

# NETL Fuel Processing R&D



## *2006 SECA Peer Review Meeting*

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**National Energy Technology Laboratory**



# Diesel Fuel Processing Roadmap

## *Future Plan – 5 year*

**2006**

**2007**

**2008**

**2009**

**2010**

### SECA Gen. 1 Diesel Reformer

SECA Cost-Reduction program ends in 2010 with Phase III Industrial Team Demonstrations. APU for truck transport, generators, and other synergistic applications (IE. Military) are important to fuel cell commercialization and are being considered. Goal is to develop adequate reforming technology to support the demonstrations in 2008 & 2010.

#### Catalyst Development – Oxide-based

**NETL** – Hexaaluminate

**ANL** – Perovskites

**Eltron** – Perovskites

**U of Mich** – Bi-metalics

#### Alternative Reforming – Eval & Dev

**NETL/Other** – RV GlideArc Plasma, RF, thermal...

#### Reactor Design –

**Goodrich / Delevan** – Fuel/Air nozzles

**TBD / SBIR 07** – Alt. Tech/Plasma

**TBD / Other** – Non-SECA Developers

Select  
Technology

Subsystem  
Demo

Industry III  
System Demo

**OTHER** – Test/Eval. Other  
Developer Fuel Processors

NETL FPU  
Test Stand

Industry II  
System Demo

?



# ***Fuel Reaction Chemistry Studies***

- **Effect of Sulfur**
- **Effect of Recycle**



# ***Effects of Sulfur on Catalytic Fuel Reforming***

## **OBJECTIVE:**

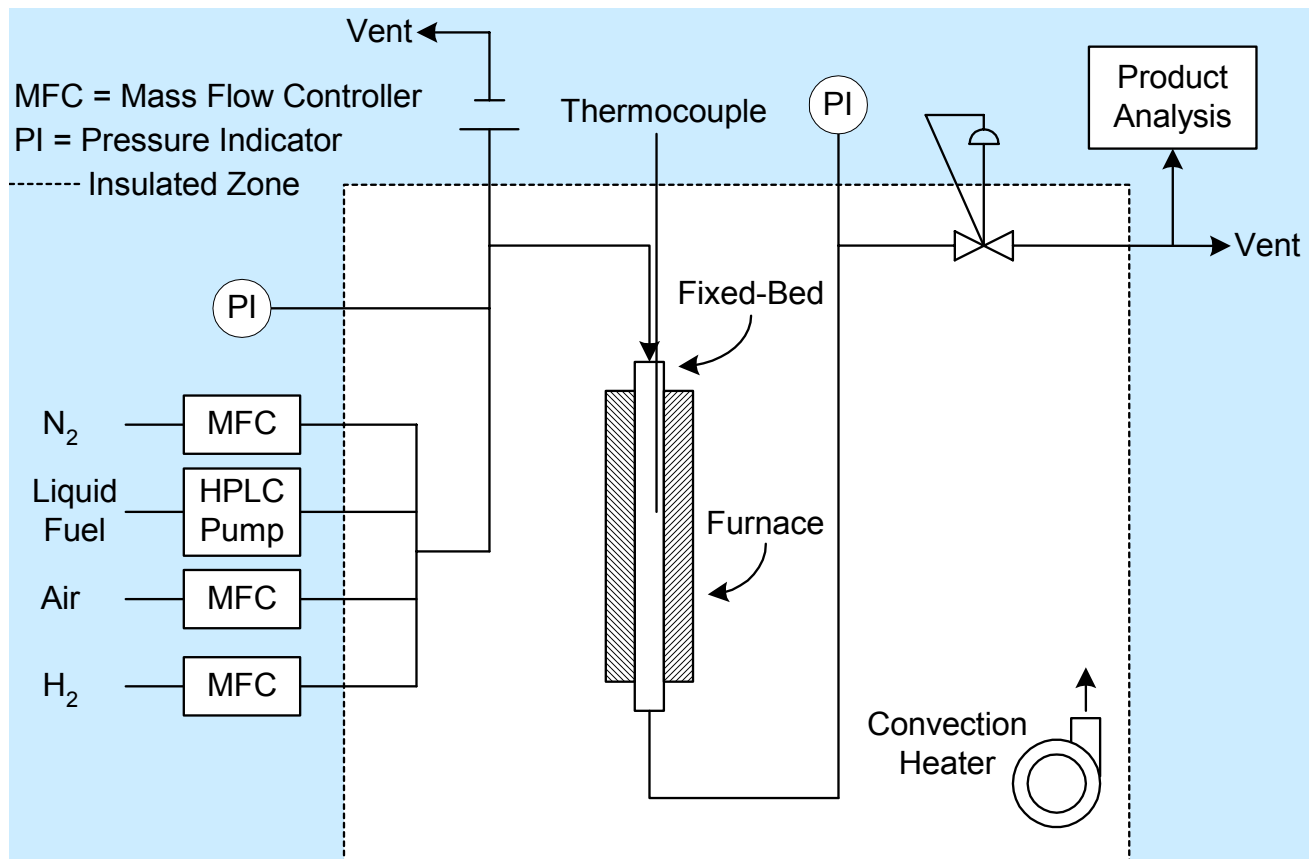
- Evaluate the effects of sulfur impurities on liquid fuel catalytic reforming.



# Sulfur Effects

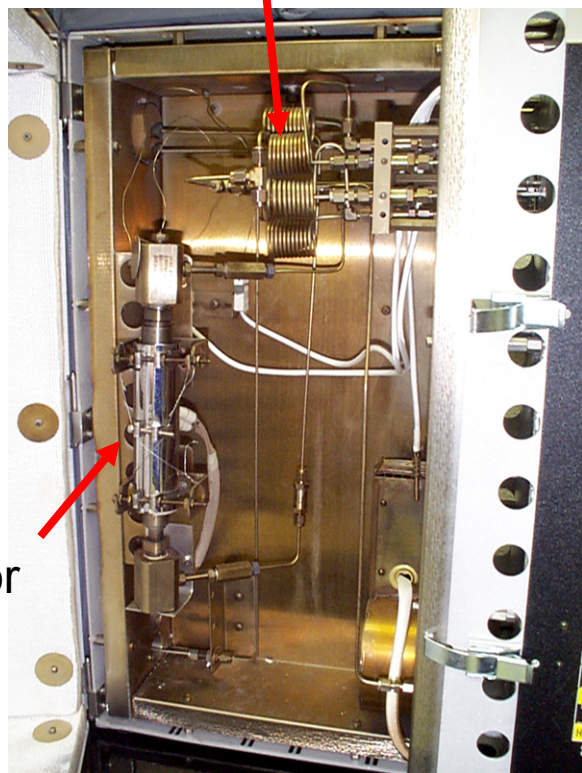
- Hard to avoid the organosulfur present in liquid hydrocarbons
- Varying range of sulfur found in liquid HC fuels
- Sulfur can be detrimental to catalyst activity
- Organic sulfur reduction
  - $R_2S + 2H_2 = H_2S + 2R-H$
- Dissociative sulfur adsorption
  - $M + H_2S (g) = M-S (a) + H_2 (g)$
  - $M + R_2S (g) = M-S (a) + R-R (g)$
  - $MO + H_2S (g) = M-S (a) + H_2O (g)$

# Experimental Setup

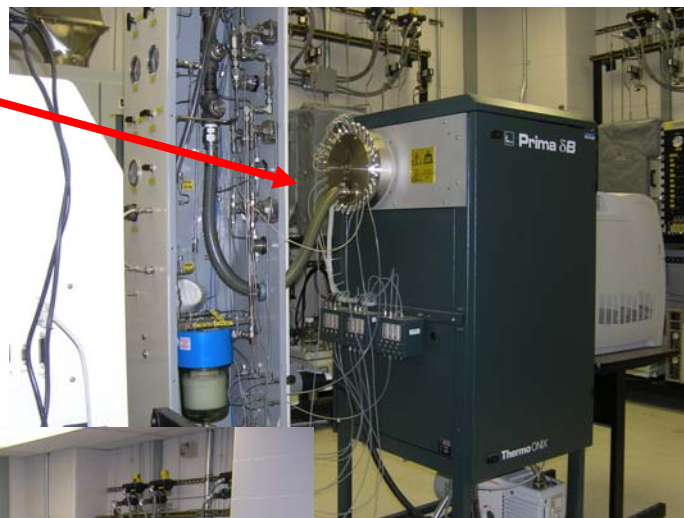


# *Laboratory Reactor*

Preheat zone



Multiple sample and calibration ports



Online Mass Spectrometer



Online GCs

Twin Micro-reactors



## Some Definitions

- Yield of product A ( $\text{H}_2$ , CO, or  $\text{CO}_2$ )

$$\text{Yield of A (\%)} = \frac{\text{Moles of A produced} \times 100}{N \times \text{moles of hydrocarbon fed to the reactor}}$$

- Yield of hydrocarbons (olefins, paraffins, and benzene)

$$\text{Hydrocarbon Yield (\%)} = \frac{m \times \text{moles of hydrocarbon produced} \times 100}{N \times \text{moles of diesel fed to the reactor}}$$

- Conversion of hydrocarbons

$$\text{Conv (\%)} = \frac{(\text{CO} + \text{CO}_2 + \sum_{i=1-7} i\text{C}_i\text{H}_r) \times 100}{N \times \text{moles of hydrocarbon fed to the reactor}}$$

Where, N is the number of moles of  $\text{H}_2$ /mole of HC for  $\text{H}_2$  yields and the number of carbons in hydrocarbon fuel for  $\text{CO}_x$ ; m is the number of carbons in the hydrocarbon product





# Experimental Conditions

- **Catalysts:**

- Hexicat (in-house hexaaluminate catalyst)
- Rh/Zirconia-doped Ceria (ZDC, oxygen-ion conducting support)
- Pt/g-alumina (Baseline catalyst)

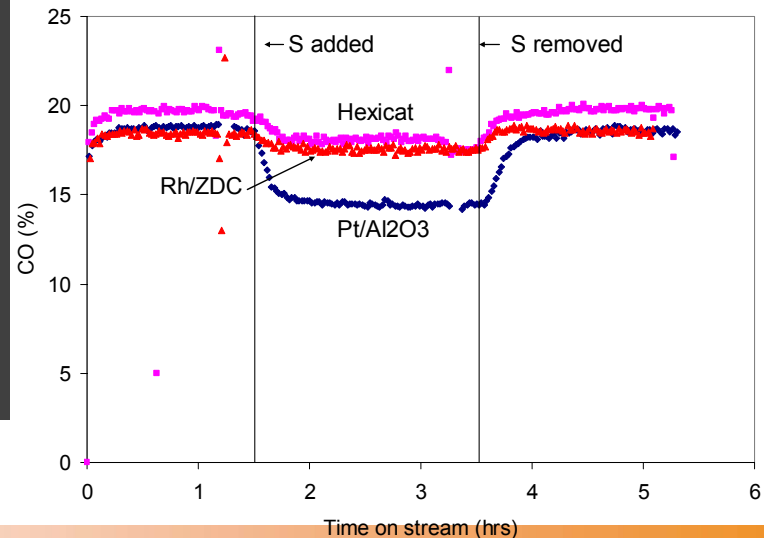
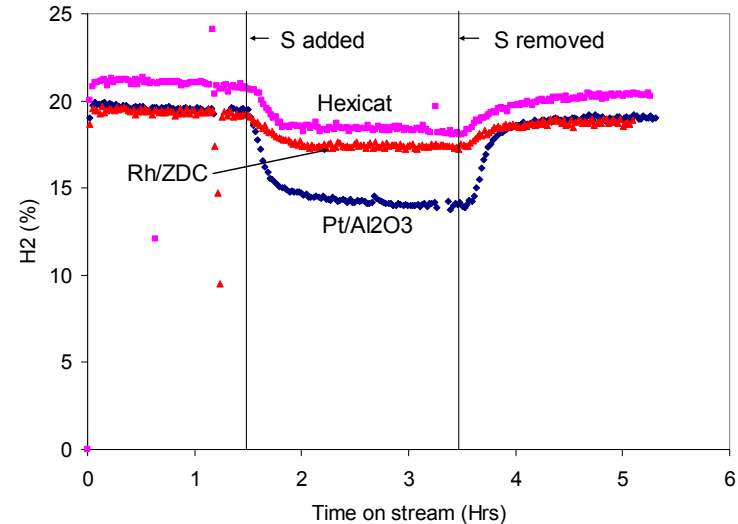
- **Operating Conditions:**

- Temperature: 850 C
- GHSV: 50,000 h<sup>-1</sup>
- O/C: 1.2
- Fuel: Tetradecane

# Sulfur Effects (50 ppm S in fuel)

(CPOX, T = 850 °C, O/C = 1.2, GHSV = 50,000 h<sup>-1</sup>)

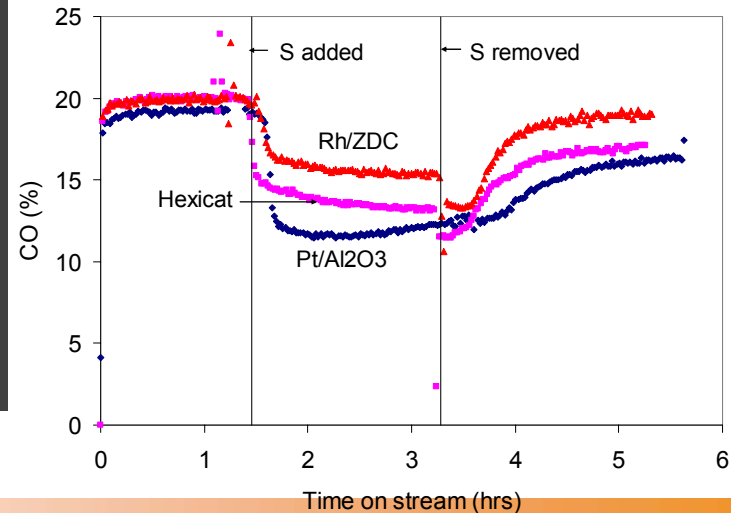
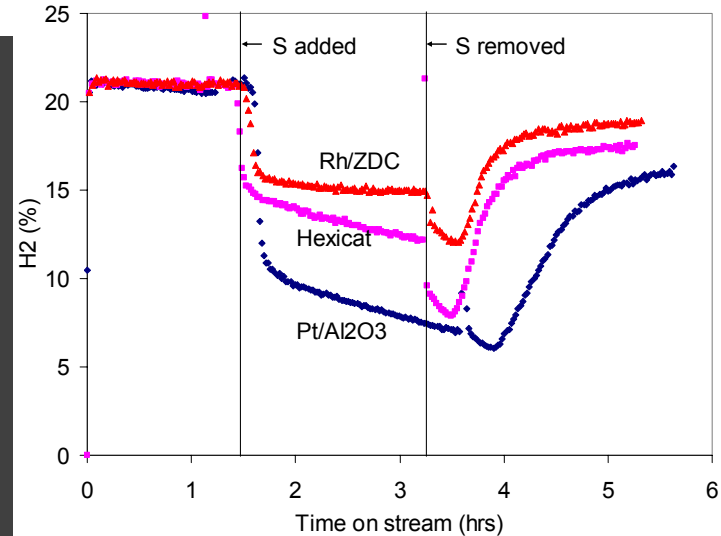
- 50 ppm of S as dibenzothiophene was introduced after 1 h TD only run
- Sulfur effects catalyst sensitive
- H<sub>2</sub> & CO yields decreased upon S introduction
  - Less significant drop from Rh/ZDC and Hexicat
- Catalyst activity restored after S removal from the feed
- Rate of carbon formation increased with S in feed
  - 0.18 g to 0.31 g for Hexicat
  - 0.21 g to 0.57 g for ZDC
  - 0.69 g to 0.92 g for Pt/alumina



# Sulfur Effects (1000 ppm S in fuel)

(CPOX, T = 850 °C, O/C = 1.2, GHSV = 50,000 h<sup>-1</sup>)

- Considerable drop in H<sub>2</sub> concentrations compared to CO concentrations
  - CO concentrations dropped to stationary levels
  - H<sub>2</sub> concentration dropped to stationary levels only for Rh/ZDC
  - Catalyst activity recovered after S removal from the feedow for Pt
- H<sub>2</sub>/CO ratio >1 before S introduction
- H<sub>2</sub>/CO ratio <1 after S introduction
  - <0.5 for Pt
- Water produced more easily on Pt catalyst compared to Rh



# Conclusions

- Sulfur effects are very catalyst sensitive
- Rate of carbon formation increased with S in feed
- Catalyst activity recovered after S removal for the Rh/ZDC and hexaaluminate catalyst and to lesser extent for the Pt system

