VII.F.3 Selective Catalytic Oxidation of Hydrogen Sulfide

Viviane Schwartz (Primary Contact), Steve Overbury, and Xianxian Wu
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831
Phone: (865) 576-6749; Fax: (865) 576-5235; E-mail: schwarts@ornl.gov

DOE Technology Development Manager: Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

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Objectives

- Develop and optimize low-cost carbon-based catalysts for the selective oxidation process to reduce sulfur levels to the parts-per-billion (ppb) range in an \( \text{H}_2 \)-rich gas stream in order to produce a low- to zero-sulfur fuel for use in fuel cells. The main reaction is represented by the following equation:

\[
\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{n}\text{S}_n
\]

- Identify activated carbon catalysts that show potential for complete conversion of \( \text{H}_2\text{S} \) without formation of undesired products.
- Investigate different activation protocols and carbon-based precursors that can lead to improved catalytic properties, and design catalysts with optimum properties.
- Perform catalytic studies of catalysts in \( \text{H}_2 \)-rich streams and model reformate gas streams to determine catalytic activity, selectivity, durability, and regeneration processes.
- Investigate reaction mechanisms and pathways for byproduct formation, such as carbonyl sulfide (COS) and sulfur dioxide (SO\(_2\)).
- Investigate reaction conditions that lead to complete and exclusive conversion of \( \text{H}_2\text{S} \) to elemental hydrogen and elemental sulfur.
- Characterize the microstructures, surface properties, and impurity levels of the catalysts and correlate them to catalytic activity, selectivity, and durability.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- I. Hydrogen Purification/Carbon Monoxide Cleanup—Reduction of emission of toxic chemicals derived from the presence of sulfur compounds in the fuel.

Technical Targets

The project is conducting fundamental studies in the development of carbon-based catalysts that can reduce sulfur levels to the ppb range in a \( \text{H}_2 \)-rich gas stream. The lab-made catalysts have demonstrated the capability to reduce sulfur levels of fuel gas streams to less than 200 ppb without formation of byproducts such as COS and SO\(_2\).
Approach

- Investigate different sources of carbon and activation processes that can lead to carbon-based materials with improved activity and selectivity for the $\text{H}_2\text{S}$ removal reaction.
- Characterize the catalysts and correlate the effects of pore volume, pore size and distribution, impurities, surface functional groups, and catalyst morphology to catalytic performance.
- Investigate the effect of reaction conditions on the activity and selectivity.
- Investigate reaction mechanisms and the formation of byproducts in $\text{H}_2$-rich streams containing variable amounts of other compounds such as water vapor and carbon monoxide.

Accomplishments

- Synthesized activated carbons that displayed superior activity and selectivity as catalysts for $\text{H}_2\text{S}$ oxidation. The synthesized catalysts are capable of converting $\text{H}_2\text{S}$ exclusively to elemental sulfur and $\text{H}_2$ in both $\text{H}_2$ and simulated reformate streams.
- Characterized surface morphology, surface area and pore size distribution, surface functionalities, and impurity composition of several commercial and laboratory-synthesized activated carbons.
- Evaluated the effect of temperature, $\text{O}_2/\text{H}_2\text{S}$ ratio, and space velocity on the activity and selectivity.
- Conducted catalytic tests for monitoring catalyst behavior in a shorter time at a relatively high $\text{H}_2\text{S}$ concentration and in several gas streams containing variable amounts of CO, $\text{CO}_2$, and $\text{H}_2\text{O}$ to evaluate formation of byproducts.
- Demonstrated the capability of lab-made catalysts to reduce sulfur levels of fuel gas streams to less than 200 ppb without formation of byproducts such as COS and $\text{SO}_2$.

Future Direction

- Design catalysts based on optimization of the synthesis process. Synthetic carbon catalysts should be produced with controlled structure, morphology, and impurity content that can lead to enhanced catalytic properties.
- Investigate durability and regeneration processes.
- Develop a systematic study to understand the importance of the impurity contribution to reaction and evaluate the roles and significance of surface functional groups.

