NATIONAL ENERGY TECHNOLOGY LABORATORY

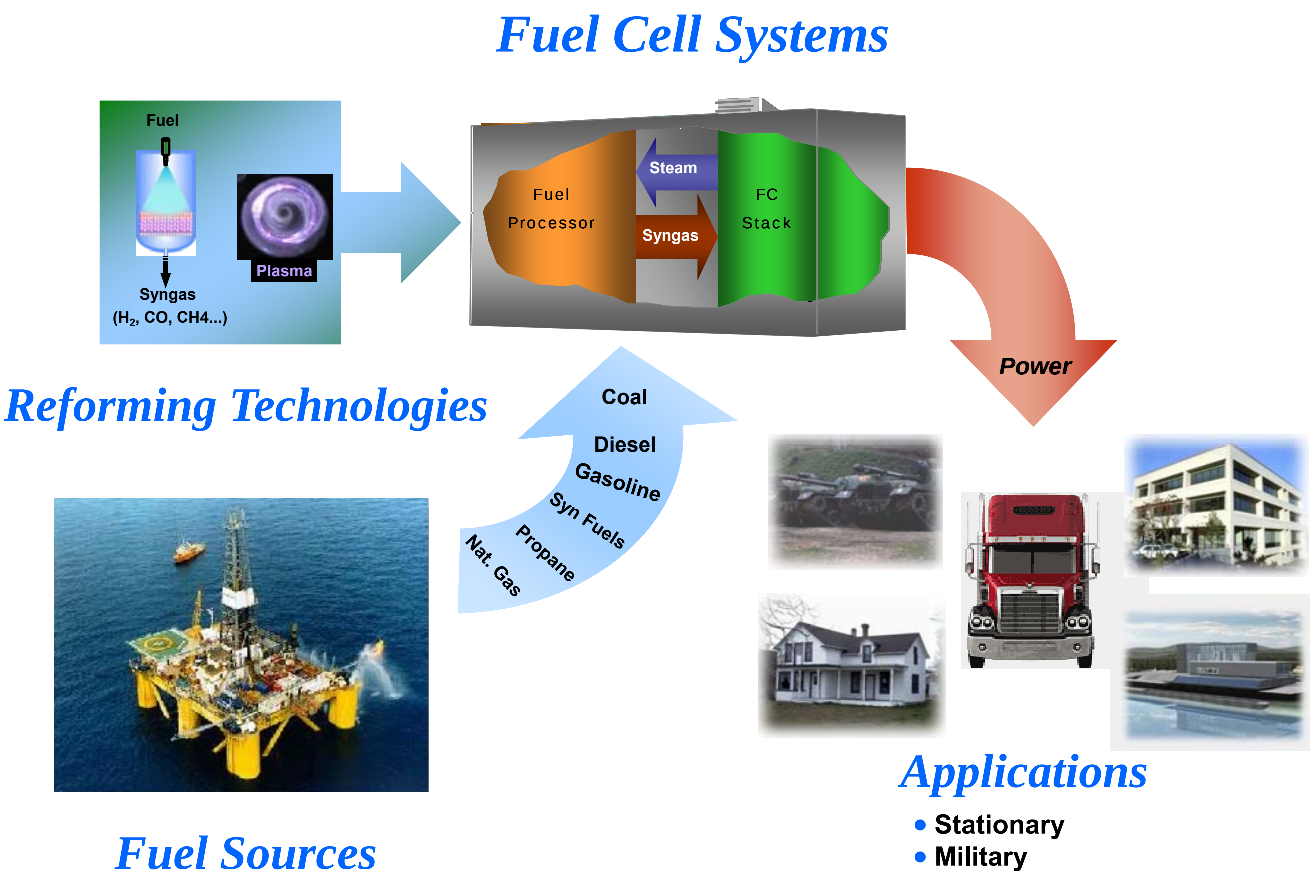
Oxide Based Reforming Catalysts & Alternative Processes: RF & Plasma

2009 SECA Annual Workshop

July 16, 2009

David A. Berry
Fuel Processing Group

Research Situation – Fuel Processing



- Stationary
- Military
- Transportation

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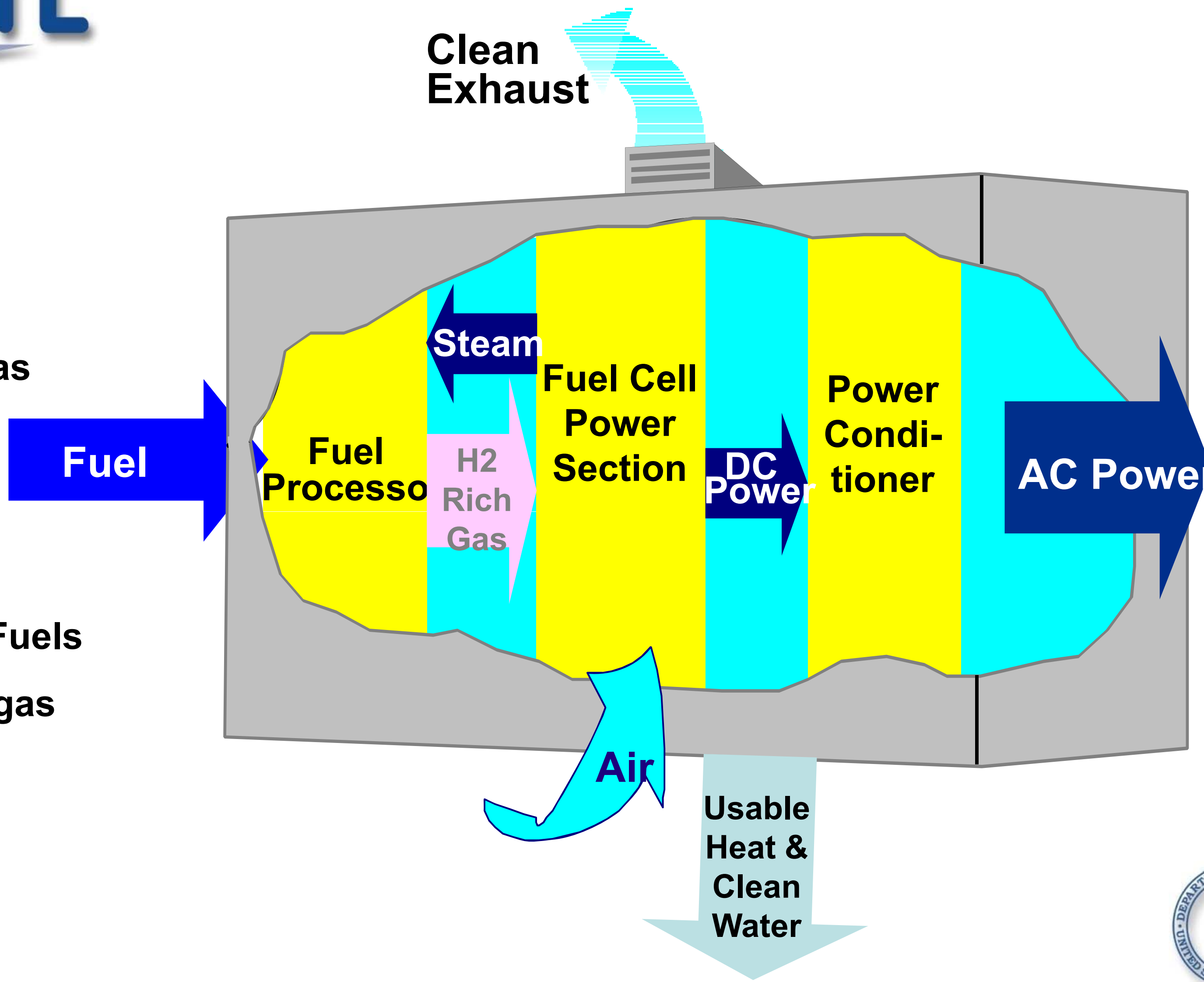
Key Enabling Technology

