Structural Selectivity of CO Oxidation on Fe/N/C Catalysts

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ABSTRACT: Fe/N/C electrocatalysts are attractive for electrocatalytic applications in fuel cells due to their low cost and high electrocatalytic activity. Because of its complex nature, the mechanism of CO oxidation on Fe/N/C electrocatalysts remains largely unknown. Aiming to provide insight into the mechanism of CO oxidation, we have performed extensive density functional theory calculations for the elementary steps in CO oxidation on Fe/N/C active sites, including Fe-N4 and Fe-N3 porphyrin-like carbon nanotube (T-FeN4 and T-FeN3), Fe-N4 porphyrin-like graphene (G-FeN4), and Fe-N2 nanoribbon (R-FeN2). It is found that CO adsorption and oxidation are very sensitive to the active site structures. CO adsorption is energetically more favorable than O2, and CO oxidation to CO2 hardly occurs on T-FeN4 and G-FeN4. In comparison, O2 prefers to adsorb and CO can easily be oxidized on T-FeN3 and R-FeN2, suggesting the CO tolerant property of T-FeN3 and R-FeN2.

1. INTRODUCTION

As one of the most promising power sources, fuel cells have received considerable attention due to their high efficiency and low environmental impact. The slow kinetics of the oxygen reduction reaction (ORR) at cathodes is one of the key factors limiting the performance of fuel cells. To date, the best material for the catalysis of the ORR is the high cost Pt-based one.1,2 To drop the cost, numerous studies have been devoted to find alternative electrocatalysts for the cathode side of fuel cells, including Pt-based alloys,3,4 carbon nanotubes-supported metal particles,5 and nitrogen/boron/phosphor doped carbon nanotubes and graphenes.6–12

Among the most investigated non-platinum systems, Fe/N/C catalysts have shown encouraging catalytic activity, and species such as FeN2Cx and FeN4Cy have been proposed to form active sites for the ORR.13–18 Especially, Fe-porphyrin-like carbon nanotubes, which incorporate 5-6-5-6 porphyrinic Fe-N4 into the graphene hexagonal side wall, exhibit an excellent oxygen reduction catalytic activity, vastly superior to the commercial Pt-C catalysts.19

The belief that the Fe atom is at the heart of these non-noble metal electrocatalysts for ORR in acid medium has been widely accepted19,20 However, some researchers proposed that the Fe ion does not form part of the active site and only catalyzes the formation of a special type of carbon containing some particular nitrogen functionalities (the principal catalytic active sites for ORR). One argument often used by these researchers to support their claims of iron-free active sites is that their catalysts are free from CO poisoning. CO poisoning of most noble-metal electrodes is a major issue in the current fuel cell technology. Recently, Birry et al. found that Fe/N/C electrocatalysts can avoid CO poisoning.21 This is rather surprising considering the strong poisoning effect of CO on hemoglobin and myoglobin, for which the active hemes are Fe porphyrins.22 Thus, the CO adsorption and oxidation on Fe/N/C catalyst should be investigated from the atomistic point of view. Rational design and tuning of their catalytic properties require detailed information of the ORR active sites and their CO tolerant property. Many theoretical works have been carried out in the framework of density function theory (DFT) for the CO oxidation on carbon nanotubes (CNT) and graphene.23–27 However, most attention in these investigations has been paid to the reactions occurring at zero Kelvin, where the effects of temperature (T) on the process of CO oxidation were neglected and not fully understood. As an important thermodynamic parameter, T plays a significant role in chemical reactions and even changes reaction directions in extreme cases.

In this paper, the CO adsorption and oxidation on four different Fe/N/C active sites are studied based on DFT, including Fe-N4 porphyrin-like CNT (T-FeN4), Fe-N3 pyridine-like CNT (T-FeN3), Fe-N4 porphyrin-like graphene (G-FeN4), and Fe-N2 nanoribbon (R-FeN2), as shown in Figure 1. Our results provide a detailed mechanism for CO oxidation on four active sites. In addition, the effect of T on the CO oxidation process is also concluded. It is found that CO oxidation exhibits a structural selectivity. Although CO oxidation is very hard on T-FeN4 and G-FeN4, CO can easily be oxidized on T-FeN3 and R-FeN2.

