Pyrite oxidation mechanism in the presence of oxygen and water

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Keywords: Mineral Sulfides, Pyrite, Acid Mining Drainage, DFT, NEB

INTRODUCTION

Pyrite (FeS_2) is the most abundant and widespread sulfide mineral at the Earth's surface. When it is exposed to the atmosphere and humidity, it is oxidized forming acid and sulfates.[1] This phenomenon is called Acid Rock Drainage (ARD) and, consequently, contributes to the acidification of aquifers. Many works[1-3] identified the formation of ARD products on the pyrite, but a molecular view of the mechanism remains to be established. Therefore, the aim of this work is to identify the oxidation mechanism of pyrite.

METHODS

The electronic structure of the systems were calculated by GGA/PBE exchange/correlation approximation of the Density Functional method (DFT) as implemented in Quantum-ESPRESSO package. Following the Monkhost-Pack scheme 1x1x1 special k-points meshes were carry out for all slabs. The Kohn-Sham (KS) electronic orbitals were expanded in a plane-wave basis set up to a kinetic cutoff of 680 eV (50 Ry). This theoretical approach assures an energy accuracy in less than 0.5 kcal.mol^{-1} for reactions calculations. Transition states were calculated by CI-NEB (Climbing Image - Nudge Elastic Band) method, and ten images converged to the minimum energy pathway using a convergence criteria of 0.025 eV.Å^{-1}.

RESULTS AND DISCUSSION

Initially the adsorption of water and oxygen molecules were investigated. Water adsorbs molecularly on the pyrite surface, and no dissociative adsorption is favored. The adsorption energy for water was estimated by our theoretical level in -14.5 kcal.mol^{-1}, in a good agreement with Thermal Programed Desorption analysis,[3] which estimates the adsorption energy in about -10 kcal.mol^{-1}. We check different adsorptions for the oxygen molecule, and the most stable adsorption occurs with the oxygen adsorbed on two iron pyrite surface sites, see Figure 1.

The initial steps of pyrite oxidation is shown in Figure 1. Oxygen molecule adsorbs and oxidizes two Fe(II) pyrite sites to Fe(III). Hydrogen transference occurs from two water molecules adsorbed near oxygen molecule, and four Fe(III)-OH$^-$ groups forms on the surface. This reaction is energetically favorable (-42.0 kcal.mol^{-1}) and the activation energy estimated in our calculations is about 2.0 kcal.mol^{-1}. The determinant ARD oxidation step is the formation of the first S-O bond on the surface. Water adsorbs by hydrogen bonding around two OH$^-$ species and hydrogen transference occurs to formation of two water molecules on the surface. The reaction energy is -23.3 kcal.mol^{-1} and activation energy is 11.6 kcal.mol^{-1} for the last reaction.
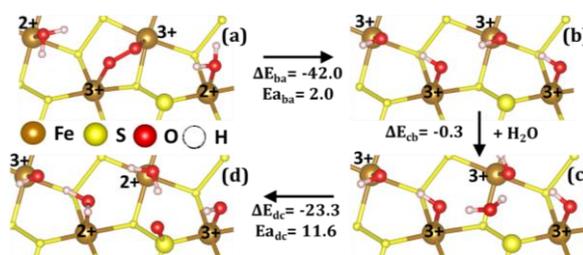

Figure 1. Fragment of the pyrite surface showing the initial oxidation mechanism steps.

CONCLUSIONS

The present study suggests a Fe(II)/Fe(III) redox cycle on the pyrite surface, in accordance with an extensive literature,[1,2] which predicted that several electron transfer between iron sites would be involved in the oxidation of pyrite. All intermediates proposed in the mechanism were observed by photoelectronic spectroscopies.[2]

ACKNOWLEDGMENTS

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