# ***Effects of Recycle on Catalytic Fuel Reforming***

## **OBJECTIVE:**

- Evaluate the effects of recycle on catalytic fuel reforming



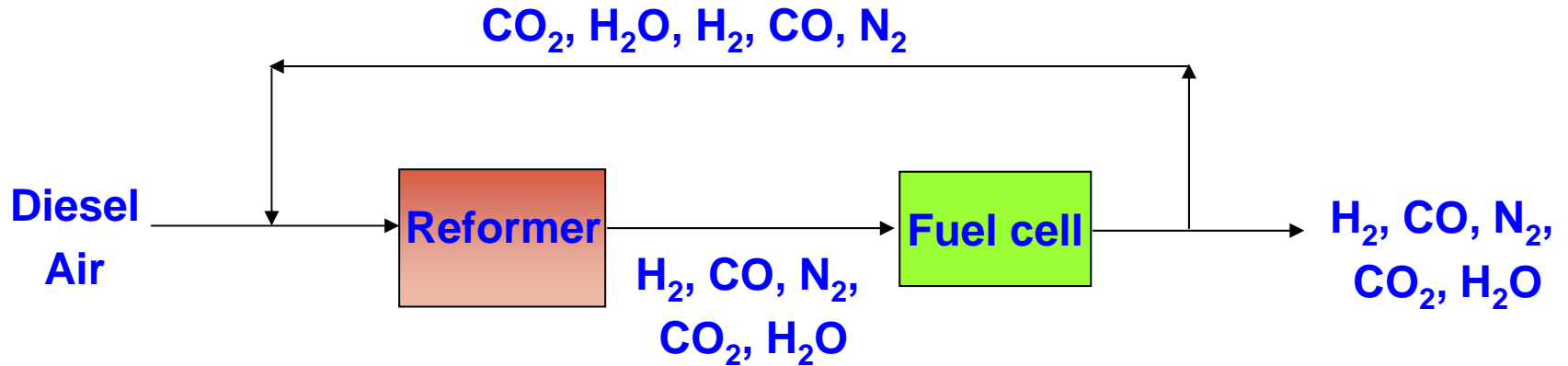
# ***Recycle Study Benefits***

- **Recycle provides benefits to “dry” reforming systems targeted for commercialization of APU and other like applications**
  - Water inhibits the carbon formation
  - Better heat integration
  - Higher efficiency
  - Higher RRs lower the catalyst temperatures and checks the catalyst sintering

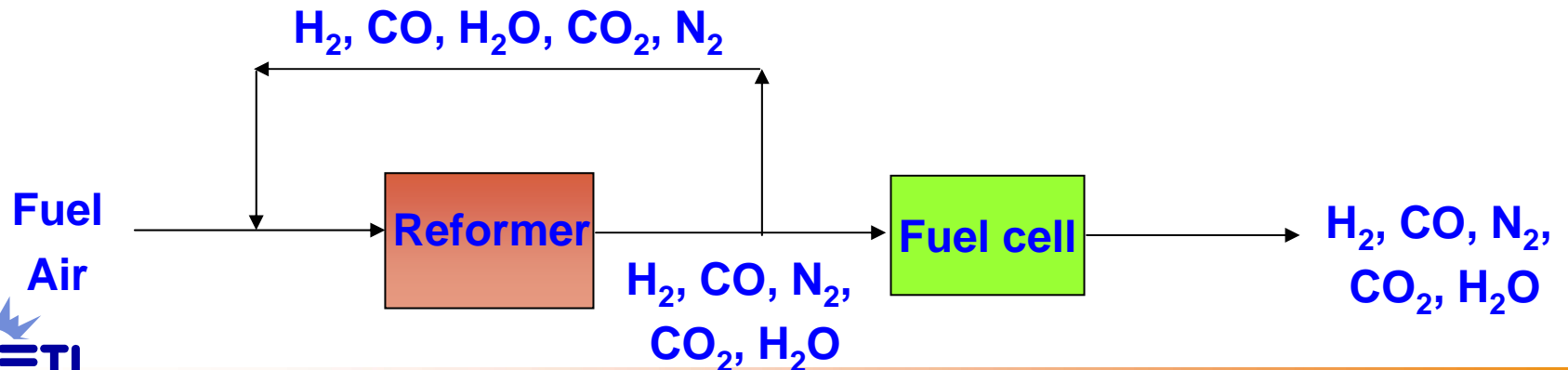


# Recycle Study Configuration

## Anode Recycle



## Reformer Recycle



# Recycle Study

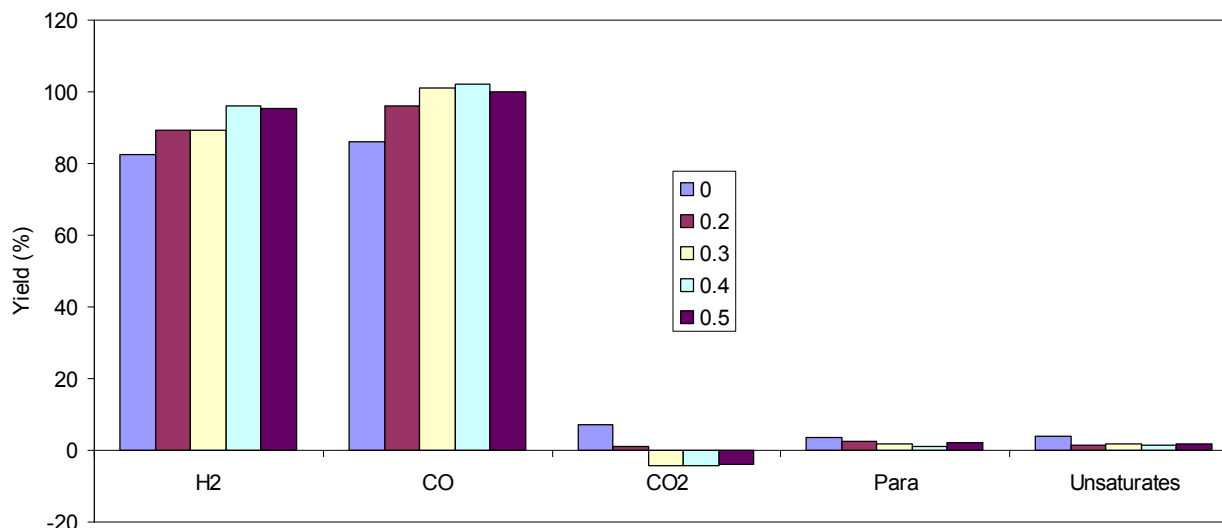
## *Runs Conditions*

- **Surrogate diesel fuel was used**
  - 40 wt% tetradecane, 20 wt% t-butylbenzene, 18 wt% t-butylcyclohexane, and 22 wt% decalin
- **Estimated equilibrium recycle stream compositions**
  - Anode recycle compositions
    - 80% conversion of syngas in fuel cell assumed
    - 24% CO<sub>2</sub>, 18% H<sub>2</sub>O, 3% H<sub>2</sub>, 3% CO
  - Reformer Recycle composition
    - 24% CO, 22% H<sub>2</sub>, 5% H<sub>2</sub>O, 1% CO<sub>2</sub>, 48% N<sub>2</sub>
- **Catalyst: Rh/Al<sub>2</sub>O<sub>3</sub> from Alfa**
- **Recycle Ratio from 0 to 0.5 studied**
- **O/C: 1.0, T: 850 °C, SV: 50,000 h<sup>-1</sup>, preheat: 325 °C**



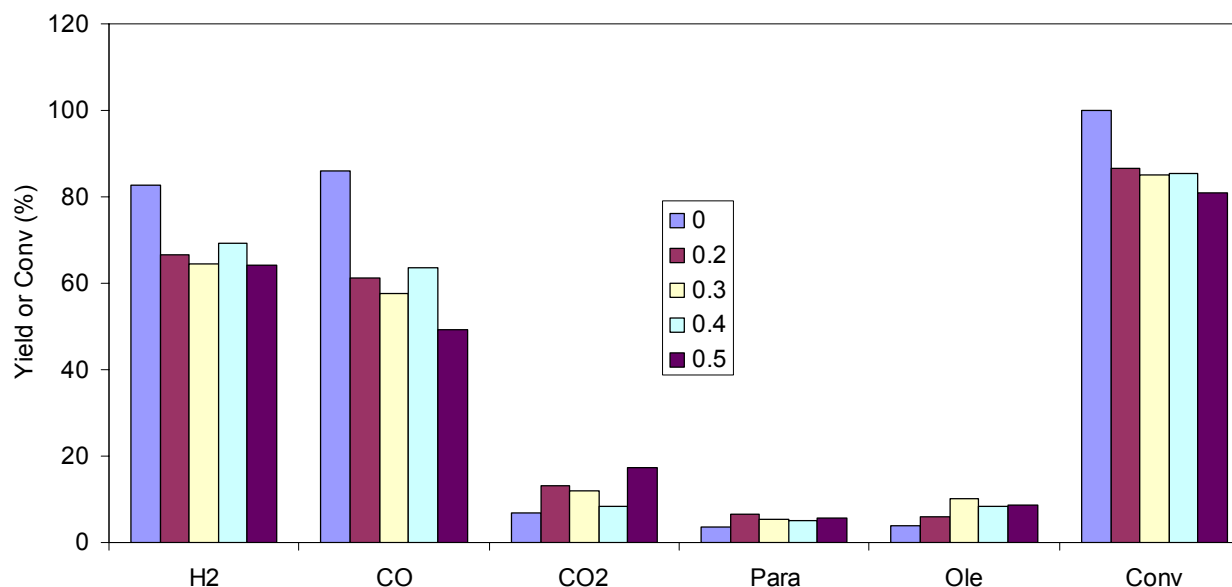


# Effect of Anode Recycle on Product Distribution



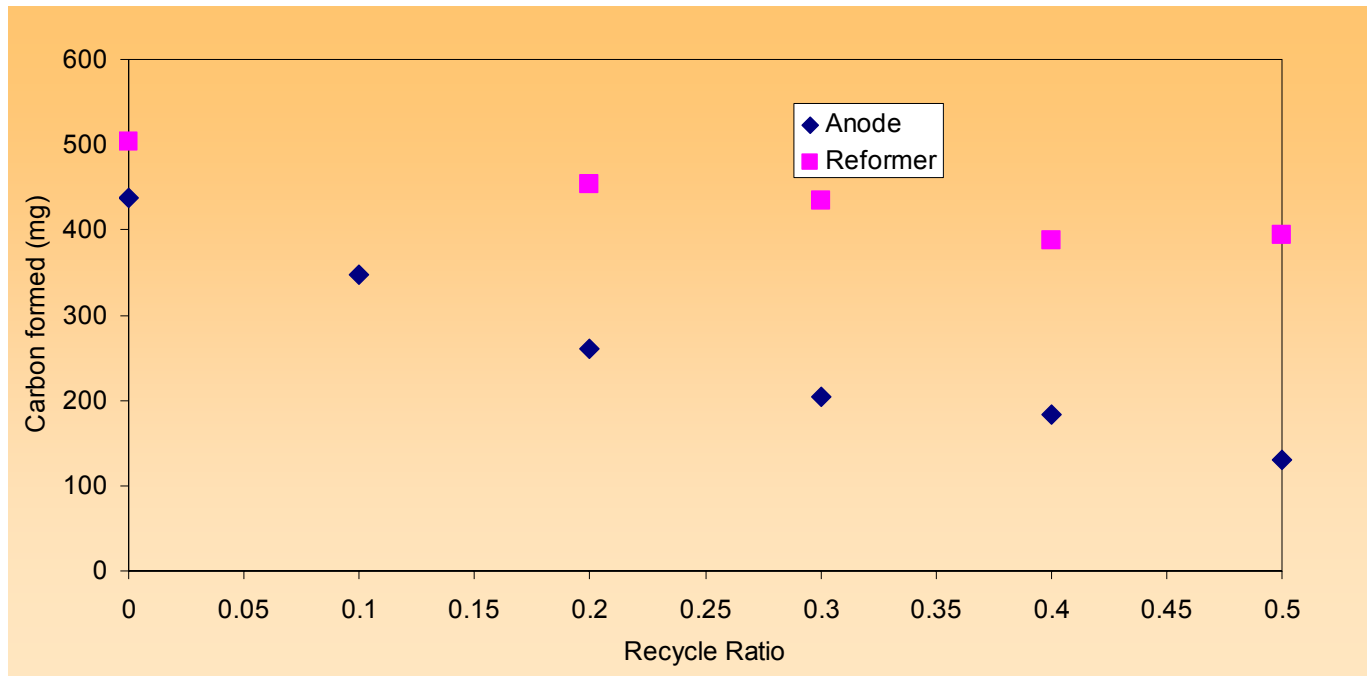
- Anode recycle: 24% CO<sub>2</sub>, 18% H<sub>2</sub>O, 3% H<sub>2</sub>, 3% CO
- H<sub>2</sub> and CO yields increase with increasing RR
- Negative CO<sub>2</sub> yields at higher RRs
  - $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$
  - Dry reforming
- HC conversion increases

# Effect of Reformer Recycle on Product Distribution



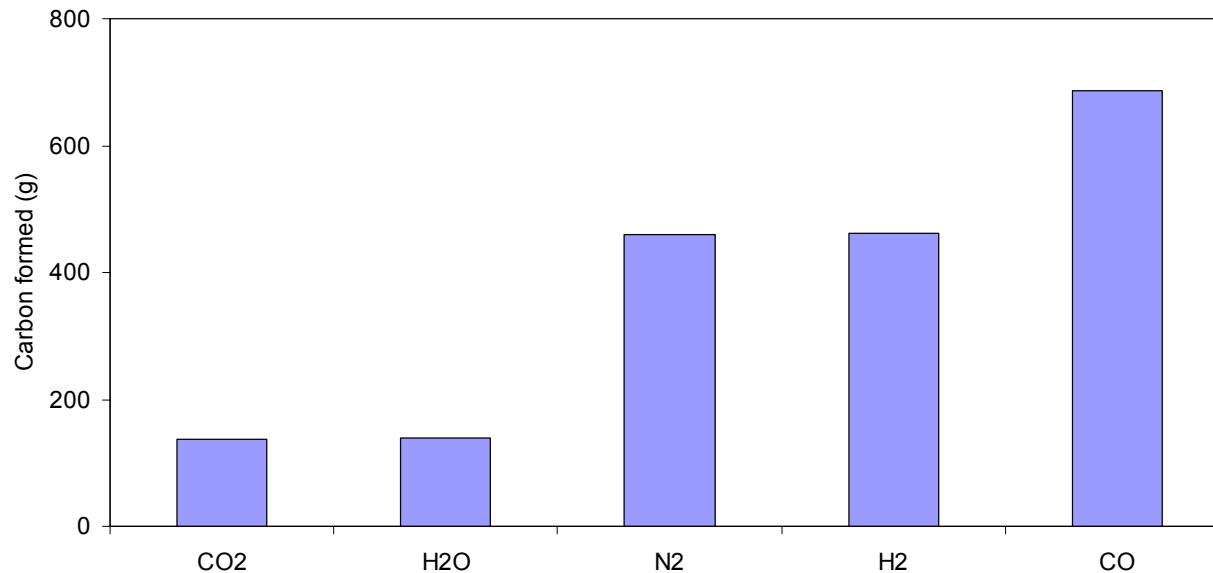
- Reformer recycle: 24% CO, 22% H<sub>2</sub>, 5% H<sub>2</sub>O, 1% CO<sub>2</sub>, 48% N<sub>2</sub>
- H<sub>2</sub> and CO yields decrease with increasing RR
- Lower HC conversion in presence of reformer recycle
- More conversion to paraffins and unsaturates
  - More carbon formed

# Effect of Recycle on carbon Formation



- Carbon formation decreases with increasing RR for anode recycle
- More carbon formed from reformer recycle stream

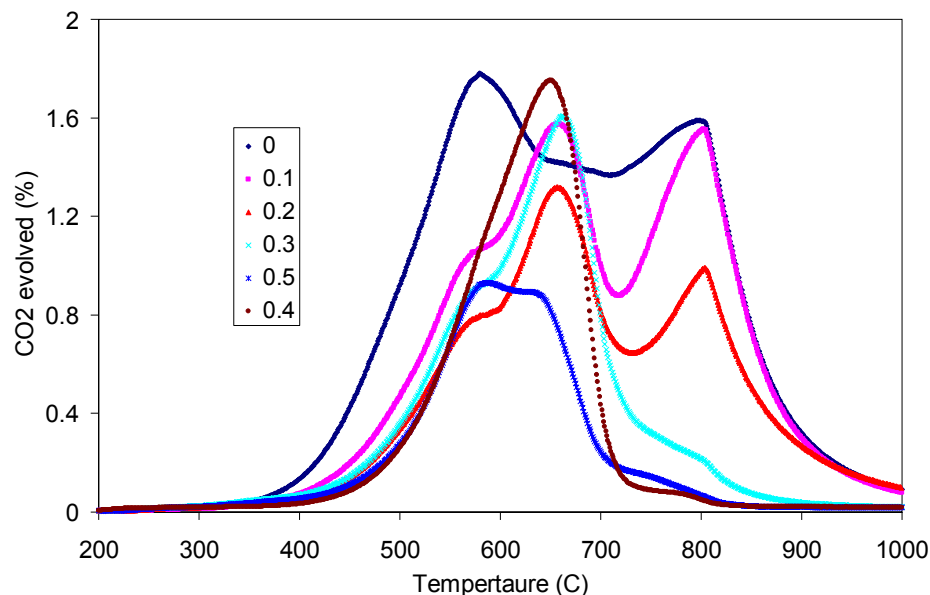
# Effect of Individual Recycle Components on carbon Formation



- **CO<sub>2</sub> and H<sub>2</sub>O have similar effects (positive)**
  - $C + CO_2 = 2CO$ ;  $C + H_2O = CO + H_2$
  - Dry reforming; steam reforming
- **H<sub>2</sub> no effects**
- **CO in recycle stream enhance the carbon formation**

# Effect of Recycle on Carbon Formation Type

## Anode Recycle



- **Mainly two peaks were observed in the TPO**
  - Low temperature peaks ( $\sim 600$  °C) can be assigned to carbon deposition on Rh metal sites<sup>5</sup>
  - High temperature peaks ( $>800$  °C) can be attributed to carbon deposited on the support<sup>5</sup>
- **High temperature peak reduces as RR increases**

<sup>5</sup>A. Shamsi, J.P. Baltrus, J.J. Spivey, Appl. Catal. A 293 (2005) 145.

