Supporting Information

Computationally Revisiting pH- and Ligand-Dependence of Fenton Reaction Selectivity and Activity in Aqueous Solution

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Section 1: Calculation method

k-point Test. In this work, we calculated the initial state (IS), transition state (TS) and final state (FS) for the O-O bond cleavage process on the Fe^{III}-complex as an example using different *k*-point meshes: $1 \times 1 \times 1$, $2 \times 1 \times 1$ and $2 \times 2 \times 1$ (Table S1). The results show that there is virtually no significant difference between the calculations for the different *k*-point meshes, indicating the ($1 \times 1 \times 1$) *k*-point mesh is sufficient in this work.

 $[(Cl^-)_3Fe^{III}(H_2O)_3]$ model. The selection of $[(Cl^-)_3Fe^{III}(H_2O)_3]$ was motivated by two primary reasons.

First, FeCl₃/FeCl₂ systems are widely used for H₂O₂ activation due to their low cost, environmental friendliness, high catalytic activity.¹⁻⁶ Given that Fe³⁺ is more stable and commonly employed as a reagent in industrial and laboratory settings, we focused on FeCl₃ as the homogeneous catalyst. The coordination environment of FeCl₃ in aqueous solutions has been extensively studied, which confirmed a mixed coordination of Cl⁻ and H₂O ligands⁷⁻¹² The reaction center Fe^{III} forms octahedral chloro complexes [Fe(H₂O)_{6-x}Cl_x]^{(3-x)+} (x = 1-3) as the predominant species.¹³⁻¹⁶

Second, from the computational perspective, we used a periodic model with VASP code. In this case, calculating a charged slab is a tricky task. To express the Fe^{III} oxidation state, we set x = 3 to achieve the initial computational structure. If we use only water as the ligands, it would require removing three electrons from the system, which introduces some uncertainties due to the influence of compensating charges, or introducing three free Cl⁻ as the counterpart in the system, which would have a significant impact on the computational time and complexity.

To further validate the robustness of our computational model, we compared Fe^{II} coordinated with two Cl⁻ ligands ([(Cl⁻)₂Fe^{II}(H₂O)₄]) with three Cl⁻ ligands ([(Cl⁻)₃Fe^{II}(H₂O)₃]⁻ with one proton in the solution). For H₂O₂ dissociation, Table S2 shows that, although the coordination environments differ, the reaction energy barrier and energy change are comparable at Fe^{II}. Similarly, the reaction energy barriers/energy change ($E_a/\Delta E$) for Fe^{IV}O²⁺ formation (Fe^{III}(OH⁻) + OH[•] \rightarrow Fe^{IV}O²⁺ + H₂O) and its competing reaction (Fe^{III}(OH⁻) + H⁺ \rightarrow Fe^{III}(H₂O)) exhibit only slight variations between the two models. These results indicate that the oxidation state of the Fe center plays a major role in determining the catalytic activity, while the role of the ligands is secondary, acting as modulators.

In addition, considering that FeCl₃ undergoes hydrolysis at pH>3, resulting in the formation of [(Cl⁻)₂Fe^{III}(OH⁻)(H₂O)₃], which serves as an alternative reaction center, we examined how hydrolysis-induced coordination variations influence catalytic activity. As shown in Table S2, the substitution of Cl⁻ with OH⁻ slightly modulates $E_a/\Delta E$, further confirming that the oxidation sate of the Fe center is the primary factor governing catalytic activity. Notably, H₂O₂ $[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{3}]$ center is dissociation at slightly more favorable than at [(Cl⁻)₂Fe^{III}(OH⁻)(H₂O)₃], likely due to the stronger binding affinity of OH⁻ compared to Cl⁻, which weakens the interaction between Fe and the reacting species in line with the bond conservation principle. More specifically, ligand-induced variations influence catalytic activity through distinct electrostatic interactions and hydrogen bonding networks involving H₂O, Cl⁻, and OH⁻.

Details on the MPA-MD method. To model the water environment surrounding the Fe-complexes, we performed ab-initio molecular dynamics (AIMD) simulations. In these simulations, latticematched bulk water, consisting of 53 randomly connected H₂O molecules at $\rho = 1$ g/cm³, was introduced to create the initial aqueous network (Figure S1a). AIMD simulations were performed over a period of 24 ps, and equilibrium was reached for all simulations after approximately 10 ps (see Figure S1a). The aqueous structures (> 5 samples) were selected from the later stage of the simulation after reaching equilibrium. For calculating the energies of homo-Fenton reaction, we employed the multi-point averaging molecular dynamics (MPA-MD) method for each intermediate state (IMS), including transition states. This method, established in our previous study, has been demonstrated to accurately calculate the solvation energies.¹⁷ The procedure consists of several basic steps. First, we selected five samples every \sim 2 ps from the equilibrium structure of AIMD and further optimized them to obtain the total energy of each structure (E_{tot}) using the PBE+U method. Second, to account for the effect of varying water networks on the total energy of each structure (E_{tot}) , we deducted the total energy of the water structure (E_{water}) and obtained the 'solvation-included energy' ($E_{sol-included}$). Therefore, the $E_{\text{sol-included}}$ includes the solvation effect for each sample while minimizing energy fluctuations by excluding the contribution of the flexible water structures. Detailed explanations regarding the 'solvation-included energy' and the 'averaging' approach are shown below.

