Diesel Reforming for Solid Oxide Fuel Cell Application

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The Critical Issues in Diesel Reforming Catalyst & Catalytic System Development

**Catalyst**
- Cost
  - Costly Rh usage
- Activity
  - Efficiency & Selectivity
  - Fuel property & chemistry
- Durability
  - Metal vaporization & agglomeration
  - Support stability
  - Sulfur poisoning
  - Coke formation

**System**
- Fuel injection & mixing
- System integration
Diesel Reforming Catalyst Development
What Constitutes an Ideal Diesel Reforming Catalyst?

- Atomically dispersed active site.
- Stably anchored over the support surface.
- Effectively cleaving C-H, C-C & C=C bonds through oxidative process.
- Competitively releasing hydrogen over oxidation to H₂O.
- Competitively oxidizing surface carbon over C=C bond growth.
- Minimum chemical binding energy with sulfur.
Objective: Developing Perovskite Based ATR Catalyst

- The Perovskite Catalyst...
  - Low cost material.
  - Stable under high temperature & redox environment.
  - Exchangeable A & B sites lead to ionic dispersion & improve catalytic activity.

Conductivities of both e⁻ and V₀⁻ of perovskite enhance catalytic active site through electron & oxygen vacancy transfers in a redox process.
Approach: ANL Perovskite Catalyst Materials

- Perovskites include chromite, aluminite, manganite, ferrite, …
- Self-combustion synthesis (Pechini method)
- B-site doped with Ru, Rh, etc…
- A-site exchanged with La, Sr, Ba, Gd, Ce, Pr, …
Catalyst Activity Study: Test Apparatus & Conditions

- **Fuel**
  - Alkane surrogate - C_{12}H_{26}
  - Organic sulfur - Dibenzothiophene (50 ppm S)
  - Other HC surrogates – Monoaromatics, Polyaromatics, Cycloparaffins …

- **Temperature**
  - Reactor: 700 °C to 800 °C
  - Preheating: 200 °C.

- **Input Mixture**
  - ATR: O_2/C = 0.3 ~0.5, H_2O/C = 1 ~ 3

- **Space Velocity**
  - Fuel Flow Rate = 2.8~5.0x10^{-3} g_{fuel}/g_{Cat}•sec
  - GHSV = 50 K ~ 100 K hr^{-1}
Catalyst Activity Study: Test Plant
Catalyst Activity Study: Investigation on ATR Catalytic Light-Off for Perovskite Material

Ru doped perovskites demonstrate low light-off temperature for hydrogen production suitable for SOFC application.
Catalyst Activity Study: Basic Performance Parameters in Catalytic ATR Reforming

Chemical Reactions in Diesel ATR Reforming:

\[ C_nH_m + xO_2 + yH_2O = nCO_2 + (m/2 + 2n -2x)H_2 + (y + 2x -2n)H_2O \]

An example:
\[ C_{12}H_{26} + 6O_2 + 12H_2O = 12CO_2 + 25H_2 \]

Definition of Reforming Performance:

\[ H_2 \text{yield} = \frac{C_{H_2}}{C_{fuel}} \]

Reforming efficiency = \( \frac{C_{H_2}\Delta H_{H_2} + C_{CO}\Delta H_{CO}}{C_{fuel}\Delta H_{fuel}} \)

COx selectivity = \( \frac{C_{CO_2} + C_{CO}}{nC_{fuel}} \)

\( C_i \) = Molar flow of \( i \),
\( \Delta H_{c_i} \) = Heat of combustion of \( i \),
\( n \) = Number of C in fuel molecule
Catalyst Activity Study: Benchmarking New Perovskite Materials with Rh-Based Catalyst

Performance of a selected group of perovskites

Reforming Efficiency (%) vs. COx Selectivity (%)

LaSrCrRu, LaCrRu, LaSrCrRh, GdCrRu, PrCrRu, LaSrAlRu, LaAlRu, LaPrFeRu, LaMnRu, LaSrCr, LaSrCrNi

Benchmark

ATR input
\( \text{O}_2/\text{C} = 0.5 \)
\( \text{H}_2\text{O}/\text{C} = 2 \)
Sulfur Tolerance Study: Recoverable Activity over Perovskite Materials

Dibenzothiophene (DBT) and its derivatives are difficult to be removed from diesel through HDS process ...

