

The interaction of pyrite {100} surfaces with O₂ and H₂O: Fundamental oxidation mechanisms

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ABSTRACT

The interaction of gaseous O₂, H₂O, and their mixtures with clean {100} surfaces of pyrite (FeS₂) were investigated in ultra-high vacuum using scanning tunneling microscopy and spectroscopy (STM-STS), ultraviolet photoelectron spectroscopy (UPS) and ab initio calculations. He I UPS spectra of O₂ exposed surfaces show that the density of states decreases at the top of the valence band but increases deeper in the valence band. These changes indicate oxidative consumption of low binding energy electrons occupying dangling bond surface states localized on surface Fe atoms, and the formation of Fe-O bonds. No such changes in the valence band spectra are observed for pyrite surfaces exposed to H₂O. However, UPS spectra of surfaces exposed to mixtures of O₂ and H₂O demonstrate that the combined gases more aggressively oxidize the surface compared to equivalent exposures of pure O₂. Atomically resolved STM images of O₂ and O₂-H₂O exposed surfaces show discrete oxidation “patches” where reacted surface Fe sites have lost surface state density to the sorbed species. STS spectra show the removal of highest occupied and lowest unoccupied surface state density associated with dangling bond states consistent with the interaction of sorbates with surface Fe sites. Ab initio cluster calculations of adsorption energies and the interaction of O₂ and water species with the surface show that O₂ dissociatively sorbs and H₂O molecularly sorbs to surface Fe. For the mixtures, the calculations indicate that H₂O dissociatively sorbs when O₂ is present on the surface. Charge population analyses also show that the surface S sites become more electropositive in this environment which should allow for easier formation of S-O surface bonds, thus promoting the production of sulfate during oxidation.