Effect of ZnO/Tourmaline on Inhibition of SRB: A Theoretical Account

Meng Gong
North China Electric Power University, Beijing 102206, P. R. China
dele333@126.com

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Abstract. Potential mechanism of inhibition of Sulfate Reducing Bacteria (SRB) at the presence of ZnO/Tourmaline was further investigated by Density Functional Theory (DFT) calculation. The structure and electronic states analysis quantitatively and qualitatively dictate the selectively catalytic generation of OH and OOH on different ZnO surface. Results confirms that OH-0.57 on ZnO(101) and OOH-0.27 on ZnO(100) is chemically active, which should act as ROS for the inhibition of SRB. Tourmaline showed synergetic effect on the accumulation of H2O on ZnO surface, which will favor the generation reaction of reactive oxygen species (ROS), hence promoting the inhibition of SRB.

Introduction

Sulfate reducing bacteria (SRB) use sulfate or other oxide sulfur compound as oxidizing agent, reducing to sulfide. SRB belong to 9 bacterial phyla and over 200 species [1]. SRB are the main reason to cause the microbially influenced corrosion by accelerating corrosion rate, inducing stress corrosion and pitting corrosion [2,3]. According to statistics of Petrochina in 1997, the financial loss due to corrosion was amount to 0.25 billion Yuan. The sterilization and inhibition of SRB is the main concern in oil field. Many biological approaches to SRB inhibition were employed in previous researches. SO4-2- reduction was inhibited by addition of NO3- in anoxic paddy soil. Nitrate reducers, and sulfate reducers compet for electron donors [4], NO2-, denitrification products NO and N2O were more competent for inhibition of bacteria than nitrate [5]. These methods is aimed to control sulfide emission rely on increasing redox potential. However, all of these methods have a problem with the high cost. Addition of oxidizing chemicals such as H2O2 or chlorines chemically oxidizes sulfide, thereby decreasing the amount of dissolved sulfide [6]. Cerium-doped TiO2 film with bactericidal activity was prepared on 304 stainless steel by a sol-gel process [7]. The intrinsic mechanism of inhibiting SNB is not investigated so far.

Herein, the potential mechanism of inhibition of SRB at the presence of the prepared nano ZnO/Tourmaline was theoretically investigated using Density Functional Theory (DFT) calculations. H2O interacts to different site of ZnO related to different reaction paths resulting in the generation of different surface species was discussed and confirmed weather they are ROS for the inhibition of SRB. The synergetic effect of Turnaline for the ZnO/Turmaline in the aqueous solution system was detected. Such fundamental understanding of the synergetic effect of Turnaline and the selective catalytic generation of ROS on different ZnO surfaces will contribute to the design and development of high-performance bacterial inhibitors for environmental science, biological sciences, medicine and materials science.

Material and Method

In reference to the catalytic reaction based on supported cluster models [8,9], DFT and periodic slab models were used to study the interaction between H2O on ZnO surface. All calculations were performed using DFT with the generalized gradient approximation (GGA) and PBE method to realize the exchange correlation energy of the system. All reactants, products, and intermediates were completely optimized. Optimization of the energy, displacement and force convergence were used as a criterion. Convergence valve were 1.0 × 10-5 eV/atom, 5.0 × 10-3 Å and 4.0 × 10-3 eV/Å respectively.
A complete linear synchronous transit (LST) and quadratic synchronous (QST) search algorithm was employed to identify the transition state of this dissociation reaction and the transition state that had a unique imaginary frequency\(^\text{[10]}\).

Molecular dynamics (MD) simulation procedures were used to investigate the adsorption of H\(_2\)O on ZnO surface. In the MD simulation, the conjugate gradient method is used for the minimization. The self-adsorption of H\(_2\)O onto ZnO surface was minimized under the conditions of constant pressure and constant temperature (NPT ensembles)\(^\text{[11]}\). The simulation protocol, with the time step of 1 fs to integrate Newton’s equation of motion and the saving frequency of every 10 ps for the coordinates of the structures, helps to ensure the stability of the simulation process. Nonbonded cut-off of 15.5 Å was applied to truncate the long-range interaction to speed up the computation. The particle-mesh Ewald method (PME) algorithm with cubic-spline interpolation (1 Å grid width) was applied to calculate electrostatic interactions efficiently\(^\text{[12]}\).

**Results and discussion**

**Potential mechanism of inhibition of SRB**

As reported, Zn\(^{2+}\) liberation and reactive oxygen species (ROS) production are thought to be the two potential toxic mechanisms of ZnO, and it is generally accepted that ROS is a major factor in the inhibition of bacteria\(^\text{[13]}\). However, it is lack of qualitative and quantitative research on the type and activity of ROS. Herein, the investigation begins with the interaction between different surfaces of ZnO under hypoxic environment.