For an IMS i in Fenton reaction, we selected and optimized j samples from AIMD simulations, and the total energy of each sample can be expressed as:

$$E_{\text{tot}}^{i,j} = E_{\text{water}}^{i,j} + E_{\text{catal}}^{i,j} + E_{\text{int}}^{i,j}$$
(S1)

where $E_{water}^{i,j}$, $E_{catal}^{i,j}$, and $E_{int}^{i,j}$ are the computed energy of water solution, catalyst (including the reaction center) and the interactions between the water solution and catalyst.

For reactions without the water molecules, $E_{tot}^{i,j} = E_{catal}^{i,j}$ and thus the reaction energy can be directly computed:

$$\Delta E_{\rm gas} = \frac{1}{j} \sum_{1}^{J} E_{\rm tot}^{i+1} - \frac{1}{j} \sum_{1}^{J} E_{\rm tot}^{i}$$
(S2)

However, for reactions in aqueous solution, different solution configuration of water network $E_{\text{water}}^{i,j}$ affects $E_{\text{tot}}^{i,j}$. Thus, we proposed to deduct the contribution of $E_{\text{water}}^{i,j}$ from $E_{\text{tot}}^{i,j}$ but keep the solvation effect into consideration. Accordingly, the solvation-including energy is defined as:

$$E_{\text{sol-included}}^{i,j} = E_{\text{catal}}^{i,j} + E_{\text{int}}^{i,j} = E_{\text{tot}}^{i,j} - E_{\text{water}}^{i,j}$$
(S3)

and the reaction energy can be computed using the 'averaging' approach:

$$\Delta E_{\text{interface}} = \frac{1}{j} \sum_{1}^{J} E_{\text{sol}-\text{included}} - \frac{1}{j} \sum_{1}^{J} E_{\text{sol}-\text{included}} \qquad (S4)$$

which not only contains the reaction energy without the water molecules, but also includes the solvation effect of the water environment.

Taking the initial state (IS) of $[(Cl^-)_3Fe^{III}(H_2O)_3]$ as an example, we present the $E_{tot}^{i,j}$, $E_{water}^{i,j}$,

and $E_{sol-included}$ for each sample in Table S3. Although the absolute energy values of $E_{tot}^{i,j}$ and

 E_{water} slightly differ, the fluctuation of relative energetics (E_{sol} -included) of [(Cl⁻)₃Fe^{III}(H₂O)₃] over the 10~24 ps period of the AIMD simulations is minimal. Furthermore, to demonstrate the effect of the equilibrium configurations sampling, we extended the AIMD simulations to 60 ps. This allows us to take samples from different time periods (10 ~ 24 ps and 34~60 ps) and calculate the corresponding solvation-included energies using the MPA-MD approach. The

results indicate that $E_{sol-included}$ of the reaction center remain consistent (Table S3). Thus, we believe that this method allows us to calculate the elementary steps in the presence of liquid phase with good accuracy. In addition, we recalculated the reaction energetics for the O-O bond and O-H bond cleavage of H₂O₂ with Fe^{III}, using more structure sampling. The results confirm that the trend of the E_a and ΔE remains consistent (Table S4), further validating the accuracy of our approach for elementary step calculations in the liquid phase.

Moreover, we employed an alternative hybrid solvation model to calculate the cleavage of O-O and O-H bond in H₂O₂ for comparison with MPA-MD method. In this approach, we incorporated 15 H₂O molecules around the reaction center within the implicit solvation model (PCM) to examine the bond cleavage in H_2O_2 (Fig. S2). The results show that the activation energies (E_a) of O-H and O-O bond cleavage using this hybrid solvation model (0.18 eV and 1.07 eV, respectively) are comparable to those obtained by MPA-MD (0.19 eV and 1.14 eV, respectively). This consistency arises because the products do not completely dissociate at the transition state, minimizing the effect of solvent water. For the final state, the energy change for OH radical formation (0.68 eV) is comparable to that obtained with the fully explicit solvation model (0.70 eV from MPA-MD), as OH is semi-hydrophobic and relatively less affected by explicit solvation. However, the highly hydrophilic H⁺ requires significant solvation energy (11.32 eV)¹⁸. Due to limitations in the hydrogen-bond network within the local solvation environment, the energy change for H⁺ formation is slightly overestimated (0.11 eV vs. -0.14 eV in MPA-MD). This suggests that the accuracy of the hybrid solvation model depends on the number of explicit water molecules included. In our test, the inclusion of 15 H₂O molecules is a relatively sufficient amount to nearly fully encapsulate the reaction center with extensive hydrogen bonding. Reducing the number of explicit water molecules would further decrease the accuracy, highlighting that the required explicit solvation environment is dictated by the most hydrophilic species in the reaction. Therefore, a fully explicit solvation model remains the preferred choice for accurately determining reaction energy changes.

Overall, the MPA-MD method has proven reliable for aqueous systems, as demonstrated in our previous work^{19,20}, which compared reaction barriers for five kinds of aqueous interface reactions between MPA-MD and state-of-the-art constrained MD methods, which show excellent agreement between the two samplings, underscoring the robustness of MPA-MD for modelling aqueous-phase reactions.