✓**Conversion of fuels to H_2 rich syngas necessary for the fuel cell**
✓**Critical for successful commercialization**

General Review

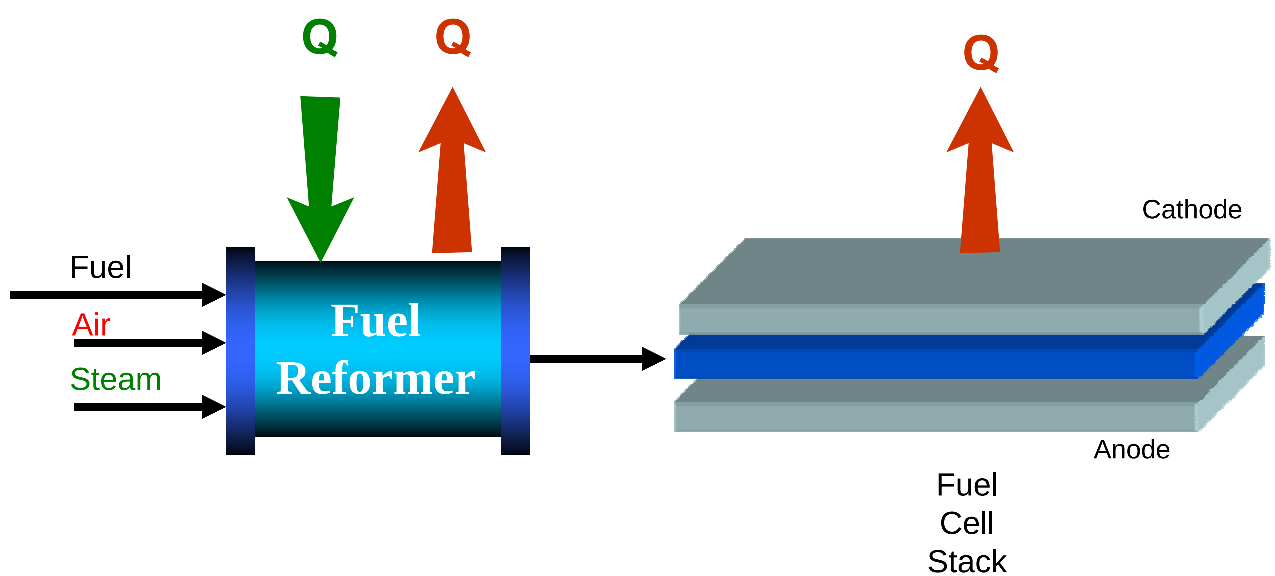
- Hydrogen
- Natural Gas
- Propane
- Gasoline
- Diesel
- Logistic Fuels
- Coal Syngas



Reformer Integration

Reforming Options:

- POx
- Steam Reforming
- Oxidative SR



Steam Reforming - Endothermic

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2$$

Pox Reforming - Exothermic

$$C_nH_m + \frac{n}{2}(O_2 + 3.76N_2) \rightarrow nCO + \frac{m}{2}H_2 + \left(3.76\frac{n}{2}\right)N_2$$

Technical Objective / Challenges

- **Desired Thermal Integration with Fuel Cell – Similar Temperature of Operation:**
  - Reduces unnecessary heat exchange and can increase system efficiency – cost & complexity savings.

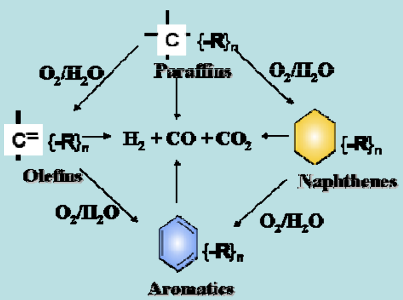
    Challenges: Thermal processes too high temperature. Can be achieved by utilizing catalysts to lower reformation temperatures. Unfortunately, most hydrocarbon fuels contain sulfur and complex hydrocarbons that deactivate catalyst systems prematurely. Commercial catalysts developed mostly for natural gas reformation & naptha.

- **Possible Low or Waterless Operation:**
  - Reduces or eliminates the complexity and cost of managing water within the system. Some applications cannot consider water addition to the process.

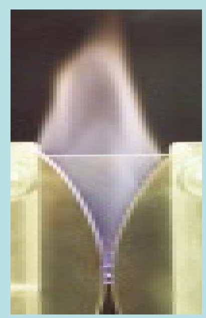
    Challenges: The use of water (usually excess) is the principle combatant to carbon formation for commercial catalysts. Water however can also increase system efficiency by increasing hydrogen concentration via steam reforming & heat utilization: *Cost vs efficiency trade-off.*

Primary Goal

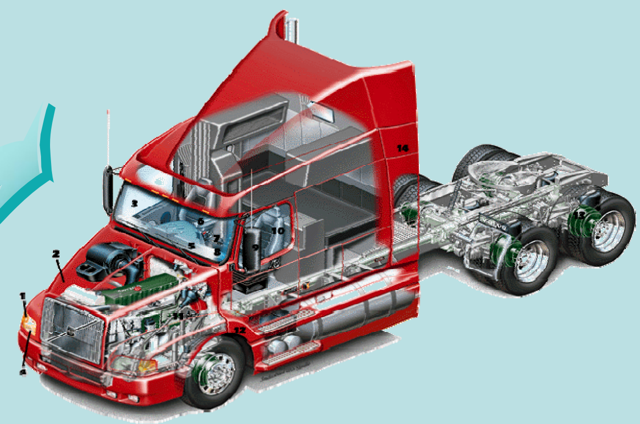
Identify, evaluate and/or develop viable hydrocarbon fuel processing technologies for high temperature solid oxide fuel cells being supported in the NETL SECA program through fundamental understanding, research, and technology demonstration.



Fuel



Technology

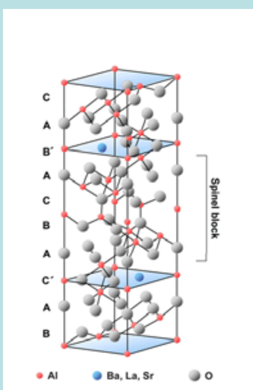


End Use

Two Project Areas

<u>Oxide-Based Catalyst Systems:</u>

Apply fundamental understanding of fuel reforming & deactivation mechanisms into intelligent design of alternative catalyst systems for long-term, stable hydrogen-rich synthesis gas production.