2. COMPUTATIONAL METHODS

All calculations are performed within DFT framework as implemented in DMOl3 code.28,29 The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional is employed to describe exchange and correlation effects.30 The
all electron relativistic core treat method is implemented for relativistic effects, which explicitly includes all electrons and introduces some relativistic effects into the core.\textsuperscript{31} The double numerical atomic orbital augmented by a polarization function is chosen as the basis set.\textsuperscript{28} A smearing of 0.005 Ha (1 Ha = 27.21 eV) to the orbital occupation is applied to achieve accurate electronic convergence. To ensure high-quality results, the real-space global orbital cutoff radius is chosen as high as 4.6 Å in the computations. The minimum energy paths (MEPs) for CO oxidation are obtained by LST/QST tools in DMOL\textsuperscript{3} code, which has been well validated to find a transition-state structure.\textsuperscript{32–36} Free energy change ($\Delta G$) is calculated as $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where $\Delta E$ denotes the total energy change directly obtained from DFT calculations, $\Delta ZPE$ shows the change in zero-point energies, and $\Delta S$ is taken as the entropy change.

In calculations, the supercell models include three unit cells of (10, 0) tubes for T-FeN4 and T-FeN3. One-dimensional periodic boundary condition is applied along the tube axial direction to simulate the infinite CNTs. The orthorhombic supercell is constructed as $30 \times 30 \times 12.678$ Å\textsuperscript{3}. Such large cells are required to minimize the interaction between CNTs in adjacent cells. For G-FeN4, all simulations are performed in a 5 × 5 graphene supercell, which includes 49 atoms. At last, for R-FeN2, three unit cells of armchair graphene ribbon with a width of $N = 7$ are embedded in a supercell with periodic boundary conditions. The minimal distance between the graphene sheet/ribbon and its mirror images is set as 15 Å, which is sufficiently large to avoid the interaction between them. The adsorption energies ($E_{\text{ad}}$) of adsorbates on Fe/N/C catalysts are calculated through

$$E_{\text{ad}} = E_{\text{ads}} + E_{\text{Fe/N/C}} - E_{\text{ads}/Fe/N/C}}$$ \hspace{1cm} (1)

where $E_{\text{ads}}$, $E_{\text{Fe/N/C}}$ and $E_{\text{ads}/Fe/N/C}}$ are the total energies of an isolated adsorbate molecule, the Fe/N/C catalysts, and the adsorption systems, respectively. By these definitions, positive $E_{\text{ad}}$ values correspond to exothermic adsorption processes.

### 3. RESULTS AND DISCUSSION

Before investigating CO oxidation reactions, we first studied the adsorption properties of O\textsubscript{2} and CO on four active sites for T-FeN4, T-FeN3, G-FeN4, and R-FeN2, which are summarized in Table 1 and Figure 2. It is found that the most energetically favorable configurations of O\textsubscript{2} on T-FeN3 and R-FeN2 are characterized by O\textsubscript{2} parallel to the CNT surface forming two chemical bonds with the Fe atom (side-on). The corresponding $E_{\text{ad}}$ values are 2.45 and 3.43 eV, respectively. O\textsubscript{2} prefers to adsorb on T-FeN4 and G-FeN4 with end-on configuration where $E_{\text{ad}}$ values are 1.13 and 0.98 eV, respectively. This is consistent with O\textsubscript{2} adsorption on metal phthalocyanine.\textsuperscript{39} The O–O bond length of the adsorbed O\textsubscript{2} on T-FeN4 and G-FeN4 are almost the same as that of the isolated gas O\textsubscript{2}, while O\textsubscript{2} on T-FeN3 and R-FeN2 are elongated nearly 0.17 Å due to the electronic charge transfer from Fe to O\textsubscript{2}-2π* orbital. As shown in Table 1, the coordination number (CN) of Fe atom increases from 2 of R-FeN2 to 4 of T-FeN3 and G-FeN4, $E_{\text{ad}}$ value of O\textsubscript{2} decreases from 3.43 eV on R-FeN2 to 0.98 eV on G-FeN4. This corresponds to the Hirshfeld population charge distribution of O\textsubscript{2} adsorption on Fe/N/C. There are only 0.15 and 0.17 charge transfer from the Fe atom to O\textsubscript{2} at T-FeN4 and G-FeN4, while the value increases to 0.28 and 0.31 e at T-FeN3 and R-FeN2, respectively. The end-on configuration is the most energetically favorable adsorption structure for CO adsorbed on T-FeN3, T-FeN4, G-FeN4, and R-FeN2 with $E_{\text{ad}}$ values of 1.79, 1.78, 1.73, and 2.28 eV, respectively. The C–O bond length increases slightly by 0.02 Å after adsorption. The charge transfer from the Fe atom to CO are quantified as 0.01, 0.01, 0.05, and 0.13 e at T-FeN4, G-FeN4, T-FeN3, and R-FeN2 according to the Hirshfeld population charge distribution.