Calculation of free energy. The free energy of elementary reaction can be calculated with $\Delta G = \Delta E + \Delta (pV) - T\Delta S + \Delta E_{ZPE}$, where ΔE is the reaction energy change, and $T\Delta S$ is the entropy change and can be obtained from the Handbook of Chemistry and Physics.²¹ $\Delta (pV)$ is

typically minimal before and after the reaction in the solution, and thus is not considered in this study. ΔE_{ZPE} is the zero-point energy correction, which can be obtained through vibrational frequency calculations. These decomposed components are shown in Table S5.

Notably, for the OH[•] and OOH[•] radical, we note that the their individual liquid-phase entropy is roughly approximated to be 1/2 of the gas-phase entropy, due to the constraints imposed by the hydrogen-bond network in the liquid phase (corresponding to 0.29 eV); this estimation is based on the relative liquid-phase entropy of H₂O and H₂O₂ compared to their respective gasphase entropy at T=300K (H₂O: 0.22 eV in liquid *versus* 0.59 eV in gas phase; H₂O₂: 0.34 eV in liquid *versus* 0.72 eV in gas phase; see *ref.* 20). While this remains an approximation, we believe it provides a more accurate representation of the liquid-phase entropy adjustment is still necessary.

The FeOCl and Fe₂O₃ model. The FeOCl(100) surface was modeled as a $p(4\times1)$ periodic slab with 4 atomic layers and the vacuum was also set to be ~15 Å. The bottom two layers were

fixed, and all other atoms were fully relaxed and $2 \times 1 \times 1$ k-point mesh was enough to apply for

this system. The Fe₂O₃(012) surface was modeled as a $p(2\times 2)$ periodic slab with 4 atomic layers with the vacuum settled to be ~15 Å. The bottom two layers were fixed, and all other atoms

were fully relaxed and $2 \times 1 \times 1$ k-point mesh was enough to apply for this system. The

FeOCl(100) surface is similar to the Fe₂O₃(012) surface in terms of Fe coordination environment (Figure S3). The DFT + U approach was applied to calculate all the elementary reaction steps, and the U term of O-2*p* and Fe-3*d* is 6.3 eV and 3.0 eV, respectively, as recommended in prior studies²²⁻²⁴. Noteworthily, the high-spin state ($\mu_B = 5$ for each Fe atom) was found to be energetically favorable for FeOCl, consistent with our previous work. For the Fe₂O₃, the antiferromagnetic state was adopted.

Section 2: Details of the microkinetic analysis

To quantitatively determine the catalytic ability of Fenton reaction on Fe-complex, the microkinetic analysis was conducted using the CATKINAS package²⁵, which is a widely used kinetic simulation package developed by our group.²⁶ The reaction kinetics were solved by utilizing a microkinetic model under the steady state condition with the continuous flow stirred tank reactor (CSTR) model, without the assumption of which step is the slowest or rate-limiting step, within the framework of transition state theory.

For each elementary step *i* in Table S6, according to the De Donder relation,²⁷ the reaction rate can be written as:

$$\begin{split} r_{1} &= \theta_{\rm H2O-Fe(III)} \cdot k_{1+} - C_{\rm H2O}/C^{\circ} \cdot \theta_{\rm Fe(III)} \cdot k_{1-} \\ r_{2} &= C_{\rm H2O2}/C^{\circ} \cdot \theta_{\rm Fe(III)} \cdot k_{2+} - \theta_{\rm H2O2-Fe(III)} \cdot k_{2-} \\ r_{3} &= \theta_{\rm H2O2} \cdot k_{3+} - C_{\rm H} + /C^{\circ} \cdot \theta_{\rm OOH-Fe(II)} \cdot k_{3-} \\ r_{4} &= \theta_{\rm OOH-Fe(II)} \cdot k_{4+} - C_{\rm OOH}/C^{\circ} \cdot \theta_{\rm Fe(II)} \cdot k_{4-} \\ r_{5} &= C_{\rm H2O2}/C^{\circ} \cdot \theta_{\rm Fe(II)} \cdot k_{5+} - \theta_{\rm H2O2-Fe(II)} \cdot k_{5-} \\ r_{6} &= \theta_{\rm H2O2-Fe(II)} \cdot k_{6+} - C_{\rm OH}/C^{\circ} \cdot \theta_{\rm OH-Fe(II)} \cdot k_{6-} \\ r_{7} &= \theta_{\rm OH-Fe(II)} \cdot k_{7+} - C_{\rm OH}/C^{\circ} \cdot \theta_{\rm Fe(II)} \cdot k_{7-} \\ r_{8} &= C_{\rm H+}/C^{\circ} \cdot \theta_{\rm OH-Fe(II)} \cdot k_{8+} - \theta_{\rm H2O-Fe(III)} \cdot k_{8-} \\ r_{9} &= C_{\rm OH}/C^{\circ} \cdot \theta_{\rm OH-Fe(II)} \cdot k_{9+} - C_{\rm H2O}/C^{\circ} \cdot C_{\rm FeO}/C^{\circ} \cdot k_{9-} \\ r_{d1} &= -C^{\circ} \cdot {\rm Flt} \cdot (C_{\rm H2O}/C^{\circ} - C_{\rm in-H+}/C^{\circ}) \\ r_{d2} &= -C^{\circ} \cdot {\rm Flt} \cdot (C_{\rm H2O}/C^{\circ} - C_{\rm in-H2O}/C^{\circ}) \\ r_{d4} &= -C^{\circ} \cdot {\rm Flt} \cdot (C_{\rm FeO}/C^{\circ} - C_{\rm in-H2O}/C^{\circ}) \\ r_{d5} &= -C^{\circ} \cdot {\rm Flt} \cdot (C_{\rm OH}/C^{\circ} - C_{\rm in-OH}/C^{\circ}) \\ r_{d6} &= -C^{\circ} \cdot {\rm Flt} \cdot (C_{\rm OOH}/C^{\circ} - C_{\rm in-OH}/C^{\circ}) \end{split}$$

