Theoretical Investigation of H_2S Corrosion of Mild Steel

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Introduction

The internal corrosion of carbon steel by carbon dioxide (CO_2) in the presence of hydrogen sulfide (H_2S), known as H_2S/CO_2 corrosion, represents a significant problem for both oil and refineries and natural gas treatment facilities. The phenomenon is complicated because CO_2 and H_2S cause different types of corrosion of carbon steel. The corrosion of CO_2 has received a lot of attention and its mechanisms are fairly understood (1-9). On the other hand, the corrosion of H_2S has not received much attention, and even though some mechanisms have been proposed (10,11) they have not been validated. The proposed H_2S corrosion mechanisms available in the literature (10,11) properly explain the behavior of experimental data but their thermodynamics and kinetics feasibility is not known. Therefore, it is unclear what the corrosion mechanism of mild steel in the presence of H_2S is. The lack of this knowledge represents a critical problem for the understanding, prevention, and control of H_2S/CO_2 corrosion.

The objective of this work is to investigate the feasibility of the mechanisms for H_2S corrosion of carbon steel proposed in the literature, using well established computational chemistry techniques such as first principle calculations and transition state theory. The most feasible mechanism for H_2S corrosion and the reaction rates and kinetics constants associated with the mechanism will be presented.

Theoretical Calculations

The mechanisms for H_2S corrosion of carbon steel proposed in the literature are based on the formation of Mackinawite film. The proposed mechanisms are given in Figure 1. The feasibility of the mechanisms given in Figure 1 was evaluated using computational chemistry. The structures of the molecules involved in the two different paths were optimized in gas phase at 0 K and 1 atm. Gaussian 98 was the first principle calculations software used for the calculations (12). B3LYP and 6-311+G(d) were the method and the basis set used for the calculations, respectively. A frequency analysis of the optimized structures was performed to determine the nature of the stationary point found by the optimization and to calculate the thermochemistry of the molecules. The STQN method was used to determine the structures for the transition states between the products and the reactants shown in each of the reactions given in Figure 1.

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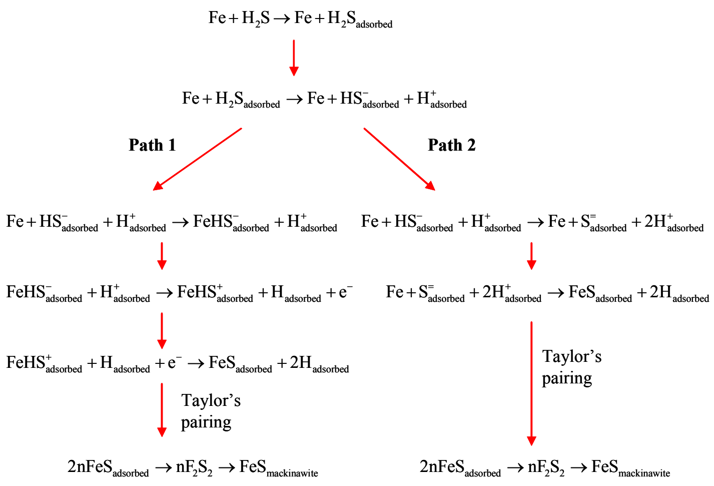

Figure 1. Proposed mechanisms for H_2S corrosion of Fe (10-11). After the initial adsorption of H_2S on the Fe surface, Mackinawite can be formed from amorphous FeS either by Path 1 (10-11) or Path 2 (11).