The above results reveal that Fe/N/C catalysts have strong interactions with O\textsubscript{2} and CO. $E_{\text{ad}}$ values of O\textsubscript{2} are larger than that of CO on T-FeN3 and R-FeN2, suggesting that Fe in T-FeN3 and R-FeN2 will be dominantly covered by the adsorbed O\textsubscript{2} if the CO/O\textsubscript{2} mixture is injected as the reaction gas. However, CO adsorption is more favorable than O\textsubscript{2} on T-FeN4 and G-FeN4, indicating that T-FeN4 and G-FeN4 may be poisoned by CO if it cannot be removed by oxidation.

In order to gain further insight into the origin of the interaction between adsorbates and Fe/N/C active sites, the electronic structures of the above substances are considered. Figures 3 and 4 illustrate the spin-polarized partial density of states (PDOS) projected onto the O–O and C–O bonds, as well as the d-projected PDOS of Fe in Fe/N/C active sites. Fe-s and Fe-p are not shown here because the interaction between them and O\textsubscript{2} is really weak. As shown in Figure 3, the dominating contributions for O\textsubscript{2} adsorption on T-FeN4 and G-FeN4 are the interactions between O\textsubscript{2}-2π* and Fe-3d orbitals, while the interactions between O\textsubscript{2}-1π and Fe-3d as well as O\textsubscript{2}-σ and Fe-3d are pretty weak. O\textsubscript{2}-4σ* is not involved in the
interaction due to its position far below the Fermi level. By contrast, Fe-3d orbitals of T-FeN3 are broadened due to the interaction with O2. Not only O2-2\pi^*, but also O2-1\pi, O2-5\sigma, and O2-4\sigma^*, interact with Fe-3d. Thus, adsorption of O2 on T-FeN3 is stronger than that on T-FeN4 and G-FeN4. At the same time, O2-2\pi^* on T-FeN4 and G-FeN4 and in gas phase is half-filled, while that on T-FeN3 becomes nearly all occupied, which can enhance the Fe-O bond and weaken the O-O bond. The spin-polarized Fe-3d orbitals and molecular orbitals of O2 dominate the magnetic moment of the system and enhance the adsorption of O2 on R-FeN2, resulting in the most stable adsorption of O2 at four sites. Fe atoms with lower CN have higher lying 3d states, which interact with the adsorbate states more strongly.

From the PDOS for the CO adsorbed on Fe/N/C in Figure 4, one can see that the CO interact with Fe chiefly through hybridization between CO-5\sigma and Fe-3d, also CO-2\pi^* and Fe-3d. The renowned mechanism of CO-metal interaction, namely, via donation from CO-5\sigma to metals and back-donation from metals to CO-2\pi^*, seems still to be applicable for CO adsorbed on Fe/N/C. This is confirmed by the fact of electron depletion at CO-5\sigma and partially occupied CO-2\pi^*, which is empty above the Fermi level in gas CO. Since the E_ad value of CO on Fe/N/C is not only related to the electron donation from CO-5\sigma to metals but also to electron back-
donation from metals to CO-2π*, our $E_{ad}$ values of CO on Fe/N/C are analogous. This differs from O$_2$ adsorption, where the more the charge transfer from Fe to O$_2$, the larger the $E_{ad}$ value is. This may be the reason why as CN of Fe decreases from 4 of T-FeN4 and G-FeN4 to 2 of R-FeN2, CO adsorption varies from energy favorable on T-FeN4 and G-FeN4 to energy unfavorable on T-FeN3 and R-FeN2 in comparison with that of O$_2$.

