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Enhanced Atomic Hydrogen Retention on Moderately Sulfidated Zero-Valent Iron Surfaces: Insights from DFT Modeling

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Sulfidation has been widely studied as a strategy to increase the reactivity, selectivity and longevity of zero-valent iron (ZVI) in groundwater remediation applications. However, the reaction mechanisms controlling the contaminant degradation at sulfidated ZVI (S-ZVI) surfaces remain debated. Recent studies suggest that reductive reactions mediated by adsorbed atomic hydrogen (H*) may dominate the degradation of key contaminants, such as chlorinated ethenes, on S-ZVI surfaces with moderate S coverage, challenging the previously proposed major role of direct electron transfer.

Herein, we employ density functional theory (DFT) to investigate the behavior of H* at S-ZVI surfaces with varying S coverage. We examine H* formation via hydrogen-evolution reaction, adsorption stability, mobility, and recombination. To account for the surface passivation occurring when S-ZVI particles undergo corrosion in water environments, we also systematically study the impact of surface oxidation and hydroxylation on the H* generation and fate.

Our results [1] show that sulfidation suppresses water adsorption and H* formation via water dissociation while weakening also H* adsorption affinity on ZVI. Despite this, S-ZVI with moderate S coverage (~¼ monolayer) retains more reduced Fe sites favorable for H* adsorption than oxidized ZVI surfaces. Adsorbed H* at the reduced Fe sites exhibits restricted mobility near S atoms, limiting H* recombination and increasing their availability for contaminant degradation.

These findings provide fundamental mechanistic insight into increased H* retention at S-ZVI surfaces, offering explanation why moderate S coverage optimizes H* retention. Thus, they can help in designing S-ZVI materials with improved reactivity and selectivity for targeted groundwater remediation applications.

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References

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