

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

# Selective Catalytic Oxidation of Hydrogen Sulfide

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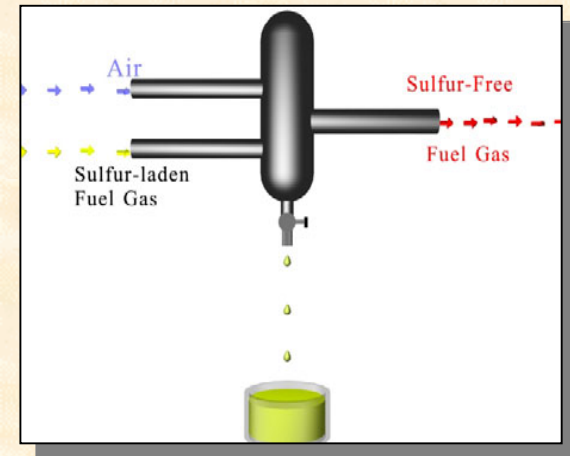
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**OAK RIDGE NATIONAL LABORATORY**  
**U. S. DEPARTMENT OF ENERGY**

# Objective

Develop and optimize an oxidative process to reduce sulfur levels to the **parts per billion** range in reformat 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

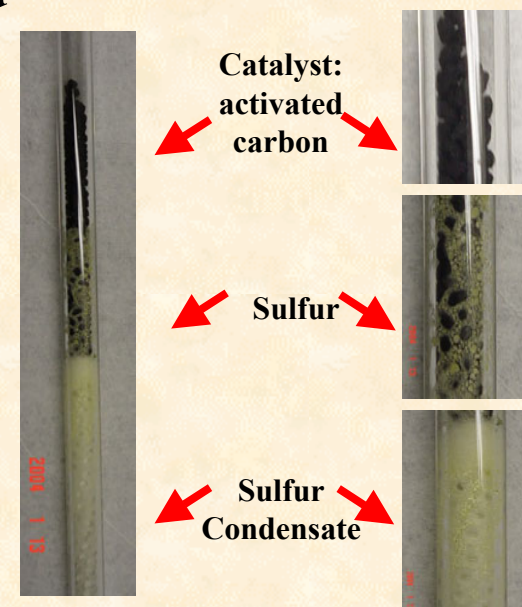
- DOE Technical Barriers for Fuel Cell Components
  - K. Emissions and Environmental Issues
  - L. Hydrogen Purification/CO Clean-up
  
- DOE Technical Target for Fuel Cell Stack System
  - Combined NO<sub>x</sub>, SO<sub>x</sub>, CO, Hydrocarbon, Particulates <9 g/1000 kWh (≈6 ppm S)

# Technical Approach

- Develop activated carbon-based catalysts with controlled microstructures for selective oxidation of H<sub>2</sub>S to elemental sulfur in reformat streams via:



- 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)



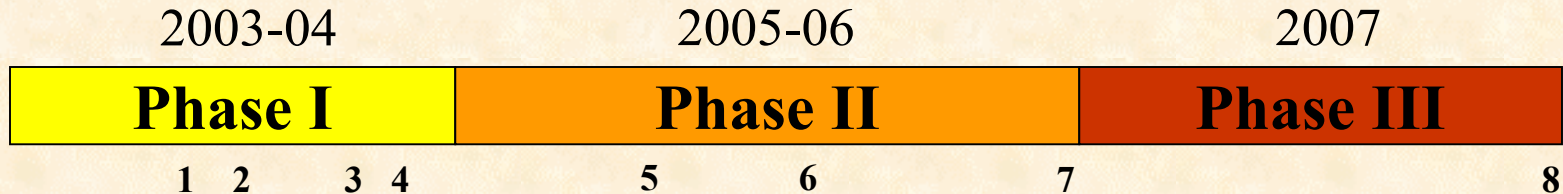


# Project Safety

- 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:

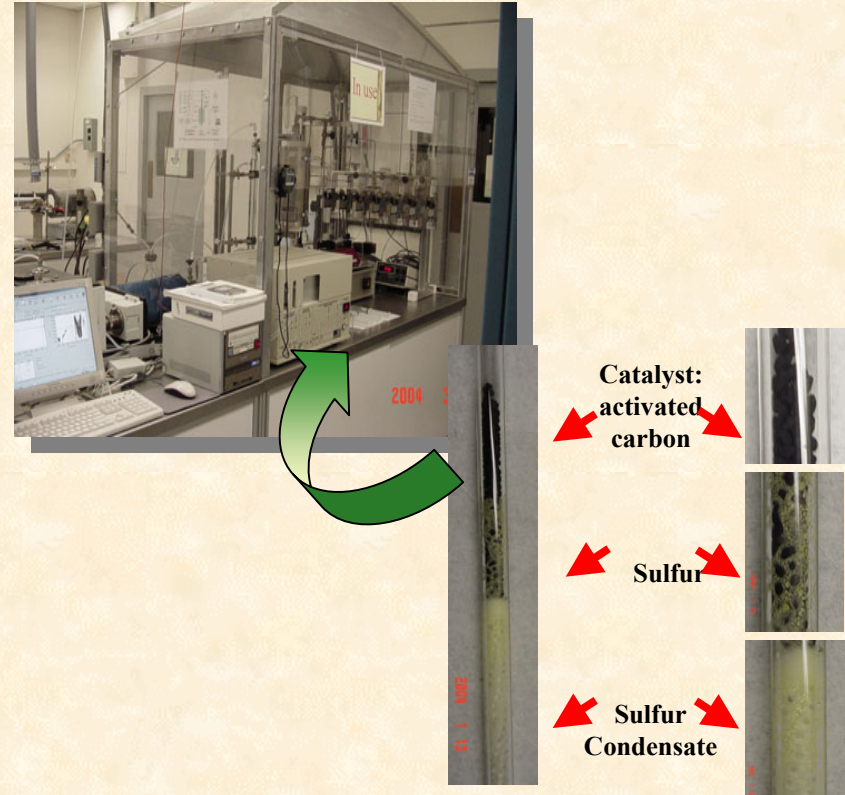
- Centaur (Calgon Carbon, bituminous coal-based, physical activation)
- WV-B (Westvaco, wood-based, chemical activation)
- VA-507 (PICA, coconut shell-based, physical activation)

### ➤ Lab-made activated carbons:

- Cellulosic materials with different purities as precursors

### ➤ Gas streams:

- Up to 10,000 ppm  $\text{H}_2\text{S}$  in  $\text{H}_2$  or  $\text{N}_2$
- Up to 1,000 ppm  $\text{H}_2\text{S}$  in simulated reformat (50-55%  $\text{H}_2$ , 12-15%  $\text{CO}_2$ , 6-9%  $\text{CO}$ , <1%  $\text{CH}_4$ , balance  $\text{H}_2\text{O}$ , < 300 ppm  $\text{H}_2\text{S}$ )
- Conditions
  - Temperature 120-200°C
  - Pressure 1 atm,
  - GHSV=>3000  $\text{h}^{-1}$ ,
  - $\text{O}_2:\text{H}_2\text{S}$  = 1:1 to 5:1



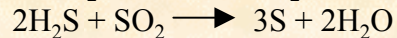
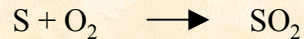
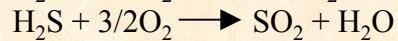
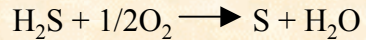
Compared to reality, the input  $\text{H}_2\text{S}$  concentration is exaggerated to demonstrate the capacity of catalyst