# Conclusions

- $H_2$  and CO yields increase while carbon formation decreases with increasing *ANODE* recycle ratio
- *REFORMER* recycle produced more carbon on the catalyst and, hence, lower hydrocarbon conversion and product yields

# Technology Transfer

- D. Shekhawat, T. H. Gardner, D. A. Berry, J. J. Spivey, Catalytic Reforming of Liquid Hydrocarbon Fuels for Fuel Cell Applications, *Catalysis*, Royal Society of Chemistry, London, 2006, Vol. 19, Chapter 6, pp. 184-253.
- D. Shekhawat, T. H. Gardner, D. A. Berry, Fuel Constituent Effects on Fuel Reforming Properties for Fuel Cell Applications, *231<sup>st</sup> ACS National Meeting*, Mar 26-30, 2006, Atlanta, GA.
- D. Shekhawat, D. A. Berry, T. H. Gardner, D. J. Haynes, J. J. Spivey, T. Xiao, M. L. H. Green, Partial Oxidation Reforming of n-Tetradecane over Pt and Carbide Catalysts: A Comparative Study, *231<sup>st</sup> ACS National Meeting*, Mar 26-30, 2006, Atlanta, GA.
- D. A. Berry, D. Shekhawat, T. H. Gardner, M. Salazar, D. J. Haynes, J. J. Spivey, Support Effects for Pt and Rh-Based Catalysts for Partial Oxidation of n-Tetradecane, *The Fourth International Conference on Fuel Cell Science, Engineering and Technology*, Jun 18-21, 2006, Irvine, CA.
- D. Shekhawat, D. A. Berry, T. H. Gardner, M. Salazar, D. J. Haynes, J. J. Spivey, Support Effects for Pt and Rh-Based Catalysts for Partial Oxidation of n-Tetradecane, *Applied Catalysis A: General*, 2006, **311**, 8-16
- D. Shekhawat, T. H. Gardner, D. A. Berry, Fuel Constituent Effects On Fuel Reforming Properties For Fuel Cell Applications, Preparing for Int. J. H2 Energy.

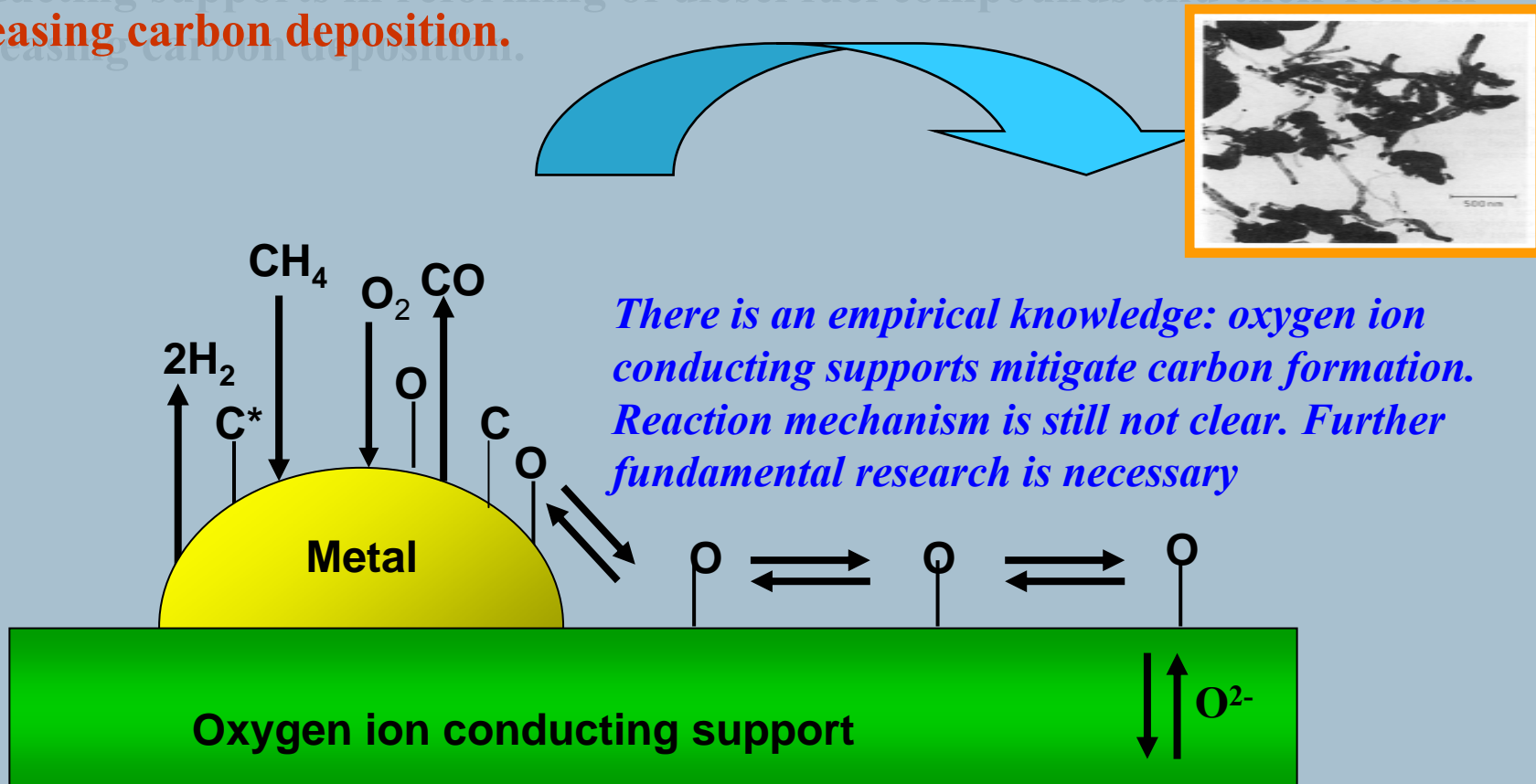
# Oxygen Conducting Catalyst Supports

## **Role of $O_2$ ion Conducting Supports on Catalytic Fuel Reforming**



# Oxygen Conducting Catalyst Supports

**Objective** To have a fundamental understanding of the role of oxygen conducting supports in reforming of diesel fuel compounds and their role in decreasing carbon deposition.



*Study is performed during cPOX of  $\text{CH}_4$ . However, results can be extrapolated to higher hydrocarbons.*

*Fundamental research will allow to use findings for catalysts synthesis and operation conditions in fuel reformers*

# Current & Prior Studies at NETL

## Performance Studies

- Effect of ionic conductivity on carbon formation
- Effect of catalyst reducibility in catalyst performance

## Characterization Studies

- Effect of Temp. & time on stream on methane conversion
- Effect of dopant type in catalyst characteristics

## \*Mechanistic Studies

- Partial Oxidation of methane in the absence of gaseous O<sub>2</sub>
- Catalyst labeling
- Isotopic oxygen uptake & exchange
  - POM Reactions



# NETL Fuel Processing R&D

## Performance and Characterization studies

Catalysts were tested to elucidate effects of:

### Support type

- Oxygen ion conducting support: *ceria based oxides*
- Non-Oxygen ion conducting supports: *alumina*

**Catalyst type** (Rh, Pt, Ni)

**Dopant type** (Zr, La, Gd)

**Dopant concentration**

**GDC10 & GDC30**

Operation variables during experimental tests included

- *Reaction Temperature*
- *O/C ratio*
- *Time on stream*
- *Space velocity*

*Parameters measured during catalytic tests and characterization*

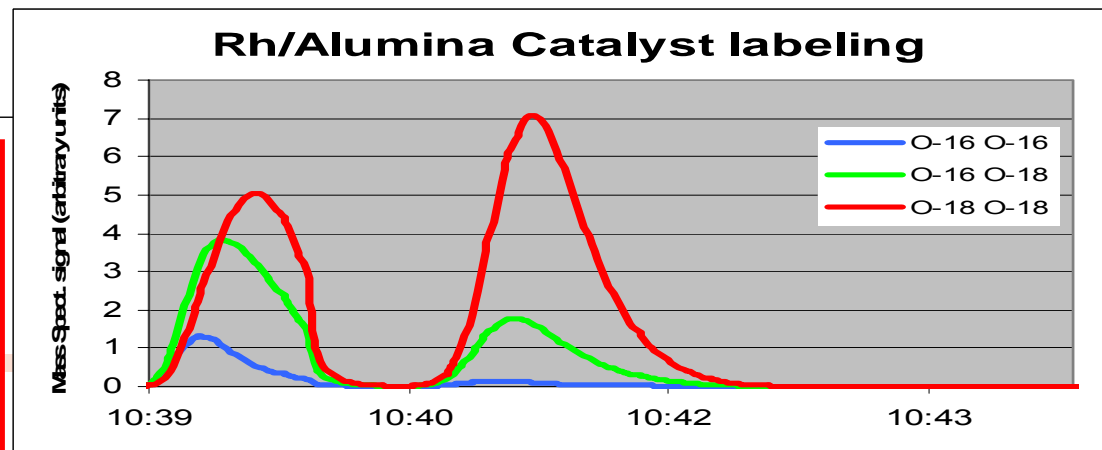
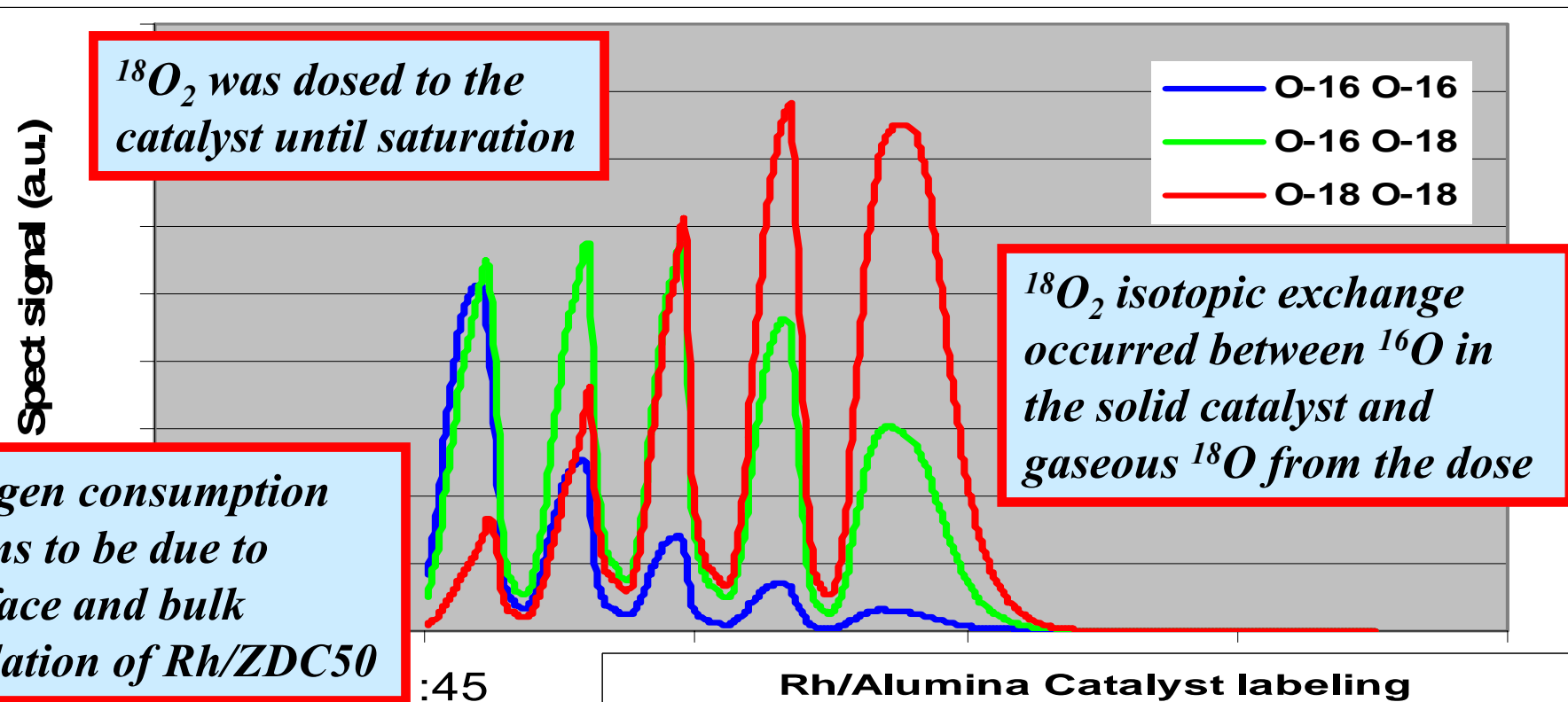
- **Catalytic activity and selectivity**
- **Amount of carbon deposition**
- **Characterization: Effect of dopant and metal addition on support reducibility.**
- **Effect of dopant addition on ionic conductivity and crystal phases**
- **Effect of Catalyst Reduction Temperature on catalytic activity and selectivity**



*100 experiments have been performed*

# Oxygen Conducting Catalyst Supports

## Isotopic tests/Cat. Labeling/Rh/ZDC50 and Rh/alumina



**Rh/ZDC50 has a significantly higher OSC and ionic conductivity than Rh/Alumina. Thus, it shows higher Isotopic Exchange**

# Isothermal Isotopic Exchange or catalyst labeling

**Suggested mechanism have been proposed for Oxygen Isotopic Exchange**

*J. Phys. Chem.* **1996**, *100*, 9429

**1- Dissociative adsorption of  $^{18}\text{O}$  on metal particles**

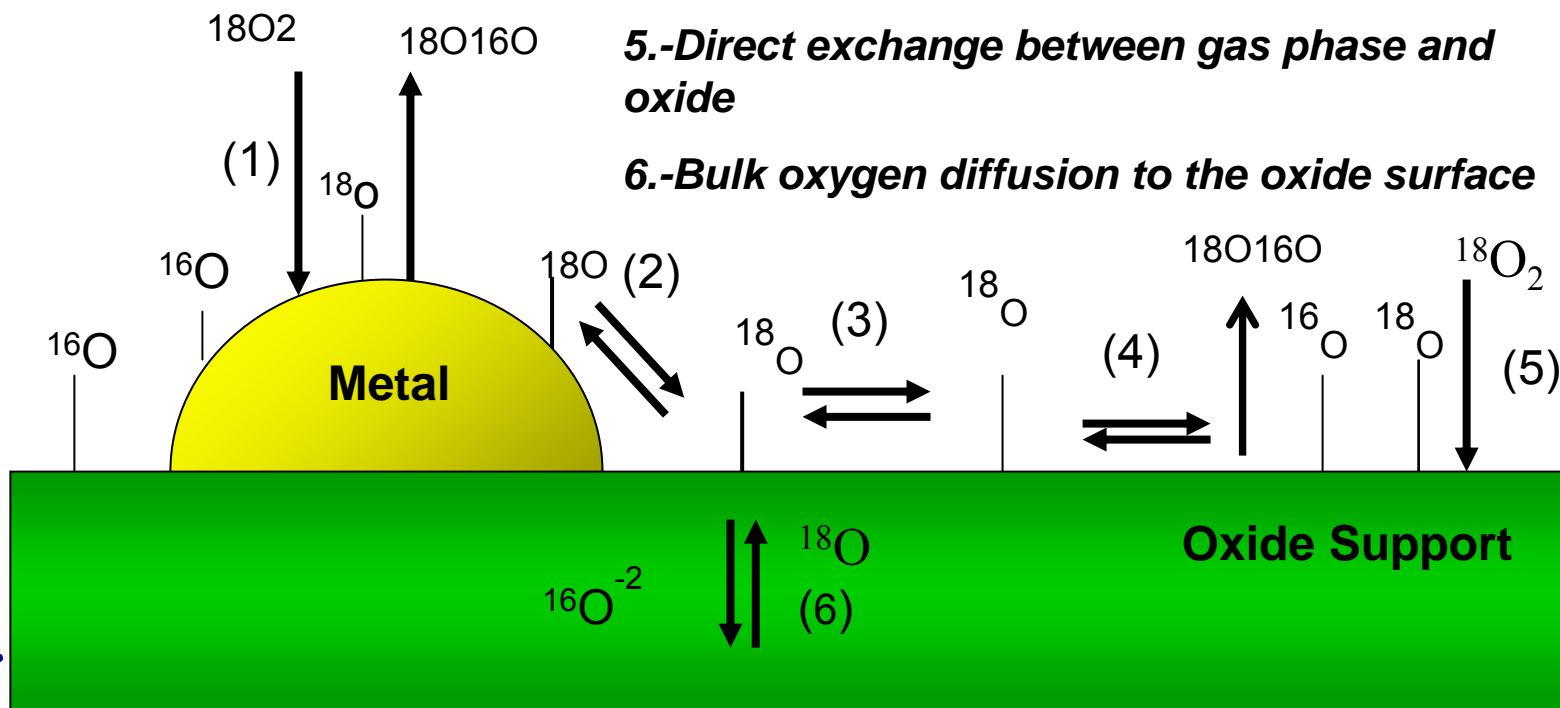
**2.-Transfer of  $^{18}\text{O}$  species from the metal to oxide surface (spillover)**