<u>Advanced Reforming Concepts:</u>

Identify and evaluate alternative non-catalytic and/or catalyst assisted processes to overcome deactivation of traditional catalytic fuel reforming of higher hydrocarbon fuel compounds.

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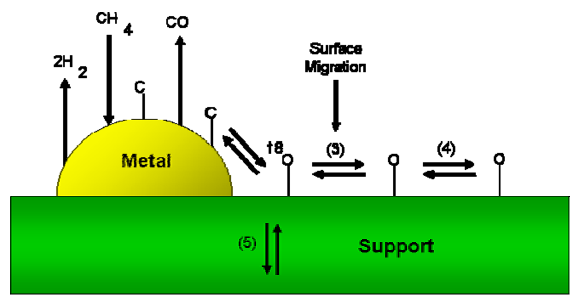
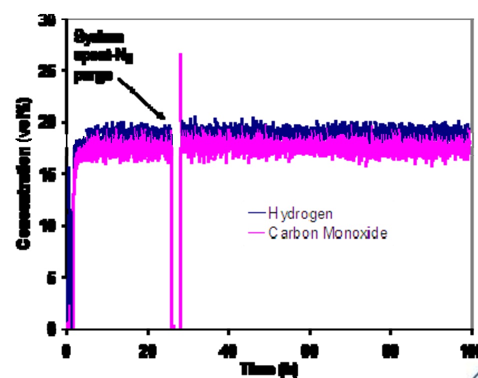
Oxide-Based Catalyst Systems

Project Objectives - Approach

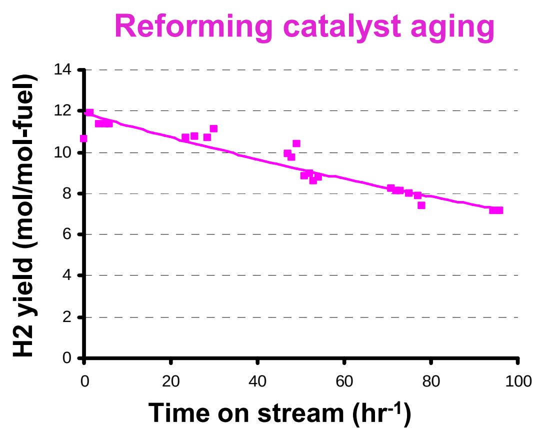
- **Gain a fundamental understanding of catalyst function and mechanism of deactivation.**

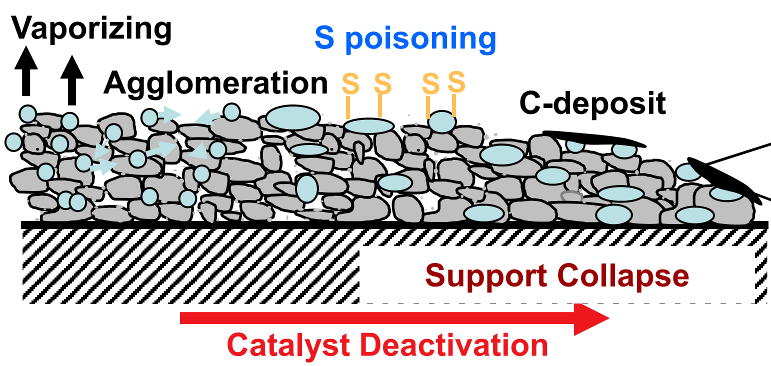


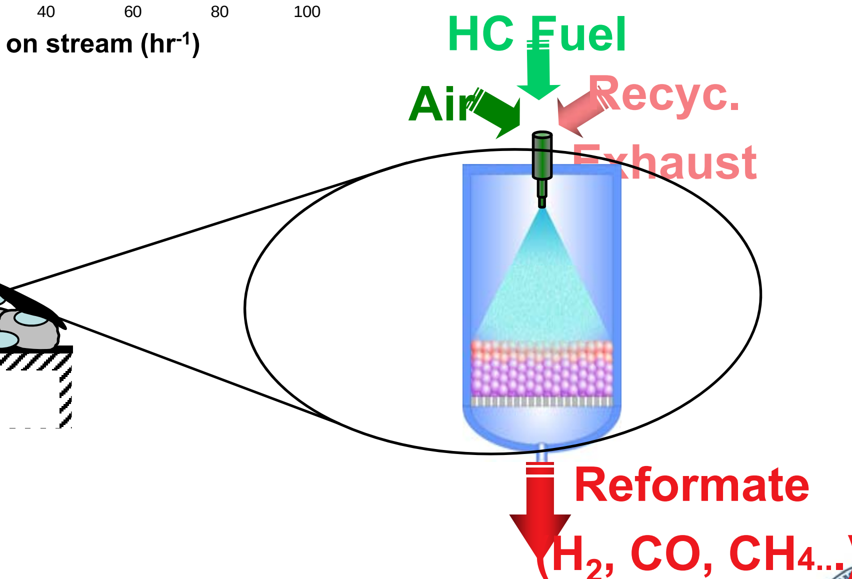
- **Apply understanding and lessons learned to design improved performance catalyst systems & demonstrate long-term performance.**



Deactivation Issues – Why?







Catalyst Progression

Traditional Inert Supported Ni

- ***Nobel Metal Additions***
  - ***Conductive Supports***
    - ***Oxide-Based Catalysts***
      - ***Oxide-Based Catalysts w/conductive supports***

➢ Ni quickly deactivates in presence of higher hydrocarbons…especially under Pox or low water conditions

