Selective Catalytic Oxidation of Hydrogen Sulfide

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Objectives

- Develop activated carbon catalysts with controlled microstructures for selective oxidation of H_2S to elemental sulfur.
- Identify key microstructural and surface chemistry features of activated carbons that promote hydrogen sulfide removal.
- Characterize the catalytic performance and reaction kinetics of commercial and laboratory-created activated carbons in model reformate gas streams.
- Understand reaction mechanisms, and explore the key microstructural features of activated carbons and the key reaction mechanisms for H_2S removal to the ppb level.

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 R,D&D Plan:

Fuel-Flexible Fuel Processors Barriers

- J. Durability

Component Barriers

- P. Durability

Approach

- Produce activated carbons for hydrogen sulfide removal that have various pore size distributions, functional groups, and inorganic impurity levels.
- Characterize the structure of commercial and laboratory-created activated carbons to be tested for catalytic oxidation of hydrogen sulfide.
- Perform catalysis tests on commercial and laboratory-created activated carbons in model reformate gases and isolate the effects of activated carbon structure and pertinent gaseous species on H_2S removal.
- Use in-situ analytical techniques and molecular modeling to determine the dependence of reaction mechanisms on activated carbon structure.

Accomplishments

- Characterized the pore structure and carbon structure of several commercial and laboratory-synthesized activated carbons.

- Preliminary results imply that using in-situ techniques such as diffuse reflectance mid-infrared Fourier transform spectroscopy (DRIFTS) holds promise in studying catalytic removal of H_2S.
- Designed and constructed a catalysis test system for catalytic oxidation of hydrogen sulfide in model reformate gas streams.
- Used Reverse Monte Carlo analysis of diffraction data to simulate the structure of activated carbon.

Future Directions

- Isolate the importance of surface functionality and impurities on pertinent reactions for hydrogen sulfide removal using catalysis experiments and in-situ analytical techniques.
- Synthesize several typical carbon-based catalysts from different sources under controlled activation processes.
- Establish processes for modifying the functional group content and impurity level of activated carbons.
- Determine optimal pore size distribution for maximum sulfur removal capacity.
- Evaluate the effect of reaction conditions on the activity and selectivity of selected catalysts.
- Study catalytic reaction kinetics and explore reaction mechanisms.

Introduction

Hydrogen is commonly produced by reforming natural gas; however, reformate contains impurities, such as hydrogen sulfide (H_2S), which can poison shift catalysts and fuel cell electrodes. Even a low concentration (a few ppm) of hydrogen sulfide dramatically shortens the life of fuel cell catalysts. Major ongoing research efforts are seeking to develop fuel cell catalysts that are more sulfur tolerant. The mission of this research project is to develop an oxidative process to reduce sulfur levels to the parts per billion range using low-cost carbon-based catalysts. This project is a new start in FY 2003, starting in March.

Selective oxidation of hydrogen sulfide to elemental sulfur on an activated carbon catalyst has been identified as a highly promising approach for the purification of fuel cell feedstocks [1]. While activated carbons are commercially used for hydrogen sulfide removal from gas streams, the key mechanisms for hydrogen sulfide removal and the critical features in an activated carbon catalyst are not well understood. Research efforts often have relied solely on commercial activated carbons, and none of the past development efforts have evaluated the use of carbon as a catalyst. In addition, the results reported by various investigators are often diverse and contradictory, especially concerning kinetics and reaction pathways. This project will emphasize the design and development of low-cost, regenerative, carbon-based catalysts that meet the required characteristics for reducing sulfur in fuel cell feedstocks to desired level. A variety of activated carbons from different sources of carbon and different activation processes will be synthesized and evaluated. The effect of operating parameters on the activity and selectivity of catalysts will be evaluated using DRIFTS (diffuse reflected infrared Fourier transform spectroscopy) (Figure 1). Based on the achievement of carbon materials with the

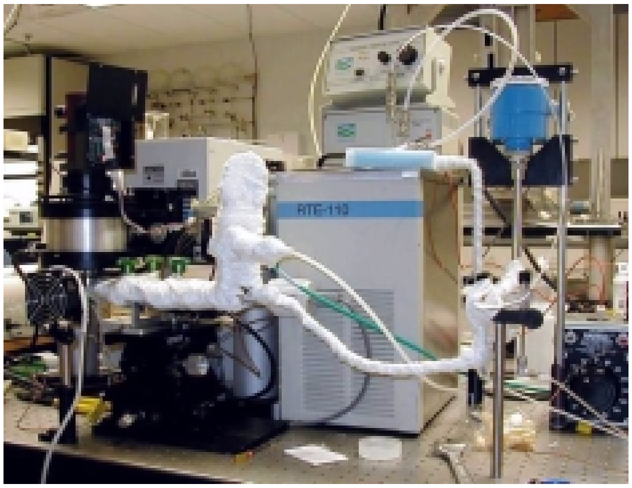

Figure 1. Picture of DRIFTS System

desired structure and surface chemistry, new insights will be provided to clarify the reaction mechanisms.

