Formation energy of the Single Atom Catalyst (SAC), oxygen formation energy, and hydrogen atom transfer energy of the four SACs models are also calculated. In order to investigate the electronic structure of the four SACs, we examined the HOMO LUMO gap values for each system. In addition, we plotted the corresponding HOMO and LUMO orbitals of each SACs models and with oxo or hydroxyl group. Through analyzing the data, I anticipated that Fe-N-C model is the easiest to synthesis and the most stable among the four models. Our work discloses the microscopic property of SACs and provides valuable suggestions to experimental scientists.

1. Introduction
Both academia and industry need high-performance heterogeneous catalysts with superior activity, selectivity, and stability. Conventional heterogeneous catalysts are subject to limited dispersion. Single atom catalyst (SAC) is an emerging class of catalyst that is able to incorporate the scalability and high dispersion [1]. Graphene is an ideal two-dimensional (2D) catalyst support because of its large surface area which allows it to have novel physical and chemical properties [2]. Metal species in SACs are all downsized into nanoparticles and are located dispersedly on a solid support, which increases the catalytic efficiency for the more exposed unsaturated reactive sites [3]. Since SACs is highly active, selective, and can be applied to various purposes, SACs has become a research hotspot in various fields such as energy and environmental protection [4]. Additionally, previous researches have shown that SACs are highly catalytically active in reactions such as CO oxidation, CO2 reduction, CH4 activation, and oxygen reduction reaction (ORR).

Typically, the metal atom in the SACs is anchored to the N sites of C framework [5]. N is an ideal heteroatom dopant because its atomic radii is similar to that of for C atom and its notable electronegativity difference comparing with C atom. In general, there are three types of configurations for the N atoms doped in the graphene lattice: graphitic, pyridinic (two C-N bonds in a hexagon), and pyrrolic (two C-N bonds in a pentagon) [6]. Different from pyridinic N, pyrrolic N has an increased
electron density on N-C sites because it has a pair of electrons in the unhybridized pz orbital [7]. Both experimental and DFT calculation have proved that pyridinic N is a more ideal doping type than graphitic or pyrrolic N because of its weaker binding energy [8]. Additionally, when trapping metal atoms, for example Fe, pyridinic N will generally have higher chemical reactivity due to its distinct charge distribution [9]. Also, pyridinic N is able to stabilize the metal center, and the activity of the catalyst will increase remarkably after adding the single metal atom.

Dodelet’s group has designed a catalyst that has Fe doping with pyridinic N in the interstices of C sheet within the micropores [11]. This design has greatly increased the catalytic activity of Fe-N-C in ORR, and has narrowed the gap between commercial Pt/C and non-metal catalysts [10]. Although there have been a lot of improvements on Fe-N-C, such as optimizing the selection of precursors for Fe and modify the pyrolysis process, the gap between Fe-N-C and commercial Pt/c regarding of durability and catalytic activity still remains [11].

Changing the electronic structures of the active sites can also slightly tune the electrocatalytic activity of the SAC. Particularly, doping atoms such as O, S, P in the metal center can create different atomic structures for the SAC [12]. However, it is difficult to illuminate the catalytic performance of different doping atoms only by time-consuming experiments. Herein, we studied four different models of single atom catalysts, Fe-N-C, Fe-O-C, Fe-P-C, and Fe-S-C, having nitrogen, oxygen, phosphorous, and sulfur coordinate with iron (II) via density functional theory. OXO and hydroxyl are introduced as two chemical groups, and were bonded to the four SACs models. Our simulation can screen all the systems efficiently and gives guidance to experiment researchers.

2. Computational Method
In this work, SACs, SACs-oxo and SACs-hydroxyl with N, O, P and S dopants were considered. All the geometry optimizations were carried out with DFT method [13] using the ωPBEh/lacvps_ecp [14] as basis set in ORCA v.4.0 [15]. Constrained calculations (constrain the axis of the flake without Fe metal) were carried out in order to investigate the SACs models with planar structure.

\[
\Delta E_{\text{formation energy}} = E_{\text{SACs}} - E_{\text{Flake}} - E_{\text{Fe(+2)}}
\]

(1)

\[
\Delta E_{\text{oxygen formation energy}} = E_{\text{SACs}=O} - E_{\text{SACs}} + E_{\text{(N2)}} - E_{\text{(N2O)}}
\]

(2)

\[
\Delta E_{\text{hydrogen atom transfer energy}} = E_{\text{(SACs-OH)}} - E_{\text{(SACs=0)}} + E_{\text{(CH3*)}} - E_{\text{(CH4)}}
\]

