Theoretical insight into hydroxyl production via H$_2$O$_2$ decomposition over the Fe$_3$O$_4$(311) surface†

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Fenton’s reagent provides a method to produce active hydroxyl radicals (‘OH) for chemical oxidation by mixing iron oxide and hydrogen peroxide, which divides into homogeneous and heterogeneous Fenton’s reagent. Heterogeneous Fenton’s reagent is fabricated from H$_2$O$_2$ and various iron oxide solid materials, such as $\alpha$-FeOOH, $\alpha$-Fe$_2$O$_3$, and Fe$_3$O$_4$. Fe$_3$O$_4$ possesses the Fe$^{2+}$/Fe$^{3+}$ mixed valence oxidational state and has been reported to have good catalytic activity. However, the reaction mechanism of H$_2$O$_2$ decomposition on Fe$_3$O$_4$ surfaces is still unclear. In this work, we performed DFT calculations to investigate the H$_2$O$_2$ decomposition mechanisms over the Fe$_3$O$_4$(311) surface. There are two iron environments for H$_2$O$_2$ adsorption and decomposition on the Fe$_3$O$_4$(311) surface, a Fe$^{2+}$/Fe$^{3+}$ environment and a Fe$^{3+}$/Fe$^{4+}$ environment. We found that the H$_2$O$_2$ can adsorb on the Fe$^{2+}$/Fe$^{3+}$ environment by molecular adsorption but by dissociative adsorption on the Fe$^{3+}$/Fe$^{4+}$ environment. Our results show that both adsorption structures can produce two OH groups on the Fe$_3$O$_4$(311) surface thermodynamically. In addition, based on the electronic property analysis, H$_2$O$_2$ on the Fe$^{2+}$/Fe$^{3+}$ environment follows the Haber–Weiss mechanism to form one OH anion and one OH radical. On the other hand, H$_2$O$_2$ on the Fe$^{3+}$/Fe$^{4+}$ environment follows the radical mechanism to form two OH radicals. In particular, the OH radical formed on Fe$^{2+}$/Fe$^{3+}$ has energy levels on both sides of the Fermi energy level. It can be expected that this OH radical has good redox activity.

Conventional homogeneous Fenton reagent composed of hydrogen peroxide (H$_2$O$_2$) and ferrous ion (Fe$^{2+}$) for the purpose of producing hydroxyl radicals. However, there are several drawbacks to the homogeneous Fenton reagent. For example, homogeneous Fenton reagent needs to react in the narrow pH range, and the aggregation of iron-containing sludge in the reaction can also limit the recycling of catalysts, which can be considered as secondary pollution in the environment. Compared to the homogeneous Fenton systems, the heterogeneous iron-based solid catalysts can serve as the other choices for the Fenton reagents, which have been reported in various previous studies. Iron oxides-based catalysts, such as $\alpha$-FeOOH, $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$, and FeO, possess good catalytic properties in many heterogeneous catalysis reactions, including Fenton reaction and Fischer–Tropsch synthesis. Theoretically, Song et al. has reported the NO oxidation mechanism over $\alpha$-Fe$_2$O$_3$ catalyst by H$_2$O$_2$. Experimentally, Li et al. have studied the $\alpha$-FeOOH material as the pCNB degradation catalyst by Fenton-like process. Furthermore, several investigations have found that the mixed valence oxidational state of iron atoms possess unique catalytic activity towards many heterogeneous catalysis reactions, including Fenton reaction, methane partial oxidation, and mercury oxidation. Among, magnetite (Fe$_3$O$_4$) is one of the iron oxide material that has a Fe$^{2+}$/Fe$^{3+}$ mix valence oxidational state. The bulk magnetite crystal structure was a member of the inverse cubic spinel group with the ferrimagnetic property.

1. Introduction

Fenton’s reagent is a well-known advanced oxidation process (AOP) that can produce reactive oxygen species (ROS), such as hydroxyl radicals (‘OH), peroxyl radical (’OOH), and superoxide radical (’O$_2$). Fenton’s reagent is usually fabricated by mixing two solutions: a reducing transition metal and hydrogen peroxide. The Fenton-type reagent has been reported as an active catalyst for various reactions such as water treatment, methane partial oxidation, and mercury removal. Most AOPs for water treatment and purification of a Fenton reaction can accelerate the application of decomposition and the least expensive. Moreover, the development of a Fenton reaction shows extraordinary ability for organic decomposition and the least expensive. Moreover, the development of a Fenton reaction can accelerate the application of AOPs for water treatment and purification on an industrial scale.