where r_i and r_{di} represent the reaction rate equations of elementary step *i* and the diffusion rate equations of liquid species, respectively. k_{i+} and k_{i-} are the forward and reverse rate constant of step *i* respectively. Flt is the standardized liquid-phase space velocity; C_j is the concentration of an individual reactant or product; C_{in-j} is the initial concentration of species *j*; θ_j is the probability of intermediate species *j* occupying an Fe site, which corresponds to the "coverage"

term in the heterogeneous catalysis; C^o is the standard solution concentration; $Z_i = \frac{Q_i}{K_{i,eq}}$ is reaction reversibility of step *i*, which approaches zero as step *i* becomes irreversible and

approaches unity as step *i* becomes quasi-equilibrated;
$$Q_i = \frac{C_{1-}C_{2-}\cdots\theta_{1-}\theta_{2-}\cdots}{C_{1+}C_{2+}\cdots\theta_{1+}\theta_{2+}\cdots};$$

 $K_{i, eq} = \exp\left(-\frac{\Delta G_i^o}{RT}\right)$ is the equilibrium constant of step *i*, respectively. k_{i+} is determined from the transition state theory, which can be written as^{17,28-32}:

$$k_{i+} = \frac{k_{\rm B}T}{h} \exp\left(\frac{\Delta S_i}{R}\right) \exp\left(-\frac{E_{a,i}}{RT}\right)$$
(S5)

where k_B and h are Boltzmann constants and Planck's constant, respectively, T is the reaction temperature.

Note: In comparison to the traditional kinetic expression based on the molar concentration (C_x) of reaction intermediate (x) used in homogeneous catalysis, our microkinetic expression follows the same fundamental principles but introduces a normalization step that accounts for individual catalytic site, which is based on the relative "concentration" (C_x/C_{Fe}). Specifically, in conventional homogenous catalysis, the second-order rate expression can be written as r_{homo} $= k_{homo} * C_A * C_x$, where C_A and C_x are the molar concentration (in unit of M or mol/L) of reactant and intermediate, respectively, and the rate constant k_{homo} has a unit depending on the reaction order (e.g., M⁻¹s⁻¹ for a second-order reaction). In contrast, our study distinguishes this expression by normalizing the concentrations of intermediate (C_x) by the catalyst concentration, defining a dimensionless relative concentration ($\theta_x = C_x/C_{\text{catalyst}}$). This results in a rate expression at the single-site level: $r_{our} = k_{our} * (C_A/C^o)(C_x/C_{catalyst})$, where C^o is the standard molar concentration, and thus $r_{\text{homo}} = r_{our} * C_{\text{catalyst}} * C^{\circ}$ and $k_{homo} = k_{our}/C^{\circ}$. In other words, this means that our approach calculates reaction rates and turnover frequencies (TOF) per Fe site; to convert to a traditional homogeneous setting, one would simply multiply by the actual Fe catalyst concentration. The rate constant k_{our} , calculated in this way, always has a unit of site-¹s⁻¹; when comparing with k_{homo} (in the unit of M⁻¹s⁻¹ for second-order reaction), we need to divide k_{our} by C° .

At a steady-state condition, the θ terms of all intermediates *j* and free sites follow the conservation rule:

$$\sum_{j} \theta_{j} = 1 \tag{S6}$$

At the steady-state condition, each θ term satisfies:

$$\frac{\partial \theta_j}{\partial t} = 0 \tag{S7}$$

Specifically, they give:

 $\begin{aligned} \theta_{\text{H2O-Fe(III)}}/\text{dt} &= r_8 - r_1 + r_9 \\ \theta_{\text{H2O2-Fe(III)}}/\text{dt} &= r_2 - r_3 \\ \theta_{\text{H2O2-Fe(III)}}/\text{dt} &= r_5 - r_6 \\ \theta_{\text{OH-Fe(II)}}/\text{dt} &= r_6 - r_7 - r_8 - r_9 \\ \theta_{\text{OOH-Fe(II)}}/\text{dt} &= r_3 - r_4 \\ \theta_{\text{Fe(II)}}/\text{dt} &= r_4 - r_5 + r_7 \\ \theta_{\text{Fe(II)}}/\text{dt} &= r_1 - r_2 \\ \text{d}C_{\text{H+}}/\text{dt} &= C_n^*(r_3 - r_8 + r_{d1}) \\ \text{d}C_{\text{H2O}}/\text{dt} &= -C_n^*(r_2 + r_5 - r_{d3}) \\ \text{d}C_{\text{FeO}}/\text{dt} &= -C_n^*(r_9 + r_{d4}) \\ \text{d}C_{\text{OOH}}/\text{dt} &= -C_n^*(r_4 + r_{d6}) \end{aligned}$

where C_n is the standardized relative total concentration in liquid phase.