Figure 1 shows the stable structures and the related calculated potential energy profiles for the adsorption of H\(_2\)O on ZnO. The interactions initiate from the optimized physisorption configuration, and then the final state relates to the dissociated adsorption of H\(_2\)O on ZnO. Results of Figure 1a suggests that H\(_2\)O chemically interacts to the bridge site between the Zn atom and O atom of ZnO(100) surface, leading to the generation of OH group and H atom, and H\(_2\)O acts as electron accepter in the adsorption system.

Figure 1b illustrates the adsorption of H\(_2\)O on the bridge site between two O atoms of ZnO(100) surface from the physisorption state to the final state, which is exothermic, and the reaction energy is -3.868 eV. At the physisorption state (reactant) there is no electron transfer and repopulation between H\(_2\)O and ZnO(100) according to the calculation of charge population. However with H\(_2\)O’s approaching to ZnO(100), OOH group and OH group generated at the intermediate state. The charge population on OOH group and OH group is -0.520 and -0.590, respectively. Then with further electronic interaction happen between ZnO(100) and OOH group and OH group, the intermediate changed into the product, which the charge population on OOH group and OH group is -0.270 and 0.600, respectively. Comparing Figure 1a with Figure 1b, we can observe that H\(_2\)O interacts to different site of ZnO(100) related to different reaction paths resulting in the generation of different surface species.

Figure 1c depicts the stable adsorption configuration of H\(_2\)O on the long bridge site between Zn atom and O atom of ZnO(101) surface from the physisorption state through the intermediate state to the product. This process has to climb over a small energy barrier of about 0.004 eV at the intermediate state and then goes into the final state with the release of 0.743 eV.

Further, we definitively identified the adsorbed species by analyzing the structure and electronic states. The bond length of the generated OH groups shown in Figure 1a, b, and c, is 0.947 Å, 0.944 Å, and 0.946 Å, respectively, which are shorter than that of the pure hydroxyl radical (0.961 Å) and the hydroxyl ion (0.951 Å). The total charge for the generated OH groups shown in Figure 1a, b, and c, is, -0.57, and -0.57, respectively, which transfer from ZnO surface making the spin zero. These generated OH groups shown in Figure 1a, b, and c can be denoted as OH\(-0.60\), OH\(-0.57\), and OH\(-0.57\), respectively. We further analyzed the density of state (DOS) and orbit of the generated OH\(-0.60\), OH-0.57, OH\(-0.57\), OOH\(-0.37\). Figure 2 depicts the DOS, integrated DOS, highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) of -OH, OH, and the generated OH group on ZnO(100).
and ZnO(101), b) DOS and integrated DOS of H$_2$O$_2$, and the generated OOH group on ZnO(100). The DOS of OH$^-$ located at around -4.5 eV and -0.5 eV with two large peaks. The DOS of OH$^-$ delocalizes at the range of -4.5 eV to -2.5 eV, and the range of -1.0 eV to 0.5 eV. According to the peak around Fermi energy (0.0 eV), the outer molecular orbit of OH$^-$ is half filled, corresponding to the integrated DOS of OH$^-$ (9 atoms) and OH$^-$ (10 atoms), respectively. The delocalization and the half fill of OH$^-$ contributed to the high reaction activity. The DOS of OH$^{0.60}$ shown in Figure 1a move to lower energy while compared to that of OH and OH$^-$, which would be less chemically active. The DOS of OH$^{0.57}$ shown in Figure 1c is delocalized and half-filled at around Fermi energy, which is very similar to the DOS of OH$. Therefore the OH$^{0.57}$ shown in Figure 1c would be high chemically active as OH for inhibition of SRB. DOS of OOH$^{0.27}$, while compared to that of H$_2$O$_2$, delocalized from -15.0 V to -11.0 eV and from -3.0 eV to 0.5 eV, the outer bonding-orbit of which is all half-filled. This property will make OOH$^{0.27}$ as reactive oxygen species.

2p-orbit of O atom contributes to the HOMO of OH and OH$^-$, respectively. However, while anti-bonding orbital (4σ*) of OH$^-$ contributes to the LUMO, the unfilled 2p-orbit of O atom contributes to the HOMO of OH$. For OH$^{0.60}$ shown in Figure 1a, 2p-orbit of O atom contributes to the HOMO and 2p-orbit of O atom together with part of O-H bond contributes to the LUMO. For OH$^{0.57}$ and OOH$^{0.27}$ shown in Figure 1b, 2p-orbit of O atom contributes to the HOMO of OH$^{0.57}$ and the anti-bonding orbital contributes to the LUMO of OH$^{0.57}$, 2p-orbits of the two O atoms contribute to both HOMO and LUMO of OOH$^{0.27}$, which corresponds to the half-filled DOS and the spin analysis.

