2005 SECA Core Technology Review

NETL On-Site Fuel Processing Activities

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by
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Investigation of Oxygen-Conducting Catalyst Supports
O2 Conducting Catalyst Supports

Goals and Objectives

**GOAL:**
To support the research for low-cost, effective, and long-duration reforming catalysts in the development of auxiliary power units (APUs) in commercial diesel trucks and other related applications as being sponsored by NETL’s SECA Fuel Cell Program.

**OBJECTIVE:**
To fundamentally understand the role of oxygen conducting supports in reforming of diesel fuel compounds and their role in decreasing carbon deposition and/or increasing sulfur tolerance.
O2 Conducting Catalyst Supports

FACTORS AFFECTING CATALYTIC PERFORMANCE AND CARBON FORMATION

- Ionic Conductivity
- Oxygen Storage Capacity
- Type of support
- O/C ratio
- Metal type
- Metal Loading

- Metal Dispersion
- Surface Area
- Particle size
- Temperature
- Synthesis Method
# O2 Conducting Catalyst Supports

## Catalysts Tested

<table>
<thead>
<tr>
<th>Material</th>
<th>Catalytic Metal</th>
<th>Material</th>
<th>Catalytic Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>none</td>
<td>GDC10</td>
<td>None</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1% Pt</td>
<td>GDC10</td>
<td>1% Pt</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1% Rh</td>
<td>GDC10</td>
<td>1% Rh</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1% Ni</td>
<td>GDC10</td>
<td>1% Ni</td>
</tr>
<tr>
<td>ZDC 50</td>
<td>none</td>
<td>GDC30</td>
<td>None</td>
</tr>
<tr>
<td>ZDC 50</td>
<td>1% Pt</td>
<td>GDC30</td>
<td>1% Pt</td>
</tr>
<tr>
<td>ZDC 50</td>
<td>1% Rh</td>
<td>GDC30</td>
<td>1% Rh</td>
</tr>
<tr>
<td>ZDC 50</td>
<td>1% Ni</td>
<td>GDC30</td>
<td>1% Ni</td>
</tr>
<tr>
<td>LDC 15</td>
<td>none</td>
<td>alumina</td>
<td>None</td>
</tr>
<tr>
<td>LDC 15</td>
<td>1% Pt</td>
<td>alumina</td>
<td>1% Pt</td>
</tr>
<tr>
<td>LDC 15</td>
<td>1% Rh</td>
<td>alumina</td>
<td>1% Rh</td>
</tr>
<tr>
<td>LDC 15</td>
<td>1% Ni</td>
<td>alumina</td>
<td>1% Ni</td>
</tr>
</tbody>
</table>
Catalysts were tested to elucidate effects of:

- Support type
- Ionic conductivity
- Reducibility
- Dopant type (Zr, La, Gd)
- Dopant concentration (GDC10 & GDC30)
- Catalyst type (Pt, Ni, Rh)
Operating variables during experimental tests included:

- Reaction Temperature
- O/C ratio
- Pressure
- Time on stream
- Space velocity
- Catalyst Reduction Temperature

-100 experiments have been performed
O2 Conducting Catalyst Supports

RESULTS
CeO₂ has high oxygen mobility and oxygen storage capacity that allows high conversion at low O/C values.

Pt/alumina shows a rapid decrease on H₂ generation.

Alumina is a non-oxygen ion conductor support that is not able to provide lattice oxygen to maintain the same CH₄ conversion.
O2 Conducting Catalyst Supports
Effect of Ionic Conductivity on Carbon Formation

Amount of carbon increases when the ionic conductivity of support decreases for all catalysts but Pt/LDC15. Lower amount of carbon was obtained on Pt/GDC. Pt/LDC15 has the highest ionic conductivity. However it has the lower dispersion.
O2 Conducting Catalyst Supports

Effect of dopant on ionic conductivity

Particular concentrations of dopants can increase the number of oxygen ion vacancies, which improves ionic conductivity.

