Catalysts for autothermal reforming

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Hydrogen, Fuel Cells, and Infrastructure Technologies
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Objectives

• Develop advanced autothermal reforming (ATR) catalysts that meet DOE targets for the Fast Start reformer
  ✓ gas-hourly space velocity (GHSV) $\geq 200,000 \text{ h}^{-1}$
  ✓ efficiency of $\geq 99.9\%$ with $\text{H}_2$ selectivity of 80%
  ✓ durability of $\geq 5000 \text{ h}$
  ✓ cost of $\leq 5$/kwe

• Develop a better understanding of reaction mechanisms to
  ✓ increase catalytic activity
  ✓ reduce deactivation
  ✓ improve sulfur tolerance

This work addresses technical barriers I, J, K, and N.
Approach

• Building on past ANL experience, we are investigating two classes of materials.
  ✓ Transition metal(s) supported on mixed oxide substrates
  ✓ Perovskites, with no precious metals

• Determine catalyst performance (H₂, CO, CO₂, and CH₄) 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 gain insight into reaction pathways.

• Work with catalyst manufacturers to optimize catalyst structure and performance.
Industry and University collaborations

• Industry
  ✓ Süd-Chemie, Inc.
    • Manufactures catalyst under a non-exclusive licensing agreement
    • ANL and Süd-Chemie working jointly to improve catalyst structure and performance

• Universities
  ✓ University of Alabama (Profs. Ramana Reddy and Alan Lane)
    • Characterization studies (SEM, TEM, XPS) of ATR catalysts
    • Kinetic and mechanistic studies of ATR catalysts
  ✓ University of Puerto Rico, Mayagüez (Prof. José Colucci)
    • Determine reaction condition boundaries for carbon formation
Reviewer’s comments from FY2002 Annual Review

• Space velocities are still low.
  
  *We have increased the GHSV by a factor of ~4 compared to data presented at last year’s review.*

• Non-CH₄ hydrocarbon outlet levels seem high.
  
  *Hydrocarbon slip has been significantly reduced. We are investigating the effect of support geometry (cell density for monoliths and monolith vs. foam) to further reduce slip.*

• Demonstrating sulfur tolerance is key.
  
  *Has proven to be challenging. Deactivation but not complete loss of activity has been observed over 100-150 h.*

• Detailed knowledge of reaction process would be helpful.
  
  *Using the Advanced Photon Source at ANL, we are studying reaction and catalyst deactivation mechanisms. Through university collaboration, catalyst characterization and kinetic/mechanistic studies are being conducted.*
Project timeline

May 1995: Initiated screening for hydrocarbon reforming catalysts

Apr 1997: Demonstrated conversion of gasoline (powder)

Nov 1997: Demonstrated catalyst in performance in engineering reactor

Aug 1999: Initiated discussions with Süd-Chemie


Oct 2000: CRADA w/H2Fuel to commercialize reformer

Aug 2001: Began work on perovskite catalysts

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

May 2000: Demonstrated 1,000 h lifetime test

Oct 2002: Demonstrated conversion of gasoline (monolith)

June 2003: Start 500 h durability test with gasoline in 5 kWe reactor

April 2003: File patents for perovskite and transition metal/oxide catalyst.


May 2000: Demonstrated 1,000 h lifetime test

Nov 2004: Catalyst w/5000 h lifetime at GHSV of 200,000 h\(^{-1}\)

June 2003: Start 500 h durability test with gasoline in 5 kWe reactor

May 1999: Initiated licensing discussions with Süd-Chemie

Sept 2004: Catalyst w/5000 h lifetime at GHSV of 200,000 h\(^{-1}\)

Oct 2000: CRADA w/H2Fuel to commercialize reformer

Oct 2002: Demonstrated conversion of gasoline (monolith)

Argonne National Laboratory
Chemical Engineering Division
FY2003 accomplishments

• For transition metal on mixed oxide supports
  ✓ Began testing monoliths with commercial grade gasoline
  ✓ Demonstrated 55% H₂ (dry, N₂-free) from sulfur-free (<450 ppb S) gasoline at GHSV of 110,000 h⁻¹
  ✓ Identified mechanisms for catalyst deactivation
  ✓ Identified new oxide substrate that is more stable than ceria under reforming conditions

• For the Ni-based perovskites
  ✓ Began testing powders with commercial grade gasoline
  ✓ Optimized composition to improve structural stability while maintaining high activity
  ✓ Demonstrated <50% loss in activity with benchmark fuel w/50 ppm S

• Filed two patent applications
Rh catalysts produced reformate with high $H_2$ concentration from sulfur-free gasoline

Fuel: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)
Feed ratio: $O_2$:C = 0.5, $H_2O$:C = 1.8, GHSV = 27,000 h$^{-1}$, Furnace Temperature is 700°C.

