UT-BATTELLE

2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies
Annual Program Review

Selective Catalytic Oxidation of Hydrogen Sulfide

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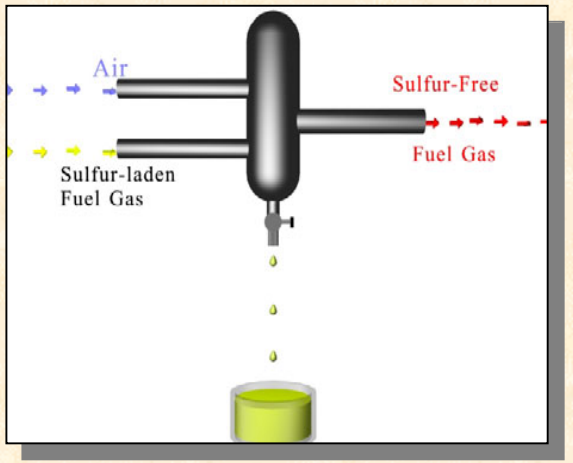
OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

Objective

Develop and optimize an oxidative process to reduce sulfur levels to the parts per billion range in reformate using low-cost carbon-based catalysts to produce a low-sulfur fuel for use in fuel cells.

- FY04 goals:
  - Development of different activation protocols in order to tailor the carbon-based catalysts.
  - Reactivity tests for determination of operational parameters for the selective oxidation reaction.
  - Demonstrate continuous removal of sulfur to 'ppbv' levels.
  - Preliminary thermodynamic analysis to verify reaction constraints.



Budget

Fiscal Year	Allocated Budget (k$)	Realized Budget (k$)	Comments
FY 2003	400	300	$100k diverted to FASTER Program
FY 2004	350	350	

Technical Targets

- DOE Technical Barriers for Fuel Cell Components
  - K. Emissions and Environmental Issues
  - L. Hydrogen Purification/CO Clean-up

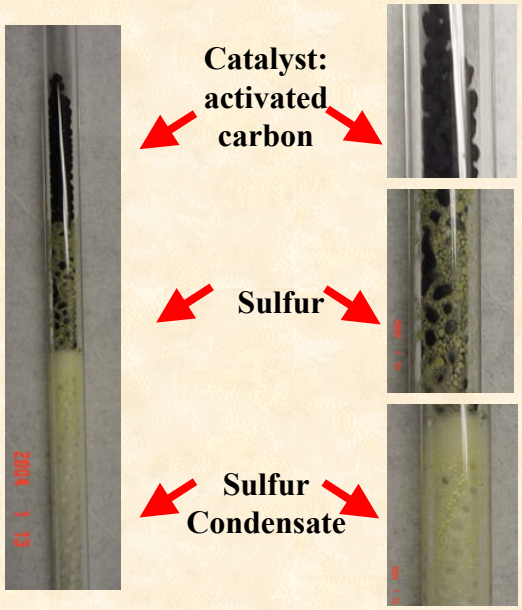
- DOE Technical Target for Fuel Cell Stack System
  - Combined NO_x, SO_x, CO, Hydrocarbon, Particulates <9 g/1000 kWh (≈6 ppm S)

Technical Approach

- Develop activated carbon-based catalysts with controlled microstructures for selective oxidation of H_2S to elemental sulfur in reformate streams via:

$$H_2S + 1/2O_2 \longrightarrow 1/nS_n + H_2O$$

  - Development of activated carbons with improved activity and selectivity
  - Correlate effects of pore volume, pore size & distribution, impurities, catalyst morphology on catalytic performance
  - Carry out long-term testing to fully characterize candidate catalysts.
  - Model reaction(s) using kinetics based thermodynamic calculations (chemKin)

