Selective Catalytic Oxidation of Hydrogen Sulfide

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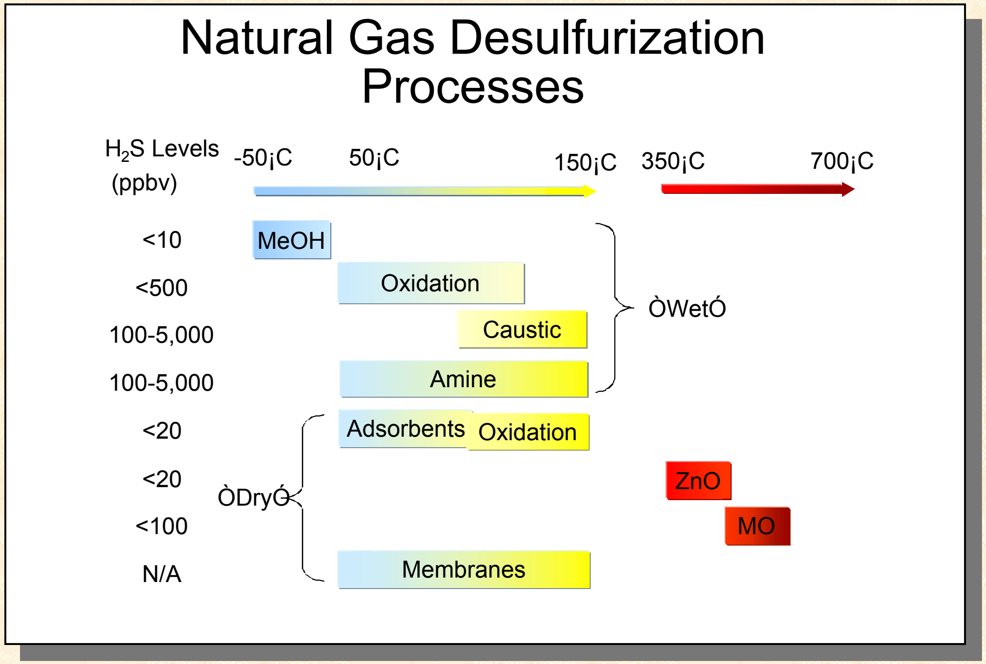
Direct Sulfur Removal

Challenge: All fossil fuels have persistent S contamination. Production of H_2 in the next several decades will be derived from fossil fuels (NG, coal, petroleum). Desulfurized H_2 is a necessity to facilitate reforming to generation of pure H_2 for storage and use in fuel cells use.

- Objective: Develop a warm temperature method direct sulfur removal technology (*gaseous sulfur to solid sulfur*) with parts per billion separation efficiency.
- Goals:
  - Lower initial capital investment
  - Synergysm with available systems
  - Removal of sulfur to ‘ppbv’ levels
    - $H_2S + 1/2O_2 \rightarrow 1/nS_n + H_2O$

Conventional H_2S removal methods

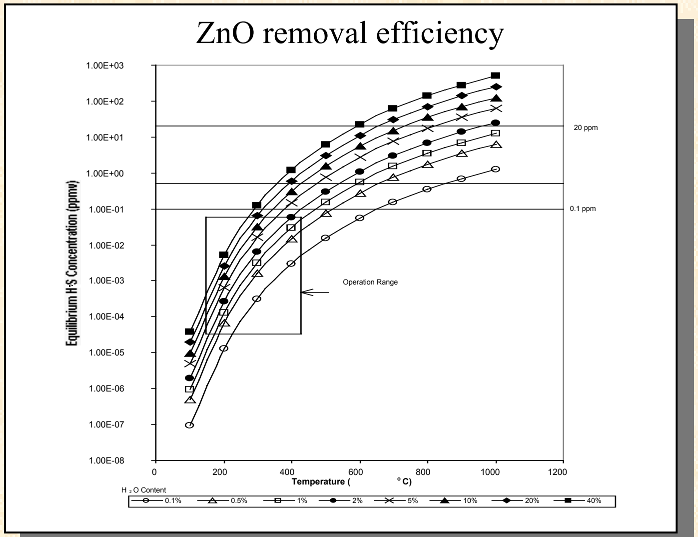


- Currently available catalysts do not meet required performance goals for any H_2 generating or utilization systems.
  – Adsorption processes remove organic sulfides and require high pressure H_2 to regenerate
  – High temperature MO catalysts have short lifetimes and show rapid decrease in activity
  – High-temperature processes generate SO_2
- Need to develop activated carbon catalysts that facilitate oxidation of H_2S:
  – High microporosity and preferential adsorption of H_2S over CO required.