Figure 1 Structures and the related calculated potential energy profiles for the adsorption of water molecule on ZnO. Distances are given in units of Å. Charges of the atoms are underlined.

Figure 2 a) DOS and integrated DOS of OH, OH$^-$, OH$^{0.60}$, OH$^{0.57}$, and OH$^{0.57}$. b) DOS and integrated DOS of H$_2$O$_2$, and OOH$^{0.27}$. 

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Figure 3 lists the density field for H\textsubscript{2}O over ZnO. The red output field represents a small density distribution of H\textsubscript{2}O over ZnO(100) and ZnO(100)/Tourmaline lattice framework while the blue output field represents a high density distribution of H\textsubscript{2}O over ZnO(100) and ZnO(100)/Tourmaline lattice framework. That more H\textsubscript{2}O molecules are adsorbed more closely to surface of ZnO(100)/Tourmaline than to the surface of ZnO(100), implying a certain synergetic effect of Tourmaline for the adsorption H\textsubscript{2}O to ZnO surface.

The adsorption isotherms of H\textsubscript{2}O on ZnO at room temperature are shown in Figure 3b, which displays the adsorption of H\textsubscript{2}O molecules per nm\textsuperscript{2} at each fugacity. The total fugacity reports the sum of the sorbate component fugacities in kPa. That the adsorption isotherms of H\textsubscript{2}O belong to Langmuir-type; i.e., the adsorption capacities initially increase quickly and almost reach the maximum value at around 2000 kPa. In Figure 3, the adsorption capacity and the slope of the adsorption curve before reaching the maximum adsorption capacity for ZnO(100)/Tourmaline is large than those for ZnO(100), suggesting that Tourmaline favour the adsorption of H\textsubscript{2}O on ZnO surface.

The adsorption energy distribution for individual isotherms can be further calculated from the general adsorption integral equation, given by:

\[ \Gamma_t(p,T) = \int \Gamma(p,T,U)f(U)dU \]  \hspace{1cm} (4)

where \( \Gamma_t \) denotes the overall adsorption isotherm, \( \Gamma \) the local adsorption isotherm on surface having an interaction energy \( U \), and \( f(U) \) is the energy distribution function to be obtained [37].

According to the adsorption isotherm of H\textsubscript{2}O on ZnO above, the local adsorption isotherm models Langmuir [38] can be applied. While the maximum adsorption potential energy for the adsorption on ZnO(100)/Tourmaline is located around -0.54 eV, the maximum adsorption potential energy for the adsorption on ZnO(100) is at around -0.48 eV (Figure 3 black line). Such effect is possibly related to the synergetic effect of Tourmaline, which can usually promote the accumulation of H\textsubscript{2}O on the surface of ZnO, hence favoring the generation of ROS to inhibit SRB.

![Figure 3 Density field for H\textsubscript{2}O over ZnO, b) adsorption isotherms and energy distribution functions P(E) of H\textsubscript{2}O over ZnO atom room temperature](image)

Conclusions

The potential mechanism of inhibition of SRB at the presence of ZnO/Turmaline were investigated qualitatively and quantitatively research using DFT calculations. H\textsubscript{2}O interacts to different site of ZnO related to different reaction paths resulting in the generation of different surface species. The generated OH groups and OOH group on ZnO surfaces can be denoted as OH\textsuperscript{-0.60}, OH\textsuperscript{-0.57}, OH\textsuperscript{-0.57}, and OOH\textsuperscript{-0.27}, respectively. We further analyzed the density of state (DOS) and orbit of the generated OH\textsuperscript{-0.60}, OH\textsuperscript{-0.57}, OH\textsuperscript{-0.57}, OOH\textsuperscript{-0.27}. The structure and electronic states analysis quantitatively and qualitatively dictate the selectively catalytic generation of OH and OOH on different ZnO surface. Results confirms that OH\textsuperscript{-0.57} on ZnO(101) and OOH\textsuperscript{-0.27} on ZnO(100) is chemically active, which should as ROS for the inhibition of SRB. Further Tourmaline promotes the interaction and accumulation of H\textsubscript{2}O on the surface...
of ZnO, hence favoring the generation of ROS to inhibit SRB. Fundamental understanding of the synergetic effect of Turnaline and the selective catalytic generation of ROS on different ZnO surfaces will contribute to the design and development of high-performance bacterial inhibitors for environmental science, biological sciences, medicine and materials science.

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References


