# **2005 SECA Core Technology Review**



# NETL On-Site Fuel Processing Activities

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by

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## 2005 SECA Core Program Review NETL Fuel Processing

# 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

Fonic 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*

Material	Catalytic Metal	Material	Catalytic Metal
CeO <sub>2</sub>	none	GDC10	None
CeO <sub>2</sub>	1% Pt	GDC10	1%Pt
CeO <sub>2</sub>	1% Rh	GDC10	1%Rh
CeO <sub>2</sub>	1% Ni	GDC10	1%Ni
<b>ZDC 50</b>	none	GDC30	None
<b>ZDC 50</b>	1% Pt	GDC30	1%Pt
<b>ZDC 50</b>	1% Rh	GDC30	1%Rh
<b>ZDC 50</b>	1% Ni	GDC30	1%Ni
LDC 15	none	alumina	None
LDC 15	1% Pt	alumina	1%Pt
LDC 15	1% Rh	alumina	1%Rh
LDC 15	1% Ni	alumina	1%Ni



#### **O2 Conducting Catalyst Supports** *Experimental tests*

**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)



## **O2 Conducting Catalyst Supports** *Experimental Equipment*



**Fixed-bed Micro-reactor** 

#### **Mass Spectrometer**



- >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**



#### **NETL Fuel Processing R&D** *Effect of support on H2 generation*





≻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 nonoxygen 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

Material	Catalytic Metal	Surface area (m <sup>2</sup> /gram)	Particle Size Support (μm)	Dispersion (percent)	ionic conductivity σ (S/cm)
ZDC 50	1% Pt	88.3	0.80	40.4	9.29E-04
GDC 10	1% Pt	45.1	0.44	58.8	2.23E-02
GDC 30	1% Pt	33.9	0.48	n/a	2.76E-02
LDC 15	1% Pt	32.5	0.44	21	3.48E-02
$CeO_2$	1% Pt	25.5	0.41	n.d.	3.78E-05
γ-Al2O3	1% Pt	182		n.d.	n.d.

# **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** 

# **O2 Conducting Catalyst Supports** *Effect of dopant on reducibility*



# **O2 Conducting Catalyst Supports** Effect of metal on H2 generation





# **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



# O2 Conducting Catalyst Supports Summary...cont.

- 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** *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*



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

#### Level 1 Intuitative Lumping

- Lumps derived from intuition (gross identification of lumping groups), e.g. paraffins, aromatics, etc.
- Little is known regarding the exact mechanism
- Psuedo-1<sup>st</sup> order
- Psuedohomogeneous phase
- Easy to develop, inexpensive
- Suitable for process simulators, e.g. ASPEN, ChemCad
- Predicts transient response and hydrocarbon slip

Mechanism Based Lumping

- Psuedohomogeneous phase
  - Based on psuedospecies lumped together based on the elucidation of a detailed mechanism
- Requires a knowledge of process chemistry
- Must possess the analytical ability to measure the psuedo-species only
- Suitable for process simulators, e.g. ASPEN, ChemCad
- Predicts transient response, hydrocarbon slip, coking and catalyst deactivation

Structure Oriented Lumping

- State of the art in complex mixture modeling
- Closely resembles pure mechanistic approach
- Involves lumping isomers only
- Detailed knowledge of process chemistry needed, expensive analytically
- Detailed kinetic studies needed for the development of lumps
- Suitable for CFD packages, e.g. Fluent

#### Level 4 Mechanistic

- Pure mechanistic approach
- Detailed kinetic studies of single components and their mixtures
- Development of experimental procedures to evaluate process chemistry
- Knowledge of catalyst properties needed
- Requires spectroscopic method
- Predicts transient response, hydrocarbon slip, coking and catalyst deactivation based on fundamentals



# **Diesel Fuel Reforming Kinetics** *Rxn Pathways*

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



- 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*





# **Diesel Fuel Reforming Kinetics** *Experimental Conditions*

	ATR	SR	ΡΟΧ
O/C	0.6	0.0	1.0
H <sub>2</sub> O/C	1.5	3.0	0.0
T (°C)	750 – 850	750 – 850	750 – 850
GHSV (h <sup>-1</sup> )	50,000 - 150,000	50,000 - 150,000	50,000 - 150,000

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



#### **Diesel Fuel Reforming Kinetics** Ternary ATR reforming Pt/Al<sub>2</sub>O<sub>3</sub>, S/C=1.5, and O<sub>2</sub>/C=0.3

