Objectives

• To develop advanced fuel processing catalysts that meet DOE performance requirements

  ➢ Compared to Ni-based steam reforming catalysts, these new catalysts will
    ▪ be able to process complex fuel mixtures, such as gasoline
    ▪ process these fuels at higher rates
    ▪ be more resistant to coking and sulfur poisoning
  
  ➢ Improve our understanding of reforming reaction mechanisms, catalyst deactivation, and sulfur poisoning
  
  ➢ Define operating parameters (e.g. air: fuel and steam: fuel ratios, temperature, gas hourly space velocities (GHSV), catalyst geometry) to optimize catalyst performance and lifetime
Budget, technical barriers and targets

• FY204 Funding: $400K

• Technical barriers for hydrogen production
  - A. Fuel Processor Capital Costs
  - G. Efficiency of Gasification, Pyrolysis, and Reforming Technologies
  - Z. Catalysts

• Technical targets for reforming catalysts
  - gas-hourly space velocity (GHSV) ≥ 200,000 h⁻¹
  - conversion ≥ 99.9% with H₂ selectivity ≥ 80%
  - lifetime > 5000 h
  - cost <$5/kWe
Approach

• Building on past ANL experience, we are investigating two classes of materials
  ➢ transition metal(s) supported on oxide substrates
  ➢ perovskites

• Determine catalyst performance (H₂ yield, COₓ selectivity, hydrocarbon breakthrough, fuel conversion) and stability as a function of:
  ➢ catalyst composition
  ➢ fuel composition and sulfur content
  ➢ operating parameters: O₂:C and H₂O:C ratios, temperature, GHSV

• Conduct catalyst characterization and mechanistic studies to identify
  ➢ factors influencing activity and selectivity
  ➢ causes of deactivation
  ➢ how sulfur affects catalyst activity
Project safety

• Internal safety reviews are performed for all aspects of this project to address ESH issues
  ➢ Catalyst synthesis
    • Synthesis procedures are performed in fumehoods to exhaust vapors of powders and solvents
    • Waste chemicals are collected and disposed of through the Laboratory’s Waste Management Operations
  ➢ Microreactor systems
    ▪ Located in fumehoods
    ▪ Equipped with safety interlocks that shut the system down if excessive temperature or pressure is sensed or the fumehood ventilation fails

• Safety reviews are updated and renewed annually
Project timeline

May 1995: Started screening reforming catalysts

Apr 1997: Demonstrated conversion of gasoline w/Pt catalyst

Nov 1997: Demonstrated catalyst performance in engineering reactor

May 1999: Initiated licensing discussions with Süd-Chemie

May 2000: Demonstrated 1,000 h lifetime test Pt catalyst


Aug 2001: Began work on perovskite catalysts

Aug 2002: Demonstrated improved formulation of ceria ATR catalyst

Feb 2002: CRADA w/Süd-Chemie to optimize catalyst performance

May 2003: Demonstrated improved ATR catalyst with more stable support

Aug 2003: Initiated development of catalyst aging process

May 2004: Completed studies of support geometry

April 2003: File patent applications for perovskite and bimetallic catalysts

DOE/EE/HFCIT Program
Refractory oxides provide a more stable support for Rh than reducible oxides

- Higher \( \text{H}_2 \) yield and lower hydrocarbon breakthrough with Rh/alumina for gasoline ATR
- Significant decrease in \( \text{H}_2 \) yield with Rh/ceria but not with Rh/alumina after aging* for isobutane ATR

<table>
<thead>
<tr>
<th>Surface Area, m(^2)/g</th>
<th>Rh dispersion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>Aged*</td>
</tr>
<tr>
<td>Rh/alumina</td>
<td>130</td>
</tr>
<tr>
<td>Rh/ceria</td>
<td>36</td>
</tr>
</tbody>
</table>

* - treated at 900°C in \( \text{H}_2/\text{H}_2\text{O} \) for 24 h
We are working to develop an aging process to simulate effects of long-term operation.