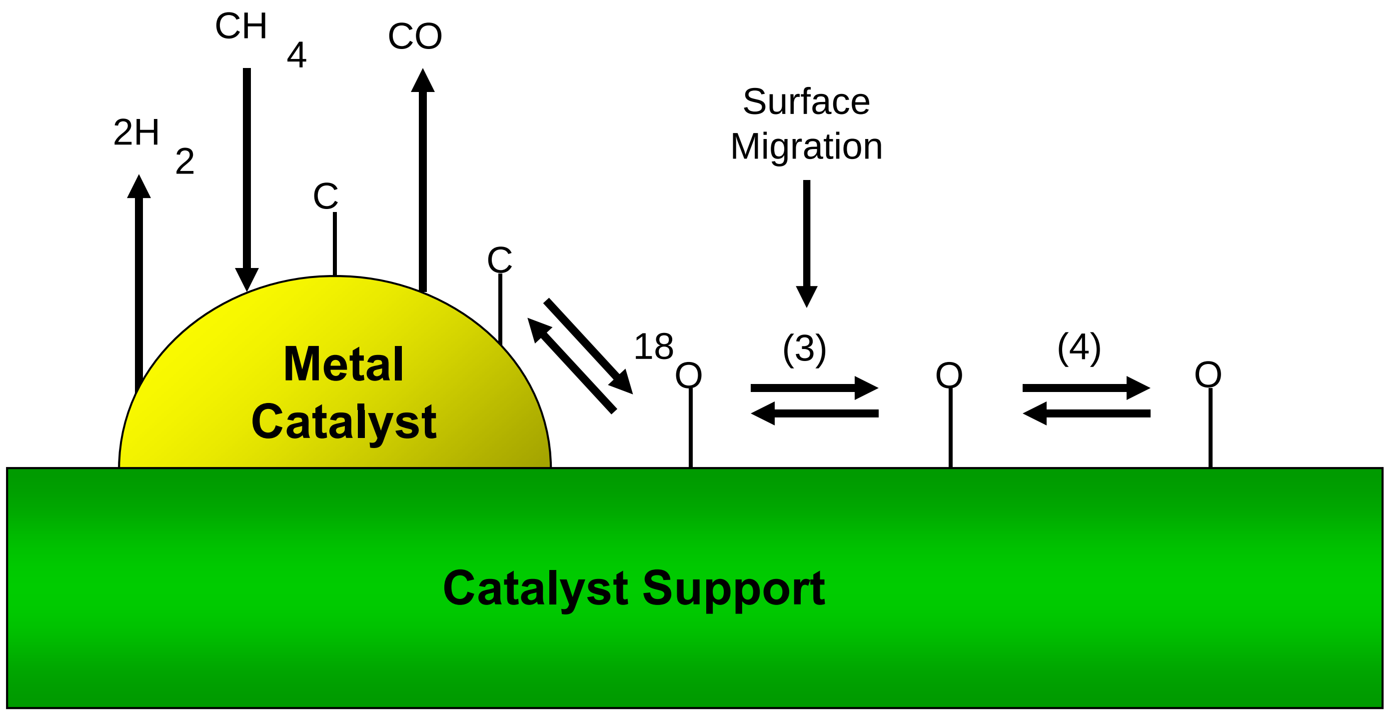
Catalyst Progression

Traditional Inert Supported Ni

- *Nobel Metal Additions*
  - *Conductive Supports*
    - *Oxide-Based Catalysts*
      - *Oxide-Based Catalysts w/conductive supports*

➢ Noble metals such as Rh demonstrated superior carbon and sulfur formation/tolerance

Carbon Formation Mechanism



- Oxygen exchange at metal/support interface would seem important for C oxidation

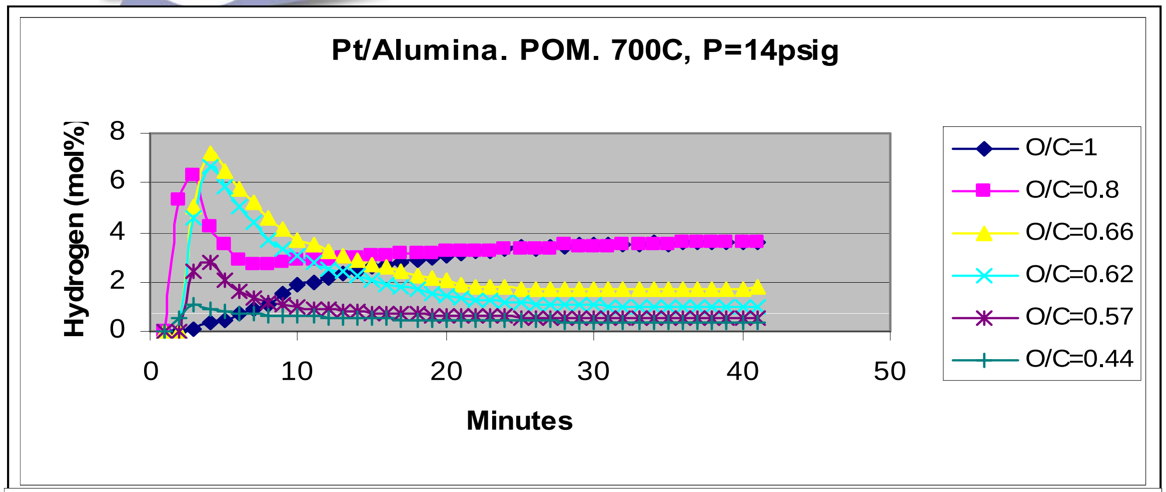
Catalyst Progression

Traditional Inert Supported Ni

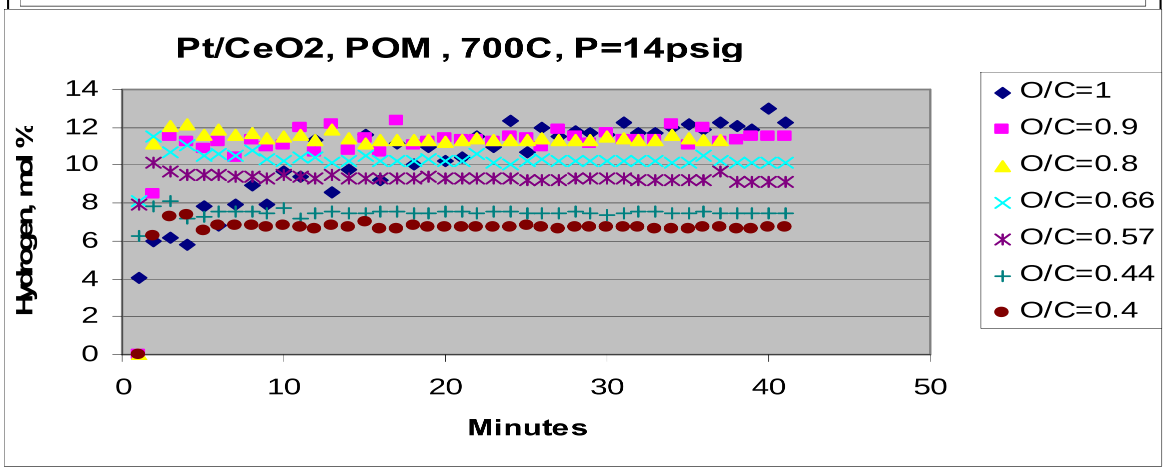
- *Nobel Metal Additions*
  - *Conductive Supports*
    - *Oxide-Based Catalysts*
      - *Oxide-Based Catalysts w/conductive supports*

- **What's the role of the support?**

Effect of support-type on H2 generation



- Pt catalysts on non-conducting supports showed both poor performance and rapid deactivation.



- Pt catalysts on oxygen ion conducting supports (CeO) exhibited stable performance even in very low oxygen environments.

