

Title: Modeling of Syngas Reactions and Hydrogen Generation over Sulfides

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1 Abstract

Introduction and Objectives

The objective of the research is to analyze pathways of reactions of hydrogen with oxides of carbon over sulfides, and to predict which characteristics of the sulfide catalyst (nature of metal, defect structure) give rise to the lowest barriers toward oxygenated hydrocarbon product. Reversal of these pathways entails the generation of hydrogen, which is also proposed for study. The activation of hydrogen on MoS₂ edges is analyzed by Density Functional Theory as the first step in hydrogenation reactions.

Accomplishments to Date

High-level density functional theory was used to model the edge defect of MoS₂ both with and without H atoms and H₂ molecules adsorbed on those edges. The structures and stabilities of the pure MoS₂ edges were finalized and published. Several MoS₂ cluster models were examined to provide insight into the behavior of the more complex edges. With that knowledge, the adsorption locations, energies, and vibrational frequencies of H adsorption were determined.

The (10 $\bar{1}$ x) edge of MoS₂ was found to be most stable, with the (1 $\bar{2}$ 1x) edge only 0.09 eV per edge MoS₂ unit less stable. The (1 $\bar{2}$ 1x) edge has not been studied previously and provides for the strongest atomic adsorption energy for H of -2.90 eV. As expected, vibrational frequencies of the H atoms are strongly dependent on the environment around them. The lowest frequency is 1223 cm⁻¹ for H bridging two Mo atoms. 1862 cm⁻¹ is characteristic of Mo–H bonds, while S–H bonds vibrate at ~2550 cm⁻¹.

The cluster calculations show that the MoS₂ monomer exists in the triplet spin state, while the H₂-MoS₂ cluster has zero spin. Coordinate driving of the H-Mo-H bond angle shows the transition from triplet to singlet and analysis of the electronic orbitals reveals interaction between the σ^* orbital of the H₂ molecule with the metal d orbitals, as predicted by Kubas [*J. Organometallic Chem.* **635** (2001) 37]. It is this interaction that breaks the H-H bond and allows the activation of the hydrogen.

Future Work

This project will expire by September 2004. The research into the modeling continues, however, along the following lines: (a) Theoretical search for catalysts for homologation of methanol to ethanol by CO/H₂, based on calculations of barriers for CO insertion into the methyl-metal bond to form acetyl, and hydrogenation thereof to ethoxide. The catalysts of choice are solid sulfides such as those studied in the present project as regards the reactivity of their surface defect sites. (b) Theoretical search for low barriers in the so-called Natta mechanism for homologation of methanol to ethanol via CO insertion into the methoxy-metal bond followed by methyl transfer from the oxygen to the carbon of the surface metallocarboxylate to form acetate. The catalysts explored for this mechanism include oxides of elements of the Group 14-15, i.e. Sn, Sb, Pb and Bi. Preliminary calculations indicate SnO as the most prospective initial choice.

2 List of Publications, Conferences, and Students Supported

Conference Presentations

- K. Klier, 19th Annual Pittsburgh Coal Conference, 2002.
- K. Klier, 20th Annual Pittsburgh Coal Conference, 2003.

Journal Articles

- J. A. Spirko, M. L. Neiman, A. M. Oelker, K. Klier, *Surface Science* **542** (2003) 192.
- J. A. Spirko, M. L. Neiman, A. M. Oelker, K. Klier, *Surface Science* (to be submitted).

Students Supported

- Michael L. Neiman, former graduate student in the Department of Chemistry. Currently a graduate student in Mathematics at Rutgers University.
- Abigail M. Oelker, former undergraduate student in the Department of Chemistry. Currently a graduate student in Chemistry at Boston University.