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There are many applications of using magnetite as pigment due to its magnetic properties, such as polishing compounds, cosmetics, medicines, polymer, and rubber filler.30-32

There are still some challenges for heterogeneous Fenton reagents, such as that the yield to produce the OH radical is low. In addition, the mechanism to produce the OH radical via heterogeneously mixed valence iron oxide catalysts such as Fe3O4 of the Fenton reaction is unclear. In literature, there have been proposed two possible mechanisms for the traditional Fenton reaction. The first mechanism had been proposed by Haber and Weiss in the 1930s, named hydroxyl free radical mechanism (Haber–Weiss mechanism),8 which involves the formation of hydroxyl radicals (•OH) in the system with the ferry (Fe3+) oxidation. This radical mechanism for the Fenton reaction with the following elementary reactions.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \cdot\text{OOH} + \text{H}^+
\end{align*}
\]

Thereafter, another mechanism was proposed by Bray and Gorin in 1932,33 which generate higher valence Fe complexes such as ferryl (Fe^IV) ion in the Fenton system, as follows:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{IV} + \cdot\text{H}_2\text{O} \\
\text{Fe}^{IV} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \cdot\text{H}_2\text{O} + \cdot\text{H}_2\text{O}
\end{align*}
\]

As a structure in the spinel family, Fe3O4 also possesses stable low-index surfaces, (100), (110), (111) facets,34-37 and a high-index surface of (311). Some studies have been reported the mercury oxidation mechanism by H2O2 over Fe3O4(001) and Fe3O4(111) surfaces.37,38 However, even though the low-index facets have relatively low surface energies, Xu et al. have successfully synthesized a polyhedral 50-facet Fe3O4 nanocrystal where only one high-index Fe3O4(311) facet can stably exist with other low-index facets jointly.39 In their results, there were even 24 high-index (311) facets in that nanocrystal, which is stable and abundant. Thus, Fe3O4(311) facet is a stable high-index surface experimentally. Because there was no investigation on the mechanism of the Fenton reaction over the Fe3O4(311) surface, in this work, we studied the adsorption and decomposition of H2O2 (Fenton reaction) over Fe3O4(311) surface using DFT calculations. We also investigated the possible reaction mechanisms of the Fenton reaction on the Fe3O4(311) surface. Moreover, we analyzed the electron density difference (EDD) and density of states (DOS) to explore the electronic interaction between H2O2/ OH and Fe3O4(311) surface. To clarify the oxidational states of iron atoms between H2O2/OH and Fe3O4(311) surface, we also calculated the Bader charge and magnetic moments for the iron atoms on the Fe3O4(311) surface.

2. Computational details

The spin-polarized periodic DFT calculations were carried out with the Vienna ab initio simulation package (VASP 5.4.1).40-43 The generalized gradient approximation (GGA) with the functional proposed by Perdew, Burke and Enzerhof (PBE) exchange-correlation functional44 was used together with a plane-wave basis set with a kinetic cutoff energy of 500 eV. The electron ion–core interactions were described by the projector augmented wave (PAW) method.45,46 In order to correctly describe the itinerant or localized behavior of the Fe 3d-orbital, it is important to account for the strong on-site Coulomb correlations.47,48 Therefore, in this work, all systems were calculated by using the Hubbard correction term U (GGA + U).

We applied the rotationally invariant approach proposed by Dudarev et al. with an effective Hubbard parameter of 4.0 eV for iron, which is the difference between the Coulomb (U) and exchange (J) parameters (Ueff = U – J). The optimized exchange-correlation functional (optB86b-vdW) was considered to determine the effect of van der Waals interactions.49

For the total energy calculations, the Brillouin zone integrations for the pristine and defect system were performed using the \(2 \times 2 \times 1\) based on the Monkhorst-Pack \(k\)-points scheme50 for all structural configuration relaxations. The convergence threshold was set to be \(10^{-5}\) eV for electronic optimization and the force convergence was set to 0.02 eV Å\(^{-1}\) for structural optimization. The adsorption energy \((E_{ads})\) of adsorbate was defined as following equation:

\[
E_{ads} = E_{Total} - E_{surf} - E_{Molecule}
\]

where \(E_{Total}\) is the total energy of the surface together with the adsorbate, \(E_{surf}\) is the total energy of the surface, and \(E_{Molecule}\) is the total energy of the free molecule in gas-phase. Therefore, a negative adsorption energy illustrated a thermodynamically-favored exothermic adsorption process. An \(8 \times 8 \times 1\) \(k\)-point grid was used to calculate electronic density difference (EDD), Bader charge analysis, and density of state (DOS) with the same cutoff energy. The imaging charge nudged elastic band (CI-NEB) method51 and dimer method was applied to find transition states and minimum energy path of all reactions. The vibrational frequencies analysis was performed for validating the optimized and transition state structures.