**3.- Surface migration of  $^{18}\text{O}$  atomic species on the oxide surface to the sites of exchange**

**4.-An exchange between  $^{18}\text{O}$  species and  $^{16}\text{O}$  species of the oxide**

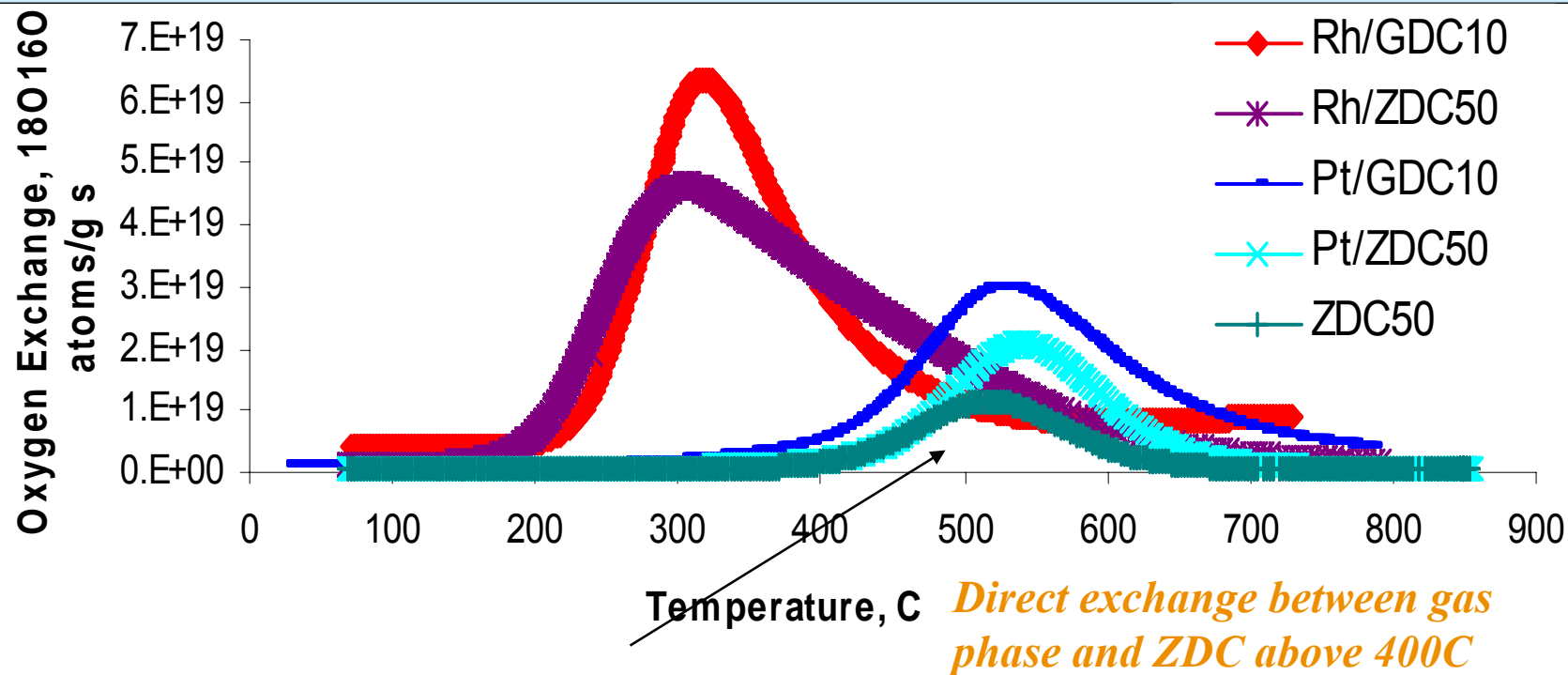
**5.-Direct exchange between gas phase and oxide**

**6.-Bulk oxygen diffusion to the oxide surface**



# Oxygen Conducting Catalyst Supports

## Isotopic Oxygen Exchange vs. Temperature



Rh and Pt enhance isotopic exchange because they accelerate the rate of  $\text{O}_2$  dissociation. Rh > Pt



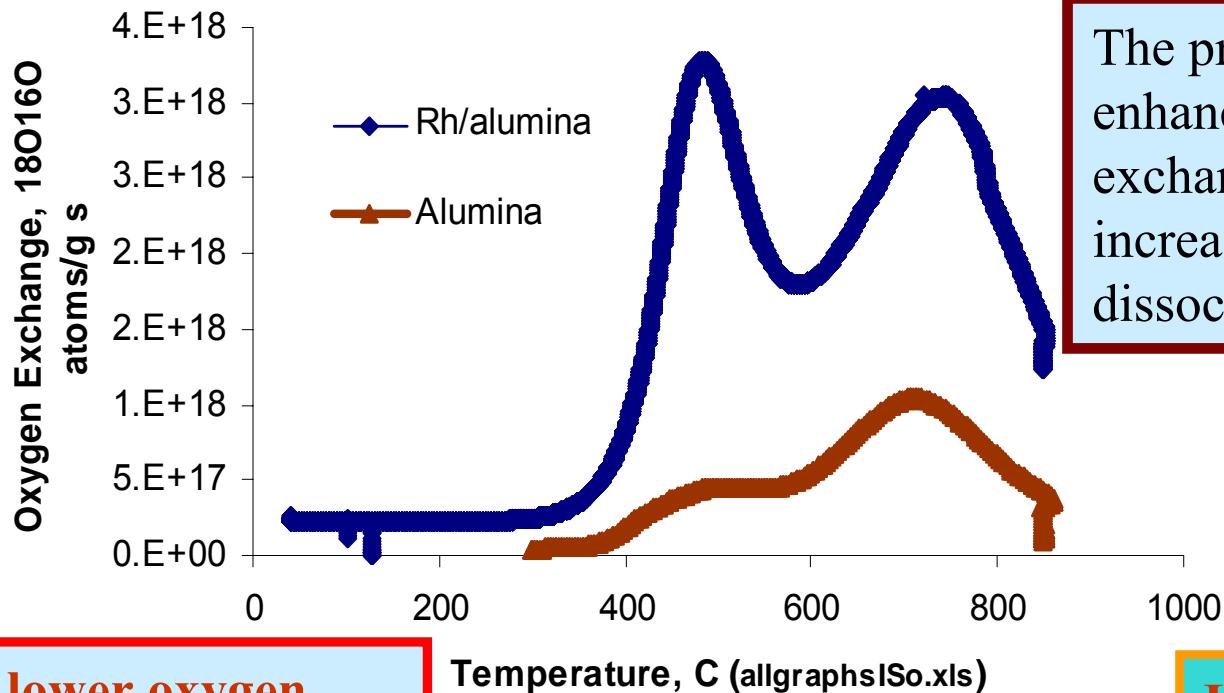
### Isotopic Oxygen Exchange trends

Rh/ZDC > ZDC (metal red. effect)

Rh/GDC10 > Rh/ZDC50 (conductivity)

Rh > Pt (oxygen binding energy)

# Isotopic Oxygen Exchange vs. Temperature



The presence of Rh enhances the isotopic exchange because it increases the rate of dissociation of oxygen

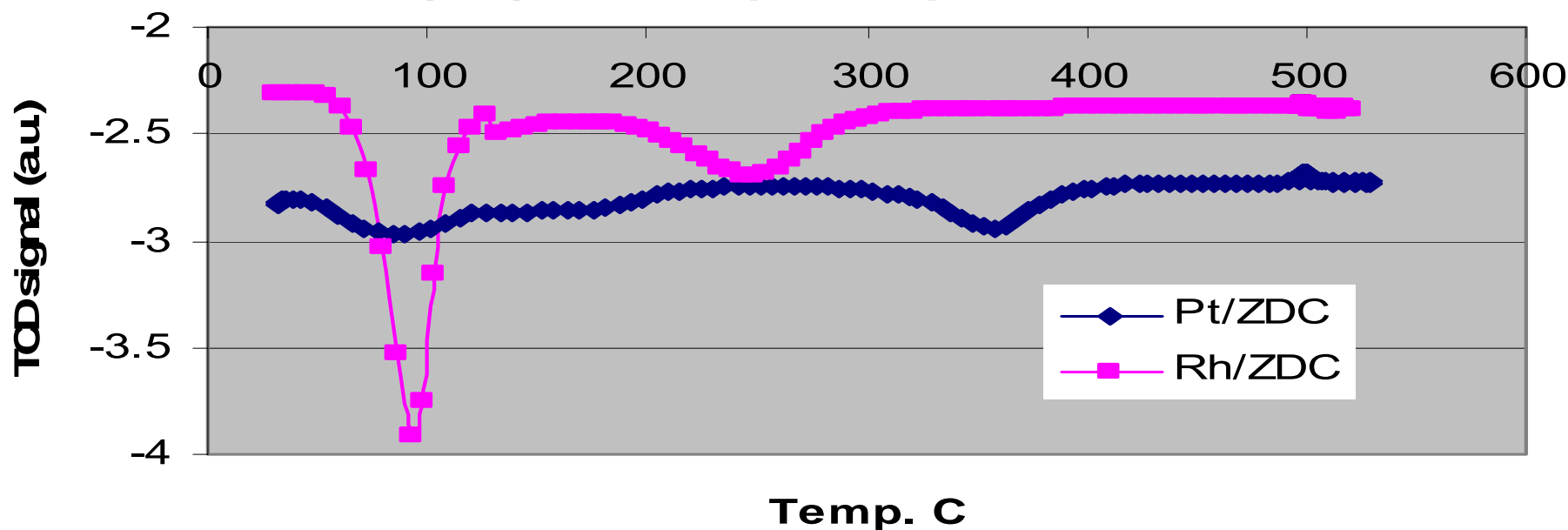
Due to lower oxygen mobility (OM) for Alumina, two peaks are detected. Higher (OM) for ceria based catalyst shows a single peak for O<sub>2</sub> exchange at metal and support.

Lower temp. peak : oxygen exchange on metal surface  
Second peak: exchange on alumina surface

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## Results/Metal reducibility

**Temperature Programmed Reduction Profiles**  
**H<sub>2</sub>(5%)/Ar, Temp. Ramp. 10C/min**



**Binding energy for neutral defects formed between oxygen ion vacancies of Ceria and Rh is lower than for Ceria-Pt, which limits its participation in further reactions**

*J. Phys. Chem. 1994,98, 13625*

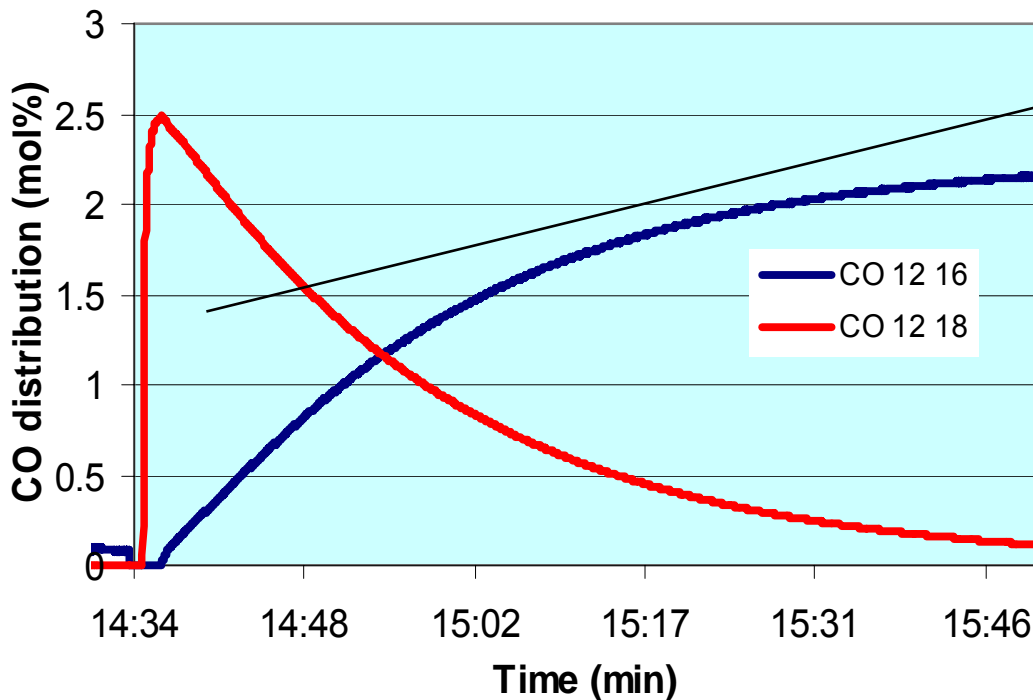




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## Results/Isotopic tests/labeled catalysts

Partial Oxidation of Methane over Labeled Rh/ZDC



This is a strong evidence for the participation of oxygen originating from the catalyst in the POM.

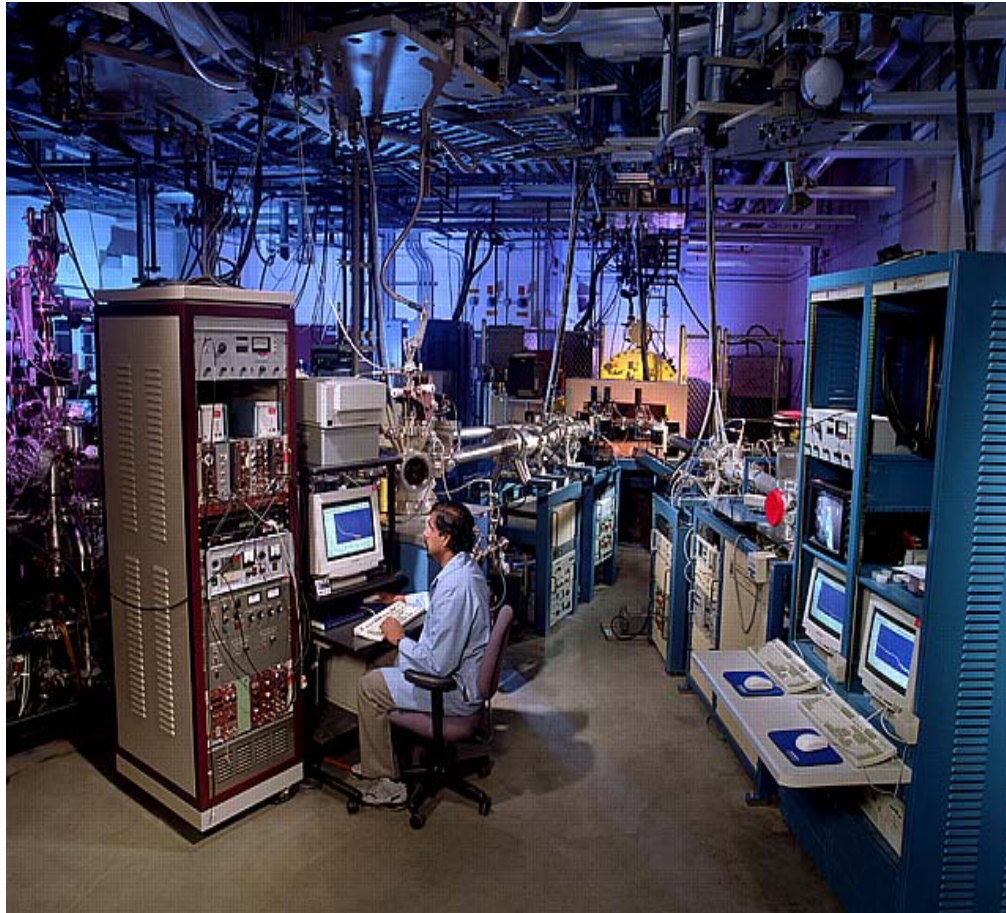
CO1216 does not form at the beginning of the reaction, which excludes the possibility of CO formation in the gas phase.