H<sub>2</sub> Production





-Higher conversions (>90%) of highly

at conditions studied

reactive paraffins





#### **Diesel Fuel Reforming Kinetics** H<sub>2</sub> production from single, binary, & ternary mixture ATR, Pt/Al<sub>2</sub>O<sub>3</sub>, S/C=1.5, and O<sub>2</sub>/C=0.3

H<sub>a</sub> Production from TD+MN+DL





60000

1025

N)

H<sub>2</sub> Production from TD

•Overall yields are not additive of yields <sup>(%)</sup> uppould <sup>(%)</sup> 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*<sub>2</sub> *production* Pt/Al<sub>2</sub>O<sub>3</sub>, S/C=1.5, O<sub>2</sub>/C=0.3, T = 850 C, and SV = 50,000 hr<sup>-1</sup>



-Reported actual yields are at the same reaction conditions, but not at optimized conditions

- -Highly reactive component consumes available O<sub>2</sub>
  - -Produces combustion products
- -O<sub>2</sub> not spared for the less reactive component
  - -Pyrolysis reaction dominates



#### **Diesel Fuel Reforming Kinetics** *Effect of aromatics content on H*<sub>2</sub> *production* Pt/Al<sub>2</sub>O<sub>3</sub>, T = 850 C, and SV = 50,000 hr<sup>-1</sup>



-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

	TD	MN	DL
Paraffins	Lots of CH <sub>4</sub> , and trace of C2-C7	Only CH₄	Mainly CH <sub>4</sub>
Olefins	C₂H₄ and C₃H <sub>6</sub> mainly	Trace	Some C <sub>2</sub> H <sub>4</sub> and C <sub>3</sub> H <sub>6</sub>
Naphthenes	None	None	None
Aromatics	Benzene only	Benzene	Benzene

Product distributions depended on the model compound, type of reforming performed, and process parameters.



# Typical Liquid Byproducts from Reforming of Different Diesel Model Components

_	TD	MN	DL
Paraffins	Mainly uconverted TD	None	None
Olefins	C7-C14 $\alpha$ -olefins, only C14 dienes and trienes	Trace	None
Naphthenes	None	None	Unconverted DL & a series of unsaturated cyclic species
Aromatics	Several including product like n- octylbenzene	Naphthelene, & unconverted 1- MN	Mainly naphthelene



# **Diesel 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<sub>2</sub>
    - Produces combustion products
- Significantly lower conversion of less reactive fuel component observed
  - O<sub>2</sub> 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



## 2005 SECA Core Program Review NETL Fuel Processing

# Hexaaluminate Catalyst Development



## Hexaaluminate Catalyst Development Approach

#### 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



Hexaalumina  $M_I(M_{II})_y AI_{12-y}O_{19.5-z}$  Structure



### Hexaaluminate Catalyst Development: Test Apparatus





## Hexaaluminate Catalyst Development: Laboratory Reactor

Online Mass Spectrometer





### Hexaaluminate Catalyst Development: Structure



NETL synthesized Co, Fe and Ni doped hexaaluminate catalysts posses similar hexaaluminate-type structure



## Hexaaluminate Catalyst Development: *Properties*



Reduction stability by temperature programmed reduction (TPR) of hexaaluminate catalysts in 5 vol%  $H_2/Ar...$ 

#### Temperature of peak maxima:

• $Co^{2+} \rightarrow Co^{0}$	1093°C
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- $Fe^{3+} \rightarrow Fe^{2+}$  407°C
- $Fe^{2+} \rightarrow Fe^{0}$  1098°C
- $Ni^{2+} \rightarrow Ni^{0}$

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 cm<sup>3</sup>/h/g



#### Hexaaluminate Catalyst Development: Various Catalysts Tested (CPOX, C<sub>14</sub>H<sub>30</sub>, O/C = 1.2, T=850°C, GHSV=50,000 cm<sup>3</sup>/h/g)



Fuel: n-tetradecane

<u>Fuel</u>: n-tetradecane/dibenzothiophene (50 ppm w/w S)



#### Hexaaluminate Catalyst Development: 100 hr *Aging Tests* (CPOX, C<sub>14</sub>H<sub>30</sub>, O/C = 1.2, T=850°C, GHSV=50,000 cm<sup>3</sup>/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