The bulk Fe3O4 was adopted the conventional Fe3O4 unit cell comprising 56 atoms (Fe2O3O2). For the Fe3O4 bulk calculations, \(8 \times 8 \times 8\) \(k\)-mesh of a grid density was employed. The optimized lattice parameters of bulk Fe3O4 were \(a = b = c = 8.396\) Å and \(\alpha = \beta = \gamma = 90^\circ\). The result of the calculation is in good agreement well with the experimental data \((a = b = c = 8.394\) Å and \(\alpha = \beta = \gamma = 90^\circ\)).52 The bulk magnetite crystal structure was inverse cubic spinel with ferrimagnet property, the structure comprises the tetrahedral iron site and octahedral iron site with different oxidation number, and the O anions form a close-packed face-centered cubic (fcc) sublattice, as shown in Fig. S1(a).† Moreover, the tetrahedral and octahedral iron sites were performed by two magnetic sub-lattices in the opposite direction to form a typical inverse spinel structure as \([\text{Fe}^{3+}]_{\text{tet}}[\text{Fe}^{3+}, \text{Fe}^{2+}]_{\text{oct}}\text{O}_4\). During the calculation, the initial atomic spin magnetic moments were \(m_s = -5\) \(\mu_B\) and \(4\) \(\mu_B\) for the tetrahedral iron and the octahedral iron sites, respectively. After structure optimization, the magnetic moment per formula unit was
calculated to be 4.0 $\mu_B$, which lies close to experiment data (4.05 $\mu_B$). The magnetic moments of Fe$^{3+}$ and Fe$^{2+}$ in the tetrahedral iron and the octahedral iron atoms were with the antiparallel alignment, creating the ferrimagnetic character. Fig. S1(b)† shows the structure of the Fe$_3$O$_4$(311) surface by constructing four molecular layer models with the bottom two layers being fully fixed. The simulated XRD pattern of Fe$_3$O$_4$ bulk structure is drawn in Fig. S1(c),† which is in a good agreement with the experimental observation.\textsuperscript{33}

### 3. Results and discussion

#### 3.1 Adsorption of H$_2$O$_2$ molecule

Fig. 1 shows the adsorption configuration of H$_2$O$_2$ on the Fe$_3$O$_4$(311) surface. There are two possible adsorption structures of H$_2$O$_2$ on the Fe$_3$O$_4$(311) surface: (1) molecular adsorption (Fig. 1(a)) and (2) dissociative adsorption (Fig. 1(b)). In the H$_2$O$_2$ molecular adsorption structure, the H$_2$O$_2$ adsorbs on the Fe$_{\text{tet}}$ site via one OH to form the Fe–O bond, while the other OH end of H$_2$O$_2$ points to the lattice oxygen to form the hydrogen bonding. The simulated XRD pattern of Fe$_3$O$_4$ bulk structure is drawn in Fig. S1(b).†

The magnetic moments of Fe$^{3+}$ and Fe$^{2+}$ in the tetrahedral iron and the octahedral iron atoms were with the antiparallel alignment, creating the ferrimagnetic character. Fig. S1(b)† shows the structure of the Fe$_3$O$_4$(311) surface by constructing four molecular layer models with the bottom two layers being fully fixed. The simulated XRD pattern of Fe$_3$O$_4$ bulk structure is drawn in Fig. S1(c),† which is in a good agreement with the experimental observation.\textsuperscript{33}

#### 3.2 The activation of H$_2$O$_2$ on Fe$_3$O$_4$

To understand the reaction mechanism of H$_2$O$_2$ decomposition, we calculated the energy barrier and reaction energy of each reaction step from both adsorption structures of H$_2$O$_2$ on the Fe$_3$O$_4$(311) surface. Two cleave aspects are considered in either molecular adsorption of H$_2$O$_2$ or dissociative adsorption of H$_2$O$_2$: (1) O–O bond-breaking into the OH group; (2) O–H bond-breaking into the OOH group. The following steps show the possible mechanisms for the molecular adsorption of H$_2$O$_2$ on the Fe$_3$O$_4$(311) surface:

$$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$$  \hspace{1cm} (1)

$$\text{H}_2\text{O}_2 \rightarrow \text{OOH} + \text{H}$$  \hspace{1cm} (2)

$$\text{OOH} \rightarrow \text{OH} + \text{O}$$  \hspace{1cm} (3)