Introduction

Hydrogen is commonly produced by reforming of natural gas; however, reformate contains impurities, such as $\text{H}_2\text{S}$, that can poison shift catalysts and fuel cell electrodes. In fuel cell applications, even a low concentration (a few ppm) of hydrogen sulfide can dramatically shorten the life of fuel cell catalysts. Therefore, the removal of sulfur-containing compounds from $\text{H}_2$-rich fuels is very important. Selective catalytic oxidation of $\text{H}_2\text{S}$ using an activated carbon catalyst is a highly promising method for the removal of $\text{H}_2\text{S}$ from fuel cell hydrocarbon feedstock [1]. The primary objective of this project is to develop a carbon-based catalyst that promotes oxidation of $\text{H}_2\text{S}$ to elemental sulfur, reducing sulfur contamination to the ppb range or better in $\text{H}_2$-rich fuel streams.

Although the use of activated carbons for selective oxidation of $\text{H}_2\text{S}$ to elemental sulfur has been suggested as a preferred approach for removal of sulfur from gas streams, the key mechanisms for $\text{H}_2\text{S}$ removal and the critical features in an activated carbon catalyst are not well understood. Additionally, one of the main difficulties with the use of this technology is the formation of byproducts such as $\text{SO}_2$ and COS. This project is focused on the design and fundamental investigation of the catalytic properties of low-cost, carbon-based catalysts that...
can successfully reduce the sulfur level in fuel cell feedstocks to meet the desired level.

**Approach**

The research is geared toward a fundamental understanding of the catalytic properties of the carbon catalyst that will enable the design of catalytic materials that can continuously remove \( \text{H}_2\text{S} \) to the ppb range in \( \text{H}_2 \)-rich fuel streams. For this purpose, an integrated effort is required that includes optimization of synthesis of carbon-based materials, structural and chemical characterization, and finally reaction studies.

The carbon materials were synthesized; and the effects of the precursor material, heat treatment, and activation process were evaluated. Activation was achieved by exposing the carbon precursor to an oxidizing gas (\( \text{CO}_2 \) or steam) for varying lengths of time in order to produce materials with variable microstructures. Different precursors were used to produce carbon catalysts with varying impurity levels. The performance of all carbon materials synthesized and obtained commercially was measured and compared in a fixed-bed reactor equipped with a gas chromatograph and an infra-red detection system. The effect of operational parameters was tested by varying the temperature, \( \text{O}_2/\text{H}_2\text{S} \) ratio, and space velocity. The formation of byproducts such as \( \text{SO}_2 \) and \( \text{COS} \) was investigated under varying gas compositions.

The characterization of the materials’ properties is being carried out to identify the surface microstructures, functionalities, and impurity contents and their relationships with the synthesis protocol and the performance of carbon catalysts. Inorganic impurities [2] and surface functional groups [3] have been shown to play an important role in the catalytic activity of the carbon-based materials. The impurities were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) screening and inductively coupled plasma optical emission spectroscopy (ICP-OES), and highly pure carbons were synthesized to isolate their effects. Another important aspect to be addressed is the kind of pore structure and the pore size distribution desired for an active, selective, and durable catalyst. Nitrogen adsorption isotherms (Bruner, Emmett and Teller surface area analysis method, BET) analysis and density functional theory calculations were performed to determine the surface area and pore size distribution of the catalysts. Thermogravimetric analysis and the Boehm titration method [4] are being applied to investigate the chemical nature of the carbon surface. Studies concerning the relationship between the activation burn-off level of activated carbons, the pore size distribution, and catalytic behavior have been conducted. Long-term reactivity tests are being used to evaluate the durability of the catalysts and regeneration processes. The lab-made catalysts are being independently tested for the removal of sulfur in coal streams through a partnership with the National Energy Technology Laboratory. Industry applications and partnering are under discussion with United Technologies, ConocoPhilips, and Chevron.

**Results**

We have developed an improved activated carbon catalyst that can selectively oxidize \( \text{H}_2\text{S} \) in \( \text{H}_2 \)-rich gas streams without consumption of \( \text{H}_2 \).