Significant concentration of CO1218 is observed for 1h, which proves that lattice oxygen reacts with methane to generate CO



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## Results/ $^{18}\text{O}$ profiles /Nuclear Reaction Analysis-PNNL

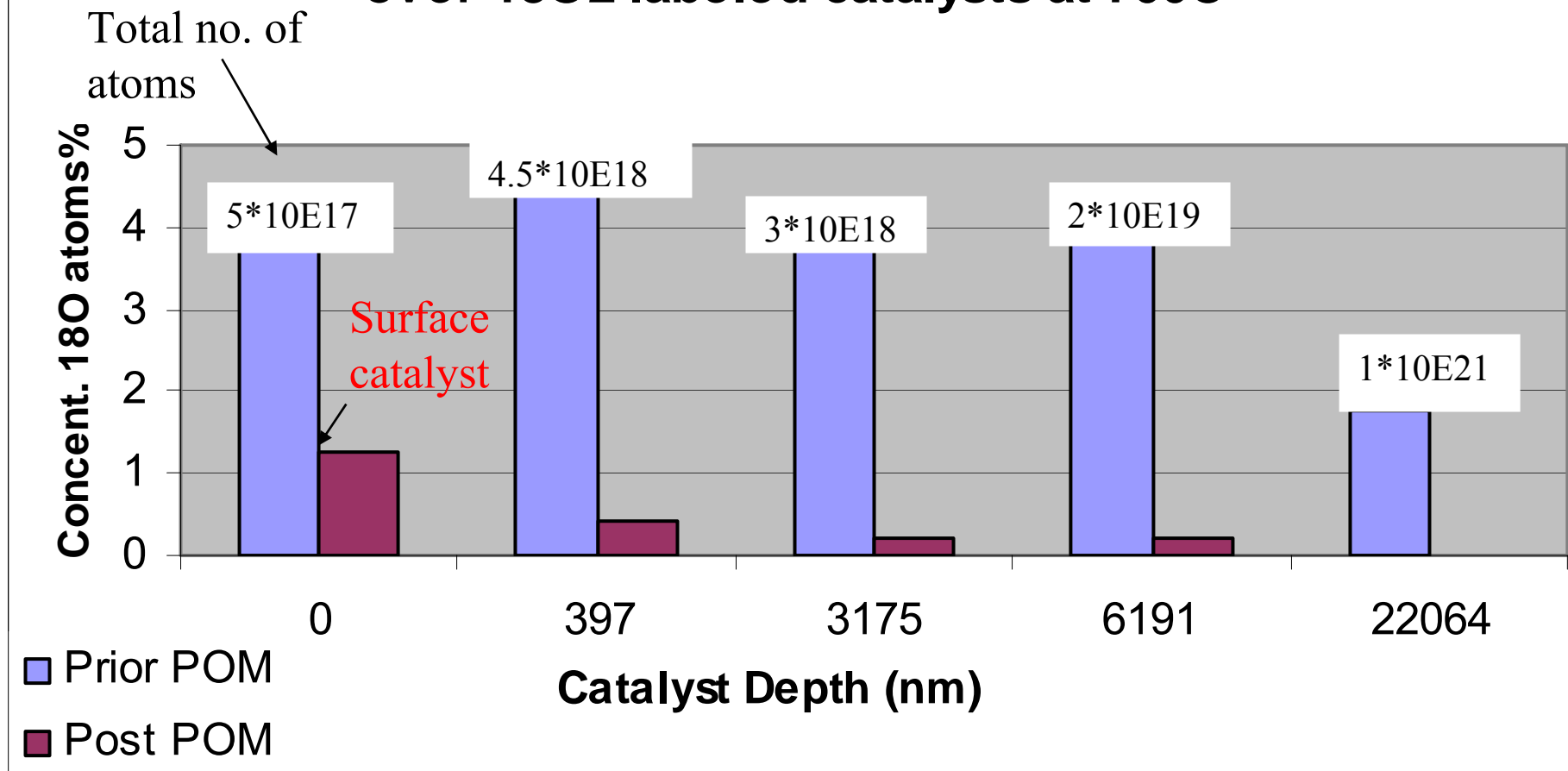


**Powder samples were pelletized and loaded into the analysis chamber. Samples were bombarded with 0.74 MeV  $\text{H}^+$  ions. The alpha particles produced during the reaction (with 3.25 MeV energy) were measured to determine the total uptake of oxygen-18 in samples**

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## Results/ $^{18}\text{O}$ concentration /Nuclear Reaction Analysis

### Concentration profiles of $^{18}\text{O}$ prior & post POM over $^{18}\text{O}_2$ labeled catalysts at 700C

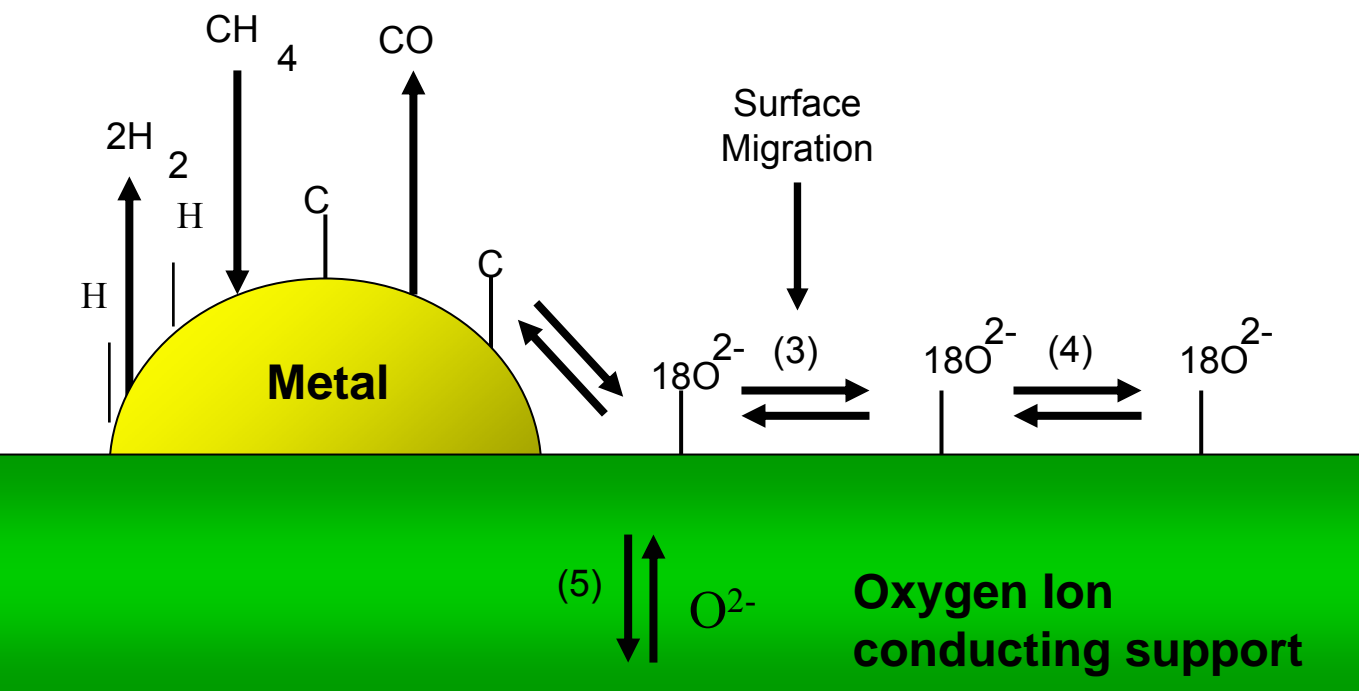


# NETL Fuel Processing R&D

## *O<sub>2</sub> Conducting Supports – Rxn Network for CH<sub>4</sub>*

- **Decomposition of methane occurs on reduced rhodium resulting on the formation of carbon and H<sub>2</sub> atoms**

- **Formation of O-C bonds is largely controlled by a redox mechanism involving lattice oxygen ions on the surface, which are not fully coordinated.**



**Lattice oxygen on the surface is replenished by bulk oxygen (fully coordinated lattice oxygen)  
This step is faster than O<sub>2</sub> dissociation**



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## *Summary – From All Studies*

- Metal catalysts dispersed on ionically conductive supports showed significantly lower carbon formation than non-conducting supports.
- The GDC support material showed the highest ionic conductivity because the similar atomic size between Gd and ceria cation. This resulted in lower carbon formation.
- Higher metal reducibility resulted in higher H<sub>2</sub> production and lower light off temperature
- Dopant and metal addition to ceria enhanced its reducibility. Especially wrt Rh as compared to Pt due to oxygen binding energies.
- Labeled catalyst POM studies and Nuclear reaction analysis showed a strong evidence for the participation of oxygen originating from the catalyst in the CO formation. Specifically lattice oxygen.
- GDC10 has been incorporated in the synthesis of hexaluminates.
- GDC10 pellets will be evaluated as packing material in the catalytic reactor for projects in this research group.



# NETL 2006 MERIT REVIEW

## Technology Transfer

### *Peer reviewed papers:*

- Salazar Maria, Berry David A., Todd H. Gardner, Shekhawat Dushyant, Floyd Donald. **Catalytic Partial Oxidation of Methane on Pt/Ceria Based Catalysts. Effect of ionic conductivity.** Applied Catalysis 310(206) 54-60
- Salazar Maria, Berry David A., Todd H. Gardner, Shekhawat Dushyant, Floyd Donald. **Synthesis gas by partial oxidation and the role of oxygen-conducting supports: A review.** Fuel Cell Science, Engineering and Technology, New York USA, FUEL CELL 2004 p 681-690.
- Salazar Maria; Berry , David A., Todd H. Gardner, Shekhawat Dushyant, **Role of lattice oxygen in the Partial Oxidation of Methane over Rh & Pt/zirconium-doped ceria. Mechanistic aspects** Preparing draft

### *Presentations:*

- Salazar Maria; Berry , David A., Todd H. Gardner, Shekhawat Dushyant, **Role of lattice oxygen in the Partial Oxidation of Methane over Rh & Pt/zirconia-doped ceria. Mechanistic aspects.** Submitted for presentation at the ACS Fall meeting 2006
- Salazar Maria; Berry , David A., Todd H. Gardner, Shekhawat Dushyant, Floyd Donald. **Catalytic Partial Oxidation of Methane on Pt-Ceria Based Catalysts.** AIChE Fall meeting, 2005
- Presentation project merit review at Spring 2004 SECA Core Meeting
- Presentation project merit review at Spring 2005 SECA Core Meeting
- FY04 Oxygen Conducting Catalyst Supports Report for SECA
- FY05 Oxygen Conducting Catalyst Supports Report for SECA



# *Hexaaluminate Catalysts Development*

## **OBJECTIVE:**

- Evaluate & develop a catalyst to reform 'extreme' hydrocarbon fuels (IE. Diesel)



# Technical Challenges

## Fuel:

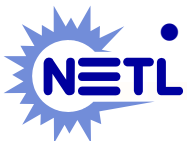
- **A wide distribution of constituents in middle distillate with...**
  - discrete physico-chemical properties
  - discrete reactivities and adsorption properties
    - Aromatics, naphthenes and paraffins
    - Organo-sulfur compounds
    - Olefin formation

## Catalyst:

- **Strongly adsorbing feed constituents result in...**
  - Active site blocking and coking of catalyst surface
- **A high temperature reducing environment results in...**
  - Vaporization and sintering of active metals

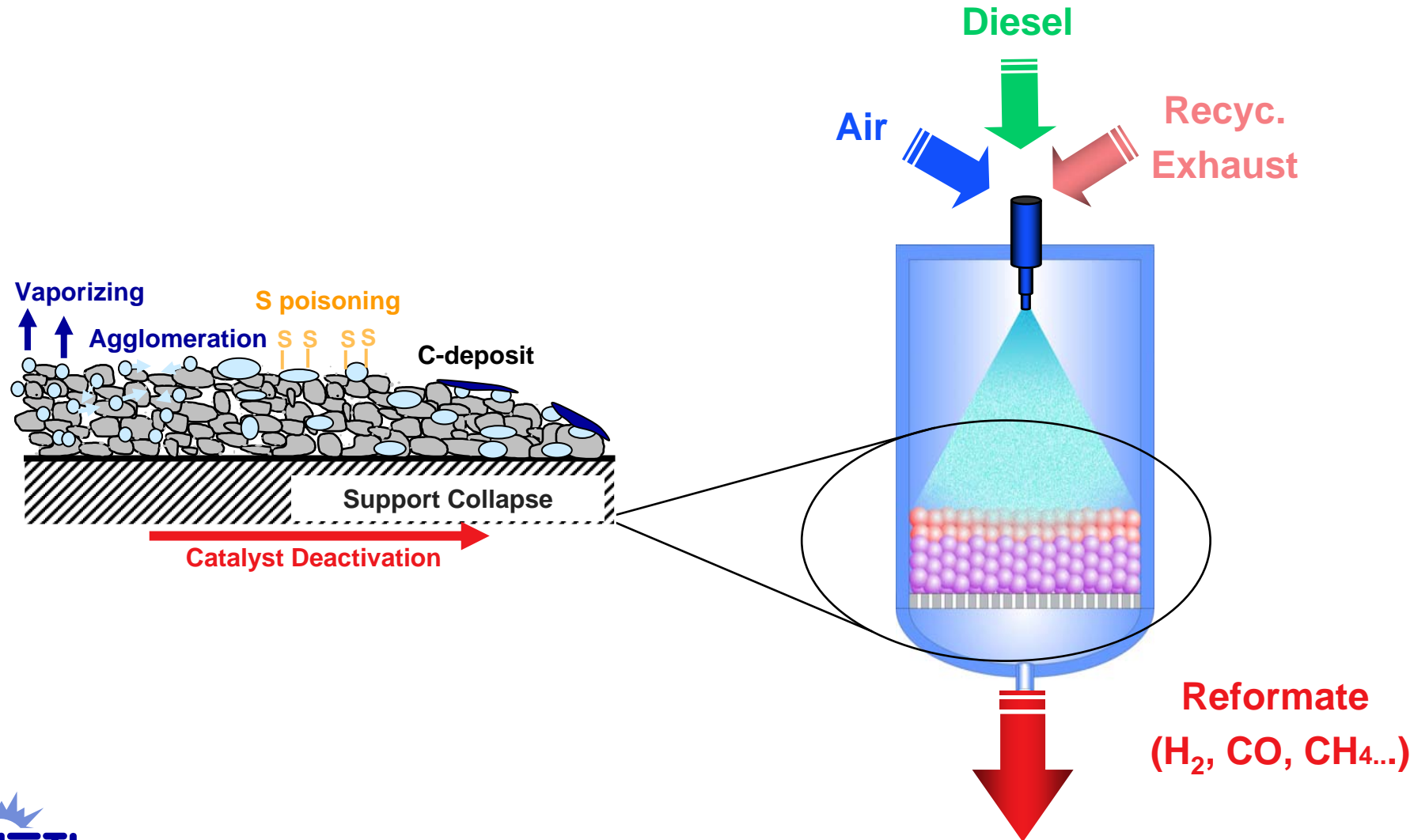
## Process:

- **Integration with SOFC**





# Catalyst/Reactor Development



# Toward a Middle Distillate Reforming Catalyst...

## Target Goals:

- A catalyst system capable of continuous long term reforming of middle distillate type fuels
  - >1,000 h
    - Low catalyst degradation rate
  - >850°C
  - Carbon deposition resistance (Aromatic <25 wt%)
  - Sulfur tolerance (<50 ppm w/w S)
  - ‘Dry’ feed

# Technical Approach

## To minimize carbon deposition and site blocking...

- Disperse catalytically active metals with elements or compounds which do not form strong chemisorption complexes
  - Hydrocarbon adsorption affected by geometric and electronic effects
    - Achieve desired effects by doping the lattice of a structural oxide