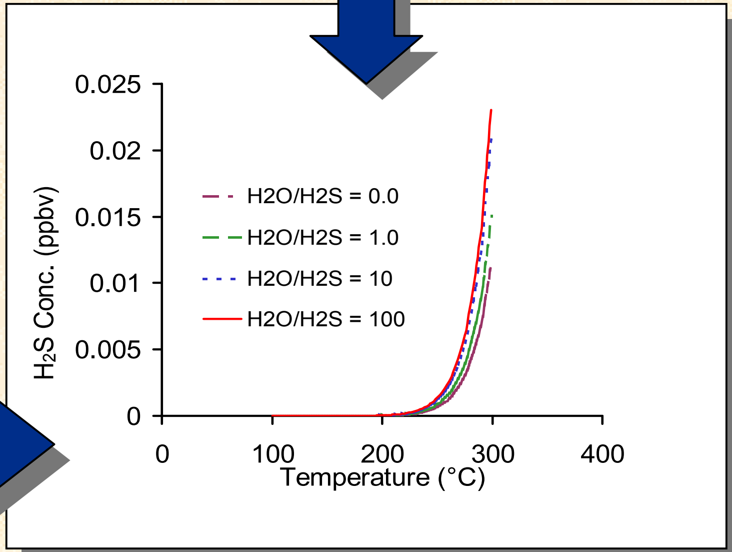
DOE technical targets assume a sulfur level of 6 ppm, *however this target requires development of sulfur tolerant catalysts and membranes.*

Advantages of SCOHS

- **Removal Efficiency:** SCOHS has part per trillion (ppt) thermodynamic sulfur removal efficiencies.
- **Water Sensitivity:** Unlike most metal oxide based systems, SCOHS is relatively insensitive to water content, which can be found in high concentrations in some reformate streams.
- **Operational Mode:** Can operate in continuous or discontinuous modes



- **Benefits:**
  - Water shift reaction catalyst
  - Separation/catalytic membranes
  - Fuel cells using natural gas, transportation fuels
  - Steam reforming catalyst

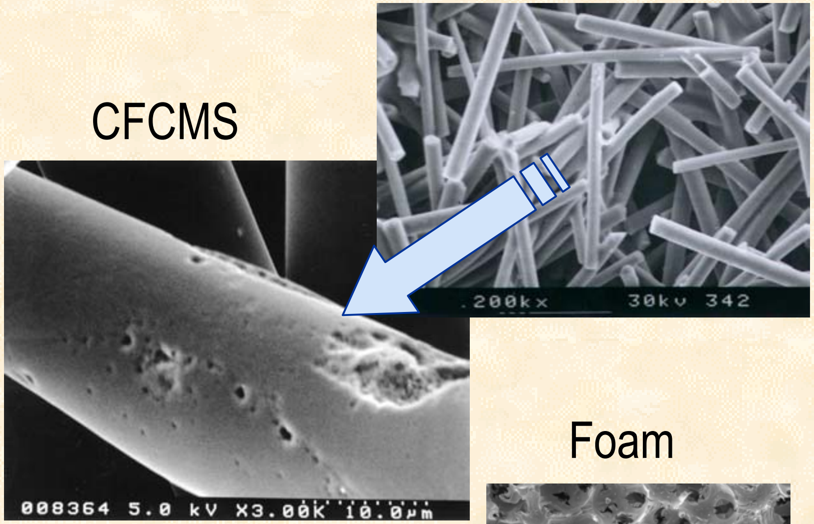


Exceptionally Low Sulfur Levels Can be Achieved with the SCOHS Process

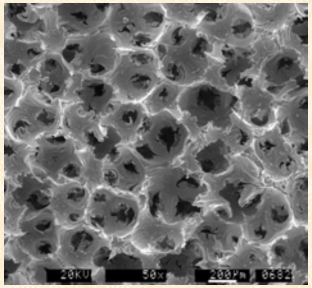
- Carbon-based catalysts offer very exciting potential to reach low (ppt) sulfur levels