- **Support type matters**

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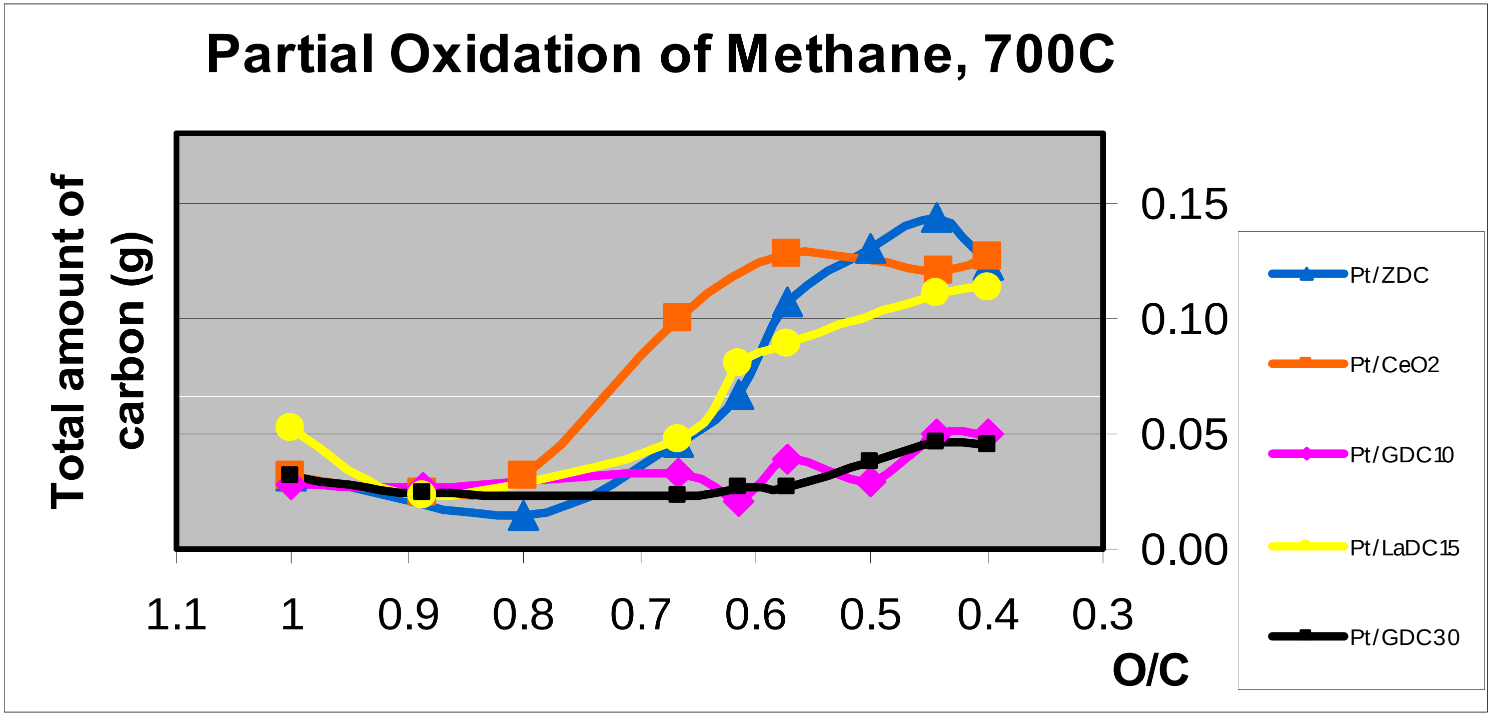
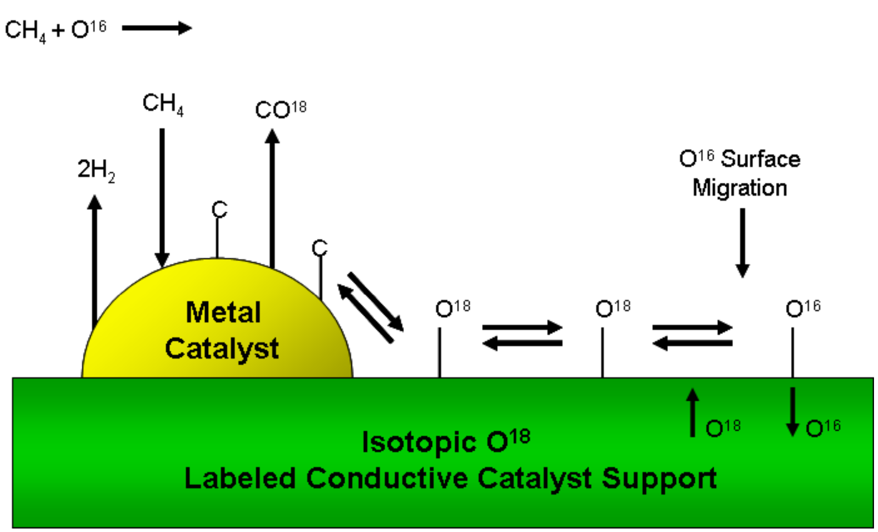
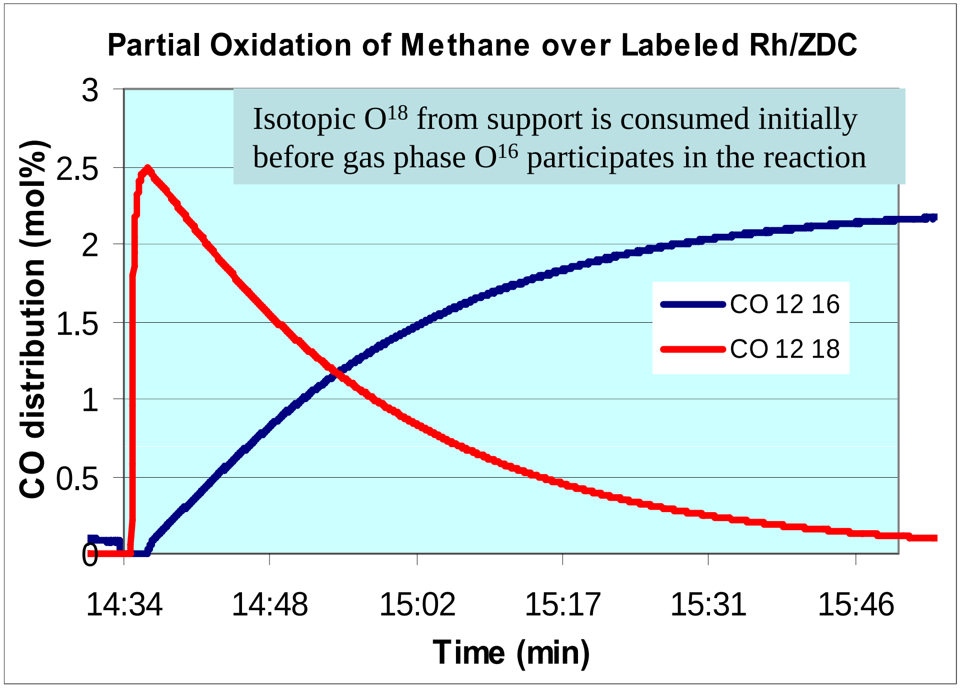
Effect of Ionic Conductivity of Support on Carbon Formation



➢**The higher the ionic conductivity of the support, the less carbon formation is observed.**