Generally, there are two well-established mechanisms for CO oxidation, namely, the Eley–Rideal (ER) mechanism and Langmuir–Hinshelwood (LH) mechanism.$^{43-51}$ In the former, CO molecules directly react with activated O$_2$, i.e., adsorbed atomic O, where the activation of O$_2$ is the rate-limiting step (RDS).$^{43}$ For the latter, coadsorbed CO and O$_2$ react to form a peroxo-type complex intermediate, which is the RDS.$^{43}$

On the basis of the adsorption results, for CO oxidation on T-FeN4 and G-FeN4, the LH reaction of CO + O$_2$ → OOCO + CO$_2$ + O is considered as a starting point, followed by the ER reaction CO + O → CO$_2$. Because the reaction pathways for CO + O$_2$ on the two active sites are very similar, here we only discuss the one on T-FeN4. The geometrical structures for CO oxidation are presented in Figure 5, and the corresponding MEP profiles are displayed in Figure 6. At the initial state, the CO adsorbs at the atop site of Fe, and O$_2$ is in the gas phase (we did locate an O$_2$ coadsorbed on FeN4 but the $E_{ad}$ is too small to adsorb). Then, O$_2$ approaches CO at the reaction site, reaching the first transition state (TS1), where O$_2$ is bonded with C of CO, imposing an activation energy ($E_a$) of 0.64 eV along the reaction pathway. Passing over TS1, a peroxo-type O–O–C–O metastable state (MS) is formed, which is 1.04 eV lower in energy than TS1. Next, the O–O bond length in the O–O–C–O complex is continually elongated from 1.476 Å to 1.812 Å, at which the system reaches the second transition state (TS2). Passing over TS2 with an $E_r$ of 0.64 eV, a CO$_2$ molecule is formed, leaving an atomic O adsorbed on Fe atom. The O adatom can easily be removed by adsorbed CO (the $E_r$ is 0.29 eV, as shown in Figure 5b) or be reduced to form H$_2$O. Similar reaction pathways have been identified on Au and Cu embedded graphene.$^{23,24}$

The energy barriers of CO oxidation are indeed substrate-sensitive.$^{52,53}$ The $E_a$ of the RDS ranges from 0.64 eV on T-FeN4 to 1.46 eV on G-FeN4. This is because the nanotubes curvature changes the chemically inert graphite surface and makes it easier to adsorb molecules on the tube surface.$^{54}$ It is also important to notice that the reaction energy ($E_f$) of CO + O$_2$ → OOCO changes from 0.40 eV exothermic on T-FeN4 to −0.62 eV endothermic on G-FeN4, highlighting that the electron transfer within the tube walls is easier on the former than on the latter due to the larger curvature of the former.$^{55}$

On the other hand, the curved structure should reduce strains in the tubes after the molecule adsorption, as confirmed by P and N doped in CNT and graphene.$^{56}$ The CO + O$_2$ reaction on T-FeN4 and G-FeN4 does not belong to a typical LH mechanism because O$_2$ does not adsorb on the two active sites when Fe was covered by CO. O$_2$ prefers to desorb rather than to react with CO on T-FeN4 and G-FeN4 sites. This may show the CO poisoning on T-FeN4 and G-FeN4 sites.

Considering explicitly the T-dependent $E_a$ and $E_r$ for CO oxidation according to the Gibbs free energy corrected at different $T$ values, a more realistic picture of the catalytic reaction can be given. As shown in Table 2, different elemental reaction steps present distinct behaviors with the increase of $T$. The $E_a$ and $E_f$ values for CO + O → CO$_2$ increase with $T$, while those for OCOO dissociation reaction decrease. $\Delta S$ is one of the most important factors determining the variation for $E_a$ and $E_r$. For CO + O → CO$_2$, the decrease of $\Delta S$ causes the increase of $E_a$ and $E_r$ as $T$ varying from 298.15 to 1000 K. On the contrary, as $\Delta S$ increases, $E_a$ and $E_r$ drop for OCOO dissociation.

For the strong adsorption of CO, Fe/N/C catalyst exposed to gas with high CO concentration may be fully covered by CO, which is confirmed by this study. It shows clearly that three CO molecules can adsorb on Fe in T-FeN3 and R-FeN2, as depicted in Figure 1i,j. The calculated $E_{ad}$ values for CO adsorption are listed in Table 1. In Figure 7, we present the MEP of a faraway O$_2$ reacting with the preadsorbed CO molecules on T-FeN3. The whole reaction process consists of two stages. The first one is that the faraway O$_2$ approaches CO adsorbed on Fe to pass the TS1 and to get to MS, in which O$_2$...
Table 2. Original and Corrected Activation Energies ($E_a$), Reaction Energies ($E_r$), and $\Delta T\Delta S$ for CO Oxidation on T-FeN4, T-FeN3, G-FeN4, and R-FeN2 under Different Temperatures$^{a}$

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<th>$E_r$ CO + O$_2$ $\rightarrow$ CO$_2$</th>
<th>$\Delta T\Delta S$</th>
<th>$E_a$ OOCO $\rightarrow$ O + CO$_2$</th>
<th>$E_r$ O + CO $\rightarrow$ CO$_2$</th>
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$^a$All results are in units of eV.