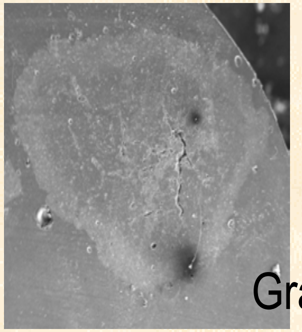
- There are several issues to address:
  - What is the mechanism for preferential adsorption of CO over H_2S?
  - Design materials selective to H_2S.
  - Can high sulfur conversion/removal efficiencies be obtained for H_2S?
  - Can carbon catalysts be synthesized with high activity?
  - What material purity/impurity are required?
  - What factors affect aging and reliability?

CFCMS



Foam





Granule

Fundamental Understanding Will Be Gained Through Kinetic Studis and In-situ Analysis

Kinetic Studies

- **Kinetics of sulfur adsorption and desorption will be monitored by temperature programmed desorption and reduction experiments and analyzed using IR spectroscopy**
- **Competitive adsorption will be monitored quantitatively using DRIFTS**

Characterization

- **In-situ EXAFS will be developed and used to investigate adsorbed sulfur species at reaction conditions (temperature and environment)**
- **NEXAFS will be investigated as a means to provide information on the electronic structure of the catalyst for correlation to its catalytic activity**
- **EDS and EELS will provide high resolution species identification of impurities and S distribution**
- **Ex-situ reactor available for understanding chemical, structural, and crystallographic changes**

Expected Results of Kinetic and In-situ Studies

Will independently quantify effects of:

[1] catalytic activity of various activated microporous carbons

[2] impurities on catalytic activity and structure

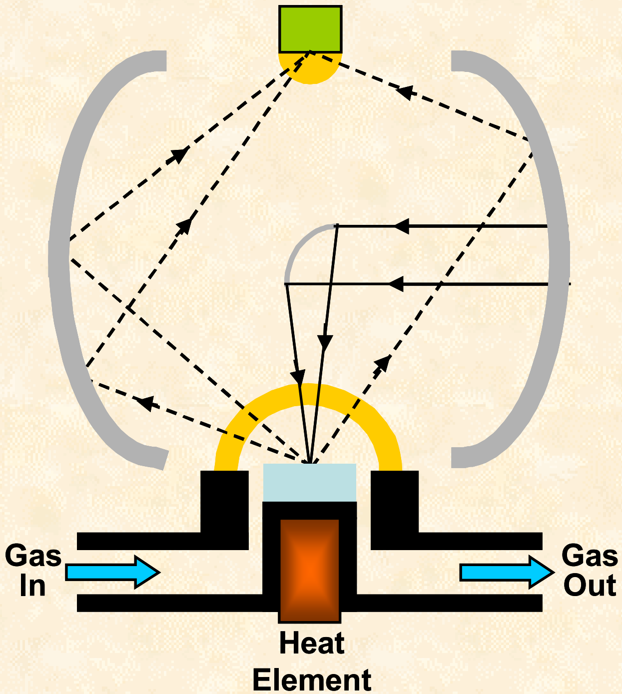
[3] Sulfur removal, conversion efficiency competitive adsorption of H_2S vs. CO

[4] competitive adsorption of H_2S vs. C on conversion efficiency

Provide fundamental scientific basis to develop breakthrough carbon catalyst technology with high sulfur and low CO selectivity for gas cleanup

