

IV.F.9 Selective Catalytic Oxidation of Hydrogen Sulfide

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Objectives

- Develop and optimize an oxidative process to reduce sulfur levels to the parts per billion range in a H₂-rich gas stream using low-cost carbon-based catalysts to produce a low- to zero-sulfur fuel for use in fuel cells.
- Develop different activation protocols and carbon-based precursors in order to tailor the catalysts for the promotion of hydrogen sulfide removal.
- Characterize the microstructures and impurity level of the catalysts and determine their relationship to catalytic activity.
- Perform studies of catalysts in H₂-rich and model reformat gas streams.
- Demonstrate the catalysts are capable of continuous removal of sulfur to 'ppbv' levels.

Technical Barriers

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

- K. Emissions and Environmental Issues
- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- Develop activated carbons with controlled microstructure for improved activity and selectivity for oxidation of hydrogen sulfide.
- Characterize the catalysts and correlate effects of pore volume, pore size and distribution, impurities, surface functional groups, and catalyst morphology to catalytic activity.
- Perform reactivity tests to determine operational parameters of the catalysts under development.
- Model the reaction using thermodynamic and kinetic models.

Accomplishments

- Synthesis of an activated carbon that demonstrated reduced sulfur levels (<5 ppb) in hydrogen-containing gas streams without formation of by-products such as COS and SO₂.
- Evaluation of numerous commercial activated carbons based on wood, coal, cellulose, and coconut shells.
- Demonstration of 99.9% removal efficiency for gas stream containing >1000 ppm H₂S for more than 20 hours.
- Initiation of discussions with several commercial end users to test the catalysts under development.

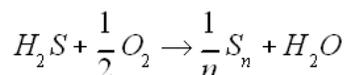
Future Directions

- Correlate the effects of catalyst morphology to the reaction kinetics in order to optimize pore size distribution.
- Demonstrate durability through long-term testing (>1000 hours).
- Correlate the impurities in the catalyst to the reaction kinetics.
- Evaluate the roles of surface sites and their significance to the reaction.
- Based on the above investigation, establish experimental protocols for modifying the functional group content and impurity level/content of activated carbons.
- Study catalytic reaction kinetics and understand the formation mechanisms of undesired products, such as SO₂ and COS.

Introduction

There are several concerns regarding sulfur contamination in the fuel stream. Environmental concerns stem from the fact that combustion products of sulfur species, largely sulfur oxides (SO_x), may be released into the atmosphere, contributing to air pollution, acid rain, and global climate change. Furthermore, scrubbing the exhaust stream to prevent this release leads to system complexity, cost, and a loss in overall efficiency due to the heat required for effective exhaust cleanup. While an H₂S limit in the fuel stream of less than 100 ppm may be reasonable to assuage environmental concerns, fuel processors for polymers and the fuel cells themselves have much more stringent sulfur control requirements.

For a variety of applications involving fuel or synthesis gas, H₂S-selective catalytic partial oxidation is a technology that may prove to be attractive. In addition to potentially being a continuous sulfur removal technology, it has the thermodynamic potential to remove sulfur to the part-per-billion level below 250°C. The supporting chemistry is simple:



Here, free energy minimization calculations [1] have shown that $n = 2, 6, \text{ or } 8$ depending on the temperature of the reaction. The elemental sulfur product is then easily separated and recovered from the fuel gas as a solid or liquid condensed phase.

High-surface-area (microporous) activated carbon has been shown to be the optimal catalyst for this process. However, one of the difficulties encountered with using this technology with sulfur-containing synthesis gas compositions is the formation of COS. It has been suggested that CO adsorbed on the catalyst surface reacts with H₂S to form COS. One possible approach to mitigate this phenomenon is to modify the catalyst to suppress the adsorption of CO and promote the adsorption of O₂ on the catalyst surface. Other difficulties with activated carbon include impurities, surface defect structure, and design of the material to maximize surface area and packing density.