- Rh and Rh-Pt catalysts produced a reformate containing $\geq 55\%$ $H_2$ ($N_2$-free, dry-basis) at a GHSV of 27,000 h$^{-1}$.
- 55% $H_2$ concentration was maintained at a GHSV of 110,000 h$^{-1}$ for Rh.
For Rh, non-CH₄ hydrocarbon slip decreased with increasing temperature (gasoline)

Fuel: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)
Feed ratio: O₂:C = 0.5, H₂O:C = 1.8, GHSV = 55,000 h⁻¹

- Increasing the O₂:C ratio to increase the reaction temperature results in a decrease in the H₂ yield.
- Raising the reaction temperature accelerates the rate of catalyst deactivation.
Tests are in progress to determine the optimal geometry for the structured support to improve fuel efficiency.

- High mass transfer rates will be crucial in operating at a GHSV of 200,000 h\(^{-1}\).
- We are evaluating the performance of the catalyst supported on different structured forms:
  - Monoliths with 600, 900, and 1200 cpsi
  - Metal foams
- Testing is being done in a kW\(_e\) reactor system under adiabatic conditions.
Deactivation and sulfur poisoning observed in long-term tests with Pt-Rh catalyst

Periodic Shutdown/Restart
Fuel: Sulfur-free benchmark fuel (75 vol% isooctane, 19 vol% xylenes, 5 vol% methylcyclohexane, x% 1-pentene)
Feed ratio: O₂:C = 0.41, H₂O:C = 1.6, GHSV = 9,000 h⁻¹

Continuous Operation
Fuels: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S), CA Tier II w/30 ppm S
Feed ratio: O₂:C = 0.45, H₂O:C = 1.6, GHSV = 57,000 h⁻¹

- Activity loss during operating cycle was mostly recovered on restart for testing involving periodic shutdown.
- Greater loss of activity due to sulfur poisoning than deactivation for testing involving continuous operation.
EXAFS showed that Pt sinters during reforming and that sulfur may further promote sintering.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>$\Delta s^2 \times 10^4$ ($\text{Å}^2$)</th>
<th>R (Å)</th>
<th>$\Delta E$ (eV)</th>
<th>$\rho$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>Pt-O</td>
<td>6.0</td>
<td>0.0</td>
<td>2.07</td>
<td>0.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Bottom - w/o S</td>
<td>Pt-O</td>
<td>1.7</td>
<td>0.3</td>
<td>2.10</td>
<td>0.0</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>Pt-Pt</td>
<td>7.3</td>
<td>0.0</td>
<td>2.78</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Top - w/o S</td>
<td>Pt-O</td>
<td>1.0</td>
<td>0.2</td>
<td>2.14</td>
<td>0.4</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>Pt-Pt</td>
<td>9.6</td>
<td>0.0</td>
<td>2.78</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Bottom - w/S</td>
<td>Pt-O</td>
<td>1.5</td>
<td>0.0</td>
<td>2.29</td>
<td>11.3</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>Pt-Pt</td>
<td>10.5</td>
<td>0.1</td>
<td>2.76</td>
<td>0.0</td>
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</tr>
<tr>
<td>Top - w/S</td>
<td>Pt-O</td>
<td>1.4</td>
<td>0.0</td>
<td>2.29</td>
<td>10.8</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>Pt-Pt</td>
<td>12.0</td>
<td>0.0</td>
<td>2.76</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

• EXAFS analysis is on going for Rh and Pt-Rh catalysts.
Sintering of ceria substrate shows need for more stable substrates

- Because of concern over loss of activity due to sintering of the ceria, we are investigating more thermally-stable supports.

- Rh/MO showed stable yields of H₂, CO, CO₂, and CH₄ over 100 h reforming sulfur-free benchmark fuel.