Introducing 50 ppm sulfur in the form of DBT temporarily suppress reforming efficiency and COx selectivity.

Catalyst re-activates after S is removed from fuel.
Sulfur Tolerance Study: Resistance to Poisoning Improves at Higher Operating Temperature

Increase reaction temperature by 100 °C significantly improved catalytic performance in the presence of sulfur.
Sulfur Tolerance Study: Stable Reforming Observed during 100-Hr Aging Test with 50 ppm S in DBT

Excellent catalytic stability was observed during 100 hour aging test with S contaminated fuel

T = 800 °C
Fuel = 50 ppm S/C_{12}H_{26}
GHSV = 50,000 hr⁻¹
### Coking Prevention Study: Issues with Heavy Hydrocarbon Components in Diesel

<table>
<thead>
<tr>
<th>Compound Type</th>
<th>Wt% Analysis, ANL</th>
<th>Wt% Analysis, Exxon</th>
<th>Ave. or Ref. Formula (ANL)</th>
<th>Representative Molecular Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>38.7</td>
<td>39.7</td>
<td>C\textsubscript{16}H\textsubscript{34}</td>
<td>![Paraffin Structure]</td>
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<tr>
<td>Cycloparaffins</td>
<td></td>
<td></td>
<td></td>
<td>![Cycloparaffin Structures]</td>
</tr>
<tr>
<td>1-ring cycloparaffins</td>
<td>29.6</td>
<td>23.6</td>
<td>C\textsubscript{10}H\textsubscript{21}</td>
<td>![1-ring Cycloparaffin Structure]</td>
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<tr>
<td>2-ring cycloparaffins</td>
<td>11.5</td>
<td>20.6</td>
<td>C\textsubscript{16}H\textsubscript{32}</td>
<td>![2-ring Cycloparaffin Structure]</td>
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<tr>
<td>3-ring cycloparaffins</td>
<td>4</td>
<td>6.5</td>
<td>C\textsubscript{22}H\textsubscript{38}</td>
<td>![3-ring Cycloparaffin Structure]</td>
</tr>
<tr>
<td>Mono-aromatics</td>
<td></td>
<td></td>
<td></td>
<td>![Mono-aromatics Structures]</td>
</tr>
<tr>
<td>Alkyl benzenes (a)</td>
<td>7.3</td>
<td>3.2</td>
<td>C\textsubscript{8}H\textsubscript{8}</td>
<td>![Alkyl Benzenes Structure]</td>
</tr>
<tr>
<td>Naphthenebenzenes (Indans (b) + Tetralins (c) + Indens (d))</td>
<td>3.2</td>
<td>0.9</td>
<td>C\textsubscript{12}H\textsubscript{16}</td>
<td>![Naphthenebenzenes Structure]</td>
</tr>
<tr>
<td>Di-aromatics</td>
<td></td>
<td></td>
<td></td>
<td>![Di-aromatics Structures]</td>
</tr>
<tr>
<td>Alkynaphthalenes (a)</td>
<td>1.8</td>
<td>1.6</td>
<td>C\textsubscript{13}H\textsubscript{14}</td>
<td>![Alkynaphthalenes Structure]</td>
</tr>
<tr>
<td>Acenaphthenes (b)/Biphenyls</td>
<td>3.5</td>
<td>2.2</td>
<td>C\textsubscript{9}H\textsubscript{12}</td>
<td>![Aacenaphthenes Structure]</td>
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<tr>
<td>Acephthalenes (c)/Fluorenes (d)</td>
<td>0.3</td>
<td>1.7</td>
<td>C\textsubscript{13}H\textsubscript{10}</td>
<td>![Acephthalenes Structure]</td>
</tr>
</tbody>
</table>
Coking Prevention Study: Correlation b/w Efficiency & Residual HC’s Formation from Diesel Components

Coking is affected by Temperature, O₂/C, H₂O/C, Catalyst & CATALYSIS CHEMISTRY of HYDROCARBONS.
Coking Prevention Study: Deactivation Mechanism & Coke Formation by Polyaromatics

- Impact on ATR reforming by 1-methylnaphthalene (1MN)
  - 1MN tentatively deactivates reforming.
  - Activity recoverable after 1MN removal.
  - Performance improves a higher T.
  - \( \text{O}_2/\text{C} \) & \( \text{H}_2\text{O}/\text{C} \) have limited impact.