**Table: Rh dispersion, %**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial</th>
<th>Reoxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td></td>
<td>81</td>
</tr>
<tr>
<td>33%H₂, 17% H₂O at 900°C - 24 h</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>&lt;1 ppm S gasoline at 700°C - 100 h</td>
<td>24</td>
<td>28</td>
</tr>
<tr>
<td>34 ppm S gasoline at 700°C - 100 h</td>
<td>3</td>
<td>13</td>
</tr>
</tbody>
</table>
Reversible adsorption of sulfur appears to be the primary cause of sulfur poisoning with Rh

- Effect of sulfur poisoning decreases with increasing temperature
- Loss in activity increases as H₂S concentration increases
- Most of the activity is recovered in ~1-2 h after sulfur is removed from feedstock

Graphs showing:
- Sulfur-free gasoline @ 700°C vs. 34 ppm S gasoline @ 800°C
- H₂ yield vs. time for different concentrations of H₂S
- Yield of H₂, CO, CO₂, CH₄ vs. time for different sulfur concentrations
- Concentration vs. time for different H₂S concentrations
Use of bimetallic formulations or sulfur-adsorbing supports has not improved the sulfur tolerance of Rh

- The addition of a second metal is known to improve the sulfur tolerance of some catalysts, such as the addition of Pd to Pt catalysts used in petroleum refining.

- Some supports, such as ceria, form a stable sulfide in the temperature range of ATR, which could serve as a potential “sink” for sulfur.

![Graph showing H₂ yield and total hydrocarbons over time for different catalysts.](image-url)
Proper selection of the structured support is critical for optimizing catalyst performance

- Performance of a Rh catalyst loaded onto 600-, 900-, and 1200-cpi monoliths and a 40-ppi metal foam for reforming gasoline is being evaluated to determine optimal support geometry

- Some preliminary observations
  - The highest temperature is observed at the exit of the first monolith
  - Nearly all of the H\textsubscript{2} is produced in the first monolith
  - CH\textsubscript{4} yield increases from the first to last monolith suggesting that methanation may be occurring as temperature decreases

- Data are being used to generate a reaction model
Less focus on perovskite catalysts

- Stability of Ni perovskite during ATR is an issue
- Results from electron microscopy and X-ray diffraction were inconclusive
- Neutron spectroscopy showed that metallic Ni particles were present
- Ni perovskites were active for gasoline ATR but the H₂ yield was low and decreased with time due to coking
- Substituting a precious metal for Ni produced a higher and more stable H₂ yield
Interactions and collaborations

- University and industrial interactions
  - University of Alabama (Prof. Ramana Reddy) to characterize ATR catalysts using SEM, TEM, and XPS
  - University of Alabama (Prof. Alan Lane) to develop more sulfur tolerant ATR catalysts
  - University of Puerto Rico, Mayagüez (Prof. Jóse Colucci) to determine operating parameters for reforming gasoline and biodiesel
  - Participant in a proposal with General Electric and University of Minnesota submitted in response to the Hydrogen Production and Delivery Research Solicitation
  - Süd-Chemie, Inc., monolith and foam studies
Response to reviewers’ comments from FY03

- More emphasis on sulfur tolerance
- Need more fundamental understanding of reaction and deactivation mechanisms
- What criteria can be used to decide when a catalyst is “good enough”
- Interaction with reforming work in the Hydrogen Program
## Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Date</th>
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<tbody>
<tr>
<td>Determine the optimal support structure (monolith vs. foam) to minimize mass transfer effects</td>
<td>01/04 (05/04)</td>
</tr>
<tr>
<td>Complete benchmarking of the ANL ATR catalyst against other reforming catalysts under development</td>
<td>05/04</td>
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<tr>
<td>Complete 1000 h test with best catalyst formulation supported on structured support using 30 ppm sulfur gasoline</td>
<td>09/04</td>
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Future work

- **Improve catalyst durability and minimize deactivation**
  - Conduct characterization studies of spent catalysts to further understanding of deactivation mechanisms
  - Validate catalyst aging process
  - Conduct long-term testing of improved catalyst formulations

- **Improve sulfur tolerance of catalysts by increasing our understanding of sulfur poisoning mechanisms**

- **Mechanistic studies to increase our understanding of reaction pathways**

- **Address catalyst issues identified in “FASTER” Program**
  - Catalyst deactivation and structural stability issues (i.e., effect of frequent and rapid startup)
  - Obtain performance data as a function of operating parameters to develop ATR/SR reaction models