We have developed improved activated carbon catalysts that can selectively oxidize H₂S in hydrogen-rich streams (also including CO and H₂O), and no consumption of H₂ has been observed. However, the key mechanisms for hydrogen sulfide removal and the critical features in an activated carbon catalyst are not well understood. Additionally, coal gas streams include high concentrations of carbon oxides, carbonyl sulfide, and potentially carbon disulfide. Therefore, it is important to investigate the catalytic activity of activated carbon for COS cleanup processes as well. An extensive evaluation of catalyst structure and the roles of catalyst impurities and surface functional groups is needed in order to make significant advances in this technological process. This project is focused on the design and fundamental understanding of the catalytic properties of low-cost carbon-based materials that can successfully reduce the sulfur level in coal gas streams.

Approach

The research is geared towards developing a fundamental understanding of the catalytic properties of the carbon catalyst to enable the design of catalytic materials that can continuously reduce hydrogen sulfide to the parts per billion (ppb) range in H₂-rich fuel streams. This requires a concerted effort that encompasses kinetic analysis, materials synthesis and characterization, and surface modeling in order to optimize the carbon-based materials.

Different precursors and activation processes were used to produce carbon catalysts with variable microstructures and impurity levels. Activation was achieved by exposing the carbon precursor to an oxidizing gas (CO₂ or steam) for variable lengths of time. Three commercial catalysts were evaluated this year: Centaur (Calgon Carbon, coal-based, physical activation), WV-B (Westvaco, wood-based, chemical activation), and VA-507 (PICA, coconut shell-based, physical activation). The activity and selectivity of the Oak Ridge National Laboratory (ORNL)-synthesized and commercial catalysts were evaluated in a laboratory fixed-bed reactor system equipped with gas chromatograph and an infrared spectrometer to monitor the concentrations of the S species in the exit gas streams. Preliminary tests were carried out to evaluate key reaction parameters, such as temperature, oxygen concentration, space velocity, H₂S concentration, and water content. The selective H₂S oxidation reaction was tested with a pure H₂ stream and a simulated reformat stream (50-55% H₂, 12-15% CO₂, 6-9% CO, <1% CH₄, balance H₂O). A relatively high input H₂S concentration was used in preliminary experimental tests for the purpose of monitoring catalyst behavior in a shorter time.

A detailed characterization study is being carried out to identify the surface microstructures, functionalities, and impurity content and their relationships with the synthesis protocol and the performance of carbon catalyst. 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. Inductively plasma source (ICP) analysis was performed in order to identify the impurities content in the synthesized and commercial catalysts, 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. The nitrogen adsorption isotherms (BET) analysis and density functional theory (DFT) calculations were performed to determine the surface area and pore size distribution of the catalysts. Long-term reactivity tests are being used to evaluate the durability of the catalysts so that potential regeneration processes can also be explored. The ORNL-synthesized catalysts were independently tested for the removal of sulfur in coal streams through partnership with the National Energy Technology Laboratory (NETL).

Results

Activated carbons were synthesized at ORNL by decomposing cellulosic materials and then activating them in a high-temperature CO₂ stream. The activation level of the lab-made catalysts was controlled by varying time at temperature. The resulting properties of the activated carbon catalyst (i.e., ash content, surface area, and pore size) were measured and are presented in Table 1. The characteristics of the commercial catalysts used in our tests were also determined and are shown for comparison (Table 1).

Table 1. Properties of Activated Carbon Samples

Sample	Holding time (h) / Burn-off (%)	Ash content (%)	BET surface area (m ² /g)	V _t (cm ³ /g)	D-R ^a micropore volume (cm ³ /g)	D-A ^b avg. pore diameter (Å)
Centaur		4.78	817	0.893	0.538	15.8
WV-B		6.30	1840	1.49	0.957	19.2
VA-507		1.08	1022	1.483	1.085	15.8
Lab-made samples						
ORNL-0	0	1.65	544	-	-	-
ORNL-1	1.0/23.8	1.65	799	0.423	0.294	11.4
ORNL-3	3.0/57.8	1.65	2230	1.148	0.833	15.6
(a) Dubinin-Raduskevich method to calculate millipore volume (b) Dubinin-Astakhov method to calculate average pore diameter						

Tests were carried out to determine the activity of the catalysts being studied. The activities were compared with respect to their ability to convert H₂S to elemental sulfur in both pure H₂ and simulated