(3)

To discuss formation energy of the SACs, \(E_{\text{SACs}}, E_{\text{Flake}}, \) and \(E_{\text{Fe(+2)}}\) are introduced, where \(E_{\text{SACs}}\) is the total energy of single atom catalysts, \(E_{\text{Flake}}\) is the total energy of the pristine flake, \(E_{\text{Fe(+2)}}\) is the energy of Iron (II) in gas phase condition. The formation energy of oxygen is calculated using formula (2): \(E_{\text{SACs}=O}\) is the energy of SACs bonded with oxygen, \(E_{\text{SACs}}\) is the energy of SACs, \(E_{\text{(N2)}}\) is the energy of nitrogen, and \(E_{\text{(N2O)}}\) is the energy of nitrous oxide. Calculation process for the energy of hydrogen atom transfer is shown in formula (3): where \(E_{\text{(SACs-OH)}}\) is the energy of SACs bonded with hydroxyl, \(E_{\text{(CH3*)}}\) is the energy of methyl, \(E_{\text{(SACs=O)}}\) is the energy of SACs bonded with oxygen, and \(E_{\text{(CH4)}}\) is the energy of methane.

3. Test Results and Discussions
In Figure 1, (a), (b), (c), and (d) show the configuration for Fe-N-C, Fe-O-C, Fe-P-C, and Fe-S-C systems. All the four SACs keep relative planar structure after constrained the frame geometry optimization (Fe atom and the flake are nearly in the same plane). The second and third row shows the top and side configuration of the SACs models bonding with oxo and hydroxyl functional groups. Different from first row, Fe atoms in (e)-(i) obviously remain out of the plane of the flake. Notably, in (f), (j), and (i), Fe-OXO and Fe-hydroxyl are not bonding with the 4 coordinated atoms in flake, which will be discussed with detail later.
Fig. 1 Optimized atomic structure of Fe-N-C, Fe-O-C, Fe-P-C, Fe-S-C with corresponding OXO and hydroxyl functional groups. White, grey, blue, orange, red, cyan, and purple stands for H, C, N, Fe, O, P, and S atoms, respectively.

Table 1 Bond length of Fe-N-C, Fe-O-C, Fe-P-C, and Fe-S-C optimized at ωPBEh/lacvps_ecp theory level. Bond length of Fe-OXO and Fe-hydroxyl, and bond angles θ₁₂ (bond angle between dopant₁-Fe-dopant₂), θ₂₃ (bond angle between dopant₂-Fe-dopant₃) are in unit: Å and θ: °.

| System | Fe-dopant₁ | Fe-dopant₂ | Fe-dopant₃ | Fe-dopant₄ | Fe-OXO | Fe-hydroxyl | θ₁₂ | θ₂₃ |
|--------|------------|------------|------------|------------|--------|-------------|-----|-----|
| Fe-N-C | 1.845      | 1.846      | 1.943      | 1.943      | 1.614  | 1.863       | 86.739 | 93.241 |
| Fe-O-C | 1.961      | 1.943      | 1.838      | 1.928      | 1.590  | 1.753       | 86.303 | 93.673 |
| Fe-P-C | 1.941      | 1.941      | 1.941      | 1.941      | 1.614  | 1.797       | 88.246 | 91.752 |
| Fe-S-C | 1.965      | 1.964      | 1.946      | 1.946      | 1.595  | 1.767       | 87.576 | 92.074 |