## To reduce metal sulfide formation...

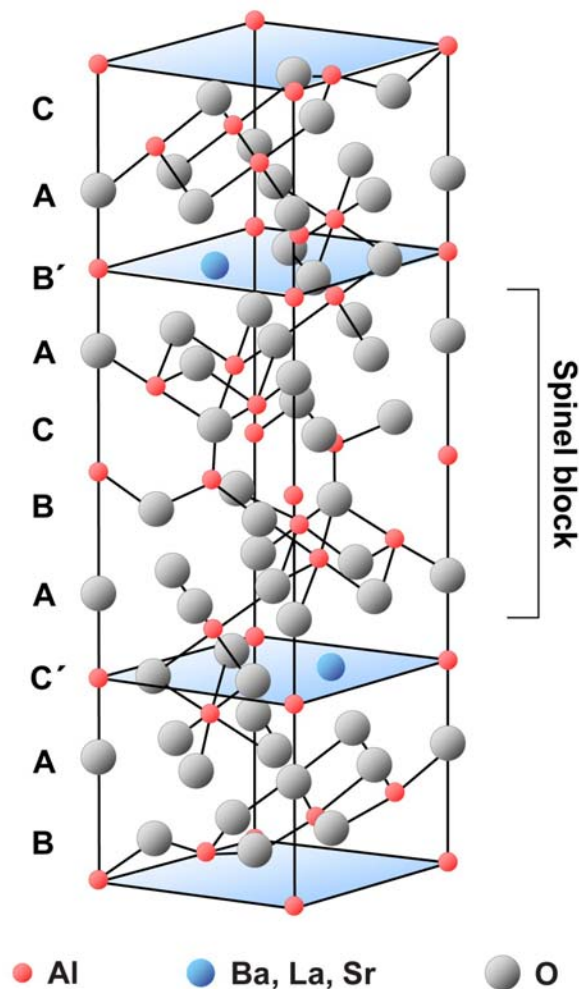
- Utilize catalytically active metals which possess unstable metal sulfides
- Disperse active sites in low coordination to reduce  $\text{H}_2\text{S}$  dissociation



# Reforming Catalyst Development

***Consider dispersing catalytically active metals into the lattice of hexaalumina - a structural oxide...***

- Al sites are exchangeable with active transition metals
- Active transition metal introduction into the lattice results in strong NNN interactions
- Defect sites<sup>4</sup> in the mirror plane region are the catalytically active site



Hexaalumina MO·6Al<sub>2</sub>O<sub>3</sub> Structure

# Advantages

- **Simplicity:** An atomically dispersed active site embedded in a refractory solid oxide
  - ‘Tunable’ catalyst activity
  - Ensemble control
- **Cost:** An inexpensive catalyst system with low transition metal loading
- **Durability:** Embedded transition metal cations are less prone to sintering, vaporization and carbon deposition

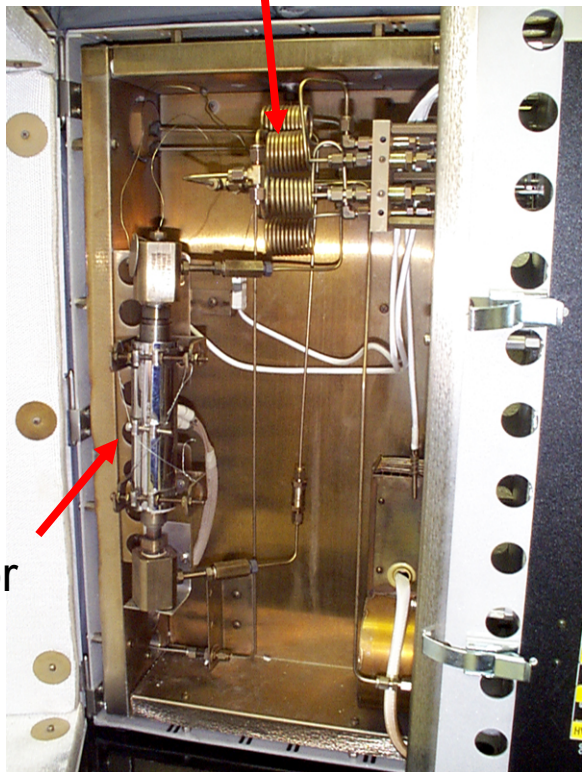


# Productivity and Results

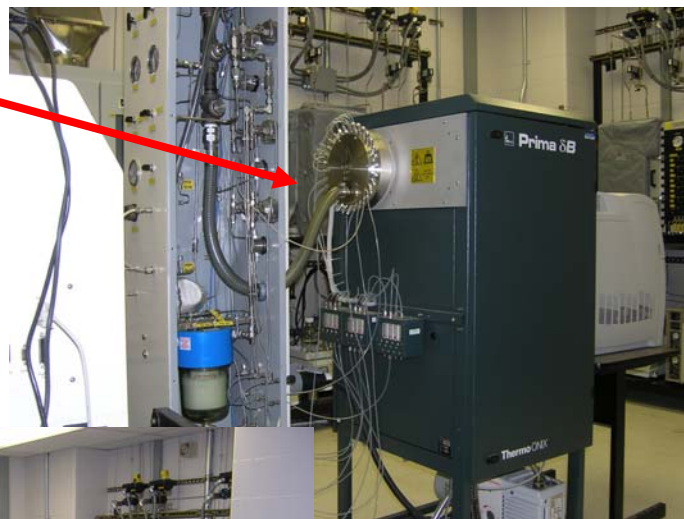
- Reactor setup and test conditions
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# NETL Laboratory Reactor Capability

Preheat zone



Multiple sample and calibration ports



Online Mass Spectrometer

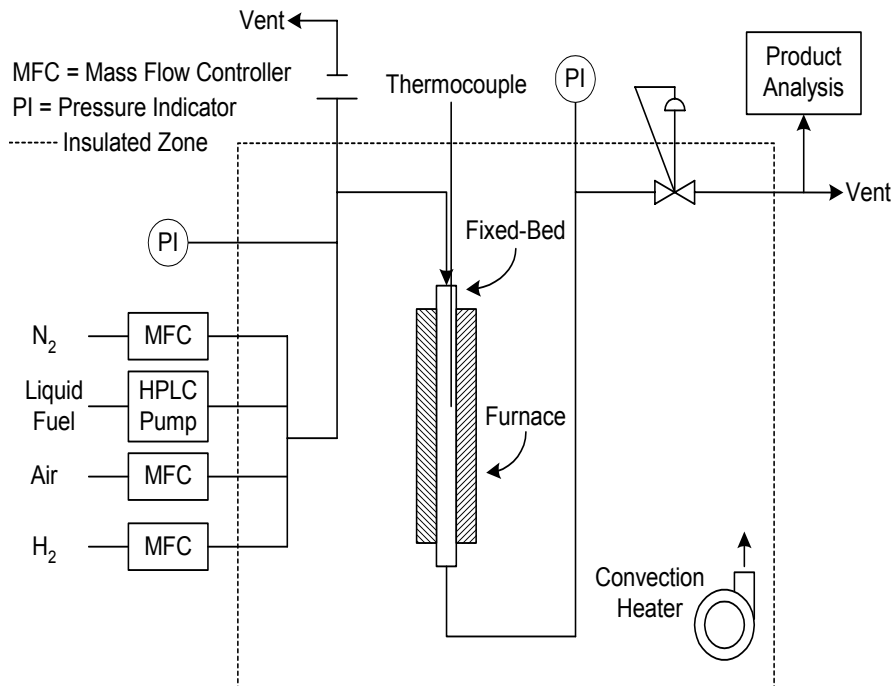


Online GCs

Twin Micro-reactors



# Test Apparatus/Reaction Conditions



## Test Fuels

- n-Tetradecane (TD)
- 50 ppm w/w S as DBT/TD
- 5 wt% 1-methylnaphthalene/TD
- DF-2 (C-T)

## Catalysts

- $MNi_yAl_{12-y}Al_{19-\delta}$  (M = Ba, La, Sr)
- HEXM catalyst series

## Test Conditions

- CPOX: O/C = 1.2
- Temp = 850-900°C
- Preheat temp = 350°C
- GHSV = 6,250 to 50,000  $\text{cm}^3\text{h}^{-1}\text{g}^{-1}$

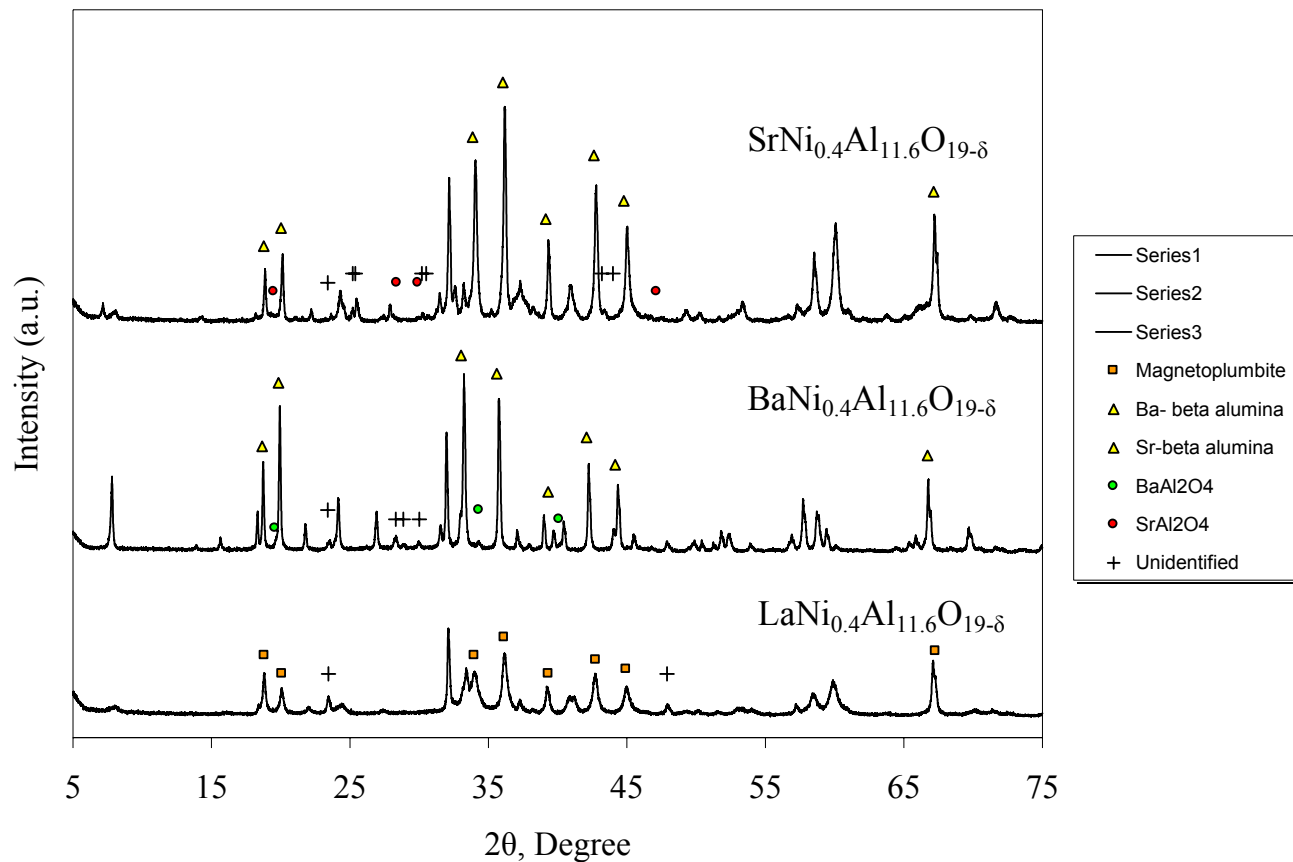


# Productivity and Results

- Reactor setup and test conditions
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# XRD Study on M-site: $\text{MNi}_y\text{Al}_{12-y}\text{O}_{19-\delta}$

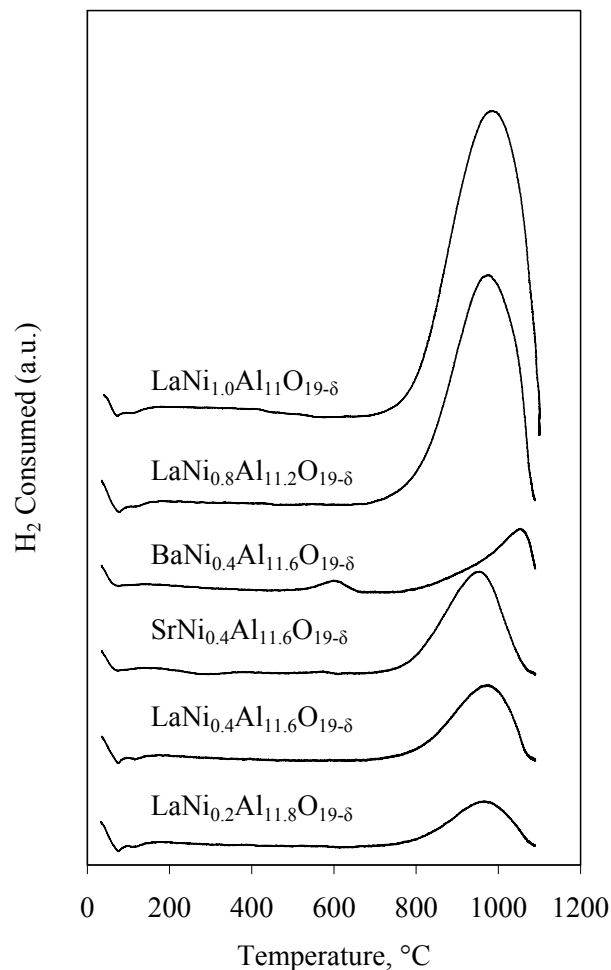
*Calcined at  $T = 1250^\circ\text{C}$ , 2 h*



➤ Substitution of Sr and Ba mirror cations resulted in  $\beta$ -alumina phase formation. La substitution resulted in a magnetoplumbite phase

# Temperature Programmed Reduction of $\text{MNi}_y\text{Al}_{12-y}\text{O}_{19-\delta}$ Catalysts

*5.15 vol%  $\text{H}_2/\text{Ar}$ , Ramp Rate = 10 K/min*



- Ni-O bond in hexaalumina lattice was influenced by the mirror cation
- Mirror cation effect suggests that Ni in the region near the mirror plane is where catalytically active defect Ni sites had formed

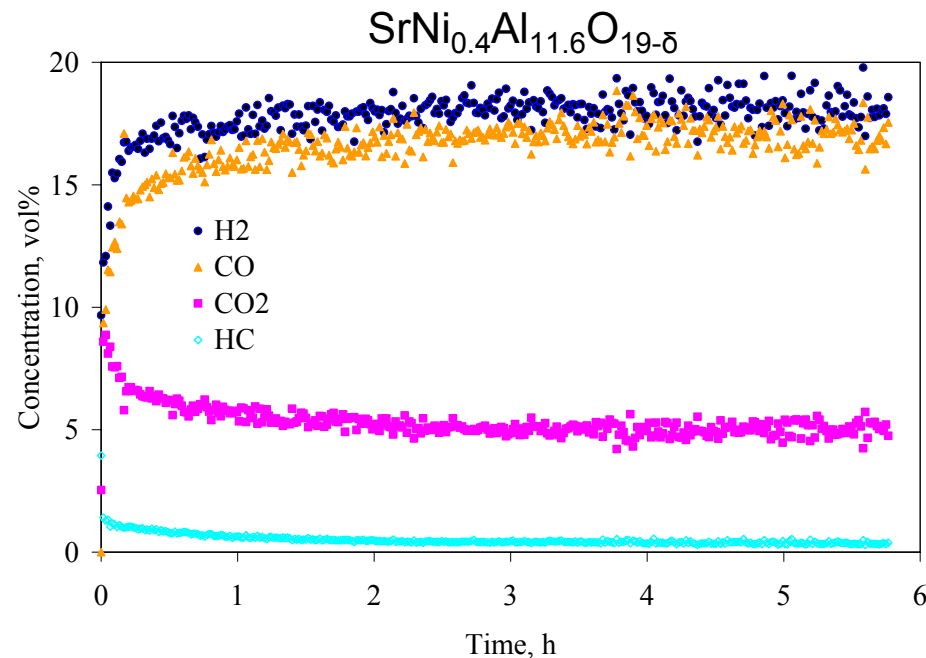
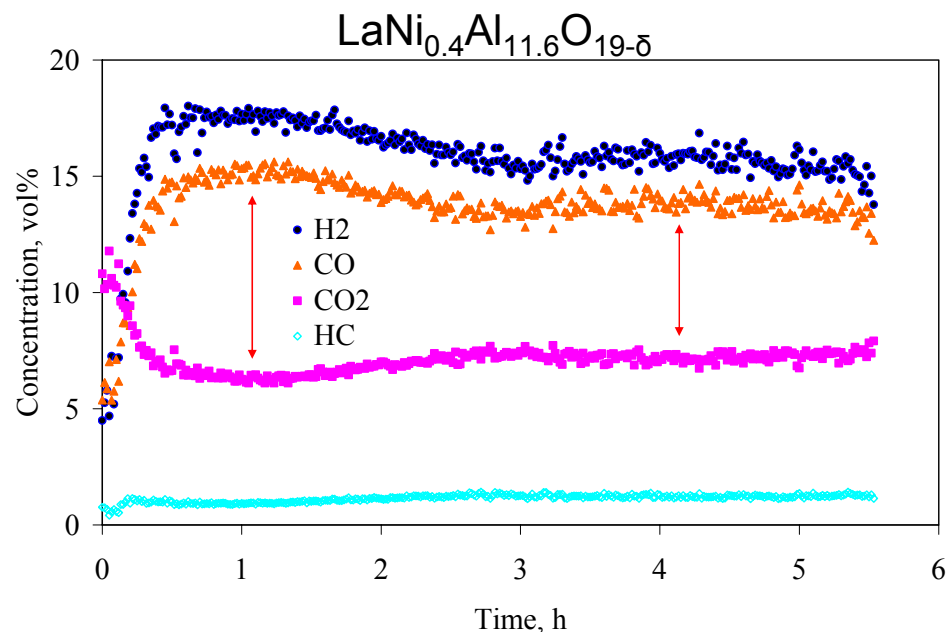
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# Effect of Mirror Cation on Catalytic Stability