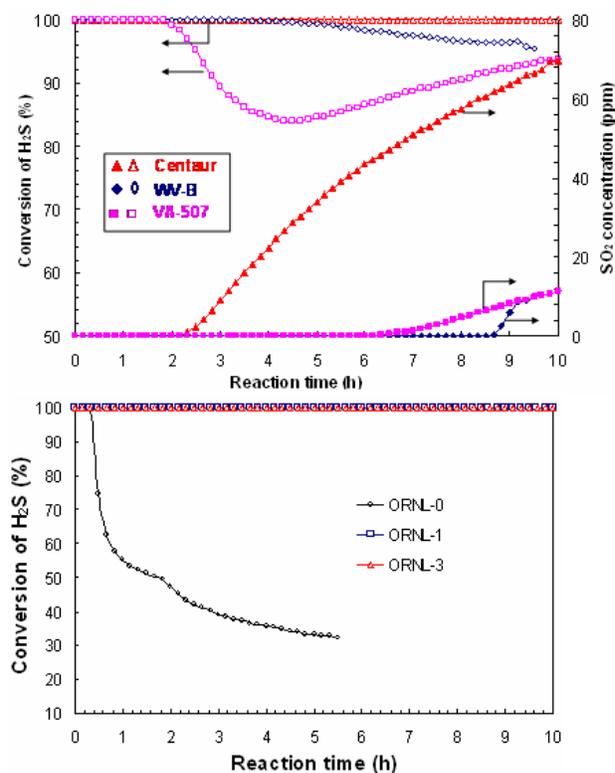


Figure 1. Selective Catalytic Oxidation of 1,000 ppm of H_2S in H_2 of (top) Three Commercial Catalysts and (bottom) ORNL-Made Catalysts (ORNL-0, ORNL-1, and ORNL-3 corresponds to nonactivated and activation times of 1 hr and 3 hrs, respectively)

reformat streams. Preliminary tests and thermodynamic analysis indicated the selection of temperature, $\text{O}_2/\text{H}_2\text{S}$ ratio, and space velocity as initial test conditions. The commercial catalysts (Figure 1, top) and the ORNL-synthesized catalysts (Figure 1, bottom) were first tested using a H_2 stream containing 1,000 ppm of H_2S . The relatively high concentration of H_2S was used with the purpose of monitoring catalyst behavior over a shorter period of time and to quickly demonstrate the capacity of the catalyst. Even though the different commercial catalysts exhibit different catalytic behavior, all three catalysts over-oxidize H_2S , forming SO_2 . On the other hand, it is clear that the activated ORNL catalysts have excellent activity and selectivity, and neither SO_2 nor H_2S was detected in the exit gas stream when tested for more than 10 hours. The importance of the activation process and the consequent formation of a micropore structure is

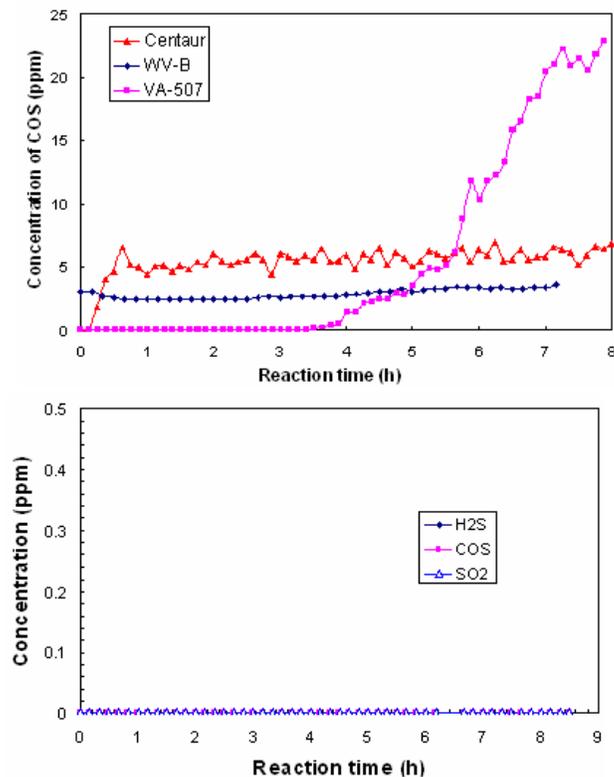


Figure 2. Selective Catalytic Oxidation of 400 ppm of H_2S in Reformat Stream of (top) Three Commercial Catalysts and (bottom) ORNL-Made Catalysts