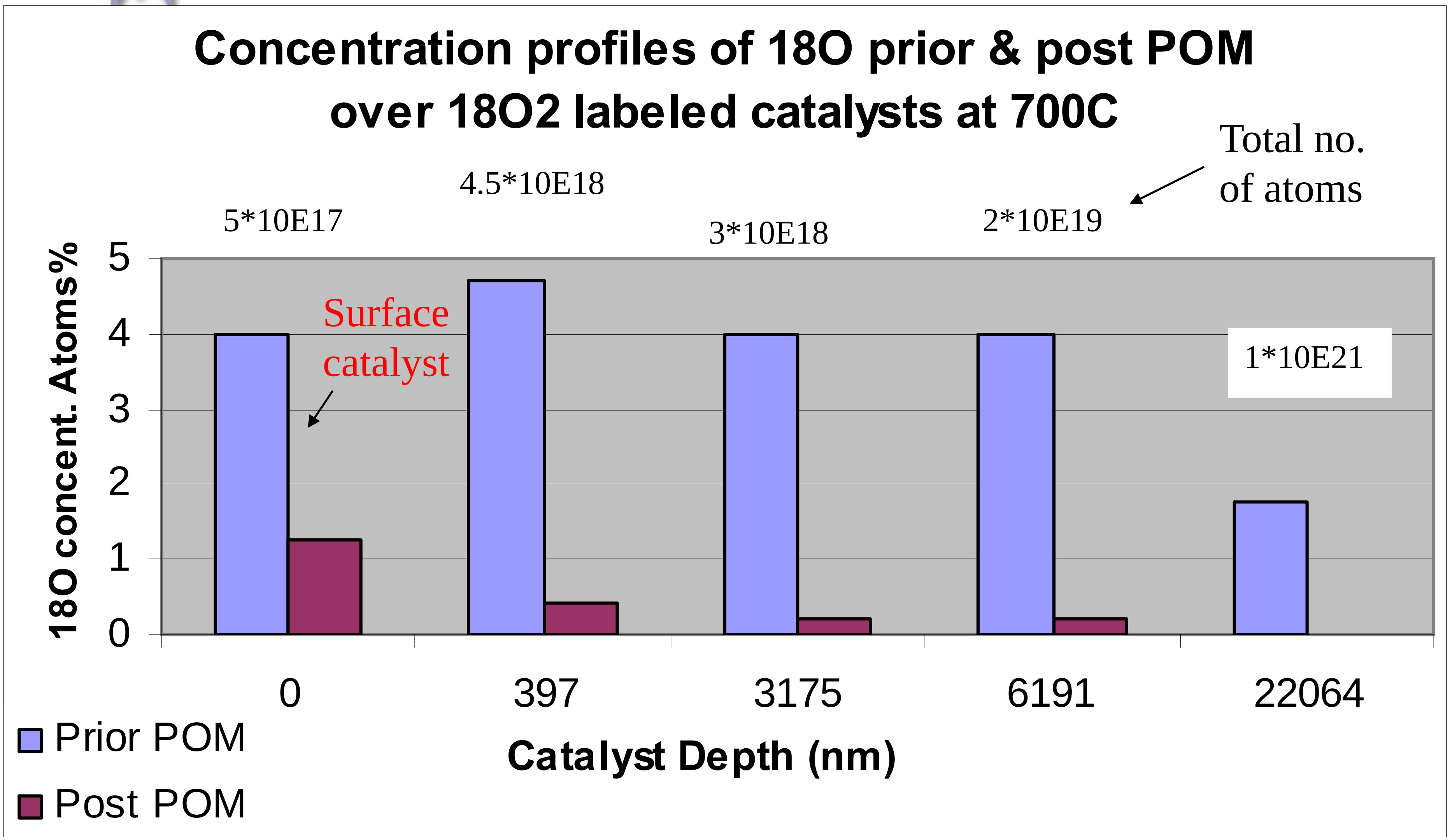
Isotopic Oxygen[18] Tracer Studies – Labeled Supports





- **Isotopic studies corroborate carbon oxidation is initiated by O_2 in the support.**

^{18}O concentration/Catalyst depth



Catalyst Progression

Traditional Inert Supported Ni

- ➢*Nobel Metal Additions*
- ➢*Conductive Supports*
- ➢*Oxide-Based Catalysts*
- ➢*Oxide-Based Catalysts w/conductive supports*

➢ **Are oxide-based catalysts beneficial?**

Additional Performance Characteristics

Other important observations:

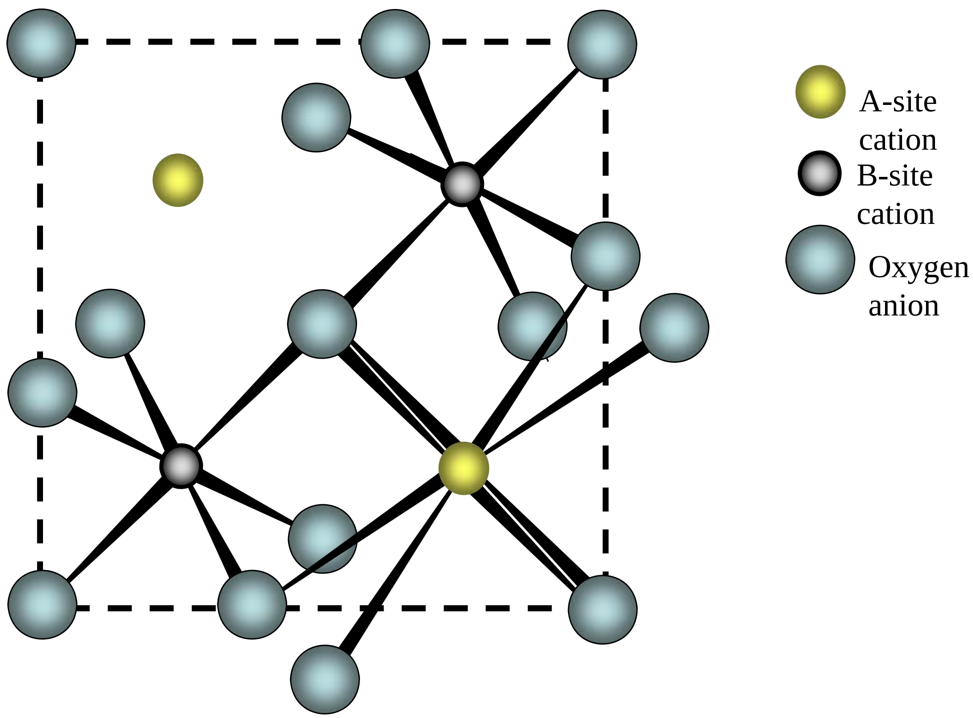
- Small "nano-sized" catalyst sites exhibit better activity and lower overall carbon formation.
- Well-dispersed active reaction sites exhibit better tolerance to sulfur and carbon deactivation.

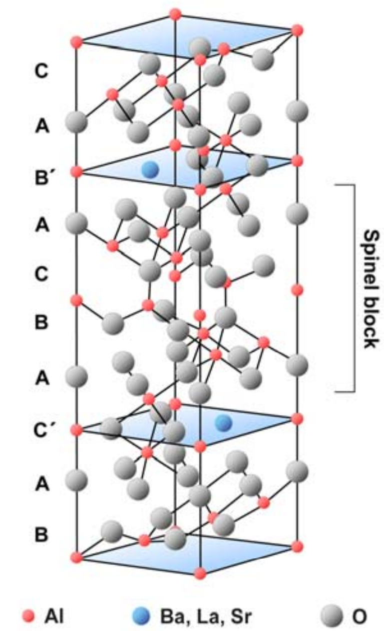
How do we take advantage of these characteristics?