For Fe-N-C and Fe-S-C systems, the bond length of Fe-dopant₁ and Fe-dopant₂, Fe-dopant₃ and Fe-dopant₄ are similar to each other. In Fe-O-C system, bond length of Fe-dopant₁, Fe-dopant₂ and Fe-dopant₄ are all greater than bond length of Fe-dopant₃. The bond length of Fe with each phosphorus dopants are almost the same. Although not mentioned in the table, bond lengths of Fe with the four dopants of SAC-OXO and SAC-hydroxyl systems (SAC= Fe-N-C, Fe-O-C, Fe-P-C, and Fe-S-C) are also investigated. Bond length of Fe-dopant₁, Fe-dopant₂, Fe-dopant₃, and Fe-dopant₄ in Fe-O-C bonded with O ion are 2.132Å, 2.832Å, 2.834Å, and 2.134 Å, respectively. In the same order, bond lengths between Fe ion and the four dopants in Fe-O-C bonded with hydroxyl are 2.474 Å, 2.521 Å, 2.532 Å, and 2.499 Å. These bond lengths suggest that Fe ion was not able to form a bonding with O dopants, because their bond lengths exceed 2.5 Å. Same problem happened in Fe-S-C bonded with O ion and hydroxyl. Bond length of Fe-dopant₁, Fe-dopant₂, Fe-dopant₃, and Fe-dopant₄ in Fe-S-C bonded with O
ion are 2.550 Å, 2.251Å, 2.359Å, and 2.842Å. The four bond lengths in Fe-S-C bonded with hydroxyl are 2.516 Å, 2.533Å, 2.532Å, and 2.513Å. Notably, most bond lengths in Fe-S-C bonded with oxo and hydroxyl are greater than 2.5Å. Therefore, the bonding between the metal ion and S dopants are considered fail. In later discussions, Fe-O-C with OXO or hydroxyl group and Fe-S-C with OXO or hydroxyl group will be excluded, since their models are not meaningful. The bond lengths of Fe with oxo (Fe-OXO) in Fe-N-C and Fe-P-C are greater than that of in Fe-O-C and Fe-P-C. Bond lengths of Fe-OXO in Fe-O-C is 1.590Å, and is slightly less than that of in Fe-P-C. The bond length of Fe-hydroxyl in Fe-N-C is 1.863Å, and is the greatest among all four systems. Fe-P-C system has the second greatest Fe-hydroxyl bond length, and Fe-O-C system has the least Fe-hydroxyl bond length. Bond angles between dopant1-Fe-dopant2(θ12) and dopant2-Fe-dopant1(θ23) in Fe-N-C and Fe-O-C systems are close. θ12 has the greatest value in Fe-P-C system, and second greatest value in Fe-S-C. θ23 is larger in Fe-N-C and Fe-O-C, and smaller in Fe-P-C and Fe-S-C.

Table 2 Formation Energy of SACs, Oxygen Formation Energy, Hydrogen Atom Transfer Energy, and HOMO-LUMO Gap of the four systems (unit: eV)

| System | Formation Energy | Oxygen Formation Energy | Hydrogen Atom Transfer Energy | HOMO-LUMO gap |
|--------|------------------|-------------------------|------------------------------|---------------|
| Fe-N-C | -34.775          | -1.879                  | 1.401                        | 0.134         |
| Fe-O-C | -29.094          | -2.905                  | 0.423                        | 0.124         |
| Fe-P-C | -32.926          | -2.346                  | 1.514                        | 0.127         |
| Fe-S-C | -29.867          | -2.146                  | -0.522                       | 0.125         |

The formation energy of Fe-N-C system is found to be -34.775eV, which is the lowest among all four systems, showing that Fe-N-C is the most stable and the easiest to synthesis among all four catalysts. In contrast, Fe-O-C system is found to have the highest formation energy of the SAC, which suggests that it is the least stable catalyst in the four. Formation energy of Fe-P-C and Fe-S-C are the second and third lowest. As shown in Table 2, oxygen formation energy is also calculated. This energy describes the amount of energy adding the oxo group on to the Fe atom would require. Ranking the four systems by having the lowest oxygen formation energy to the highest, it would be from Fe-O-C, Fe-P-C, Fe-S-C, to Fe-N-C. Although Fe-O-C possesses the lowest oxygen formation energy, its metal center did not successfully bond with the OXO group, as shown in Figure 1, (f) and (j). To investigate the stability of the four SACs after bonding with hydroxyl, we calculated the hydrogen atom transfer energy, which describes the amount of energy required to remove the H atom from its present bonding with the SACs. The larger the hydrogen atom transfer energy is, the more energy is needed to break the O-H bond. As shown in Table 2., Fe-P-C is found to have the largest hydrogen atom transfer energy as 1.514 eV, and Fe-N-C has the second greatest hydrogen atom transfer energy as 1.401 eV, indicating that Fe-N-C and Fe-P-C are more preferable catalysts. It is worth noting that the hydrogen atom transfer energy for Fe-S-C and Fe-O-S are remarkably less than that of for Fe-N-C and Fe-P-C, which suggest that Fe-S-C and Fe-O-C are a lot easier to lose the H atom. HOMO and LUMO are two types of molecular orbital: HOMO stands for highest occupied molecular orbital, and LUMO stands for lowest unoccupied molecular orbital. Since HOMO and LUMO are the two orbitals closest in energy among all orbitals, the HOMO-LUMO gap is where excitation is most likely to occur in a system. The smaller the HOMO-LUMO gap is, the better the conductivity the system has; the greater the HOMO-LUMO gap is, the better performance as semiconductors the system is. The HOMO LUMO gap of Fe-N-C, Fe-O-C, Fe-P-C, Fe-S-C catalysts are estimated to be 0.134 eV, 0.124 eV, 0.127 eV, 0.125 eV. The relatively small values of HOMO-LUMO gap suggest that all four catalysts have comparatively strong conductivity. Based on the date of HOMO-LUMO gap in Table 2, the conductivity of the four systems should follow this order: Fe-O-C > Fe-S-C > Fe-P-C > Fe-N-C.
Figure 2 shows the HOMO (red) and LUMO (blue) electron distribution of Fe-N-C, Fe-O-C, Fe-P-C, Fe-S-C with corresponding OXO and hydroxyl. The positive and negative density of electron are shown in red and blue in the figure, respectively. The isosurface value of 0.02 was used for all the systems.