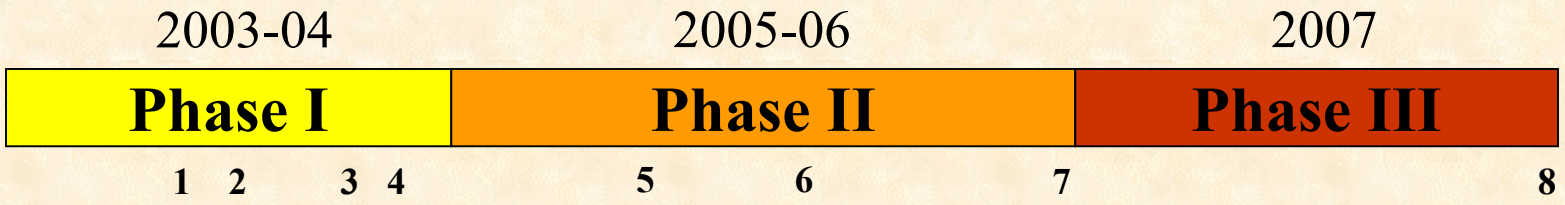


Project Safety

- Project has undergone "Integrated Safety Management Pre-Planning and Work Control" (Research Hazard Analysis and Control)
  - Definition of task
  - Identification of hazards
  - Design of work controls
  - Conduct of work
  - Feedback
- Each work process is authorized on the basis of a Research Safety Summary (RSS) reviewed by ESH subject matter experts and approved by PI's and cognizant managers
- The RSS is reviewed/revised yearly, or sooner if a change in the work is needed
- Experienced Subject Matter Experts are required for all Work Control for Hydrogen R&D including
- Periodic safety reviews of installed systems

Project Timeline

(Project initiated April 2003)

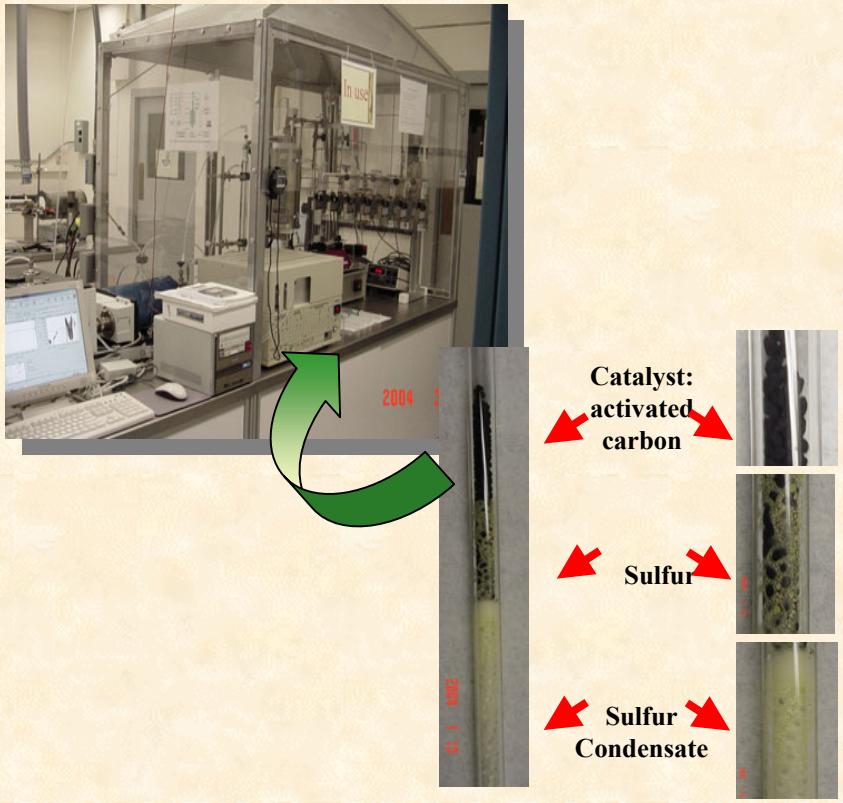


- Phase I: Proof of Principle
  1. Evaluate commercial catalysts
  2. Complete system thermodynamic analysis
  3. Development of different activation protocols
  4. Demonstrate 99% removal efficiency with S levels <500 ppb
- Phase II: Development Testing and Evaluation
  5. Complete analysis of effects of impurities, microstructure, surface functionalization, and morphology on catalytic performance
  6. Synthesize supported catalyst
  7. Develop catalysts that meet durability goals
- Phase III: Optimization, Scale up and Tech Transfer
  8. Complete scale up and transition to industry

Technical Accomplishments

Materials:

- Commercial activated carbons:
  - Centaur (Calgon Carbon, bituminous coal-based, physical activation)
  - WV-B (Westvaco, wood-based, chemical activation)
  - VA-507 (PICA, coconut shell-based, physical activation)
- Lab-made activated carbons:
  - Cellulosic materials with different purities as precursors
- Gas streams:
  - Up to 10,000 ppm H_2S in H_2 or N_2
  - Up to 1,000 ppm H_2S in simulated reformate (50-55% H_2, 12-15%CO_2, 6-9%CO, <1%CH_4, balance H_2O, < 300 ppm H_2S)
  - Conditions
    - Temperature 120-200°C
    - Pressure 1 atm,
    - GHSV=>3000 h^{-1},
    - O_2:H_2S = 1:1 to 5:1



Compared to reality, the input H_2S concentration is exaggerated to demonstrate the capacity of catalyst

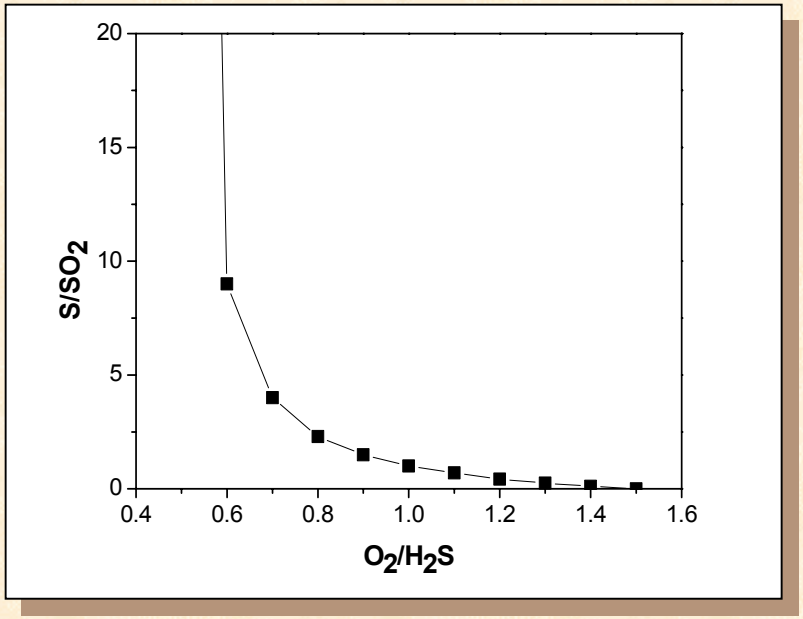
Thermodynamic Evaluation: Analysis of Operation Regime

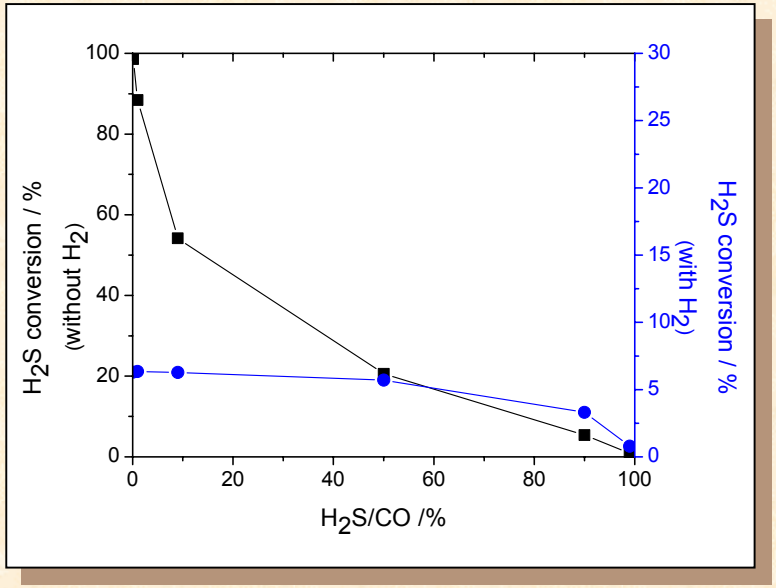
- Equilibrium calculations:
  - T = 400 K:

$$H_2S + 1/2O_2 \longrightarrow S + H_2O$$
$$H_2S + 3/2O_2 \longrightarrow SO_2 + H_2O$$
$$S + O_2 \longrightarrow SO_2$$
$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