Approach

The assembled research team allows for a processing-to-product approach to tackle the timely issue of hydrogen sulfide removal from reformate feedstocks of hydrogen. The feedback between materials processing, molecular modeling, reaction mechanism studies, and engineering evaluation provides a synergistic approach for the development of an activated carbon catalyst.

Different precursors and variations in activation conditions can produce dramatically different microstructures in carbon materials. A focused effort to identify their relationships and the influence of the resultant pore structure (pore volume, pore size and distribution) on the performance of carbon catalyst is necessary. Surface functional groups play an important role in the catalytic activity of the catalyst [2]; thus, it is important to identify the initial surface functional groups and then develop techniques to modify or alter surface functionality. To produce an optimal activated carbon catalyst, the functional group content should be tailored to optimize hydrogen sulfide adsorption and minimize side reactions, such as adsorption of CO and H_2O, that could result in the formation of sequestered hydrogen sulfide products.

Inorganic impurities have also been shown to strongly catalyze hydrogen sulfide oxidation [3]. In order to understand the influence of catalytic impurities on the reactions of interest, highly pure carbons will need to be synthesized to isolate their effects. Inorganic impurities must also be added to activated carbons in order to elucidate their role in adsorption and catalysis. It is commonly accepted that metal impurities in activated carbons play important roles in catalytic performance. Key issues that must be clarified include 1) identification of the reaction mechanisms associated with specific impurities, 2) the activity and selectivity of those impurities, and 3) the efficacy of these impurities after extensive sulfur deposition and catalyst regeneration.

Reaction mechanisms will be determined using a combination of catalytic reactor experiments on simple gas mixtures, in-situ analytical techniques (such as DRIFTS), and molecular modeling. Together, these techniques can isolate individual gas-carbon reactions, explore competition between gases for reaction sites, determine the mechanisms for deleterious side reactions, and predict ideal carbon structures for H_2S removal. This combination of analysis methods provides multiple perspectives of catalyst reactions, ranging from idealized thermodynamic reaction predictions to measured catalyst surface interactions to an overall perspective of downstream gas composition. Key reaction parameters include temperature, pressure, oxygen concentration, H_2S concentration, water content, and the concentration of other impurities.

Ultimately, an activated carbon catalyst is only successful for hydrogen sulfide removal if it can perform to required concentrations in an actual reformate gas stream for a reasonable time period using a practical reactor geometry. A catalyst must remove and retain hydrogen sulfide in the presence of the wide range of impurities found in reformate feedstocks. Optimized activated carbon catalysts will be tested on simulated reformate feedstocks of hydrogen. The potential of promising catalyst candidates for regeneration also needs to be explored. Partnering with laboratories and industry will be explored as a means to evaluate down-selected catalysts on actual reformed gas streams.

Results

The porosity and carbon structure of several commercial and laboratory-created activated carbons have been determined. Typical results are listed in Table 1 and Table 2. The activated carbons are derived from different precursors (pitch-derived carbon, coconut shell carbon, coal, and low-ash charcoal) in order to determine the effects of common inorganic impurities. Also, preliminary experiments have sought to accurately determine their functional group content.

An in-situ study has been initiated to understand the interaction of gas species such as H_2S, O_2 and

Table 1. X-ray Diffraction Parameters of Assorted Commercial and Laboratory Activated Carbons

	Precursor	Interplanar spacing (nm)	Crystallite height (nm)	Crystallite diameter (nm)
Anshan 1000 m^2/g	pitch fiber	0.3667	1.127	1.775
Anshan 1500 m^2/g	pitch fiber	0.3660	1.134	1.803
Calgon Centaur 4x6	coal	0.3574	1.157	1.813
Calgon OLC 12x40	coconut shell	0.3662	1.080	1.810
Calgon OVC 4x10	coconut shell	0.3764	1.107	1.847
ORNL SMM-19	carbon fiber monolith	0.3742	1.058	1.757
ORNL SMS-48	carbon fiber monolith	0.3743	1.081	1.736
PICA G55C-1	coconut shell	0.3737	1.037	1.821
PICA VA507	coconut shell	0.3767	1.053	1.886
Westvaco Ultramicroporous	wood	-	-	1.720