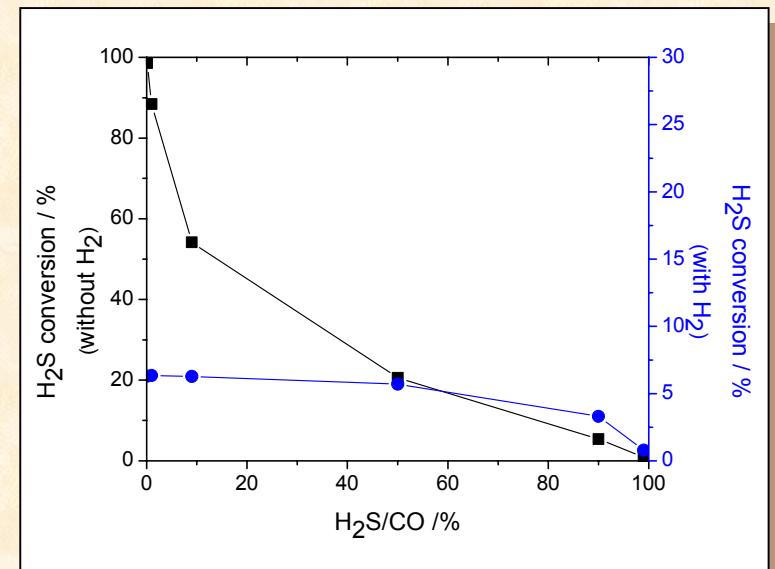
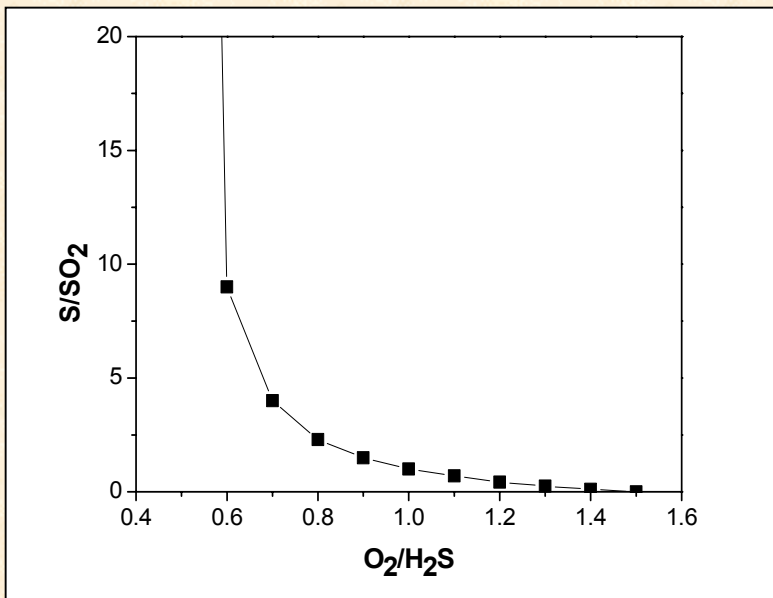
# Thermodynamic Evaluation: Analysis of Operation Regime

- Equilibrium calculations:

➤ T = 400 K:



➤ (T = 400 K):

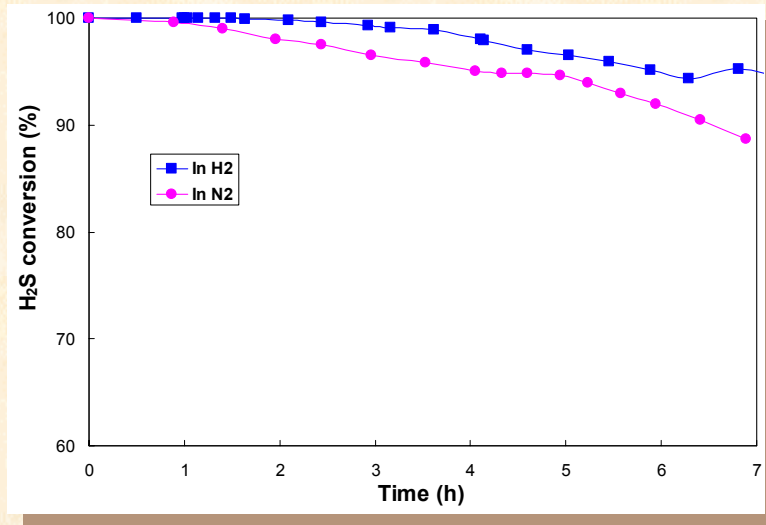


- Thermodynamic equilibrium calculations confirms increasing selectivity as a stoichiometric O<sub>2</sub>:H<sub>2</sub>S ratio is approached;
- COS formation is suppressed by presence of H<sub>2</sub> in gas stream

# Thermodynamic Evaluation: Effect of Gas Composition

Commercial catalyst: Centaur at 130°C and 1 atm

H<sub>2</sub>S inlet Conc.=10,000 ppm in N<sub>2</sub> or H<sub>2</sub>,



Equilibrium results predict:

In H<sub>2</sub>: no conversion of H<sub>2</sub>S

In N<sub>2</sub>: 100% conversion

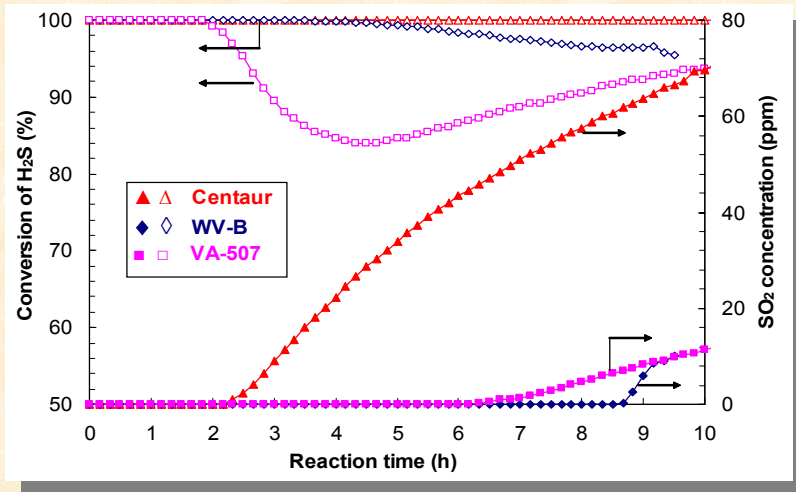
(400 ppm H<sub>2</sub>S)

- Equilibrium thermodynamic analysis predicts oxidation of H<sub>2</sub> 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

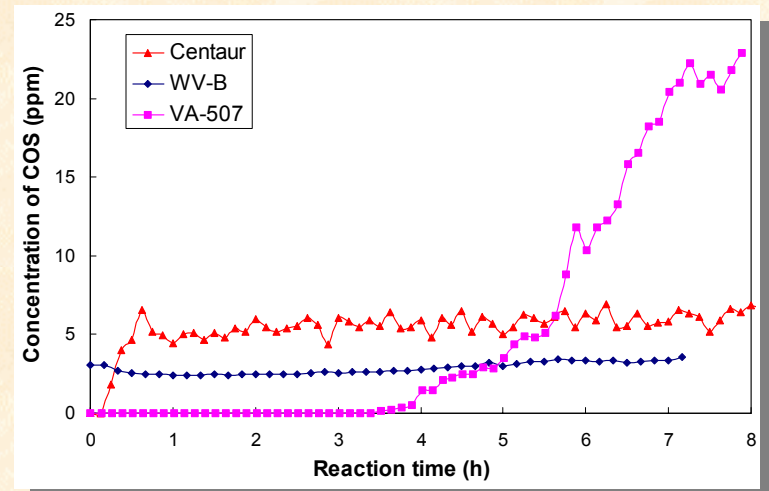


# Commercial Carbon Materials Showed Differing Catalytic Behavior

1000 ppm H<sub>2</sub>S in H<sub>2</sub> stream



400 ppm H<sub>2</sub>S in reformat (50%H<sub>2</sub>, 15%CO<sub>2</sub>, 9%CO, 1%N<sub>2</sub>, balance H<sub>2</sub>O ~24%)



Commercial carbon samples exhibited differing catalytic activity and selectivity:

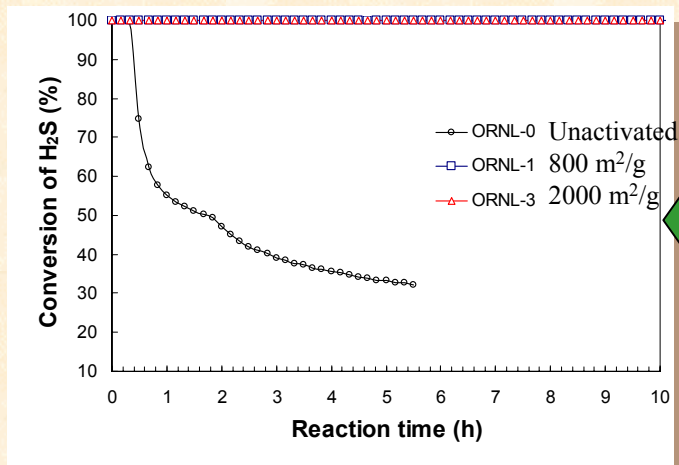
- Centaur sample (coal-based) has 100% conversion of H<sub>2</sub>S, but it over-oxidized S to SO<sub>2</sub>
- VA-507 sample (Coconut shell based) shows the lowest activity
- WV-B sample (wood-based) displays good selectivity and 100% conversion of H<sub>2</sub>S at the beginning, but both H<sub>2</sub>S and SO<sub>2</sub> were observed after several hours on stream