  - (T = 400 K):

$$H_2S + CO \longrightarrow COS + H_2$$



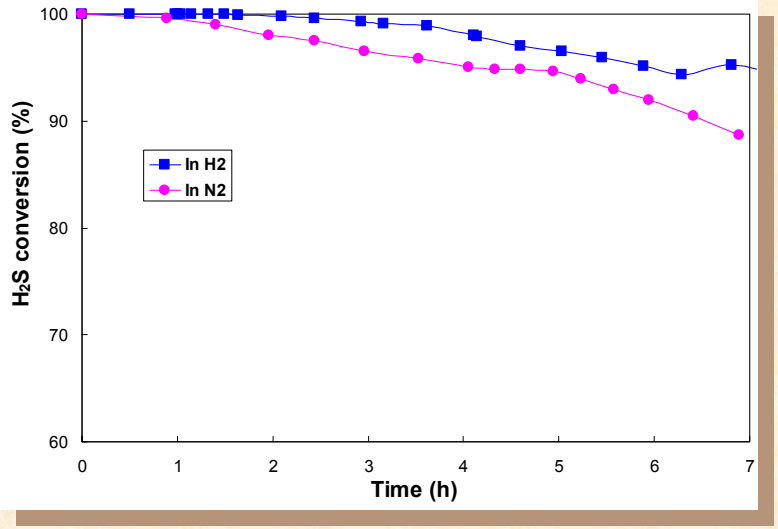


- Thermodynamic equilibrium calculations confirms increasing selectivity as a stoichiometric O_2:H_2S ratio is approached;
- COS formation is suppressed by presence of H_2 in gas stream

Thermodynamic Evaluation: Effect of Gas Composition

Commercial catalyst: Centaur at 130°C and 1 atm

H_2S inlet Conc.=10,000 ppm in N_2 or H_2,

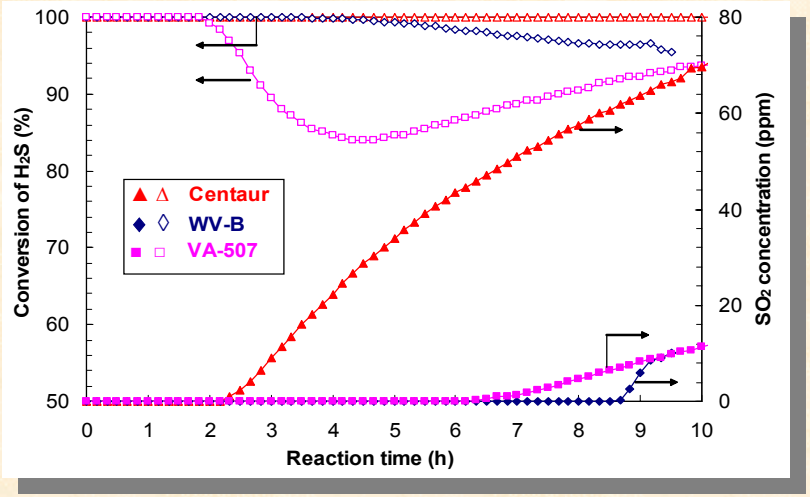


Equilibrium results predict:
In H_2: no conversion of H_2S
In N_2: 100% conversion
(400 ppm H_2S)

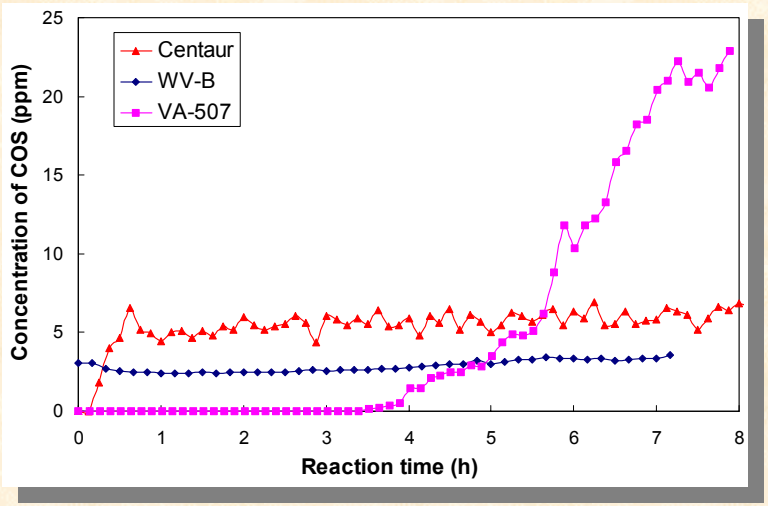
- Equilibrium thermodynamic analysis predicts oxidation of H2 and CO in multicomponent gas streams
- Experimental results show superior selectivity to elemental sulfur than predicted by equilibrium calculations.
  Reaction is dominated by kinetics and never achieves thermal equilibrium