*CPOX:  $n\text{-C}_{14}\text{H}_{30}$ ,  $\text{O/C} = 1.2$ ,  $T = 850^\circ\text{C}$ ,  $P = 2 \text{ atm}$ ,  $\text{WHSV} = 50,000 \text{ cm}^3\text{h}^{-1}\text{g}^{-1}$*

**NETL developed hexaaluminate catalysts are very active for the partial oxidation of large hydrocarbons...**



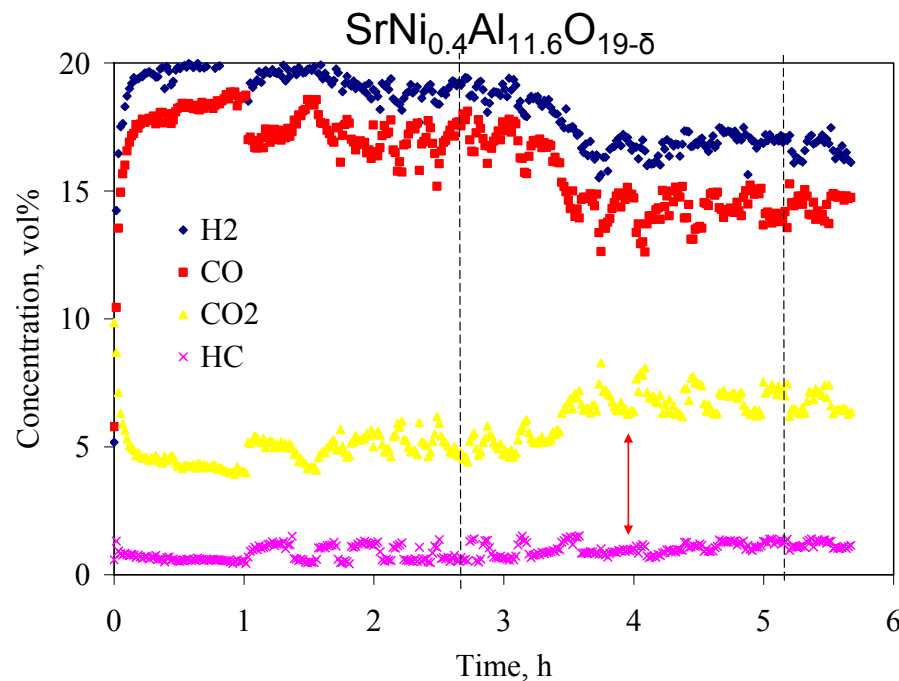
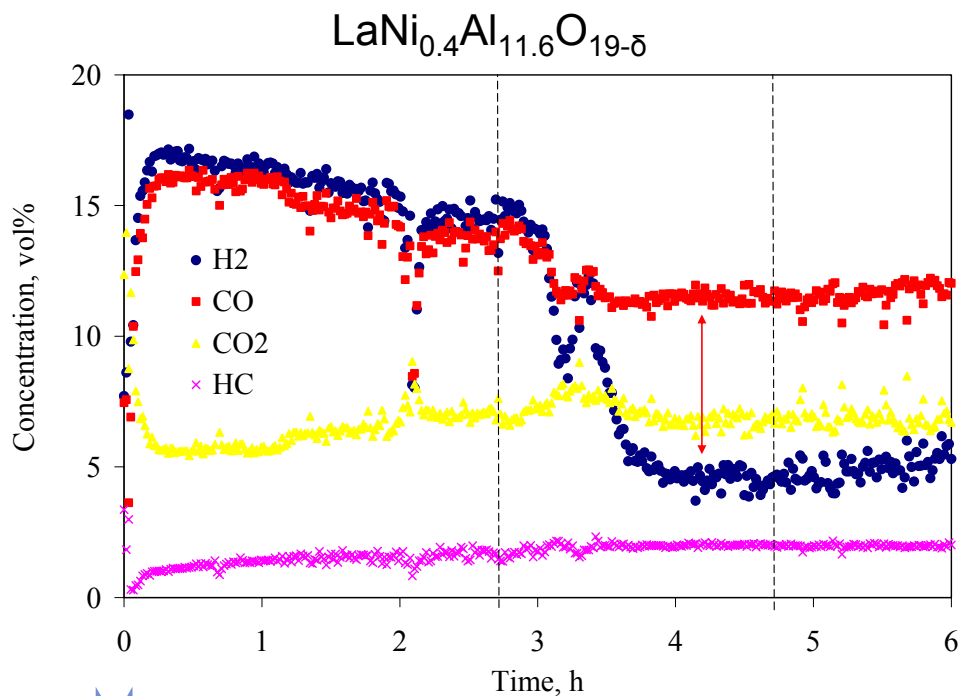
- The structural effect induced by the mirror cation influences catalyst stability
- High coordination Ni sites result in excessively strong HC adsorption



# Effect of Mirror Cation on Sulfur Poisoning

*CPOX:  $n\text{-C}_{14}\text{H}_{30}$ ,  $\text{O/C} = 1.2$ ,  $T = 850^\circ\text{C}$ ,  $P = 2\text{ atm}$ ,  $\text{WHSV} = 50,000\text{ cm}^3\text{h}^{-1}\text{g}^{-1}$ ,  
Step response to 50 ppm w/w S as DBT/  $n\text{-C}_{14}\text{H}_{30}$*

**Dibenzothiophene (DBT) and its derivatives are difficult to remove from diesel through hydrodesulfurization...**

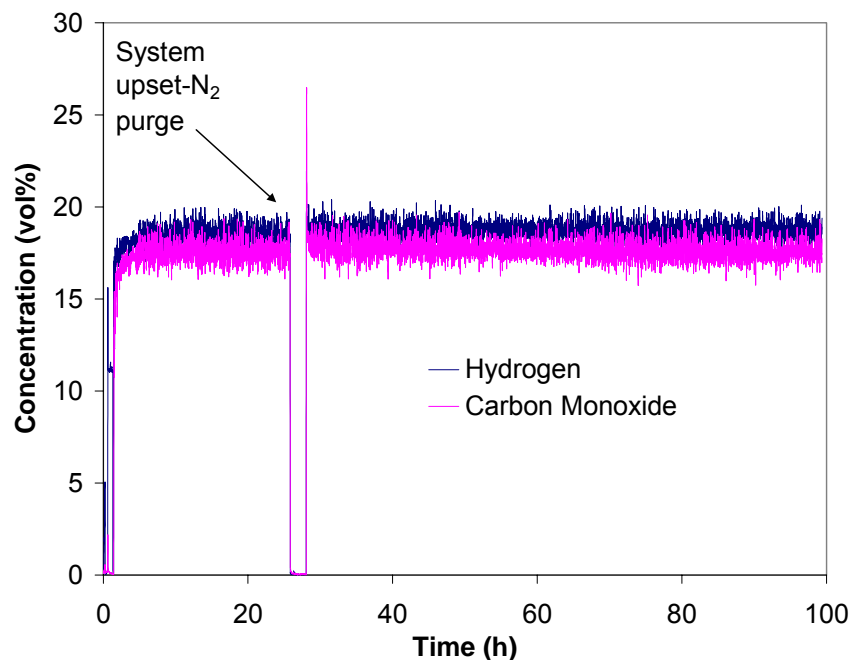


- The mirror cation produces a structural effect on the Ni ensemble
- High coordination Ni sites result in excessively strong S adsorption

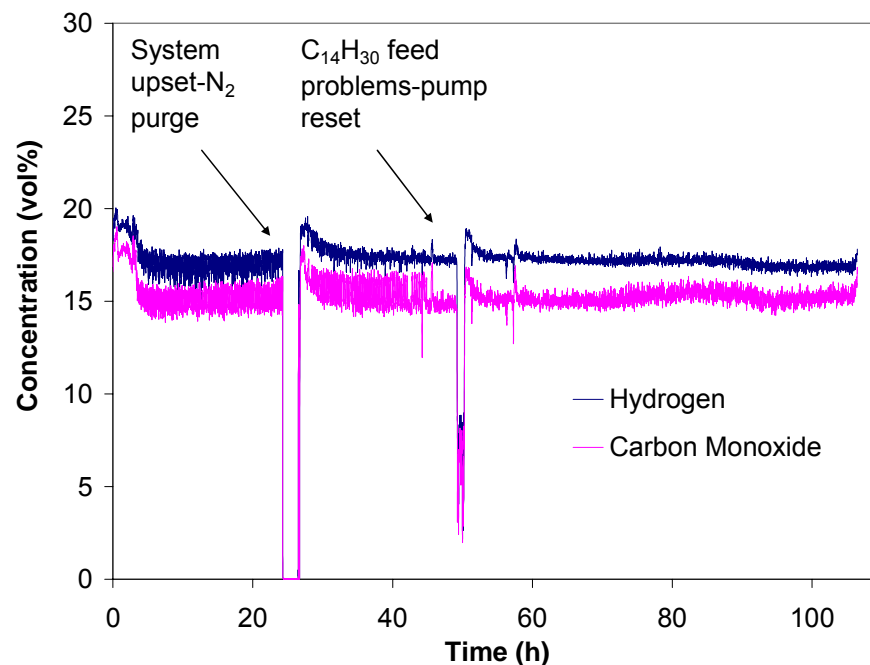


# Hexaaluminate Catalyst Stability: 100 hr Aging Tests

*CPOX:  $n\text{-C}_{14}\text{H}_{30}$ ,  $\text{O/C} = 1.2$ ,  $T = 850^\circ\text{C}$ ,  $P = 2 \text{ atm}$ ,  $\text{WHSV} = 50,000 \text{ cm}^3\text{h}^{-1}\text{g}^{-1}$*



**Catalyst:**  $\text{BaNi}_{0.4}\text{Al}_{11.6}\text{O}_{19.5}$   
**Fuel:** n-tetradecane



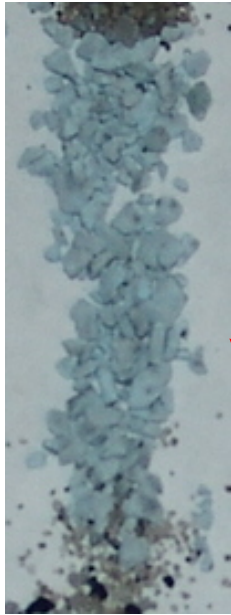
**Catalyst:** 0.1 wt%  $\text{Rh/SrNi}_{0.4}\text{Al}_{11.6}\text{O}_{19.5}$   
**Fuel:** n-tetradecane/dibenzothiophene (50 ppm w/w S)

Hexaaluminate catalysts showed good stability over 100 hr

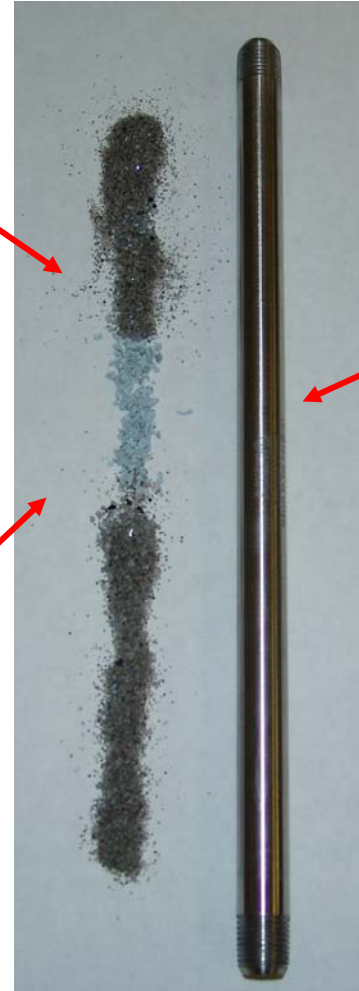


# Hexaaluminate Catalyst / Reactor

Quartz chips  
used to disperse  
the catalyst



$\text{BaNi}_{0.4}\text{Al}_{11.6}\text{O}_{19-\delta}$  catalyst after 100 h  
CPOX on 50 ppm w/w DBT/n-  
tetradecane. The catalyst remained  
relatively carbon free.



Laboratory  
Reactor  
(Incoloy  
800HT,  
950°C, 80  
psig)



# Summary Points

- Active sites are defective Ni sites in the mirror plane region (coordinatively unsaturated Ni)
- Geometric distribution of Ni dispersed within the mirror plane was affected by the mirror cation
- The excellent stability observed with nickel substituted hexaaluminate catalysts resulted from an atomically dispersed active site present in low coordination

# Productivity and Results

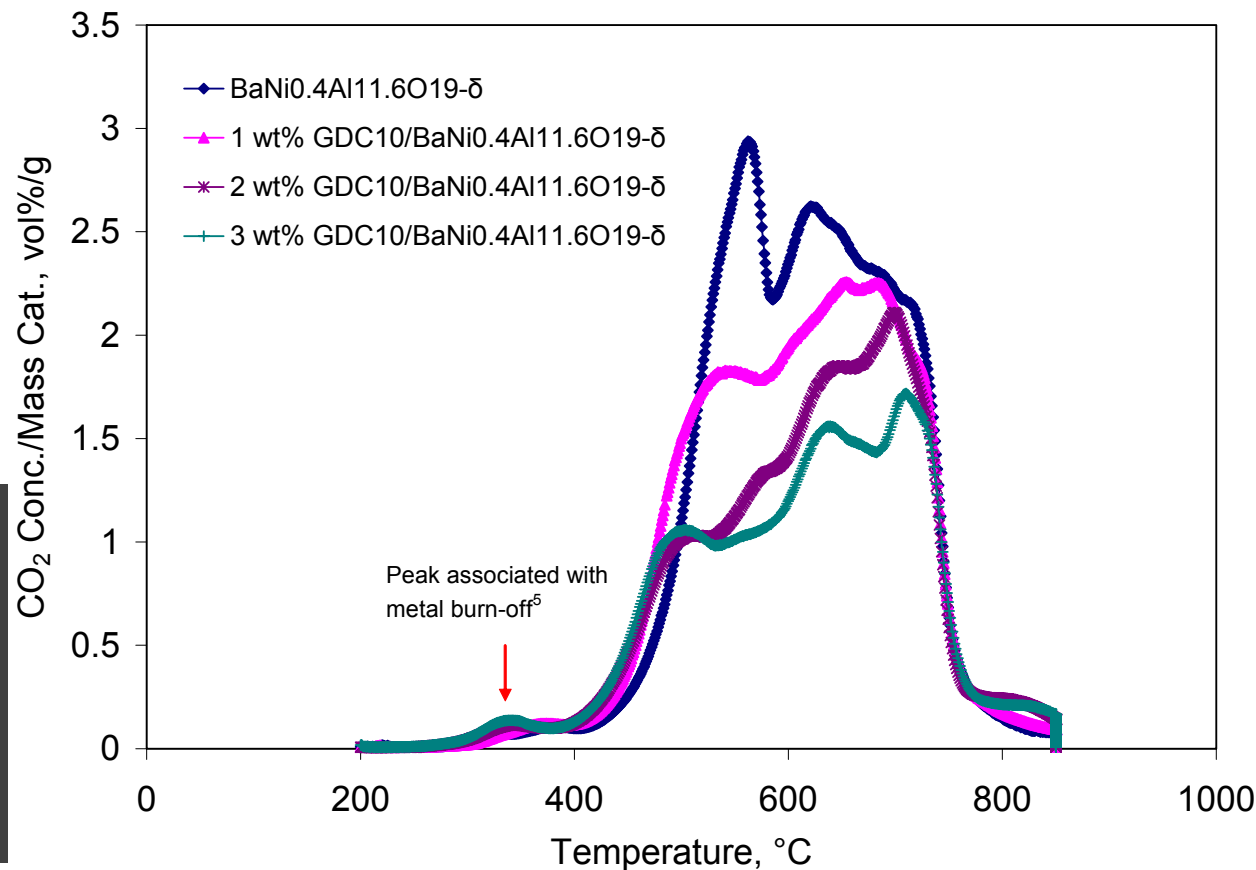
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# Minimization of Carbon Deposition with $\text{CeO}_2$ -Based Surface Treatments