Table 2. Pore Structure Characterization of Assorted Commercial and Laboratory Activated Carbons from Nitrogen Adsorption Analysis

	BET surface area (m^2/g)	D-R micropore volume (cc/g)	D-A average pore diameter (Å)
Anshan 1500 m^2/g	1393	0.756	22.3
Calgon Centaur 4x6	1144	0.506	21.3
Calgon OLC 12x40	1110	0.506	21.3
Calgon OVC 4x10	884	0.391	19.7
ORNL SMM-19	1730	0.895	22.8
ORNL SMS-48	1404	0.619	20.7

CO with carbon surface and interpret the reaction mechanisms of H_2S oxidation and undesired side reactions for the formation of COS and SO_2. A DRIFTS reactor which is capable of in-situ measurement up to 500°C is being used to identify the change of carbon surface chemistry in various gas atmospheres. A preliminary study on the interaction of CO with activated carbon has provided positive support for this approach, and typical results are shown in Figure 2.

Reverse Monte Carlo modeling has been applied to diffraction data to produce a theoretical activated carbon microstructure. By introducing select modifications to theoretical microstructures, carbon microstructural variables can be kept constant except for a specific feature of interest (functional group content, pore size, carbon structural order, etc.), and the effect of specific feature changes on the thermodynamics and kinetics of H_2S removal can be predicted. Slight modifications of these theoretical microstructures will later be used to model the behavior of actual activated carbons by incorporating the measured microstructural features of activated carbons.

A catalytic reactor system for hydrogen sulfide has been designed and is being constructed. A schematic representation of the system is shown in Figure 3.

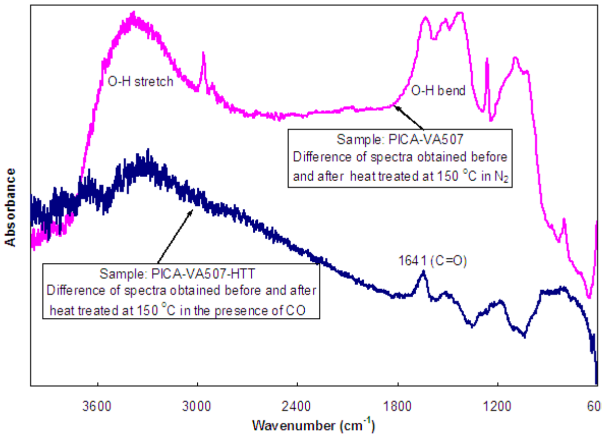

Figure 2. Preliminary Results on the Interaction of CO with Activated Carbon Observed by DRIFTS

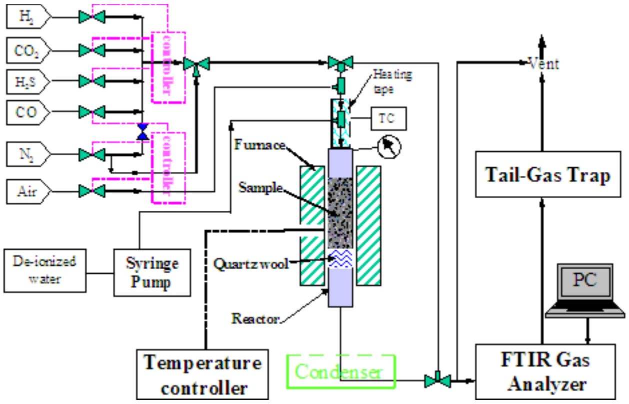

Figure 3. Schematic Representation of the Experimental Setup for Testing Carbon-Based Catalyst (FTIR=Fourier transform infrared)

Conclusions

- The microstructures of several activated carbon materials have been characterized for subsequent correlation to catalysis results.
- Preliminary results imply a promise of using *in-situ* techniques such as DRIFTS in studying catalytic removal of H_2S.
- Reverse Monte Carlo methods have been applied to diffraction data to create a theoretical model of the microstructure of activated carbon in order to identify reaction sites.

FY 2003 Publications/Presentations

1. Gardner TH, Berry DA, Lyons KD, Beer SK, Freed AD. Fuel processor integrated H_2S catalytic partial oxidation technology for sulfur removal in fuel cell power plants, **Fuel,** 81, 2157-2166 (2002).
2. Rodriguez-Reinoso F. The role of carbon materials in heterogeneous catalysis, **Carbon**, 36, 159-175 (1998).
3. Steijns M, Mars P. Catalytic oxidation of hydrogen sulfide: Influence of pore structure and chemical composition of various porous substances, **Industrial and Engineering Chemistry Product Research and Development**, 16, 35-41 (1977).