<table>
<thead>
<tr>
<th></th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As prepared</td>
</tr>
<tr>
<td>Rh/doped-CeO₂</td>
<td>36</td>
</tr>
<tr>
<td>Rh/MO</td>
<td>37</td>
</tr>
</tbody>
</table>

* 24-h at 900°C in 33% H₂, 17% H₂O, bal N₂

Conditions: Benchmark fuel, O₂:C = 0.45, H₂O:C = 1.6, GHSV = 82,000 h⁻¹
Some highlights from our collaborations with the University of Alabama

- TEM study to determine the effect of H\(_2\) reduction on Rh particles and ceria grains.
  - Significant increase in ceria grain size after reduction
  - Sharp interface between Rh and ceria observed on calcined samples becomes diffuse after reduction suggesting poorer interaction between metal and ceria

- Kinetic study of isobutane steam reforming catalyzed by PtCe\(_{1-x}\)Gd\(_x\)O\(_{2-(x/2)}\)
  - Rate is proportional to Pt dispersion
  - Effect of Gd concentration over the range of 0 \(\leq x \leq 0.2\) is minimal
  - A rate equation based on the Langmuir-Hinshelwood-Watson kinetic model has been developed

Relationship between Pt dispersion and H\(_2\) yield for Pt-CGO at different Gd concentrations
Cost targets can be achieved

• With a GHSV of 200,000 h\(^{-1}\), the cost target of ≤ $5/kWe is achievable, even with a precious metal catalyst.

• The estimated materials cost (structure, oxide substrate, precious metal), not including manufacturing cost, is $1.50-$2.50/kWe.
We have focused on increasing the stability of Ni-based perovskites

- Lanthanum on the A-site of $\text{ACr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ gave the best performance in terms of $\text{H}_2$ yield, fuel conversion, and avoiding coke formation.

- Cr was the best dopant on the B-site of $\text{LaB}_{0.9}\text{Ni}_{0.1}\text{O}_3$ for stabilizing the perovskite structure while maintaining high reforming activity.

<table>
<thead>
<tr>
<th>A-site</th>
<th>$\text{H}_2$ Yield*</th>
<th>Conv., %</th>
<th>C, Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>13.1</td>
<td>96.9</td>
<td>0.63</td>
</tr>
<tr>
<td>Pr</td>
<td>11.3</td>
<td>87.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Nd</td>
<td>11.9</td>
<td>97.0</td>
<td>6.3</td>
</tr>
<tr>
<td>Gd</td>
<td>13.3</td>
<td>99.9</td>
<td>5.1</td>
</tr>
<tr>
<td>Er</td>
<td>13.9</td>
<td>97.7</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Fuel: Isooctane, Feed ratio: Temperature = 700°C, $\text{O}_2$:$\text{C} = 0.37$, $\text{H}_2\text{O}$:$\text{C} = 1.15$, GHSV = 22,800 h$^{-1}$
Perovskites are susceptible to sulfur poisoning with most activity lost during the first 10 h

Fuel: Benchmark fuel (78 vol% isoctane, 16 vol% xylenes, 5 vol% methylcyclohexane, 1% 1-pentene) with sulfur added as benzo thiophene
Feed ratio: Temperature = 700°C, O₂:C = 0.45, H₂O:C = 1.6, GHSV = 25,000 h⁻¹
$La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ exhibited <5% loss in $H_2$ yield over 24-h in test with sulfur-free gasoline.

Fuels: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)
Feed ratio: $O_2$:C = 0.45, $H_2O$:C = 1.6, GHSV = 25,000 h⁻¹
## FY2003 milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demonstrate 60% H\textsubscript{2} from California Tier II low sulfur</td>
<td>02/03</td>
</tr>
<tr>
<td>gasoline at 700-800°C and a space velocity of 100,000 h\textsuperscript{-1}</td>
<td></td>
</tr>
<tr>
<td>with structured form of metal-doped ceria or perovskite catalyst (N\textsubscript{2}, H\textsubscript{2}O-free basis).</td>
<td></td>
</tr>
</tbody>
</table>

*Demonstrated 55% H\textsubscript{2} from no sulfur gasoline at 110,00h h\textsuperscript{-1} in a microreactor. Testing with gasoline with 30 ppm sulfur to be conducted in 5-kWe adiabatic reactor.*

Demonstrate improved sulfur tolerance of non-Pt catalysts with benchmark fuel containing 30 ppm S (less than 50% loss in activity over a 100-h period compared to activity measured with sulfur-free benchmark fuel.)

*In progress – Less than 50% loss in H\textsubscript{2} yield over 24-h.*
Future work

- Evaluate catalyst performance on a larger scale using 1-5 kWe adiabatic reactors.
  - Confirm microreactor results
  - Better evaluate long-term performance
  - Determine optimal geometry for structured support
- Work to decrease precious metal loading while improving catalyst stability and sulfur tolerance.
- Work to improve catalyst activity and sulfur tolerance of perovskite catalysts.
- Address the effect of rapid startup on catalyst stability.
- Increase our fundamental understanding of reaction processes and mechanisms for deactivation and sulfur poisoning.