The optimum ionic size of Gd & La in ceria lattice causes almost no ceria expansion or contraction around the dopant, which causes high ionic conductivity, Solid State Ionics, V131, pp.281-290
Higher metal reducibility gives higher catalytic performance wrt H2
Rh/ZDC yielded the highest catalytic performance for H2 generation
There was no large effect of type of dopant on reducibility of Pt which caused no big difference on catalytic performance.
O2 Conducting Catalyst Supports

Effect of metal on H2 generation

Pt/ZDC, POM, 700C

Rh/ZDC, POM, 700C

Ni/ZDC, POM, 700C

- Pt presented the most stable catalytic performance
- Ni presented the lowest metal dispersion
O2 Conducting Catalyst Supports

Regeneration of catalysts after carbon formation

Catalyst regeneration was possible after carbon build up
O2 Conducting Catalyst Supports

Summary

- Amount of carbon generated was directly proportional to catalyst ionic conductivity
  - Higher amount of carbon, obtained by: Pt/CeO2 > Pt/ZDC > Pt/LDC15 > Pt/GDC10 > Pt/GDC30

- Amount of carbon increased when the ionic conductivity of support decreased for all catalysts but Pt/LDC15, which has the highest ionic conductivity but lower dispersion

- Amount of carbon increased when the ionic conductivity of support decreased for all catalysts but Pt/LDC15, which has the highest ionic conductivity but lower dispersion
Lower amount of carbon was obtained on Pt/GDC10 and Pt/GDC30.

Lower conversion was obtained on alumina based catalysts, which may be due to the fact that alumina is a non-oxygen conducting support.

Full regeneration of catalytic activity was demonstrated for the Pt base catalysts after sequential carbon build up.

In general carbon generation during the partial oxidation of methane is complex and likely influenced by: Ionic Conductivity, Oxygen Storage Capacity, Type of support, Metal type, Metal Loading, O/C ratio, Metal Dispersion, Surface Area, Particle size and Metal-support interaction.
O2 Conducting Catalyst Supports

Future Plans

- **Continue Analysis of Existing Data**:  
  - Much data yet to consider wrt catalyst parameters/characterization and performance (product yields and carbon deposition).
  - Consider effects of sulfur on oxygen conducting supported catalyst performance.

- **Initiate Mechanistic Studies**  
  - Utilize O18 for correlation of oxygen isotopic exchange with rate of carbon deposition and catalytic performance to elucidate pathways or mechanisms for O2 conducting supports

- **Technology Transfer**  
  - Continue dissemination of results through publications and program interaction. Peer-reviewed publication planned in FY05.
2005 SECA Core Program Review
NETL Fuel Processing

Diesel Fuel Reforming Kinetics
Diesel Fuel Reforming Kinetics

Goals & Objectives

**GOAL:**
- Provide kinetic reaction rate and process information of diesel fuel reforming to support the development of auxiliary power units (APUs) in commercial diesel truck transport and other related applications as being sponsored by NETL’s SECA Fuel Cell Program

**OBJECTIVE:**
- Correlate fuel reforming rates versus process conditions, and catalyst type for individual, and combined diesel constituents (surrogate diesel fuel).
Diesel Fuel Reforming Kinetics

Applicability

- Diesel-based fuel cell APUs are considered a significant high volume market for SOFC’s.

- Fundamental understanding of diesel reforming and general methodology for kinetic rate determination would be beneficial to catalyst developers. May extend to hydrocarbon fuels in general.

- Fuel reforming kinetics would be useful to fuel reforming developers and system integrators to evaluate steady-state and transient performance, develop control strategies, maximize efficiency, and minimize cost.
Diesel Fuel Reforming Kinetics

Benefits of Study

System integration & reformer operation / design

Insights for catalyst improvement & design
Diesel Fuel Reforming Kinetics

**Methodology**

- **Response surface methodology**
  - Process parameter optimization study for the diesel ATR
  - Elucidation of complex chemical networks for the diesel ATR
- **Propose mechanism / model**
- **Develop kinetic rates**
  - Carry out kinetic measurements
    - Representative model compounds: single component & surrogate fuel mixtures
    - Real diesel
- **Validate model**
  - Experimental data
# Diesel Fuel Reforming Kinetics