revealed by comparing the activity of the lab-made carbonized material without activation (ORNL-0) and after increasing activation times (ORNL-1 and ORNL-3). Additionally, the selectivity of the oxidation reaction is demonstrated since H_2O production was not detected under reaction conditions and, consequently, no hydrogen co-oxidation took place.

One of the difficulties encountered with using this technology with sulfur-containing synthesis gas compositions is the formation of COS. Therefore, it is particularly important to verify the performance of the commercial and lab-synthesized catalysts in the presence of a wide range of compounds found in hydrogen-containing gas streams, including CO, CO_2 , and H_2O . Tests using a simulated reformat gas stream were carried out with 400 ppm of H_2S . Figure 2 presents the results for the commercial catalysts (top) and the ORNL-synthesized and activated catalysts (bottom). In the case of the

commercial catalysts, COS was almost immediately detected, whereas, in the case of the ORNL catalysts, no H₂S, SO₂, or COS were detected. The ORNL activated carbon catalysts consistently remove H₂S to levels below 200 ppb without formation of side-reaction products, such as SO₂ and COS, and with 100% selectivity to elemental sulfur. The same selectivity and activity were reached by the ORNL catalysts when using a simulated coal gas stream containing high CO levels (20%) for up to 8 hours, as independently measured by NETL. Recent studies indicate that the ORNL catalysts have more basic surface sites than their equivalent commercial counterparts.

Our on-going effort is to completely characterize the activated carbons in order to systematically determine the factors that affect the activity, selectivity, and durability of the catalysts. Those factors include the choice of precursors, the impurity types, the impurity content, burn-off level, and the surface features. ICP analysis of each of the commercial and the lab-made catalysts was carried out so that the major impurities could be identified and quantified. Impurities such as phosphorous, sodium, calcium, potassium, and iron have been identified as major components in these catalysts. The pore size distribution derived from DFT analysis reveals that all pores are smaller than 50 Å for the commercial catalysts, whereas a significant volume is in pores smaller than 10 Å in the case of the ORNL-synthesized catalysts.

Conclusions

- ORNL-synthesized catalysts achieved total conversion and excellent selectivity for H₂S. The results were greatly superior to commercial carbons.
- Synthesized activated carbon that demonstrated reduce sulfur levels (<50 ppb) in hydrogen-containing gas streams without formation of by-products, such as COS and SO₂.
- Demonstrated 99.9% removal efficiency for gas stream containing >1000 ppm H₂S for more than 20 hours.

FY 2004 Publications/Presentations

1. Xianxian Wu, Andrew K. Kercher, Timothy R. Armstrong, Viviane Schwartz, and Steven H. Overbury, "Activated carbons for the selective catalytic oxidation of hydrogen sulfide to sulfur," submitted to Chemical Communications.
2. Xianxian Wu, Andrew K. Kercher, Nidia Gallego, Viviane Schwartz, Steven H. Overbury, and Timothy R. Armstrong, "Activated carbons as catalyst for selective partial oxidation of hydrogen sulfide," oral presentation at the 2004 International Carbon Conference, RI (2004).
3. Xianxian Wu, Andrew K. Kercher, Viviane Schwartz, Steven H. Overbury, and Timothy R. Armstrong, "Removing hydrogen sulfide from hydrogen-rich gas streams by selective catalytic oxidation," oral presentation at the 2004 ACS meeting, Philadelphia, PA (2004).
4. Viviane Schwartz, Xianxian Wu, Andrew Kercher, Steve Overbury, and Timothy Armstrong, "Sulfur removal in hydrogen-rich gas streams by selective oxidation of hydrogen sulfide using activated carbon catalysts," poster presentation at the 2004 Fuel Cell Seminar, TX (2004).

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2. Rodriguez-Reinoso F., **Carbon**, 36, 159-175 (1998).
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