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DFT Investigation of Chalcopyrite Oxidation Mechanism

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Sulfide minerals are an economically important group of minerals, serving as the primary source of metals such as copper, zinc, lead, gold, and silver. Chalcopyrite, for instance, is the planet's main source of copper, extracted through both pyrometallurgical and hydrometallurgical processes. Hydrometallurgy provides benefits for low-grade ores and enhances environmental control. However, pyrometallurgy remains the sole viable process for high-grade ores due to surface transformations under hydrometallurgical conditions[1-2]. In light of this, our objective is to elucidate the surface phenomena that occur on chalcopyrite, proposing an oxidative mechanism for the surfaces of chalcopyrite. Our calculations are based on Density Functional Theory (DFT), implemented in Quantum Espresso[3], version 7.0, using the exchange-correlation energy functional employed was Perdew–Burke–Ernzerhof (PBE)[4] and plane waves. Hubbard parameters were applied to iron atoms to improve the description of d electrons. Our adsorption models use chalcopyrite surfaces terminated with (001) and (112) sulfur atoms. As part of our proposed mechanism, we initiated a study on the adsorption of water and oxygen on these surfaces. Several configurations were tested to determine the most stable configuration for further investigation of the mechanism. In the first step, water preferentially adsorbs on iron sites, while oxygen prefers to adsorb on sites containing both iron and sulfur, as shown in Figure 1. Density of States (DOS) calculations support these adsorption preferences. For these systems, the adsorption energy was calculated to be -15.94 kcal mol^{-1}. In the second step, various possibilities are being explored, with the most likely outcome being the dissociation of O_2. Thermodynamic, electronic, kinetic, and spectroscopic properties will be calculated to understand the formation reactions of sulfur oxides on the chalcopyrite surface.

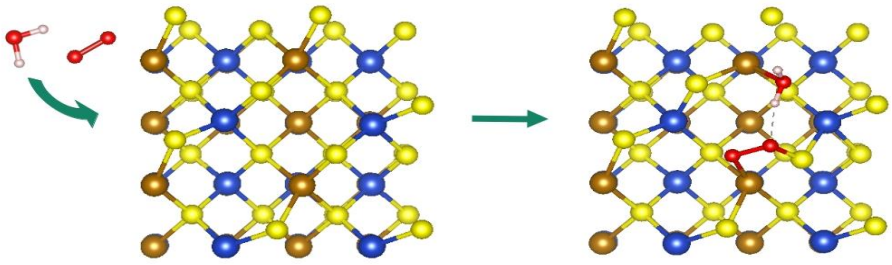

Figure 1: Atomic configuration after the first co-adsorption step of H_2O and O_2 on a chalcopyrite (001) surface. Atoms are colored as follows: red (O), white (H), yellow (S), blue (Cu), and brown (Fe).

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