In eqn (1), the reaction barrier is 0.76 eV of that the H$_2$O$_2$ molecule cleaves the O–O bond to form two OH groups on one Fe$_{\text{tet}}$ site and one Fe$_{\text{oct}}$ site, and the reaction energy of this reaction is significant endothermic by 1.44 eV. Fig. S2(a)† depicts the structures of the initial state, transition state, and final state of this reaction. In eqn (2), the pathway starts from the deprotonation of H$_2$O$_2$ to deliver one hydrogen atom to the lattice oxygen, then forming an OOH group and the surface hydroxyl group. The oxygen atoms of the OOH group are separately adsorbed on both Fe$_{\text{tet}}$ and Fe$_{\text{oct}}$ as shown in Fig. S2(b).† The calculated energy barrier of this reaction is 0.52 eV by a slight endothermicity of 0.22 eV. Comparing the pathways via O–O bond breaking and deprotonation, the reaction in the former is more thermodynamically favorable to produce the two OH groups, but it has larger activation energy for O–O bond scission, whereas the reaction in the latter possesses a smaller energy barrier to form the OOH group.

When the decomposition reaction starts from the dissociative adsorption of H$_2$O$_2$ (H + OOH), the reaction can also divide into O–O bond breaking and OH deprotonation reactions. The first pathway is the O–O bond decomposition of OOH to form O atom and OH group on two Fe$_{\text{oct}}$ sites of the surface. The calculated energy barrier and reaction energy of this elementary step (OOH $\rightarrow$ O + OH) is 0.24 eV and 0.20 eV, respectively. The activated O–O bond length in the transition state structure is 1.70 Å, and the intermediate state will form a hydrogen bonding interaction between the O atom and OH group with a distance of 1.86 Å after dissociation, as shown in Fig. S3(a).† However, the dissociated O atom is unstable so that this O atom can attract the atomic H of the surface hydroxyl group to form another OH group on the Fe$_{\text{oct}}$ site via the hydrogen bonding networks, which results in a large exothermic reaction by 1.44 eV due to the stability of forming two OH groups. The second pathway is that deprotonation from OOH to transfer one H atom to the lattice oxygen to form dioxygen on the two octahedral iron sites, as shown in Fig. S3(b).† This process is
a thermal neutral process with an activation energy of 0.79 eV. This result demonstrates that the most favorable pathway from the decomposition reaction of the dissociative adsorption of H$_2$O$_2$ is to produce two OH groups on the Fe$_3$O$_4$(311) surface. Table 2 summarizes the calculated reaction energy and activated barriers of the elementary steps of the O–O bond and O–H bond dissociation of H$_2$O$_2$ on Fe$_3$O$_4$(311) surface. Fig. 2 depicts the potential energy profiles for H$_2$O$_2$ decomposition on different sites over Fe$_3$O$_4$(311) surface. Our results show that it is thermodynamically favorable to produce the two hydroxyl groups on the Fe$_3$O$_4$(311) surface from both molecular adsorption and dissociative adsorption.

### Table 1
The adsorption energy and geometrical parameters of H$_2$O$_2$ via different adsorption configurations on the Fe$_3$O$_4$(311) surface

| Adsorption type       | $E_{ads}$ (eV) | O–O bond length (Å) | O–H$_1$ bond length (Å) | O–H$_2$ bond length (Å) |
|-----------------------|----------------|---------------------|-------------------------|-------------------------|
| Gas phase             | —              | 1.472               | 0.98                    | 0.98                    |
| Molecular adsorption  | −1.17          | 1.475               | 1.016                   | 1.061                   |
| Dissociate adsorption | −1.57          | 1.483               | 2.135                   | 0.983                   |

### Table 2
Calculated reaction barriers ($E_a$ in eV), reaction energies ($\Delta E$ in eV), and imaginary frequencies (IMF, cm$^{-1}$) for elementary reactions of H$_2$O$_2$ decomposition on the Fe$_3$O$_4$(311) surface

| Elemental steps        | $E_a$ (eV) | $\Delta E$ (eV) | IMF (cm$^{-1}$) |
|------------------------|------------|-----------------|-----------------|
| **Molecular adsorption** |            |                 |                 |
| H$_2$O$_2$(gas) → H$_2$O$_2$* | —          | −1.17           |                 |
| H$_2$O$_2$* → 2OH*     | 0.76       | −1.44           | i424            |
| H$_2$O$_2$* → H* + OOH*| 0.52       | 0.22            | i493            |
| **Dissociate adsorption** |            |                 |                 |
| H$_2$O$_2$*(gas) → H* + OOH* | —          | −1.57           |                 |
| H* + OOH* → H* + O* + OH* | 0.24       | 0.20            | i641            |
| H* + O* + OH* → 2OH*  | —          | −1.44           |                 |
| H* + OOH* → OO* + 2H* | 0.79       | 0.002           | i943            |