- Proposed Model of PAH impact on Reforming and C-formation
  - Low cetane# / high Tig make them hard to oxidize.
  - Competition b/w oxidation vs. C growth

1 MN tentatively deactivates reforming.
Activity recoverable after 1MN removal.
Performance improves a higher T.
\( \text{O}_2/\text{C} \) & \( \text{H}_2\text{O}/\text{C} \) have limited impact.

Long resident time and slow decomposition of PAH over active site reduce reforming rate & increase residual HC’s & coke formation!
Coking Prevention Study: Fishbone Analysis on Root Cause of Coking

We are currently working on coking reduction through both catalyst & engineering improvements.
Catalyst Characterization: Identifying Perovskite Structure & Ru Active Site

Conventional (XRD, SEM, ICP, TPR, BET…) and Advanced (EXAFS, XANES) characterization methods were used to study structure-activity relationship.

XRD confirms perovskite structure

EXAFS reveals Ru embedded in perovskite

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N</th>
<th>R (Å)</th>
<th>σ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCSR1200</td>
<td>6.0</td>
<td>1.943</td>
<td>2.5x10⁻⁵</td>
</tr>
<tr>
<td>LCSR800</td>
<td>4.7</td>
<td>1.953</td>
<td>2.5x10⁻⁵</td>
</tr>
<tr>
<td>LCR800</td>
<td>4.3</td>
<td>1.962</td>
<td>1.0x10⁻⁵</td>
</tr>
</tbody>
</table>
Summary: Knowledge Gained on Perovskite Catalyst & Its Applicability to SECA

- Ru doped perovskites demonstrated excellent catalytic reforming activities comparing with Rh based catalysts.
- Active catalysts are the perovskites containing Ru at B site with oxygen vacancy and high surface area.
- Improved sulfur tolerance and perovskite stability were demonstrated through 100-hr aging at higher operating temperature.
- Root cause of catalyst deactivation through coking by aromatics was identified. Improvement through catalyst material refinement and new reactor engineering approach is underway.

Perovskite ATR catalysts provide new low-cost alternatives in fuel reforming for SECA.
Diesel Fuel Mixing & Cool Flame Study
Critical Issues in Fuel Mixing

- Completed vaporized fuel is essential for catalytic reforming.
- Diesel fuel cannot be evaporated without fractioning.
- Incomplete mixing creates “hot spots” on the catalyst and leads to sintering & coke formation.
ANL Approach: Diesel Injection Technology Improvement & Pre-reforming through Cool Flame

- **Diesel Injection** – A joint effort between ANL and International Truck and Engine Corporation (ITEC)
  - ANL is currently building a test facility for air-steam-fuel-exhaust gas mixing study with catalyst testing capability for ANL autothermal reforming process.
  - ITEC provides diesel-fuel injectors and fuel-injection control system.

- **Cool Flame** – An alternative method to further improve fuel mixing and pre-reforming.
  - What is cool flame?
  - How it may benefit SECA fuel reforming effort?
  - Our approach – Investigating operating condition and gas composition in cool flame.

*L. Hartmann, K. Lucka, and H. Kohne, 2003*
Diesel Mixing Study: Fuel-Air-Steam Mixing Facility Under Construction
Diesel Mixing Study: ITEC Diesel Fuel Injector

- Pulsed injection with pulse rate of
  10 ~ 70 Hz (500 ~ 4000 rpm for 4-cylinder engine)
- Injection duration
  Below 1 ms at idle to 20 ms at high load
- Injection nozzles
  6 holes around
- Fuel injection rate
  Peak : 105 mm³/stroke at 240 bar and 600 rpm
  Idle : 9.2 mm³/stroke at 45 bar and 600 rpm
Diesel Mixing Study: Demonstration of Fuel Injection Test Chamber
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