Based on the reaction barriers (E_a) and free energy change (ΔG) of each elementary reaction step *i* (see detailed data in Table S6) obtained using the VASP code, the kinetic analysis was performed with CATKINAS. We note that the kinetic calculations refer to each site, with the turnover frequency (TOF) representing the number of reactant molecules converted per second at a single Fe site. The concentration of reactants was set relative to the amount of Fe to represent the collision probability between the reactants and the catalyst. Therefore, the TOF calculated in this way has unit of s⁻¹. In this approach, the ratio of H₂O₂ to Fe was set according to the typical experimental range of 1 to 10³ times³³⁻³⁷. For illustration, we used a 100:1 ratio as an example for TOF calculation. The kinetic equations were addressed under the condition of $C_{\text{H2O2}}/C_{\text{Fe}}$ = 100, $C_{\text{H2O}}/C_{\text{Fe}}$ = 5500, and T = 300 K.

Notably, since explicitly simulating the system at a given pH using AIMD simulations requires a significantly larger simulation cell and incurs a much higher computational cost, the pH effect is instead introduced in the microkinetic modeling by adjusting the chemical potential of protons. Specifically, the chemical potential of proton is corrected by a term of $-RT \ln(C_{H^+}/C^0)$ (i.e., -2.303 RT pH), which accounts for the proton concentration at different pH values. This is a widely adopted approximation in chemical modeling.

Moreover, we further investigated the influences of different kinetic barriers of O-O bond and O-H bond breakage on the total turnover frequency (TOF, which is a quantitative measure of the overall rate) when pH=0, by applying a similar approach with the method proposed in *ref.* 37, that is the degree of rate control. Specifically, we keep the barriers of other steps constant, meanwhile mapping the TOF value (solving the kinetic equations at every single point) in the *x*-axis range of (0, 0.6) for the O-O bond breakage barrier at intervals of 0.05 and in the *y*-axis range of (0, 0.06) at intervals of 0.05, corresponding to a mesh density of 13×13 in the figure (Figure S10).

Regarding the selectivity of OH[•] versus $Fe^{IV}O^{2+}$, it can be explained by the reaction rate at the steady-state condition. Specifically, the competing reaction for the oxidation process (S9) where Fe^{III} –OH⁻ can also react with the aqueous protons (S8).

$$Fe^{III} - OH^- + H^+ \rightarrow Fe^{III} - H_2O$$
(S8)

$$Fe^{III} - OH^- + OH^\bullet \rightarrow Fe^{IV}O^{2+} + H_2O$$
(S9)

When the reaction reaches equilibrium, the equilibrium constant can be written as:

$$K_{eq8} = \frac{C_{Fe^{III} - H_2O}}{C_{Fe^{III} - OH} - C_{H} +}$$
(S10)
$$K_{eq13} = \frac{C_{Fe^{III} - OH} - C_{H} +}{C_{Fe^{III} - OH} - C_{OH} +}$$
(S11)

where the K_{eq8} and K_{eq13} refer to equilibrium constant of S8 and S9, respectively. With equation (S10) and (S11), we can derive the selectivity (S) as:

$$S = \frac{C_{OH}}{C_{Fe}^{IV}O^{2} +} = \frac{K_{eq8}}{K_{eq13}} \cdot \frac{C_{H}}{C_{Fe}^{III} - H_{2}O}$$
(S12)

Section 3: The analysis of Fe^{IV}O²⁺ formation mechanism

For pathway (iv), involving O-O bond cleavage of H_2O_2 on Fe^{II} to form Fe^{III}(OH⁻) and OH⁺. The formed OH radical may diffuse in the aqueous solution via a hydrogen atom transfer mechanism between OH[•] radical and water molecules (OH^{••••}H₂O \rightarrow H₂O^{•••}OH[•]), enabling them to oxidize OH. scavengers such as DMSO. However, due to the constraints of the hydrogen bonding network, the escape of the nascent OH' radicals requires overcoming a free energy barrier of ~0.17 eV.³⁹ In contrast, the Fe^{III}(OH⁻) and OH[•] radical formed after O-O bond of H₂O remain in close proximity, with an O-O distance of 2.567 Å (Fig. S6), suggesting a weak bonding interaction between the nascent OH[•] radical and Fe^{III}(OH⁻). The reaction of Fe^{III}(OH⁻) with OH[•] is much easier with the barrier only 0.01 eV, making it kinetically more favourable than the escape of the nascent OH radicals into the bulk solution. We also note that while the direct reaction of OH with DSMO is typically fast, it still requires overcoming an energy barrier, which is estimated to be ~ 0.2 eV based on the experimental rate constant ($\sim 10^9$ $M^{-1} s^{-1}$ ⁴⁰ using the Eyring–Polanyi equation. It is worth noting that the reaction rate of the OH[•] scavenger also depends on its concentration. At very high scavenger concentration, the collision probability between OH radical and scavenger increases significantly, making it less favourable to observe pathway (iv), as the OH radical is oxidized by the scavenger. Under this condition, the pathway (iii) may become dominant for Fe^{IV}O²⁺ formation, which involves deprotonation of H₂O₂ on Fe^{II} to form OOH⁻, which then undergoes O-O bond cleavage. The formed OH⁻ is then released into the solution. However, our study focuses primarily on scenarios where OH[•] is not fully scavenged, thus allowing pathway (iv) to occur. Additionally, we performed microkinetic simulations to compare the reaction rates of both pathways as pH changes. As shown in Fig. S9, the reaction rates of both pathways increase and then decrease with increasing pH. Notably, when pH > 4.5, the rate of pathway (iv) exceeds that of pathway (iii), suggesting that pathway (iii) is more favorable under alkaline conditions. However, under realistic conditions, pH typically ranges from 1 to 4.