3.3 Solvent effect

To realistically simulate the effect of the catalytic environment on Fenton’s reaction, we carried out the implicit solvent model by using VASPsol. The implicit solvent effect of water was adopted in this work, where the corresponding dielectric constant of water was 78.3553. As listed in Table S1† the reaction barriers of either O–O bond breaking or O–H bond breaking of the H$_2$O$_2$ molecule in an aqueous solution become smaller than that of the H$_2$O$_2$ molecule in the vacuum, which is contributed by the solvent effects. Besides, the OH groups production is still the most thermodynamically favorable pathway via O–O bond breaking of the H$_2$O$_2$ on the Fe$_3$O$_4$(311) surface, as shown in Fig. S4. Thus, with/without the solvent effect, the reaction trend of H$_2$O$_2$ decomposition on the Fe$_3$O$_4$(311) surface is similar.

### 3.4 Electronic property analysis

#### 3.4.1 H$_2$O$_2$ molecular adsorption

To analyze the interactions between H$_2$O$_2$ and Fe atoms upon adsorption on different sites over Fe$_3$O$_4$(311) surface. Our results show that it is thermodynamically favorable to produce the two hydroxyl groups on the Fe$_3$O$_4$(311) surface from both molecular adsorption and dissociative adsorption.

Fig. 2 The potential energy profiles of the decomposition of H$_2$O$_2$ on the Fe$_3$O$_4$(311) surface via (a) H$_2$O$_2$ molecular adsorption and (b) H$_2$O$_2$ dissociative adsorption.
Fe₃O₄(311) surface, we calculate the electron density difference (EDD) and density of states (DOS). Fig. 3(a) and (b) show the different views of 2D EDD contour plots of H₂O₂ molecular adsorption. Fig. 3(a) illustrates the accumulation of electron region between the OH group and Fe₄ oct site, representing that the oxygen donates electrons to the iron atom to form a dative bond between oxygen and iron atom. On the other hand, Fig. 3(b) shows the cutting plane along with the other H atom and the O–O bond (H₂–O–O), which displays the electron density accumulation (red contour) between the OH group and the lattice O. This EDD plot in Fig. 3(b) indicates that the H₂O₂ donates the electron transfer from the lattice O to the OH group via the hydrogen bonding interaction. In addition, Fig. 4(a) shows the PDOS diagram of the H₂O₂ molecule before and after its adsorption. One can observe that the spin up and spin down of the peaks of H₂O₂ is getting splitting after adsorption. Moreover, as can be seen in Fig. S5(a) and (b)† the projected d orbitals of Fe₄oct and Fe₄tet atoms show that the d orbitals of Fe₄tet have obviously changed, and the peak is getting broad. In comparison, the peaks of the Fe₄oct changed slightly after H₂O₂ adsorption. Additionally, the d orbitals of the Fe₄tet atom have an overlap with the p orbitals of H₂O₂ around −0.50 eV, reflecting the dative bond between H₂O₂ and Fe₄tet atom.

3.4.2 H₂O₂ dissociative adsorption. Fig. 3(c) shows the 2D EDD plot of the OOH group of the H₂O₂ dissociative adsorption configuration, and the cutting plane is along the bridge between two Fe₄oct atoms and the O–O bond (Fe₄oct–O–O–Fe₄oct). The blue contour around the OOH group reveals that the OOH group loses electrons electron. There is also a broad electron density accumulation (red contour) around the bound OOH and two
Fe\textsubscript{oct} atoms, and the region around the OOH group, which indicates the strong electron interactions between Fe atoms and the OOH group. The strong electronic interactions mean that the OOH can form a dative chemical bond with the Fe atoms.

Further, the PDOS plots, as shown in Fig. 4(b), demonstrated that the peaks of the OOH (from the dissociative adsorption of H\textsubscript{2}O\textsubscript{2}) has a significant splitting on both spin up and spin down, reflecting the strong radical property of the OOH group. The peaks around $-1.50$ eV and $-1.00$ eV belong to $\pi$-HOMO and $\beta$-HOMO, respectively, as well as the peak around $0.50$ eV represents the LUMO of the OOH group before adsorption (black line in Fig. 4(b)). For the dissociative adsorption configuration of H\textsubscript{2}O\textsubscript{2}, the peaks of the OOH group (red line in Fig. 4(a)) display a broad region above Fermi level energy to $3.00$ eV, but the peaks around $0.50$ eV disappear. It reflects that the OOH group can gain electrons from the Fe atoms. After dissociative adsorption configuration of H\textsubscript{2}O\textsubscript{2}, the peaks still show a notable splitting on both spin up and spin down, representing the strong radical property of the OOH group. Besides, as can be seen in Fig. S5(c) and (d), the d orbital of the Fe\textsubscript{oct} atom shows a more remarkable change than that of the Fe\textsubscript{tet} atom before and after OOH group formation, indicating the strong interaction between the Fe\textsubscript{oct} atom and the OOH group.