DRIFTS

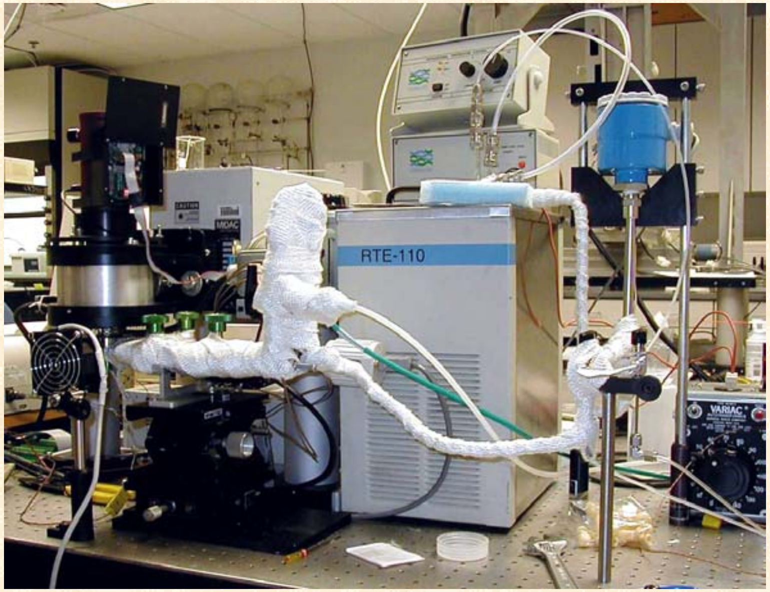
D*iffuse* ***R****eflectance mid-* ***I****nfrared* ***F****ourier* ***T****ransform* ***S****pectroscopy*



DRIFTS can provide quantitative in-situ analysis of catalytic reactions by analyzing spectroscopic changes due to the functional group content

DRIFTS instrument made available through ORNL-NTRC collaboration:

- MIDAC FTIR spectrometer
- Harrick DRIFT accessory
- Spectral range 4000-500 cm-1
- 1 cm^{-1} resolution



Graphics courtesy of ORNL-NTRC

Prototype Structures for Activated Carbon Materials

- Generate prototype carbon structures consistent with experiment
  - STM studies
- Perform adsorption studies on a number of local configurations
  - activated carbon is amorphous: Adsorption occurs locally
  - Provide information on the variety and strength of bonding, heats of formation of key molecules (I.e. CO-S, etc.) on specific local environments
- This information would be used in conjunction with experiment to try to process out local atomic arrangements that favor CO-S formation
- First Principles Total Energy calculations
  - Input: atomic species
  - Local density approximation to density functional theory
    - Treating the quantum many body of effects of electron exchange and correlation

H_2S Catalytic Partial Oxidation Process Chemistry

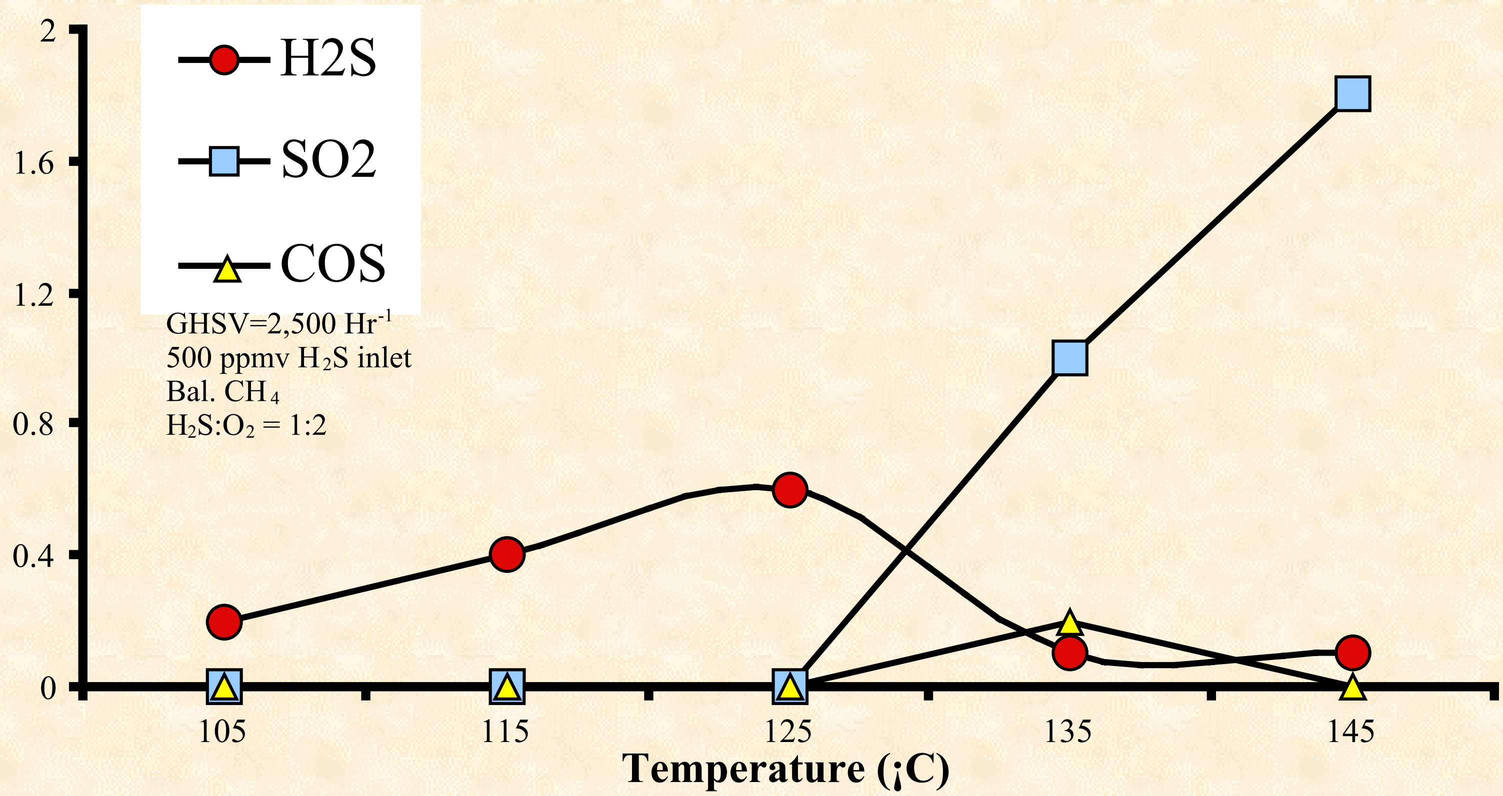
- H_2S partial oxidation reaction
  - Discovered 1883 by Carl F. Claus