Commercial Carbon Materials Showed Differing Catalytic Behavior

1000 ppm H_2S in H_2 stream



400 ppm H_2S in reformate (50%H_2, 15%CO_2, 9%CO, 1%N_2, balance H_2O ~24%)



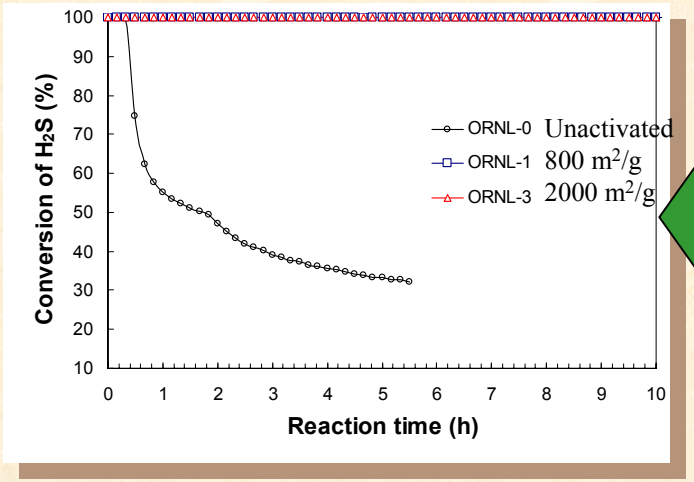
Commercial carbon samples exhibited differing catalytic activity and selectivity:

- Centaur sample (coal-based) has 100% conversion of H_2S, but it over-oxidized S to SO_2
- VA-507 sample (Coconut shell based) shows the lowest activity
- WV-B sample (wood-based) displays good selectivity and 100% conversion of H_2S at the beginning, but both H_2S and SO_2 were observed after several hours on stream

Proof of Concept Demonstrated with ORNL Catalyts

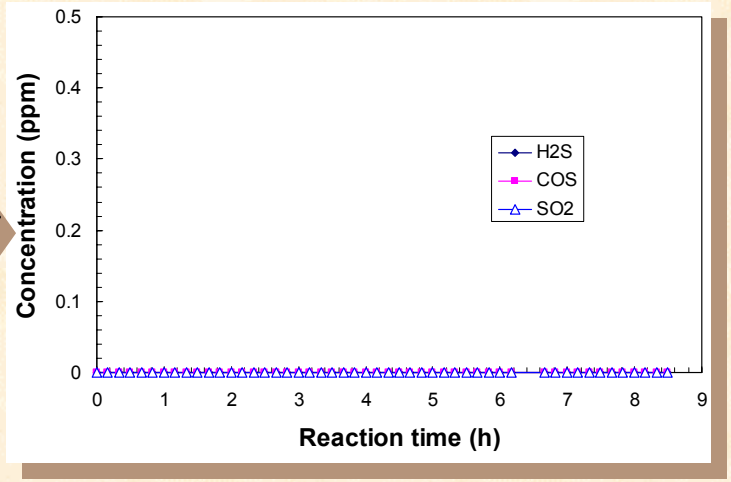
(S levels reduced to < 200 ppb)

1000 ppm H_2S in H_2 stream



No H_2S, SO_2, or COS were Detected over 10 h

400 ppm H_2S in reformate (50%H_2, 15%CO_2, 9%CO, 1%N_2, balance H_2O ~24%)