Figure S1. (a) Energy profile of AIMD simulation for Fe^{III}-complex in aqueous solution. The side views of the input water structure and the water structure obtained after the MD simulation. The red arrow indicates roughly the point that the structures start to further optimization. (b) Energy profiles of AIMD simulation for 60 ps. The shadow under the curves represents the error bar. (c) The optimized structure of Fe^{III}-complex in the gas and explicit water environment. The bond lengths of Fe with ligands are marked (unit: Å).

Note: As shown in Figure S1a, the energy oscillation describes the free energy variation relative to the average energy of simulation during of $10 \sim 20$ ps, and the oscillation range of $10 \sim 20$ ps is approximately between ± 2.5 eV, which achieves a low RMSE value of 3.51 meV/atom. In addition, to verify that the simulation reaches the equilibrium stage after ~ 10 ps, we extended

the AIMD simulations to an additional period of 60 ps (Figure S1b), which further shows the simulations reach equilibrium after ~ 10 ps with a low RMSE. Comparing the lengths of the Fe-O and Fe-Cl bonds in the gas model (Figure S1c), we found that the Fe-O bond becomes slightly shorter, while the Fe-Cl bond is slightly longer due to the H-bonds formation. Thus, the inclusion of the explicit solvent can more accurately simulate the structure of the reaction centre, especially through H-bond interactions.



Figure S2. The structures and energetic information for O-H bond cleavage and O-O bond cleavage of H_2O_2 at Fe^{III} by the hybrid solvation model.



Figure S3. The structures of FeOCl(001) (a) and $Fe_2O_3(012)$ (b), in which the surface-exposed active sites were marked.



Figure S4. The energy scan for the O-O bond breakage of H_2O_2 at the Fe^{III} site with the gasphase (a) and PCM (b) model.



Figure S5. The structures for the initial state (IS), transition state (TS) and finial state (FS) for the O-O bond cleavage of $[(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}(OOH^{-})]^{2-}$ with the key bond length marked by black arrow; unit: Å.



 $[(CI^{-})_{3}Fe^{III}(H_{2}O)_{2}(OOH^{-})]^{-} \rightarrow [(CI^{-})_{3}Fe^{III}(H_{2}O)_{2}(O_{2}{}^{2-})]^{-} + H^{+}$

Figure S6. The related geometric structures in the Fenton reaction. IS, TS and FS indicate the initial state, transition state and final state, respectively.



Figure S7. Related geometric structures in Fenton reaction with OOH group present.



Figure S8. Correlations of E_a of O-O bond cleavage and $E_b(OH)$ on FeOCl(100) (a) and Fe₂O₃(012) (b).



Figure S9. The TOF of the $Fe^{IV}O^{2+}$ formation by pathway (iii) and (iv).



Figure S10. TOF of the OH[•] generation as a function of the O-H bond and O-O bond cleavages.



Figure S11. The structures of Fe^{II}-complex with different ligands. Yellow, S; blue, N.

 $1 \times 1 \times 1$ 2×1×1 2×2×1 State IS /eV -851.67 -851.66 -851.65 TS /eV -850.07 -850.1 / FS /eV -851.19 -851.21 -851.2

 Table S1. Reaction energetics of IS, TS and FS at different k-points.

Table S2. The energy barrier (E_a) and energy change (ΔE) of some key steps on different