## Modeling Approaches

<table>
<thead>
<tr>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
<th>Level 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intuitive Lumping</td>
<td>Mechanism Based Lumping</td>
<td>Structure Oriented Lumping</td>
<td>Mechanistic</td>
</tr>
<tr>
<td>Lumps derived from intuition (gross identification of lumping groups), e.g., paraffins, aromatics, etc.</td>
<td>Psuedo-homogeneous phase</td>
<td>State of the art in complex mixture modeling</td>
<td>Pure mechanistic approach</td>
</tr>
<tr>
<td>Little is known regarding the exact mechanism</td>
<td>Based on psuedo-species lumped together based on the elucidation of a detailed mechanism</td>
<td>Closely resembles pure mechanistic approach</td>
<td>Detailed kinetic studies of single components and their mixtures</td>
</tr>
<tr>
<td>Psuedo-1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>Requires a knowledge of process chemistry</td>
<td>Involves lumping isomers only</td>
<td>Development of experimental procedures to evaluate process chemistry</td>
</tr>
<tr>
<td>Psuedo-homogeneous phase</td>
<td>Must possess the analytical ability to measure the psuedo-species only</td>
<td>Detailed knowledge of process chemistry needed, expensive analytically</td>
<td>Knowledge of catalyst properties needed</td>
</tr>
<tr>
<td>Easy to develop, inexpensive</td>
<td>Suitable for process simulators, e.g. ASPEN, ChemCad</td>
<td>Detailed kinetic studies needed for the development of lumps</td>
<td>Requires spectroscopic method</td>
</tr>
<tr>
<td>Suitable for process simulators, e.g. ASPEN, ChemCad</td>
<td>Predicts transient response, hydrocarbon slip, coking and catalyst deactivation</td>
<td>Suitable for CFD packages, e.g. Fluent</td>
<td>Predicts transient response, hydrocarbon slip, coking and catalyst deactivation based on fundamentals</td>
</tr>
<tr>
<td>Predicts transient response and hydrocarbon slip</td>
<td>Predicts transient response, hydrocarbon slip, coking and catalyst deactivation</td>
<td>Predicts transient response, hydrocarbon slip, coking and catalyst deactivation based on fundamentals</td>
<td></td>
</tr>
</tbody>
</table>
Diesel Fuel Reforming Kinetics

*Rxn Pathways*

- Different reaction schemes for each class proposed based on RSM studies, e.g. for SR,

\[
\begin{align*}
P & \xrightarrow{k_1} LP \\
LP & \xrightarrow{k_2} OL \\
P & \xrightarrow{k_3} OL \\
OL & \xleftarrow{k_4} AR \\
\end{align*}
\]

\[
\begin{align*}
P + H_2O & \xrightarrow{k_6} \text{Syngas} \\
LP + H_2O & \xrightarrow{k_7} \text{Syngas} \\
OL + H_2O & \xrightarrow{k_8} \text{Syngas} \\
AR + H_2O & \xrightarrow{k_9} \text{Syngas} \\
\end{align*}
\]

- Following criteria utilized to assess the validity of model:
  - calculated rate constants (positive values and Arrhenius Law)
  - minimized value of objective function
  - calculated profile of species concentration variations.
Diesel Fuel Reforming Kinetics

**Testing Approach**

- Conduct single-, binary-, ternary-component and surrogate diesel reforming studies in sequential manner.
- Conduct “similarity studies” within a class to evaluate behavior/effect.
- Evaluate the effect of sulfur on performance of fuel reforming catalysts
- Select representative model compounds within each class:
  - Paraffin: n-Tetradecane (TD); Naphthene: Decalin (DL); and Aromatic: 1-Methylnaphthalene (MN)
Diesel Fuel Reforming Kinetics

Experimental Setup

- MFC = Mass Flow Controller
- PI = Pressure Indicator
- Insulated Zone
- Vent
- Thermocouple
- Product Analysis
- Fixed-Bed
- Convection Heater
- N₂
- Liquid Fuel
- Air
- H₂

MFC
HPLC Pump
MFC
MFC

HPLC = High-Performance Liquid Chromatography
# Diesel Fuel Reforming Kinetics

## Experimental Conditions

<table>
<thead>
<tr>
<th></th>
<th>ATR</th>
<th>SR</th>
<th>POX</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/C</td>
<td>0.6</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>H₂O/C</td>
<td>1.5</td>
<td>3.0</td>
<td>0.0</td>
</tr>
<tr>
<td>T (°C)</td>
<td>750 – 850</td>
<td>750 – 850</td>
<td>750 – 850</td>
</tr>
<tr>
<td>GHSV (h⁻¹)</td>
<td>50,000 - 150,000</td>
<td>50,000 - 150,000</td>
<td>50,000 - 150,000</td>
</tr>
</tbody>
</table>

