Fe(110) 표면의 피리딘 옥심 결합 메커니즘 및 전자 구조 해명: 전산 연구

Unraveling Bonding Mechanisms and Electronic Structure of Pyridine Oximes on Fe(110) Surface: A Computational Study

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Abstract : The development of corrosion inhibitors with outstanding performance is a never-ending and complex process engaged in by researchers, engineers and practitioners. Computational assessment of organic corrosion inhibitors performance is a crucial step towards the design of new task-pecific materials. Herein, electronic features, adsorption characteristics and bonding mechanisms of two pyridine oximes, namely 2-pyridylaldoxime (2POH) and 3-pyridylaldoxime (3POH) with the iron surface were investigated using molecular dynamics (MD), and self-consistent-charge density-unctional tight-binding (SCC-DFTB) simulations. SCC-DFTB simulations revealed that 3POH molecule can form covalent bonds with iron atoms in its neutral and protonated states, while 2POH molecule can only bond with iron through its protonated form, resulting in interaction energies of -2.534, -2.007, -1.897, and -0.007 eV for 3POH, 3POH+, 2POH+, and 2POH, respectively. Projected density of states (PDOSs) analysis of pyridines-Fe(110) interactions indicated that pyridine molecules chemically adsorbed on the iron surface.

키워드 : 부식, 연강, 전산 계산, 부식 억제제
Keywords : corrosion, mild steel, computational calculation, corrosion inhibitor.

1. Introduction

Pyridines are one of the most prevalent heterocyclic structural scaffolds which have a broad spectrum of applications in different fields such as pharmaceuticals, organic synthesis, dyes, additives, agrochemicals, materials science, among others. Pyridine derivatives have been a viable option to inhibit corrosion of iron alloys, copper, and aluminum[1]. The importance of these heterocycles in corrosion inhibition studies comes from their electron-rich structures and the presence of several active sites. It is well-documented that organic corrosion inhibitors act by adsorption on metal surfaces, forming a protective barrier that prevents further corrosion[2].

Despite their enduring importance in providing essential information about the inhibition efficiency and general corrosion protection mechanisms, experimental studies are time and resource-intensive and unable to reveal insights into the direct interactions between molecules and metal surfaces. In an attempt to overcome this limitation, researchers have proposed several computational approaches.

The present study reports computational assessment of 2-pyridylaldoxime (2POH) and 3-pyridylaldoxime (3POH) through molecular dynamics (MD) simulation and self-consistent charge density functional tight-binding (SCC-DFTB) simulations.

2. Materials and Method

Herein, the inhibitor-iron interactions were fully optimized by spin polarized SCC-DFTB method, including dispersion interaction with Slater-Koster trans3d using the DFTB+ code. The generalized gradient approximation (GGA) within its PBE formulation was used for the electron exchange and correlation. The adsorption systems were fully optimized using a SCC tolerance of 10-8 au, thermal smearing (Methfessel-Paxton smearing distribution function), and Broyden mixing scheme.

The electronic energy of pyridine-Fe(110) surface was converged on (2×2×1) k-point grid. The adsorption models were generated by constructing Fe(110) iron surface consisting of a (3×3) supercell and a vacuum spacing of 20 Å along the z-direction separating periodic image in each direction. Then, neutral and protonated forms of molecules were placed on the top side of the slab and all atoms were allowed to relax except the two bottom-most atomic layers. MD equilibrium process was carried out for 5000 ps in canonical ensemble

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(NVT) using COMPASSIII force field.

3. Results and Discussion

Adsorption geometries of neutral and protonated molecules on Fe(110) surface were optimized by SCC-DFTB simulation as shown in Figure 1. Inhibitor molecules can adsorb on the iron surface through physical and/or chemical interactions. An interatomic distance within the sum of the covalent radii of interacting atoms mainly indicates a chemical bonding while physical interactions usually occur at interatomic distances beyond 3 Å. Looking at optimized adsorption geometries of neutral molecules, one can notice that 2POH and 3POH have a very different adsorption mode on Fe(110) surface. The 2POH molecule (Figure 1(a)) approaches the iron surface but with a long adsorption distance, therefore no chemical bonding is formed. However, in contrast to 2POH, it can be observed that 3POH molecule (Figure 1(b)) is stabilized in a nearly vertical adsorption mode on the Fe(110) surface, with formation of three bonds with iron atoms.

The adsorption strength of pyridine oximes on the iron surface can be characterized by the interaction energies analyzed from the optimized adsorption geometries. The neutral form of 3POH molecule exhibits the highest magnitude of interaction energy, reinforcing the fact that it has the strongest contribution to the adsorption of 3POH compound and it is followed by its protonated form. Both neutral and protonated forms of 3POH have a strong negative interaction energy of -2.534 and -2.007 eV, respectively, attributable to their thermodynamically favorable adsorption properties and affinity to iron atoms. In the case of 2POH compound, although the neutral molecule has a favorable adsorption ability on Fe(110) surface as evidenced by its negative interaction energy, it is just -0.007 eV because of the long adsorption distance and absence of chemical bonds.

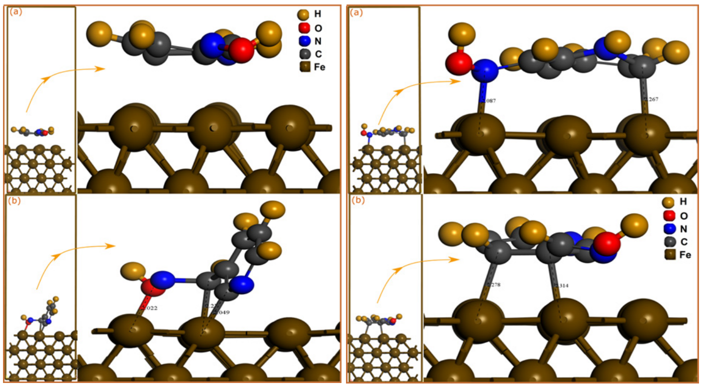

Figure 1. Adsorption geometries of 2POH (left) and 3POH (right) obtained by DFTB simulations; (a) Neutral, (b) Protonated.

MD simulations were conducted to identify the most stable adsorption configurations of pyridine oximes on the Fe(110) surface in absence and presence of water molecules, chlorides, and hydronium ions at 303 K.

4. Conclusion

In the present work, adsorption characteristics and bonding mechanisms of two pyridine oximes, namely 2-pyridylaldoxime (2POH) and 3-pyridylaldoxime (3POH) on Fe(110) surface were investigated using molecular dynamics simulations and SCC-DFTB simulations. Atomistic simulations by SCC-DFTB revealed that 3POH compound had a strong affinity to iron atoms through its neutral and protonated forms whereas only protonated form of 2POH compound showed bonding ability with the iron surface.

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