### 3.4.3 OH on the Fe\textsubscript{tet}/Fe\textsubscript{oct} of the Fe\textsubscript{3}O\textsubscript{4}(311) surface.

According to the calculated results, both molecular adsorption of H\textsubscript{2}O\textsubscript{2} and dissociative adsorption of H\textsubscript{2}O\textsubscript{2} can produce two OH groups on either Fe\textsubscript{tet} or Fe\textsubscript{oct} atoms of the Fe\textsubscript{3}O\textsubscript{4}(311) surface. Because Fenton’s reaction involves the redox reaction, we did the electronic property analysis to understand the electronic and magnetic properties after H\textsubscript{2}O\textsubscript{2} decomposition. Fig. S6(a) and (b) show the EDD plots of the adsorption of the OH group on the Fe\textsubscript{tet} and Fe\textsubscript{oct} sites after H\textsubscript{2}O\textsubscript{2} decomposition, respectively. It shows wide regions of electron density accumulation (red lines) between the OH group and either Fe\textsubscript{tet} or Fe\textsubscript{oct} atoms, which shows the electron transferred from the OH group to the Fe atoms. Fig. 4(c) represents the PDOS of the OH groups on the Fe\textsubscript{tet} and Fe\textsubscript{oct} sites after H\textsubscript{2}O\textsubscript{2} decomposition. For the OH on the Fe\textsubscript{oct} atom, there are peaks with similar intensity on both sides of the Fermi level, indicating that the oxygen atom on OH has unpaired electrons after H\textsubscript{2}O\textsubscript{2} decomposition. Since the peaks are close to the Fermi level, we can expect that the OH group on the Fe\textsubscript{oct} atom should be very active. Besides, it can be observed from Fig. S7(a) that the DOS distribution of Fe\textsubscript{tet} changes significantly before and after adsorption, whereas from Fig. S7(b) that the DOS distribution of Fe\textsubscript{oct} is very similar after H\textsubscript{2}O\textsubscript{2} dissociation. The changes of the DOS distribution of Fe\textsubscript{tet} implies that Fe\textsuperscript{2+} might have been oxidized to Fe\textsuperscript{3+}.

Further, the PDOS plots, as shown in Fig. 4(b), demonstrated that the peaks of the OOH (from the dissociative adsorption of H\textsubscript{2}O\textsubscript{2}) has a significant splitting on both spin up and spin down, reflecting the strong radical property of the OOH group. The peaks around $-1.50$ eV and $-1.00$ eV belong to $\pi$-HOMO and $\beta$-HOMO, respectively, as well as the peak around $0.50$ eV represents the LUMO of the OOH group before adsorption (black line in Fig. 4(b)). For the dissociative adsorption configuration of H\textsubscript{2}O\textsubscript{2}, the peaks of the OOH group (red line in Fig. 4(a)) display a broad region above Fermi level energy to $3.00$ eV, but the peaks around $0.50$ eV disappear. It reflects that the OOH group can gain electrons from the Fe atoms. After dissociative adsorption configuration of H\textsubscript{2}O\textsubscript{2}, the peaks still show a notable splitting on both spin up and spin down, representing the strong radical property of the OOH group. Besides, as can be seen in Fig. S5(c) and (d), the d orbital of the Fe\textsubscript{oct} atom shows a more remarkable change than that of the Fe\textsubscript{tet} atom before and after OOH group formation, indicating the strong interaction between the Fe\textsubscript{oct} atom and the OOH group.