# Proof of Concept Demonstrated with ORNL Catalysts

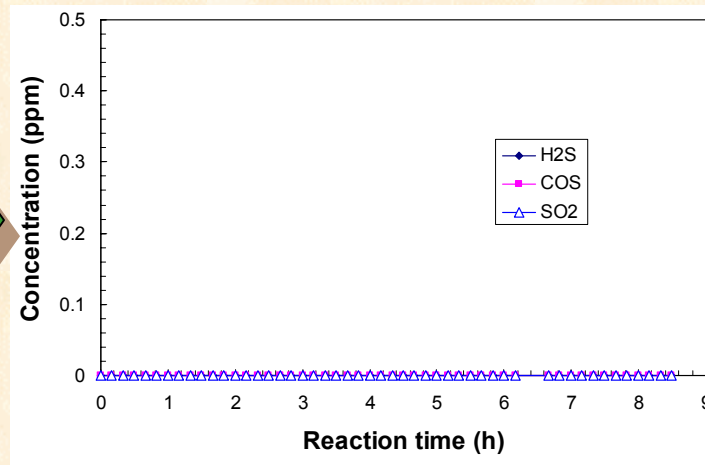
(S levels reduced to < 200 ppb)

1000 ppm H<sub>2</sub>S in H<sub>2</sub> stream

400 ppm H<sub>2</sub>S in reformat (50%H<sub>2</sub>,  
15%CO<sub>2</sub>, 9%CO, 1%N<sub>2</sub>, balance  
H<sub>2</sub>O ~24%)



No H<sub>2</sub>S,  
SO<sub>2</sub>, or  
COS were  
Detected  
over 10 h



- Excellent activity and selectivity were observed for activated carbons (ORNL-1 and ORNL-3)
- No SO<sub>2</sub>, H<sub>2</sub>S, COS was detected in more than 10 h
- The unactivated sample (ORNL-0) showed a low catalytic activity

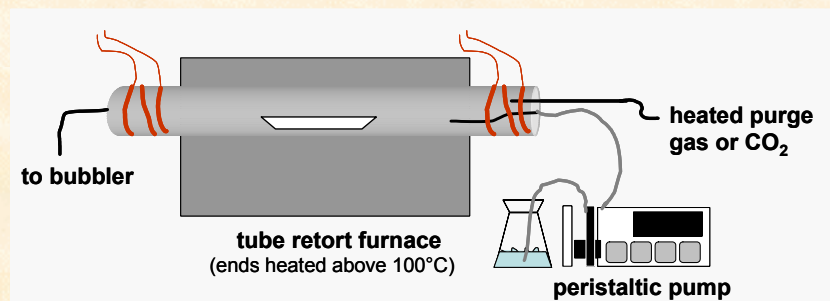


# Catalysts Development, Characterization and Activity Analysis

- Commercial catalysts**

Sample	Ash content	Surface area (m <sup>2</sup> /g)	Avg pore diameter (Å)	Activity	Selectivity
Centaur	4.78 %	817	15.6	<b>High</b>	<b>Low</b>
WV-B	6.30 %	1840	19.2	<b>Medium</b>	<b>Medium</b>
VA-507	1.08 %	1022	15.6	<b>Low</b>	<b>Medium/Low</b>

- ORNL catalysts** – carbon precursors are physically activated with steam and/or CO<sub>2</sub>. Thermal processing is varied to obtain different pore distribution.



Sample	Ash content	Holding Time(h)/ Burn-off (%)	Surface area (m <sup>2</sup> /g)	Avg pore diameter (Å)	Activity	Selectivity
ORNL-0	1.65 %	0			<b>Low</b>	<b>High</b>
ORNL-1	1.65 %	1.0/23.8	799	11.4	<b>High</b>	<b>High</b>
ORNL-3	1.65 %	3.0/57.8	2230	15.6	<b>High</b>	<b>High</b>

# Summary

- ORNL synthesized catalysts achieved total conversion and excellent selectivity for  $\text{H}_2\text{S}$  - *superior* than commercial carbons
  - No by products ( $\text{COS}$ ,  $\text{SO}_2$ ) were formed
  - 99.98% removal efficiency in single pass
  - Sulfur levels of reformat reduced to less than 200 ppb
  - No steam sensitivity observed
- Role of impurities: commercial catalysts with highest purity, has lowest activity.
- A relatively high  $\text{H}_2\text{S}$  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,  $\text{GHSV}=50,000 \text{ h}^{-1}$ , because only trace  $\text{H}_2\text{S}$  is present in the fuel gas streams like reformat (*e.g.*,  $<300 \text{ ppm}$ ).



# 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  $\text{SO}_2$  and COS.
- Optimize activation process.