Bonds with C in the two adjacent CO molecules. The second stage starts from the MS, passes TS2, and reaches the final state (FS) of two produced CO$_2$ to leave the catalyst and a CO molecule left. Both reaction stages are likely to proceed because of the low $E_a$ involved. The $E_a$ values associated with these two reaction stages are 0.12 and 0.67 eV, and the corresponding energy releases are 0.33 and 3.55 eV, respectively.

In the presence of a preadsorbed CO on T-FeN3, O$_2$ can be adsorbed with $E_{ad}$ = 1.83 eV. As results, both of CO and O$_2$ can be readily coadsorbed on the embedded-Fe atom. After adsorption, O$_2$ first dissociates rather than reacts with CO to form O–O–CO complex intermediate. The atomic configurations at various states along the reaction path are displayed in Figure 8a. This pathway possesses an $E_r$ of 0.98 eV. However, an O$_2$ molecule can react with H to form H$_2$O via OOH mechanism and leave an O atom adsorbed on the Fe atom.$^{59}$ And then, the $E_r$ of CO oxidation can be reduced to only 0.23 eV, as shown in Figure 8b. The effect of $T$ on CO
oxidation on T-FeN3 is similar to that on G-FeN4. The $E_a$ and $E_r$ values for the combination reactions increase with $T$, while those for the OCOOCO dissociation reaction decrease. For CO oxidation on T-FeN3, the RDS comes from the oxidation of the third CO by O$_2$ whose $E_a$ decreases to 0.75 eV at 298.15 K, implying that this reaction can be preceded more easily at elevated $T$.

There is a little difference for CO oxidation on R-FeN2 compared with that on T-FeN3, as summarized in Figures 9 and 10. O$_2$ first is adsorbed on Fe instead of reacting with two CO to form COOOOC complex. And then, O$_2$ reacts with CO one by one and a CO molecule is left. When O$_2$ is coadsorbed with CO, the $E_{ad}$ value decreases to 2.46 eV. Similar to CO oxidation on T-FeN3, the third CO oxidized by the O atom is easier than that by the O$_2$ molecule with an $E_a$ of 0.84 eV, compared with 1.15 eV, as shown in Figure 10. These results show that the CO covered on T-FeN3 and R-FeN2 could be removed by oxidation. In contrast with T-FeN3, the $E_a$ values of RDS in R-FeN2 increase with $T$. As shown in Table 2, the $E_a$ value for the third CO oxidation by O$_2$ is 1.10 eV at 298.15 K, which is 0.19 eV larger than that by the O atom. According to a previous study, reactions with a barrier about 0.91 eV (21 kcal/mol) or less will proceed readily at $T = 298.15$ K. Thus, the third CO could not be oxidized by O$_2$ directly, which shows a different case from T-FeN3. Generally speaking, $T$ presents varied effects on different elemental reactions, determined by $\Delta S$, and consequently affects the whole reaction rate. Specifically, the $E_a$ values of RDS on G-FeN4 and R-FeN2 increase with $T$, while those on T-FeN4 and T-FeN3 decrease.

It should be mentioned that undercoordinated CN of Fe in Fe/N/C catalysts is one of the most important properties for CO oxidation. As CN of Fe decreases from 4 of T-FeN4 and G-FeN4 to 3 of T-FeN3 and 2 of R-FeN2, more empty Fe-3d orbitals adsorb more adsorbates, which favors CO oxidation.
This is the case of Au clusters in supported or unsupported states.\(^{52,53,58,59}\) Recently, Fe/N/C electrocatalysts are found to be free from CO poisoning.\(^{21}\) Our results imply that -FeN4 configuration may be not the active site for ORR because both T-FeN4 and G-FeN4 sites are CO intolerant.

4. CONCLUSION

On the basis of the first principles calculation, CO adsorption and oxidation on four different active sites of Fe/N/C catalysts are studied. It is found that CO adsorption and oxidation exhibit structural selectivity. CO adsorption is energetically favorable than O\(_2\), and CO oxidation to CO\(_2\) is very hard on T-FeN4 and G-FeN4, indicating that these two configurations may be poisoned by CO adsorption. By contrast, O\(_2\) prefers to absorb on T-FeN3 and R-FeN2, and CO can easily be oxidized by O\(_2\), suggesting the CO tolerant property of T-FeN3 and R-FeN2.

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Notes

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