The density of electrons of Fe-N-C, Fe-O-C, Fe-P-C, Fe-S-C, and after bonded with oxo or hydroxyl are shown in Figure 2. Since the metal center did not successfully form a bond with the O or S dopants after OXO or hydroxyl was added in Fe-O-C and Fe-S-C, these four models are excluded from our discussion here, leaving eight models to investigate. The spatial distribution of HOMO and LUMO energy levels of those eight models are shown in Figure 2. We employed graphical representations because it is important to understand the properties and geometries of the HOMO and LUMO of each SAC model. From Fig.2 (a), it is clear that in Fe-N-C, the HOMO is localized in lower half of the system and the LUMO is localized in the upper half of the system. After bonding with the OXO group, the positively charged electrons in the HOMO of Fe-N-C OXO have increased notably, as shown in Fig2. (e). However, positively charged electrons in the HOMO of Fe-N-C hydroxyl have decreased significantly compared with that of in Fe-N-C OXO. It can also be observed in Fig2. (e) that the HOMO of Fe-N-C OXO is principally restricted on Fe and N. As shown in Fig.2 (b), the HOMO of Fe-O-C is mainly localized in the upper half of the system, and the LUMO of Fe-O-C is localized in the lower half of the system. HOMO and LUMO in Fe-S-C are mainly localized on the graphene nanoflake. Compare the HOMO of Fe-P-C and Fe-P-C OXO, it can be seen that the positive and negative density of electrons become centralized in the center after the OXO group is bonded to Fe-P-C, and HOMO is mainly localized in Fe in Fe-P-C OXO. In contrast, HOMO in Fe-P-C OXO is not as centralized as it is in Fe-P-C OXO. It can also be observed from Fig2. that both the HOMO and LUMO of Fe-N-C only have a vertical line of symmetry. However, after bonded with the OXO or hydroxyl group, the HOMO and LUMO of Fe-N-C start to have two lines of symmetry, one vertically and one horizontally, as shown in Fig2. (e) and (f). Besides Fe-N-C OXO and Fe-N-C hydroxyl, Fe-P-C, Fe-P-C OXO, and Fe-P-C hydroxyl models also are found to have two lines of symmetry, as shown in Fig2. (c), (g), and (h). In addition, we found out that there is a straight relation between the energy gap of HOMO-LUMO and the stability of the SAC. Based on the results from Table 2, we can rank the four system from having the lowest formation energy to highest formation energy and the order is: Fe-N-C < Fe-P-C < Fe-S-C < Fe-O-C. This shows a trend that the higher the energy gap of HOMO-LUMO is, the lower the formation energy is, and the more stable the system is.
4. Conclusion
In this work, we employed DFT calculations to investigate the properties of Fe-N-C, Fe-O-C, Fe-P-C, Fe-S-C, and each after bonded with oxo or hydroxyl group. Fe-N-C is found to have the lowest formation energy of the SAC, which suggests that it is the easiest to synthesis and most stable among the four models. Also, we found that Fe-N-C has the highest oxygen formation energy and Fe-O-C has the lowest oxygen formation energy. The collected data also shows that Fe-P-C has the highest hydrogen atom transfer energy, Fe-N-C has the second highest hydrogen atom transfer energy, and Fe-S-C has the lowest hydrogen atom transfer energy. Thus, we can conclude that Fe-N-C is a more preferable catalyst than Fe-O-C, Fe-P-C, or Fe-S-C from synthesis and energy perspectives. In addition, we found that Fe-N-C has the largest HOMO LUMO gap value among the four SAC models, which indicates that it might be a good candidate for semiconductors. Fe-S-C is found to have the lowest HOMO LUMO gap, which suggests that its conductivity is the best among the four SACs. Our simulation screens all the systems efficiently and give guidance to experiment researchers.

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