Oxide-based Catalyst Systems

General Formula

ABO





Doping the lattice of certain oxide-based compounds with catalytic metals results in…

•A structured catalytic surface with nano-sized metallic crystallites that serves as a template to control metallic crystallite size and dispersion.

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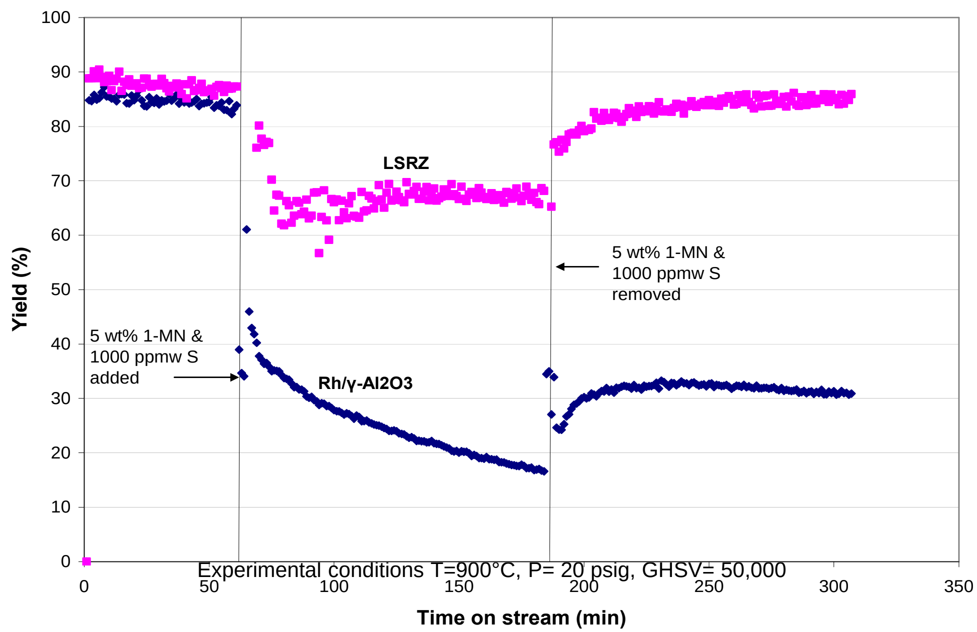
Oxide-Based Catalyst Performance



A **conductive oxide-based catalyst** was doped with 1% Rh along with a SOA Rh catalyst on alumina. After exposure to a severely carbon producing fuel compound, the oxide-based catalyst performance remained stable, while the non-conducting supported catalyst deactivated significantly.

➢ **Oxide based catalysts appear to exhibit better stability/performance than their bulk metal catalyst counterpart.**

Catalyst Progression

Traditional Inert Supported Ni

- ***Nobel Metal Additions***
  - ***Conductive Supports***
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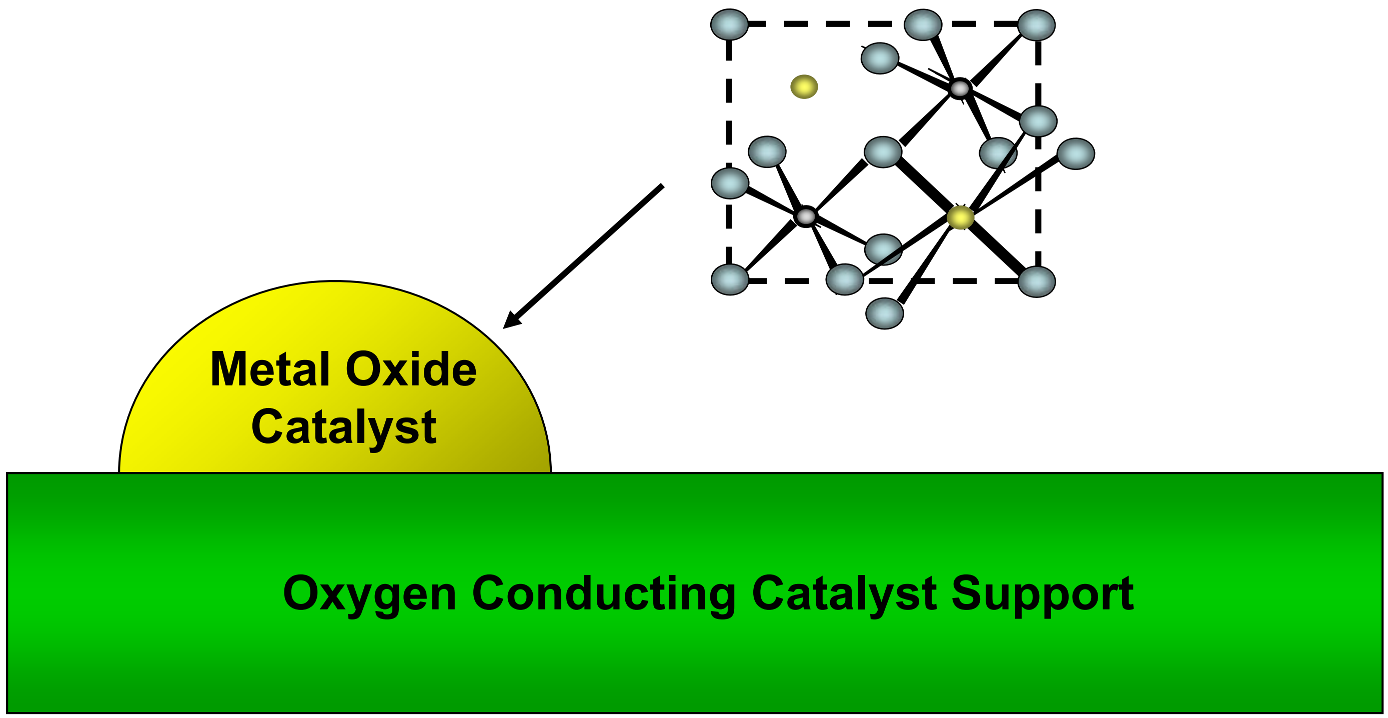
- **Is there a benefit?**