### Table 3 Calculated Bader charge and magnetization for Fe atoms, H\textsubscript{2}O\textsubscript{2}, and OH groups before and after H\textsubscript{2}O\textsubscript{2} decomposition.

| Species | Bader charge | Magnetization | Species | Bader charge | Magnetization |
|---------|--------------|---------------|---------|--------------|---------------|
| Fe\textsubscript{tet} | 1.32 | 3.782 | Fe\textsubscript{oct} | 1.67 | 4.240 |
| Molecular adsorption | | | | | |
| Fe\textsubscript{tet} | 1.36 | 3.804 | Fe\textsubscript{oct} | 1.67 | 4.243 |
| H\textsubscript{2}O\textsubscript{2} | $-0.012$ | — | OH on the Fe\textsubscript{tet}/Fe\textsubscript{oct} | | |
| Fe\textsubscript{tet} | 1.69 | 4.249 | Fe\textsubscript{oct} | 1.71 | 4.234 |
| OH-Fe\textsubscript{tet} | $-0.47$ | — | OH-Fe\textsubscript{oct} | | |
| OH-Fe\textsubscript{oct} | $-0.51$ | — | Free surface | | |
| Fe\textsubscript{tet} | 1.68 | 4.248 | Fe\textsubscript{oct} | 1.69 | 4.262 |
| Dissociative adsorption | | | | | |
| Fe\textsubscript{tet} | 1.73 | 4.258 | Fe\textsubscript{oct} | 1.71 | 4.276 |
| H-OOH | $-0.09$ | — | OH on the Fe\textsubscript{tet}/Fe\textsubscript{oct} | | |
| Fe\textsubscript{tet} | 1.69 | 4.258 | Fe\textsubscript{oct} | 1.70 | 4.278 |
| OH-Fe\textsubscript{tet} | $-0.50$ | — | OH-Fe\textsubscript{oct} | | |
| OH-Fe\textsubscript{oct} | $-0.45$ | — | Free surface | | |

\[ \text{H}_2\text{O}_2 \rightarrow '\text{OH} + '\text{OH} \]

\[ \text{Fe}_{\text{tet}}^{2+} + '\text{OH} \rightarrow \text{Fe}_{\text{tet}}^{3+} + '\text{OH}^- \]

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3.4.4 OH on the Fe\textsubscript{oct}/Fe\textsubscript{oct2} of the Fe\textsubscript{3}O\textsubscript{4}(311) surface.

After the decomposition of the H\textsubscript{2}O\textsubscript{2} to two OH groups on the Fe\textsubscript{oct} and Fe\textsubscript{oct2} atoms, we also investigated the electronic interaction between these OH groups and the Fe\textsubscript{oct} atoms via EDD, PDOS, Bader charge and magnetisation analyses. Fig. S6(c) and (d)† show the EDD contour plots from the different perspective cutting planes of these two OH groups. These EDD plots display a wide region with electron density accumulation (red color) between the OH group and either Fe\textsubscript{oct} or Fe\textsubscript{oct2} atoms, demonstrating the OH group has a strong interaction with either Fe\textsubscript{oct} or Fe\textsubscript{oct2} atoms. In Fig. 4(d), the peaks of OH groups show a little split, which also denotes the radical character for these OH groups. Besides, the PDOS of the d orbital of either Fe\textsubscript{oct} atom or Fe\textsubscript{oct2} atom display only slightly changes before and after H\textsubscript{2}O\textsubscript{2} decomposition, as shown in Fig. S7(c) and (d).† This result implies that the redox reactivity between OH groups and Fe\textsubscript{oct}/Fe\textsubscript{oct2} atoms is weak.

The calculated Bader charge values have slight changes on both Fe\textsubscript{oct} and Fe\textsubscript{oct2} atoms before and after O–O decomposition, where the value of Fe\textsubscript{oct} atom changes from 1.68|e| to 1.73|e|, and the value of Fe\textsubscript{oct2} atom from 1.69|e| becomes 1.71|e|. The calculated magnetic moment values of both Fe\textsubscript{oct1} and Fe\textsubscript{oct2} atoms remain around 4.25 μ\textsubscript{B} before and after O–O decomposition. These results indicate that both Fe\textsubscript{oct1} and Fe\textsubscript{oct2} atoms are the ferric ions (Fe\textsuperscript{3+}) initially and the Fe atoms will get hardly further oxidized after forming the OH group on these Fe atoms. Thus, the OH groups on these ferric ions (Fe\textsuperscript{3+}) also possess a radical character after H\textsubscript{2}O\textsubscript{2} decomposition. The calculated Bader charge and magnetic moment values are listed in Table 3.