Reaction center	Reaction equations	$E_{\rm a}/{\rm eV}$	$\Delta E / eV$	
	$[(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}(H_{2}O_{2})]^{-} \rightarrow$	0.27	0.27	
	$[(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}(OOH^{-})]^{2-} + H^{+}(aq)$	0.37	0.27	
	$[(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}(H_{2}O_{2})]^{-} \rightarrow$	0.42	0.06	
$[(C^{1-}) E_{2}][(U, O)]^{-}$	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + OH^{\bullet}(aq)$	0.42	0.00	
[(C1)3Fe-(H2O)3]	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + OH^{\bullet}(aq) \rightarrow$	0.01	0.22	
	$[(Cl^{-})_{3}(Fe^{IV}O)^{2+}(H_{2}O)_{2}]^{-} + H_{2}O(aq)$	0.01	-0.25	
	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + H^{+}(aq) \rightarrow$	0.00	0.22	
	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{3}]$	0.09	-0.52	
	$[(Cl^{-})_{2}Fe^{II}(H_{2}O)_{3}(H_{2}O_{2})] \rightarrow$	0.41	0.20	
	$[(Cl^{-})_{3}Fe^{II}(H_{2}O)_{3}(OOH^{-})]^{-} + H^{+}(aq)$	0.41	0.30	
	$[(Cl^{-})_{2}Fe^{II}(H_{2}O)_{3}(H_{2}O_{2})] \rightarrow$	0.22	0.08	
$[(C1^{-}) E_{\alpha} \mathbb{I}(U_{\alpha})]$	$[(Cl-)_2Fe^{III}(H_2O)_3(OH-)] + OH^{\bullet}(aq)$	0.55	0.00	
$[(C1)_{2}^{1}C(11_{2}^{0})_{4}]$	$[(Cl^{-})_{2}Fe^{III}(H_{2}O)_{3}(OH^{-})] + OH^{\bullet}(aq) \rightarrow$	0.02	0.26	
	$[(Cl^{-})_{2}(Fe^{IV}O)^{2+}(H_{2}O)_{3}] + H_{2}O(aq)$	0.03	-0.20	
	$[(Cl^{-})_{2}Fe^{III}(H_{2}O)_{3}(OH^{-})] + H^{+}(aq) \rightarrow$	0.13	0.38	
	$[(Cl^{-})_{2}Fe^{III}(H_{2}O)_{4}]^{+}$	0.15	-0.38	
	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(H_{2}O_{2})] \rightarrow$	0.10	0.14	
$[(C^{1-}) E_{c} = [(U \cap C)]$	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OOH^{-})]^{-} + H^{+}(aq)$	0.19	-0.14	
$[(C1)_{3}Fe^{-1}(\Pi_{2}O)_{3}]$	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(H_{2}O_{2})] \rightarrow$	1 1 4	0.70	
	$[(Cl-)_3Fe^{III}(H_2O)_2(OH)] + OH^{\bullet}(aq)$	1.14	0.70	
	$[(Cl^{-})_{2}Fe^{III}(OH^{-})(H_{2}O)_{2}(H_{2}O_{2})] \rightarrow$	0.22	0.00	
$[(C1^{-}) \cdot Fall(OH^{-})(H \cdot O) \cdot]$	(II O) [(Cl ⁻) ₂ Fe ^{III} (OH ⁻)(H ₂ O) ₂ (OOH ⁻)] ⁻ + H ⁺ (aq)		-0.09	
	$[(Cl^{-})_{2}Fe^{III}(OH^{-})(H_{2}O)_{2}(H_{2}O_{2})] \rightarrow$	1 26 0		
	$[(Cl-)_{3}Fe^{III}(OH-)(H_{2}O)_{2}(OH)] + OH^{\bullet}(aq)$		0.01	

reaction centers.

10-24 ps (j)	$E_{tot}^{i, j}$	$E_{water}^{i, j}$	$E_{sol}^{ \ \ i,j}$ - included	24-60 ps (j)	$E_{tot}^{i, j}$	$E_{water}^{\ \ i,\ j}$	i, j E _{sol} - included
1	-851.65	-786.62	-65.03	6	-851.61	-786.45	-65.16
2	-851.28	-786.28	-65.00	7	-851.91	-786.92	-64.99
3	-851.50	-786.62	-64.89	8	-852.14	-787.18	-64.96
4	-851.54	-786.36	-65.14	9	-851.88	-786.74	-65.14
5	-851.36	-786.44	-64.92	10	-852.17	-787.32	-64.84

Table S3. The $E_{tot}^{i,j}$, $E_{water}^{i,j}$ and $E_{sol-included}$ of every sample of $[(Cl^{-})_3 Fe^{III}(H_2O)_3]$ for the 10-24 ps and 24-60 ps time period of AIMD simulations (unit: eV).

Table S4. The E_a and ΔE for O-H bond cleavage and O-O bond cleavage of Fe^{III}(H₂O₂) for the 10-24 ps and 24-60 ps time period of AIMD simulations (unit: eV).

10-24 ps	0	-H	0	-0	24-60 ps	0	-H	0	-0
(j)	$E_{\rm a}$	ΔE	$E_{\rm a}$	ΔE	(j)	$E_{\rm a}$	ΔE	E_{a}	ΔE
1	0.14	-0.29	1.04	0.42	6	0.11	-0.14	1.17	0.81
2	0.21	-0.19	1.28	0.52	7	0.23	-0.16	1.22	0.53
3	0.29	-0.15	1.21	0.82	8	0.19	-0.11	0.95	0.71
4	0.20	-0.18	1.06	1.21					
5	0.12	-0.14	1.13	0.54					
Ave	0.19	-0.15	1.14	0.70	Ave	0.18	-0.14	1.11	0.68

Table S5. Entropy (T ΔS) and zero-point-energy (ΔZPE) contribution (unit: eV).

Steps	1	2	3	4	5	6	7	8	9
$T\Delta S$	-0.21	-0.34	0.00	-0.37	-0.34	-0.34	-0.29	0.00	0.12
ΔΖΡΕ	-0.01	0.10	0.06	0.02	0.10	0.08	0.10	-0.03	0.03

	Reaction equations		$\Delta G/ \mathrm{eV}$	
No.			pH-	$E_{\rm a}/{\rm eV}$
		DFT	correction	
1	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{3}] \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}] + H_{2}O(aq)$	0.06	/	/
2	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}] + H_{2}O_{2}(aq) \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(H_{2}O_{2})]$	0.15	/	/
3	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(H_{2}O_{2})] \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OOH^{-})]^{-} + H^{+}(aq)$	-0.08	2.303 <i>RT</i> pH	0.19
4	$[(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}(OOH^{-})]^{-} \rightarrow [(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}]^{-} + ^{\bullet}OOH$	0.06	/	/
5	$H_2O_2(aq) + [(Cl^-)_3Fe^{II}(H_2O)_2]^- \rightarrow [(Cl^-)_3Fe^{II}(H_2O)_2(H_2O_2)]^-$	0.12	/	/
6	$[(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}(H_{2}O_{2})]^{-} \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + OH^{\bullet}(aq)$	-0.20	/	0.42
7	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} \rightarrow [(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}]^{-} + OH^{\bullet}(aq)$	1.06	/	/
8	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + H^{+}(aq) \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{3}]$	-0.35	-2.303 <i>RT</i> pH	0.09
9	$ [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + OH^{\bullet}(aq) \rightarrow [(Cl^{-})_{3}(Fe^{IV}O)^{2+}(H_{2}O)_{2}]^{-} + H_{2}O(aq) $		/	0.01

Table S3. Reaction energetics of each elementary step for solving the microkinetic model.