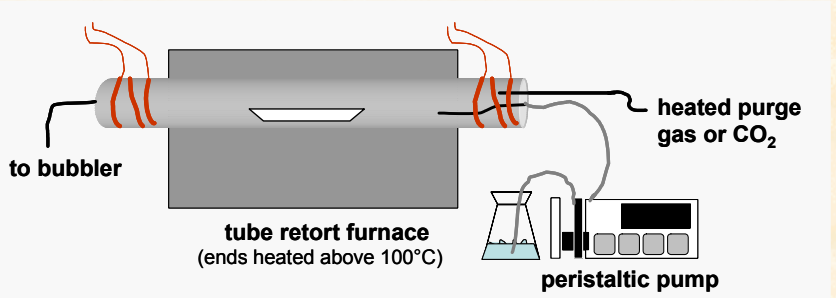
- Excellent activity and selectivity were observed for activated carbons (ORNL-1 and ORNL-3)
- No SO_2, H_2S, COS was detected in more than 10 h
- The unactivated sample (ORNL-0) showed a low catalytic activity

Catalysts Development, Characterization and Activity Analysis

- **Commercial catalysts**

Sample	Ash content	Surface area (m2/g)	Avg pore diameter (Å)	Activity	Selectivity
Centaur	4.78 %	817	15.6	**High**	**Low**
WV-B	6.30 %	1840	19.2	**Medium**	**Medium**
VA-507	1.08 %	1022	15.6	**Low**	**Medium/Low**

- **ORNL catalysts –** carbon precursors are physically activated with steam and/or CO_2. Thermal processing is varied to obtain different pore distribution.



Sample	Ash content	Holding Time(h)/ Burn-off (%)	Surface area (m2/g)	Avg pore diameter (Å)	Activity	Selectivity
ORNL-0	1.65 %	0			**Low**	**High**
ORNL-1	1.65 %	1.0/23.8	799	11.4	**High**	**High**
ORNL-3	1.65 %	3.0/57.8	2230	15.6	**High**	**High**

Summary

- ORNL synthesized catalysts achieved total conversion and excellent selectivity for H_2S - *superior* than commercial carbons
  - No by products (COS, SO_2) were formed
  - 99.98% removal efficiency in single pass
  - Sulfur levels of reformate reduced to less than 200 ppb
  - No steam sensitivity observed
- Role of impurities: commercial catalysts with highest purity, has lowest activity.
- A relatively high H_2S concentration is used in experimental test for the purpose of monitoring catalyst behavior in a shorter time.
- It is possible to reach DOE target space velocity, GHSV=50,000 h^{-1}, because only trace H_2S is present in the fuel gas streams like reformate (*e.g.*, <300 ppm).

Interactions and Collaborations

- **National Energy Technology Laboratory:** David Berry, Dushyant Shekhawat, and Todd Gardner - catalyst testing (verification studies), process design, testing for sulfur removal from coal gas

- Discussions on implementation of technology in:
  - fuel cell systems - **United Technologies**
  - refinery processes - **ConocoPhilips and ChevronTexaco**
  - distributed fueling stations **- Kraus Global**

Responses to Previous Year Reviewers' Comments

- Project needs to be developed and show progress:
  - Laboratory scale reaction system was designed, constructed, and fully tested. Followed by evaluation of the reaction conditions.
  - Significant results obtained:
    - Synthesis of activated carbons with high activity and selectivity.
    - Evaluation of catalytic performance of commercial and lab-made catalysts.
    - Initiated characterization of the catalyst microstructures.
  - Research is going to be presented in important congresses in the field of carbon chemistry (2004 International Carbon Conference, RI, July 11-16) , fuel cells (2004 Fuel Cell Seminar, TX, Nov. 1-5), and catalysis (Gordon Conference, NH, June 27- July2).
- Need of comparison between experimental data and equilibrium calculations:
  - Performance of equilibrium calculations and comparison with experimental data.
- Outside collaborations and potential customers need developed:
  - since last year we have interacted with (4) end users/developer and are working with NETL for catalyst testing and process development

Future Work

- Correlate the effects of catalyst morphology of activated carbons with the reaction kinetics to define the optimized pore size distribution desired for a good catalyst.
- Develop understanding of impurity contribution to reaction to determine which impurity (or impurities) has catalytic effect and which one does not.
- Evaluate the roles and significance of surface functional groups.
- Understand the formation mechanisms of SO_2 and COS.
- Optimize activation process.