Ternary fuel composition: n-tetradecane (40 wt%), decalin (40 wt%), and 1-methylnaphthelene (20 wt%)
Diesel Fuel Reforming Kinetics

*Ternary ATR reforming*

**Pt/Al₂O₃, S/C=1.5, and O₂/C=0.3**

- Results very similar to binary reforming
- No conversion of less reactive aromatics at conditions studied
- Higher conversions (>90%) of highly reactive paraffins
- Olefins formation was significantly lower compared to only TD reforming
Diesel Fuel Reforming Kinetics

$H_2$ production from single, binary, & ternary mixture

ATR, Pt/Al$_2$O$_3$, S/C=1.5, and O$_2$/C=0.3

- Overall yields are not additive of yields from individual fuel components
- Relative reactivity of one fuel component considerably affects the conversion pattern of other
- More the difference in relative reactivity; larger the effect
Diesel Fuel Reforming Kinetics  
*Effect of aromatics content on \( H_2 \) production*

Pt/Al\(_2\)O\(_3\), S/C=1.5, \( O_2/C=0.3 \), T = 850 C, and SV = 50,000 hr\(^{-1}\)

- Reported actual yields are at the same reaction conditions, but not at optimized conditions
- Highly reactive component consumes available \( O_2 \)
  - Produces combustion products
- \( O_2 \) not spared for the less reactive component
  - Pyrolysis reaction dominates
Diesel Fuel Reforming Kinetics

Effect of aromatics content on $H_2$ production

Pt/Al$_2$O$_3$, $T = 850$ C, and $SV = 50,000$ hr$^{-1}$

-MN+DL+TD is 20 wt% MN + 40 wt% DL + 40 wt% TD (22 C% MN + 39 C% DL + 39 C% TD)
## Typical Gaseous Byproducts from Reforming of Different Diesel Model Components

<table>
<thead>
<tr>
<th></th>
<th>TD</th>
<th>MN</th>
<th>DL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>Lots of CH$_4$, and trace of C2-C7</td>
<td>Only CH$_4$</td>
<td>Mainly CH$_4$</td>
</tr>
<tr>
<td>Olefins</td>
<td>C$_2$H$_4$ and C$_3$H$_6$ mainly</td>
<td>Trace</td>
<td>Some C$_2$H$_4$ and C$_3$H$_6$</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Benzene only</td>
<td>Benzene</td>
<td>Benzene</td>
</tr>
</tbody>
</table>

Product distributions depended on the model compound, type of reforming performed, and process parameters.
## Typical Liquid Byproducts from Reforming of Different Diesel Model Components

<table>
<thead>
<tr>
<th></th>
<th>TD</th>
<th>MN</th>
<th>DL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Paraffins</strong></td>
<td>Mainly unconverted TD</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Olefins</strong></td>
<td>C7-C14 α-olefins, only C14 dienes and trienes</td>
<td>Trace</td>
<td>None</td>
</tr>
<tr>
<td><strong>Naphthenes</strong></td>
<td>None</td>
<td>None</td>
<td>Unconverted DL &amp; a series of unsaturated cyclic species</td>
</tr>
<tr>
<td><strong>Aromatics</strong></td>
<td>Several including product like n-octylbenzene</td>
<td>Naphthelene, &amp; unconverted 1-MN</td>
<td>Mainly naphthelene</td>
</tr>
</tbody>
</table>
Diezel Fuel Reforming Kinetics

*Conclusions to Date*

- Overall yields from a multi-component fuel are not additive of yields from individual fuel components.

- Relative reactivity of one fuel component considerably affects the conversion pattern of other.

- Conversion of highly reactive fuel component proceeds towards completion:
  - Highly reactive component consumes available O$_2$
    - Produces combustion products.