Our lab-made catalysts have demonstrated the capability for continuous removal of sulfur to less than 200 ppb levels. Figure 1 illustrates the differences among the lab-made catalyst and several commercial catalysts tested using a model reformate stream containing 1000 ppm of \( \text{H}_2\text{S} \) in 50% \( \text{H}_2 \), 15% \( \text{CO}_2 \), 9% \( \text{CO} \), 2% \( \text{CH}_4 \), and 23% \( \text{H}_2\text{O} \). The conversion of \( \text{H}_2\text{S} \) and sulfur yield were calculated using these equations:

\[
\text{Conversion of } \text{H}_2\text{S} (\%) = \frac{C_{\text{H}_2\text{S,in}} - C_{\text{H}_2\text{S,out}}}{C_{\text{H}_2\text{S,in}}} \times 100
\]

\[
\text{Selectivity to sulfur (}) = \frac{C_{\text{H}_2\text{S,in}} - C_{\text{H}_2\text{S,out}} - C_{\text{SO}_2}\text{out} - C_{\text{COS}\text{out}}}{C_{\text{H}_2\text{S,in}}} \times 100
\]

It is clear from Figure 1 that the undesired formation of gaseous sulfur byproducts such as \( \text{SO}_2 \) and \( \text{COS} \) is a key aspect for the successful performance of the lab-made catalysts, and it is the main problem for the commercial carbon materials.

Besides the catalyst properties, the operational conditions must be optimized in order to achieve high conversion and selectivity. The effects of temperature, \( \text{O}_2/\text{H}_2\text{S} \) ratio, and space velocity were
investigated. Our studies showed that the activity and selectivity of activated carbons are strongly dependent upon the test conditions and the gas components. For instance, Figure 2 shows the influence of the O$_2$/H$_2$S ratio on the catalytic behavior of activated carbons in an H$_2$ stream at 150°C. It can be observed that a higher O$_2$/H$_2$S ratio results in a higher emission of SO$_2$ but does not significantly shift the SO$_2$ breakthrough time. In a reformate stream (Figure 3), an increase of the O$_2$/H$_2$S ratio suppressed the formation of COS, but the effect was not significant for ratios higher than 2:1.

The formation of byproducts was studied by varying the gas composition. Figure 4 shows the measured H$_2$S conversion and COS emission when a lab-made catalyst was tested using different gas streams. It was found that the formation of byproducts such as COS is strongly dependent on the reactive mixture and that different reaction routes might be responsible for the changes in selectivity observed during this study. The most significant result from this effort is that our lab-made catalyst demonstrated a unique capability to partially oxidize COS as

\[
\text{COS} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 + \frac{1}{n}\text{S}_n
\]

The surface area, impurity content, and carbon structure of several commercial and lab-made...
Conclusions

- Activated carbons are inexpensive and can be used to remove sulfur to ppb levels from H₂-rich gas streams. Several activated carbon materials have been synthesized and tested for the selective catalytic oxidation of H₂S.
- The process operates at low temperatures, and the ORNL-synthesized activated carbon demonstrated good activity and high selectivity toward H₂S oxidation, whereas side reactions are a problem for commercial activated carbons.
- The conversion and selectivity of H₂S are strongly dependent on operational conditions. Increased conversion can be achieved using a higher O₂/H₂S ratio, lower space velocities, and higher temperatures. However, these factors show little effect on achieving exclusive conversion to elemental sulfur.
- The emission of byproducts such as COS and SO₂ seems to be dependent upon the sulfur vapor pressure level. The microstructures of the lab-made catalyst may be responsible for the build-up of sulfur in its micropores before the sulfur vapor pressure becomes high enough to form byproducts. Additionally, the lab-made carbon catalysts demonstrated a unique capability to partially oxidize COS.
- Many factors, such as impurities, microporosity, and surface functional groups may contribute to the differences in activity and are under investigation.

FY 2005 Publications/Presentations/Patents


References