Theory and Applications for Sulfur Chemistry: Hydrogen from Hydrogen Sulfide

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Technical Summary

In this thesis, I explore the chemistry of reacting sulfur species computationally and experimentally.

Chemical systems often resist simplification because the number of important species and reactions far exceeds anyone's definition of simple. However in spite of the inherent complexity, understanding the detailed chemistry of reacting systems is crucial to a wide variety of pursuits, both academic and commercial. Automatic reaction mechanism generation is a powerful tool to understand complex reactive systems and describe the detailed chemistry. The Reaction Mechanism Generator (RMG) software is an implementation of this concept that allows the user to create detailed kinetic models for use in the design, optimization, or understanding of reactors, engines, or fuels. The computational section of this thesis centers on creating the capability to automatically predict the thermochemical properties of arbitrary sulfur molecules and the kinetic parameters of reactions between these species in the context of automatic mechanism generation. A demonstration of this enhanced capability is shown in the automatic creation of detailed chemical mechanism describing the partial oxidation of dimethyl sulfide.

The experimental work focuses on a hydrogen generating chemical cycle that uses hydrogen sulfide as a feedstock. Novel hydrogen sulfide processing and hydrogen production technologies are timely given the rising production of increasingly sulfur-rich hydrocarbons, the more strict government and industry limits on the sulfur content of fuels, and the need for new, non-hydrocarbon based, methods of hydrogen production to reduce the carbon intensity of chemical industry.

Initially exploring the reactivity of hydrogen sulfide, water, and iodine mixtures to form hydroiodic acid, two competing pathways were discovered. The more interesting pathway involved the reaction of hydrogen sulfide with iodine and water to form hydroiodic acid and sulfur dioxide. A bench-top prototype was created demonstrating the creation of hydrogen gas from hydrogen sulfide through this pathway. Technoeconomic modeling of the proposed process was conducted, suggesting both commercial and environmental motivation for adoption. The thesis concludes with a brief discussion of future research directions and progress toward the commercialization of the described technology.