*Catalysts exposed to  $n\text{-C}_{14}\text{H}_{30}$  CPOX, O/C = 1.2 for 5 h at 850°C*

**Consider the application of a thin film of  $\text{CeO}_2$  to the surface of the catalyst as a method of minimizing carbon deposition...**

➤ TPO experiment reveals that carbon deposited onto the hexaaluminate catalyst surface correlates with the concentration of the  $\text{CeO}_2$  treatment



# Productivity and Results

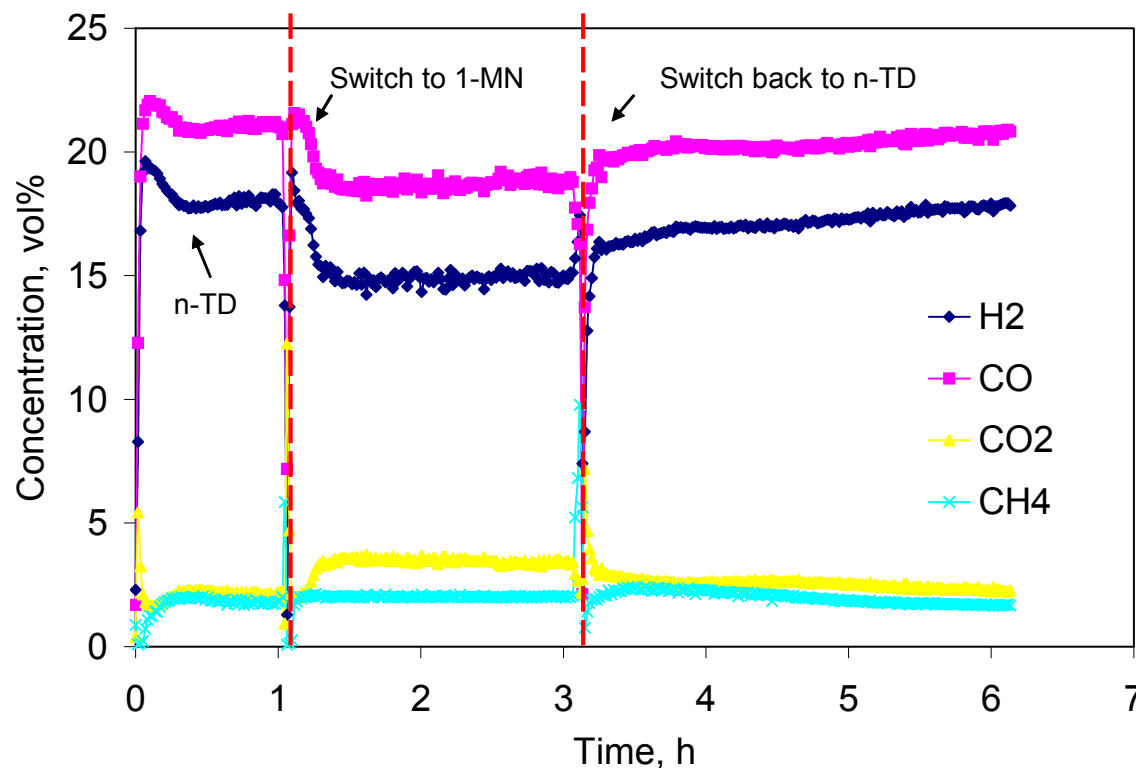
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# Catalyst Step Response Methods

*CPOX:  $O/C = 1.2$ ,  $T = 900^{\circ}\text{C}$ ,  $P = 2 \text{ atm}$ ,  $WHSV = 25,000 \text{ cm}^3\text{h}^{-1}\text{g}^{-1}$*

**How do hexaaluminate catalysts respond to the step addition of aromatic compounds (1-MN)?**

- Strong adsorption tendencies have been minimized
- HEXM series catalyst exhibited excellent recovery



**Catalyst: HEXM-1**

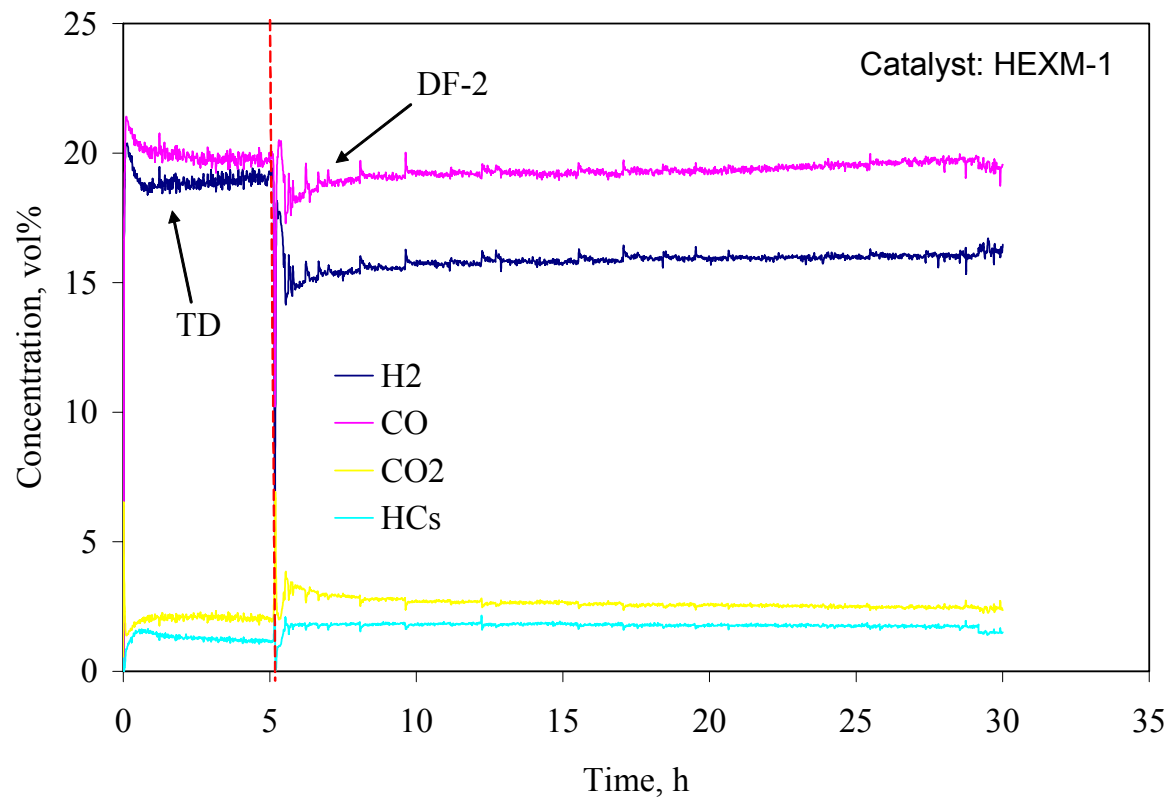
**Step response:  $n\text{-C}_{14}\text{H}_{30}$  to 5 wt% 1-MN/ $n\text{-C}_{14}\text{H}_{30}$  and back to  $n\text{-C}_{14}\text{H}_{30}$**

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# Hexaaluminate Catalyst Stability

*CPOX: DF-2 (9 ppm w/w S), O/C = 1.2, T = 900°C, P = 2 atm,  
WHSV = 25,000 cm<sup>3</sup>h<sup>-1</sup>g<sup>-1</sup>*

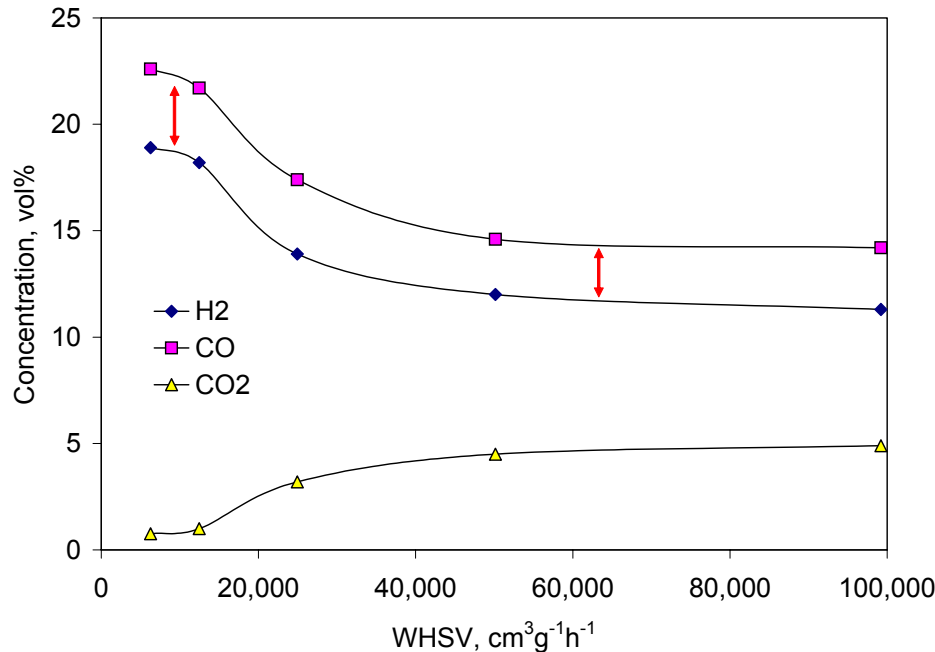


NETL Hexaaluminate catalysts show excellent stability over 30 h on DF-2



# Effect of Residence Time

**CPOX: DF-2 (9 ppm w/w S), O/C = 1.2, T = 900°C, P = 2 atm**

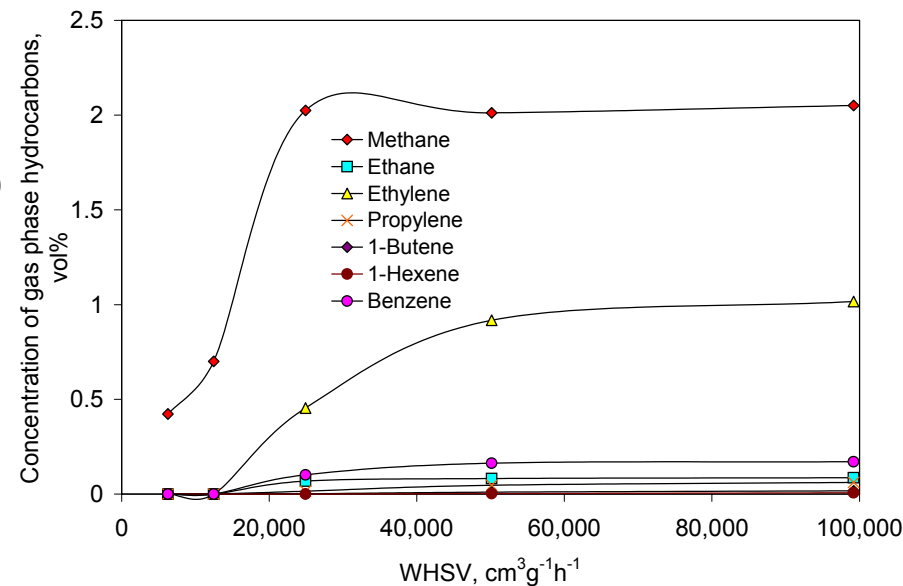


Catalyst: HEXM-1

Data collected after 2 h online

As  $\text{WHSV} > 12,500 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$  olefin formation becomes significant. At  $\text{WHSV} < 12,500 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$  only  $\text{CH}_4$  is present...

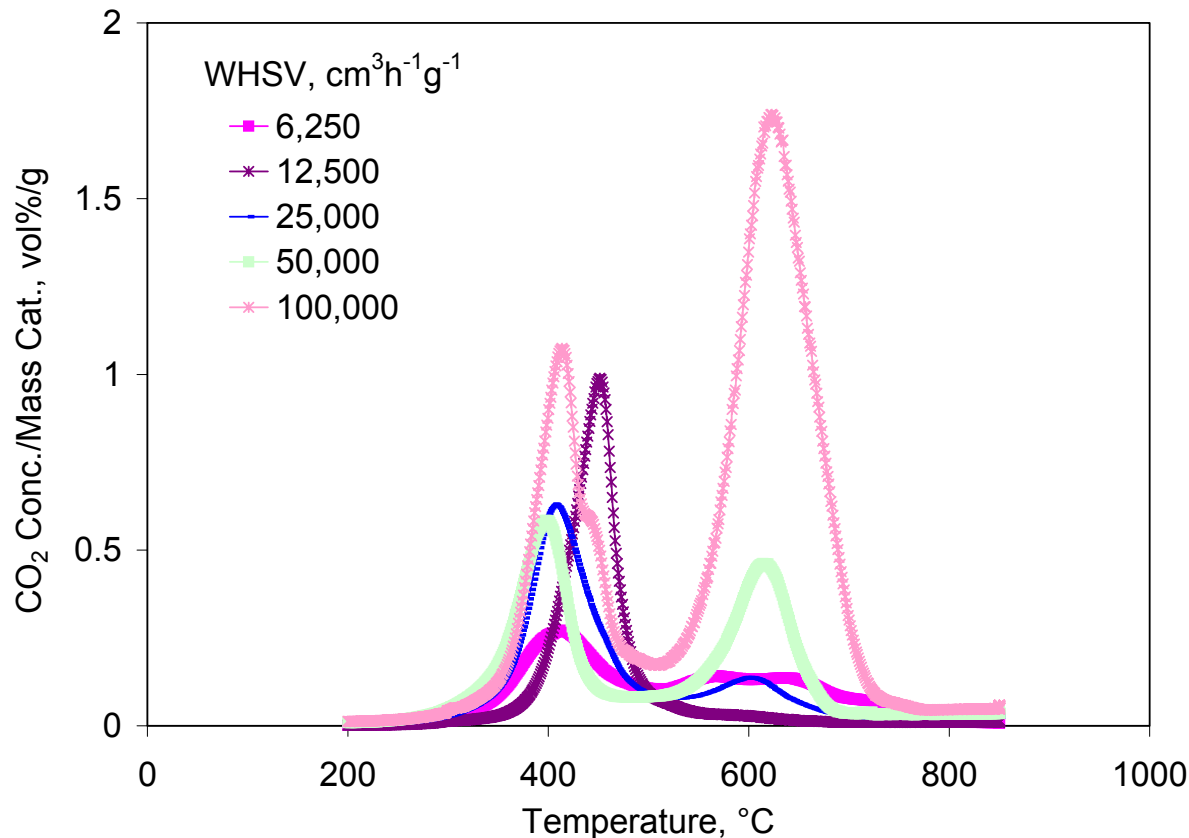
$\text{H}_2/\text{CO}$  selectivity remained the same over all residence times. As WHSV was increased, gas phase chemistry became more significant...





# Effect of Residence Time on Carbon Deposition

*CPOX: DF-2 (9 ppm w/w S), O/C = 1.2, T = 900°C, P = 2 atm*



***What is the influence of WHSV on carbon deposition?***

➤ Carbon deposition increases with increasing WHSV

# Proposed Future Work

## Catalyst Development:

- **Continue on series with Hexaalumina & HEXM**
  - Address selectivity issues
  - Demonstrate long-term diesel fuel operation
  - Test engineered catalyst forms with commercial catalysts companies



# Relevant Literature

## **Patents**

Gardner, T., Berry, D., Shekhawat, D., "Hexaaluminate-type catalysts for the reforming of hydrocarbon fuels to hydrogen and carbon monoxide and method for making the same," U. S. patent pending

## **Book Chapter**

Shekhawat, D., Berry, D., Gardner, T. and Spivey, J., "Catalytic Reforming of Liquid Hydrocarbon Fuels for Fuel Cell Applications," *Catalysis*, Vol. 19, 2006, pp. 214-220

## **Refereed Journal Papers**

Gardner, T., Shekhawat, D., Berry, D., Smith, M., Salazar, M. and Kugler, E., "Effect of Nickel Hexaaluminate Mirror Cation on Structure Sensitive Reactions During n-Tetradecane Partial Oxidation," *Accepted Applied Catalysis: A*

## **Conference Papers**

Gardner, T., Shekawat, D. and Berry, D. "Hexaaluminate Catalysts for the Partial Oxidation of Middle Distillate Fuels," *Proceedings of the 2006 ACS Spring Conference*, Atlanta, GA, March 2006.

Gardner, T., Shekawat, D. and Berry, D. "Partial Oxidation of n-Tetradecane over Lanthanum Ni-Hexaaluminate Catalysts," *Proceedings of the 2004 AIChE Fall Conference*, Austin, TX, Nov. 2004.

## **Project Reports**

Gardner, T., Shekawat D. and Berry, D., "Development of Hexaaluminate Catalysts," *Solid State Energy Conversion Alliance FY 2005 Progress Report*

Gardner, T., Shekhawat D. and Berry, D., "Development of Hexaaluminate Catalysts," *Solid State Energy Conversion Alliance FY 2004 Progress Report*, pp. 1-6.