Table S6. Reaction energetics of each elementary step for solving the microkinetic model

No.	Reaction equations	$\Delta G/\mathrm{eV}$	$E_{\rm a}/{\rm eV}$
1	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{3}] \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}] + H_{2}O(aq)$	0.06	/
2	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}] + H_{2}O_{2}(aq) \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(H_{2}O_{2})]$	0.15	/
3	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(H_{2}O_{2})] \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OOH^{-})]^{-} + H^{+}(aq)$	-0.08	0.19
4	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OOH^{-})]^{-} \rightarrow [(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}]^{-} + OOH$	0.06	/
5	$\mathrm{H}_{2}\mathrm{O}_{2}(\mathrm{aq}) + [(\mathrm{Cl}^{-})_{3}\mathrm{Fe}^{\mathrm{II}}(\mathrm{H}_{2}\mathrm{O})_{2}]^{-} \rightarrow [(\mathrm{Cl}^{-})_{3}\mathrm{Fe}^{\mathrm{II}}(\mathrm{H}_{2}\mathrm{O})_{2}(\mathrm{H}_{2}\mathrm{O}_{2})]^{-}$	0.12	/
6	$[(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}(H_{2}O_{2})]^{-} \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + OH^{\bullet}(aq)$	-0.20	0.42
7	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} \rightarrow [(Cl^{-})_{3}Fe^{II}(H_{2}O)_{2}]^{-} + OH^{\bullet}(aq)$	1.06	/
8	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + H^{+}(aq) \rightarrow [(Cl^{-})_{3}Fe^{III}(H_{2}O)_{3}]$	-0.35	0.09
9	$[(Cl^{-})_{3}Fe^{III}(H_{2}O)_{2}(OH^{-})]^{-} + OH^{\bullet}(aq) \rightarrow [(Cl^{-})_{3}(Fe^{IV}O)^{2+}(H_{2}O)_{2}]^{-} + H_{2}O(aq)$	-0.07	0.01

Table S7. Reaction rate equations for each elementary step of Fenton reaction and reaction rate constant (*k*). Specifically, the calculated results include the forward/reverse rate constant (k_+/k_-), the net rate (r_n), and the reversibility (Z_i) of step *i* under given conditions (C_{H2O2}/C_{Fe(III)} = 100; C_{H2O}/C_{Fe(III)} = 5500; Flt = 1.0 M⁻¹s⁻¹; pH= 0; T= 300K).

No.	Reaction rate equations	$k_{+}/{\rm site}^{-1}{\rm s}^{-1}$	$k_{-}/{\rm site^{-1}s^{-1}}$	r_n /site ⁻¹ s ⁻¹	Z_i
1	$r_1 = k_{1+} \cdot \theta_{\text{FeIII(H2O)}} \cdot (1 - Z_1)$	6.14×10 ¹¹	6.25×10 ¹²	2.37	0.999999999999613787
2	$r_2 = k_{2+} \cdot \theta_{\text{FeIII}} \cdot C_{\text{H2O2}} / C^o \cdot (1 - Z_2)$	1.89×10^{10}	6.25×10 ¹²	2.37	0.99999992614904909
3	$r_3 = k_{3+} \cdot \theta_{\text{FeIII}(\text{H2O2})} \cdot (1 - Z_3)$	4.02×10 ⁹	1.82×10^{8}	2.37	0.99988512858626344
4	$r_4 = k_{4+} \cdot \theta_{\text{FeIII(OOH-)}} \cdot (1 - Z_4)$	6.14×10 ¹¹	6.25×10 ¹²	2.37	0.99999996592615148
5	$r_5 = k_{5+} \cdot \theta_{\text{FeII}} \cdot C_{\text{H2O2}} / C^o \cdot (1 - Z_5)$	6.03×10 ¹⁰	6.25×10 ¹²	2.37	0.99999991206108219
6	$r_6 = k_{6+} \cdot \theta_{\text{FeII}(\text{H2O2})} \cdot (1 - Z_6)$	5.50×10 ⁵	2.40×10 ²	2.37	3.17×10-4
7	$r_7 = k_{7+} \cdot \theta_{\text{FeIII(OH-)}} \cdot (1 - Z_7)$	9.74×10 ⁻⁶	6.25×10 ¹²	4.38×10 ⁻¹⁹	0.99999996592615148
8	$r_8 = k_{8+} \cdot C_{\mathrm{H}+} / C^o \cdot \theta_{\mathrm{FeIII(OH-)}} \cdot (1 - Z_8)$	1.92×10 ¹¹	2.54×10 ⁵	2.37	0.99999065608040272
9	$r_9 = k_{9+} \cdot C_{\text{OH}} / C^o \cdot \theta_{\text{FeIII(OH})} \cdot (1 - Z_9)$	4.25×10 ¹²	2.83×10 ¹¹	4.69×10-5	0.999999999999646771

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