Reaction	ΔH_r^{400K} (KJ/mol)	ΔG_r^{400K} (KJ/mol)
$H_2S + {}^1/_2O_2 \longrightarrow {}^1/_8S_8 + H_2O$	-208.3	-182.6
${}^1/_8S_8^{(s,l)} \longleftrightarrow {}^1/_nS_n^{(g)}$	P_v^{400K} = 6.92 Pa	
	P_v^{500K} = 764 Pa	

- Possible side reactions

Reaction	ΔH_r^{400K} (KJ/mol)	ΔG_r^{400K} (KJ/mol)
${}^1/_nS_n + O_2 \longrightarrow SO_2$	-300.2	-300.9
$H_2S + {}^3/_2O_2 \longrightarrow SO_2 + H_2O$	-518.6	-487.5
${}^1/_nS_n + CO \longrightarrow COS$	-31.0	-28.4
$2CO \longrightarrow C^{(s)} + CO_2$	-173.3	-101.9
$CO + {}^1/_2O_2 \longrightarrow CO_2$	-283.5	-248.3

H_2S Partial Catalytic Oxidation Performance in Natural Gas



Testing and analysis carried out by NETL

Program Milestones

- **Fabricate and test several different types of catalysts from activated granular carbons to more sophisticated activated nanowebs and monolithic fibrous structures. (9/03)**
- **Establish a working simulation model capable of describing the catalytic reaction that can be used to guide catalyst synthesis. (9/03)**

Anticipated Developments

- Development a reliable (ppb level) desulfurization catalyst with minimal or no CO adsorption
- Develop a continuous desulfurization process
- Develop an understanding of role of surface impurities and defects on adsorption of H_2S and CO in activated carbon

Relevance to DoE R&D Plan

The presence of sulfur and other impurities is a fundamental barrier to the practical implementation of fuel cell concepts. In particular, fuel cell durability is strongly affected by impurity content.

- Sulfur affects the durability of *fuel cell components*, *fuel processors and distributed energy systems.*

Fuel-Flexible Fuel Processors Technical Barriers:

H_2 Purification/ CO Clean-up	"Liquid fuels contain impurities such as sulfur compounds. These compounds and their derivatives as well as CO must be removed to prevent loss of performance in the fuel cell."

Significant Collaborations

- **Collaboration with NETL on reactor design and test methods**
- **Discussions with SGL Carbon on carbon materials development**
- **Interest in technology from:**
  - **ChevronTexaco**
  - **ConocoPhillips**