- Significantly lower conversion of less reactive fuel component observed:
  - O$_2$ not spared for the less reactive component
    - Pyrolysis reaction dominates.
Diesel Fuel Reforming Kinetics

Future Plans

- **Continue Surface Response Mapping:**
  - Evaluate other fuel compounds within a classification to examine if similar reforming behavior exists
  - Continue evaluation of carbon formation
  - Evaluate the effect of sulfur on performance of fuel reforming catalysts

- **Develop Kinetic Submodels**
  - Develop intuitive kinetic models for individual model compounds and benchmark fuel for particular catalyst types. Collaboration with Dr. Lanny Schmidt (U of MN).

- **Technology Transfer**
  - Continue dissemination of results through publications and program interaction with fuel cell / catalyst developers
Hexaaluminate Catalyst Development
The hexaaluminate catalyst….  

- Is stable under high temperature reducing and oxidizing environments  
  - A property of its unique unit cell structure consisting of a spinel block and two mirrored planes

- Has aluminum sites that are exchangeable with transition metals  
  - Doping results in strong interactions with neighboring atoms that suppresses active metal mobility  
  - Dispersed active metals are less susceptible to carbon formation

Hexaaluminate $M_i(\text{M}_{II})_y\text{Al}_{12-y}\text{O}_{19.5-z}$ Structure
Hexaaluminate Catalyst Development: 
*Test Apparatus*

MFC = Mass Flow Controller
PI = Pressure Indicator

- Insulated Zone
- Vent
- Thermocouple
- Product Analysis
- Fixed-Bed
- Furnace
- Convection Heater
- Vent

- N₂
- Liquid Fuel
- Air
- H₂

**Diagram Labels:**
- HPLC Pump
- MFC

**Legend:**
- PI = Pressure Indicator
- MFC = Mass Flow Controller
Hexaaluminate Catalyst Development: *Laboratory Reactor*

- Preheat zone
- Twin Micro-reactors
- Multiple sample and calibration ports
- Online Mass Spectrometer
- Online GCs
Hexaaluminate Catalyst Development: Structure

NETL synthesized Co, Fe and Ni doped hexaaluminate catalysts possess similar hexaaluminate-type structure
Hexaaluminate Catalyst Development: Properties

Reduction stability by temperature programmed reduction (TPR) of hexaaluminate catalysts in 5 vol% H₂/Ar...

Temperature of peak maxima:
- Co⁺⁺ → Co⁰ 1093°C
- Fe³⁺ → Fe²⁺ 407°C
- Fe²⁺ → Fe⁰ 1098°C
- Ni²⁺ → Ni⁰ 996°C

Peak reduction temperatures of transition metals doped into hexaalumina are shifted to significantly higher temperatures.
Hexaaluminate Catalyst Development:  
*Test Conditions*

**Test Fuels**
- n-Tetradecane
- n-Tetradecane/Dibenzothiophene (50 ppm w/w S)

**Catalysts**
- Ni and Co doped hexaalumina
- Ni and Co doped hexaalumina/promoter (0.1 wt% Rh)
  - Improved activity & light-off characteristics

**Test Conditions**
- CPOX: O/C = 1.2
- Temp = 850°C
- Preheat temp = 350°C
- GHSV = 50,000 cm³/h/g
Hexaaluminate Catalyst Development: Various Catalysts Tested

(CPOX, C_{14}H_{30}, O/C = 1.2, T=850°C, GHSV=50,000 cm³/h/g)

Fuel: n-tetradecane

Fuel: n-tetradecane/dibenzothiophene (50 ppm w/w S)
Hexaaluminate Catalyst Development: 100 hr

**Aging Tests**

\((CPOX, \ C_{14}H_{30}, O/C = 1.2, T=850°C, \ GHSV=50,000 \ cm^3/h/g)\)

Hexaaluminate catalysts showed good stability over 100 hr
Hexaaluminate Catalyst Development

Summary

- Inexpensive catalysts based on Ni and Co doped hexaaluminates have shown good catalytic activity and selectivity.

- XRD and TPR characterization of catalysts indicates that they are Co and Ni doped hexaalumina.

- Good catalytic stability was observed with sulfur and sulfur free n-Tetradecane partial oxidation for 100 hour on Ni doped hexaaluminate catalysts.
Hexaaluminate Catalyst Development

**Future Work**

Examine the effects of...

- Active metal substutional level on hexaaluminate phase formation and catalytic activity

- Gas composition on catalytic performance
  - ATR – steam addition
  - SR – steam reforming

- Operating conditions
  - Temperature
  - Space velocity