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

<table>
<thead>
<tr>
<th>Fiscal Year</th>
<th>Allocated Budget (k$)</th>
<th>Realized Budget (k$)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY 2003</td>
<td>400</td>
<td>300</td>
<td>$100k diverted to FASTER Program</td>
</tr>
<tr>
<td>FY 2004</td>
<td>350</td>
<td>350</td>
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</tbody>
</table>
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\textsubscript{x}, SO\textsubscript{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 $\text{H}_2\text{S}$ to elemental sulfur in reformate streams via:

$$\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{n}\text{S}_n + \text{H}_2\text{O}$$

- 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 H₂S in H₂ or N₂
  - Up to 1,000 ppm H₂S in simulated reformate (50-55% H₂, 12-15%CO₂, 6-9%CO, <1%CH₄, balance H₂O, <300 ppm H₂S)
  - Conditions
    - Temperature 120-200°C
    - Pressure 1 atm,
    - GHSV=>3000 h⁻¹,
    - O₂:H₂S = 1:1 to 5:1

Compared to reality, the input H₂S concentration is exaggerated to demonstrate the capacity of catalyst.
Thermodynamic Evaluation: Analysis of Operation Regime

- Equilibrium calculations:
  - \( T = 400 \text{ K} \):
    - \( \text{H}_2\text{S} + 1/2\text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O} \)
    - \( \text{H}_2\text{S} + 3/2\text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} \)
    - \( \text{S} + \text{O}_2 \rightarrow \text{SO}_2 \)
    - \( 2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O} \)
  - \( (T = 400 \text{ K}) \):
    - \( \text{H}_2\text{S} + \text{CO} \rightarrow \text{COS} + \text{H}_2 \)

- Thermodynamic equilibrium calculations confirms increasing selectivity as a stoichiometric \( \text{O}_2: \text{H}_2\text{S} \) ratio is approached;
- COS formation is suppressed by presence of \( \text{H}_2 \) in gas stream
Thermodynamic Evaluation: Effect of Gas Composition

Commercial catalyst: Centaur at 130°C and 1 atm
H₂S inlet Conc.=10,000 ppm in N₂ or H₂,

Equilibrium results predict:
- In H₂: no conversion of H₂S
- In N₂: 100% conversion (400 ppm H₂S)

► 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 samples exhibited differing catalytic activity and selectivity:

- Centaur sample (coal-based) has 100% conversion of H₂S, but it over-oxidized S to SO₂.
- VA-507 sample (Coconut shell based) shows the lowest activity.
- WV-B sample (wood-based) displays good selectivity and 100% conversion of H₂S at the beginning, but both H₂S and SO₂ were observed after several hours on stream.

400 ppm H₂S in reformate (50%H₂, 15%CO₂, 9%CO, 1%N₂, balance H₂O ~24%)
Proof of Concept Demonstrated with ORNL Catalysts
(S levels reduced to < 200 ppb)

1000 ppm H₂S in H₂ stream

400 ppm H₂S in reformate (50%H₂, 15%CO₂, 9%CO, 1%N₂, balance H₂O ~24%)

- Excellent activity and selectivity were observed for activated carbons (ORNL-1 and ORNL-3)
- No SO₂, H₂S, 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ash content</th>
<th>Surface area (m²/g)</th>
<th>Avg pore diameter (Å)</th>
<th>Activity</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>4.78 %</td>
<td>817</td>
<td>15.6</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>WV-B</td>
<td>6.30 %</td>
<td>1840</td>
<td>19.2</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>VA-507</td>
<td>1.08 %</td>
<td>1022</td>
<td>15.6</td>
<td>Low</td>
<td>Medium/Low</td>
</tr>
</tbody>
</table>

#### ORNL Catalysts

Carbon precursors are physically activated with steam and/or CO₂. Thermal processing is varied to obtain different pore distribution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ash content</th>
<th>Holding Time(h)/Burn-off (%)</th>
<th>Surface area (m²/g)</th>
<th>Avg pore diameter (Å)</th>
<th>Activity</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORNL-0</td>
<td>1.65 %</td>
<td>0</td>
<td>799</td>
<td>11.4</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>ORNL-1</td>
<td>1.65 %</td>
<td>1.0/23.8</td>
<td>799</td>
<td>11.4</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>ORNL-3</td>
<td>1.65 %</td>
<td>3.0/57.8</td>
<td>2230</td>
<td>15.6</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>
Summary

- ORNL synthesized catalysts achieved total conversion and excellent selectivity for $\text{H}_2\text{S} - \textit{superior} \text{ than commercial carbons}
  - No by products ($\text{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 $\text{H}_2\text{S}$ 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, GHSV=50,000 h$^{-1}$, because only trace $\text{H}_2\text{S}$ 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.