Finally, in a comparison of two mechanisms of H\textsubscript{2}O\textsubscript{2} decomposition on the Fe\textsubscript{3}O\textsubscript{4}(311) surface, we found that it can occur a redox reaction between H\textsubscript{2}O\textsubscript{2} and Fe\textsubscript{3}O\textsubscript{4}(311) surface when H\textsubscript{2}O\textsubscript{2} adsorbed on both Fe\textsubscript{oct} and Fe\textsubscript{oct2} sites. The mechanism obeys the Haber–Weiss mechanism to produce one OH anion and one OH radical, which has a strong redox activity. On the other hand, while H\textsubscript{2}O\textsubscript{2} adsorbed on two Fe\textsubscript{oct} sites, H\textsubscript{2}O\textsubscript{2} can dissociate into two OH radicals without oxidizing the Fe\textsubscript{oct} atoms, which is the radical mechanism of H\textsubscript{2}O\textsubscript{2} decomposition. Based on these results, we could predict that the active OH radicals would be the surface abundant species on the Fe\textsubscript{3}O\textsubscript{4}(311) surface. Moreover, the calculated desorption energies of OH radicals are 2.84 eV and 2.94 eV at Fe\textsubscript{oct}\textsuperscript{2+}/Fe\textsubscript{oct}\textsuperscript{3+} and Fe\textsubscript{oct}\textsuperscript{3+}/Fe\textsubscript{oct}\textsuperscript{3+} sites, respectively. The desorption energy indicated that the hydroxyl radicals might be challenging to desorb from the Fe\textsubscript{3}O\textsubscript{4}(311) surface. Therefore, in our study, we predict that the surface OH groups might go through surface heterogeneous oxidation reactions.

4. Conclusions

In this work, we have employed DFT calculations to study the H\textsubscript{2}O\textsubscript{2} adsorption and the decomposition mechanism on the Fe\textsubscript{3}O\textsubscript{4}(311) surface. Fe\textsubscript{3}O\textsubscript{4}(311) surface possesses a mixed valence (Fe\textsuperscript{2+}/Fe\textsuperscript{3+}) state so that there are two possible adsorption sites for H\textsubscript{2}O\textsubscript{2} adsorption. When H\textsubscript{2}O\textsubscript{2} adsors on the Fe\textsubscript{oct}\textsuperscript{2+}/Fe\textsubscript{oct}\textsuperscript{3+} sites, the adsorption structure is molecular adsorption, whereas the adsorption structure of H\textsubscript{2}O\textsubscript{2} on Fe\textsubscript{oct}\textsuperscript{3+}/Fe\textsubscript{oct}\textsuperscript{3+} sites becomes dissociative adsorption [OOH + H]. We found that the molecular adsorption of H\textsubscript{2}O\textsubscript{2} can proceed O–H or O–O bond scission to form OOH or 2OH on the Fe\textsubscript{3}O\textsubscript{4}(311) surface, respectively. The O–H and O–O bond dissociation is kinetic control and thermodynamic control of the decomposition reaction for the molecular adsorption of H\textsubscript{2}O\textsubscript{2}, respectively. On the contrary, the dissociative adsorption of H\textsubscript{2}O\textsubscript{2} only prefers to go through the O–O bond scission to produce 2OH on the Fe\textsubscript{3}O\textsubscript{4}(311) surface with a small energy barrier of 0.24 eV. In addition, according to various electronic property calculations, DOS, EDD, Bader charge, and magnetic moments, we observed that the reaction from H\textsubscript{2}O\textsubscript{2} to 2OH on the Fe\textsubscript{oct}\textsuperscript{2+}/Fe\textsubscript{oct}\textsuperscript{3+} sites obeys the Haber–Weiss mechanism of the Fenton reaction. The Fe\textsubscript{oct}\textsuperscript{2+} site can be oxidized to Fe\textsubscript{oct}\textsuperscript{3+}, while the other Fe\textsubscript{oct}\textsuperscript{3+} site maintains its original oxidation state. Thus, the 2OH formed from the molecular adsorption of H\textsubscript{2}O\textsubscript{2} is a composition of OH anion and OH radical. On the contrary, the 2OH produced from the dissociative adsorption of H\textsubscript{2}O\textsubscript{2} is two radicals because the Fe\textsubscript{oct}\textsuperscript{3+}/Fe\textsubscript{oct}\textsuperscript{3+} sites did not change their oxidation states, which belongs to the radical mechanism. Compared to two mechanisms, it can produce an active OH radical on the surface via either the Haber–Weiss mechanism or radical mechanism, where the oxidation state of Fe on the Fe\textsubscript{3}O\textsubscript{4}(311) surface can stay at Fe\textsuperscript{3+} instead of further oxidation. As a result, our results predict that these OH radicals from the Fenton-like reaction of H\textsubscript{2}O\textsubscript{2} on the Fe\textsubscript{3}O\textsubscript{4}(311) surface might be a candidate of oxidant for other heterogeneous catalysis reactions.

Conflicts of interest

There are no conflicts to declare.

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