Oxide Catalyst on O2 Conducting Supports



- Metal oxide-based catalyst on oxygen-conducting supports may perform better

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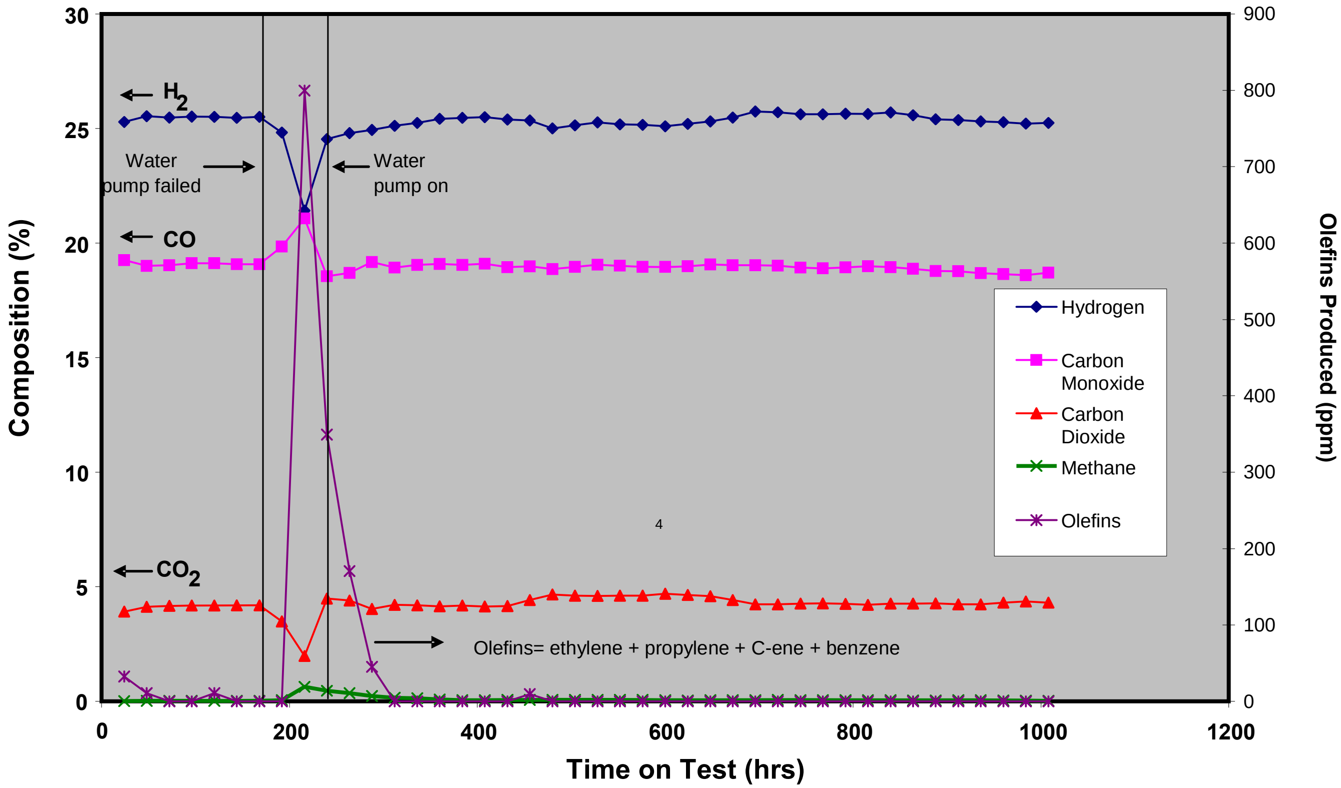
Long-Term Testing

- **1000 hour Endurance Test**
  - ✓**Fully reformed local pump diesel**
  - ✓ **Equilibrium syngas yields achieved**
  - ✓**Survived multiple system upsets**
  - ✓ **O/C=1, H_2O/C=0.5**



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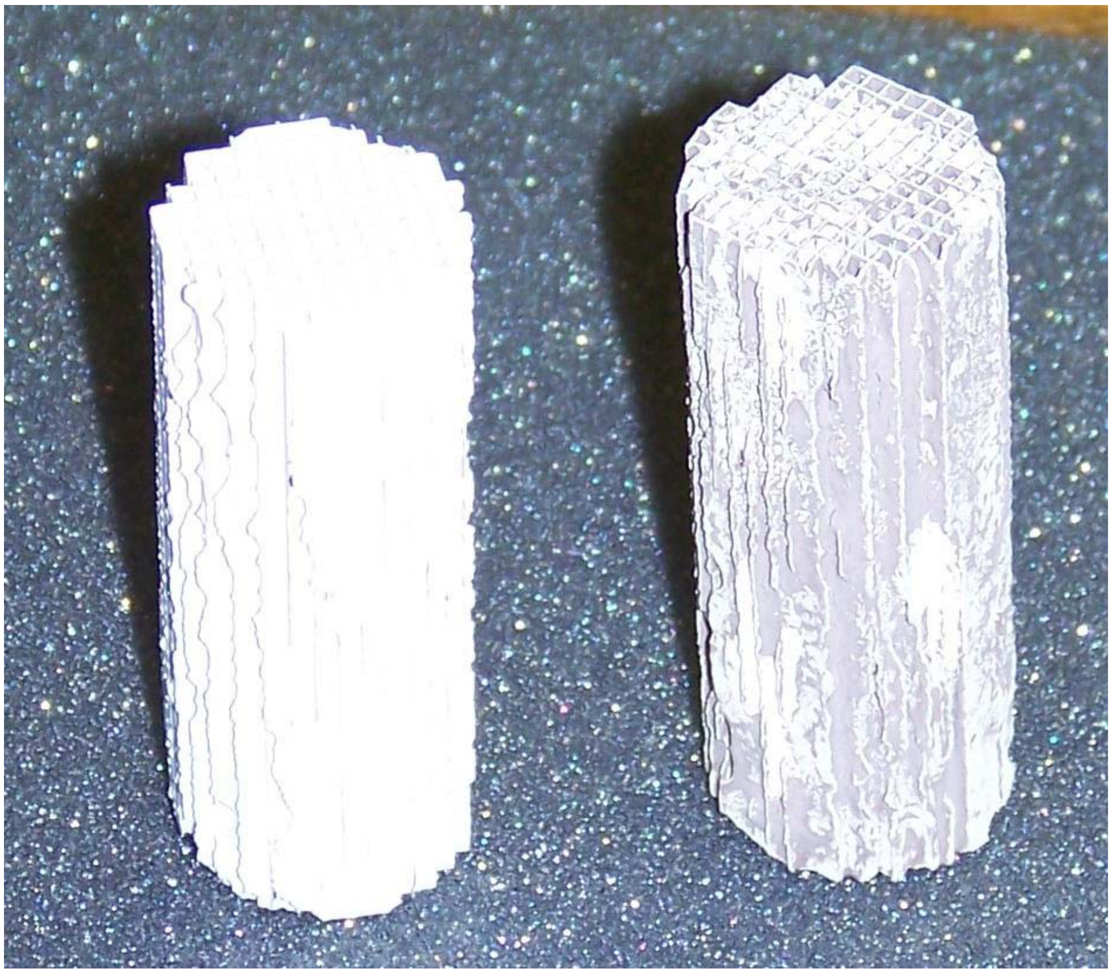
Monolithic Reforming Catalyst

Base Support: 400 cpi alumina-based



Coated Monolith: Incorporates NETL pyrochlore catalyst system

Tech Transfer Activities

2009 | **2010**

Catalyst Development

Strategy: Develop long-term test data for FC fuel reforming to share with developers & catalyst companies to encourage tech transfer, licensing and collaboration.

-Contract with Nextech for coated monoliths

-Collaboration w/PCI for microlith catalyst evaluation

-- Discussions w/Sud Cheme

Long-term Powder Data (NETL)

Monolithic Catalyst Test (NETL)

CRADA Commercial Partner (TBD)

Patent Application

Monolithic Catalyst Fab (Nextech)

PCI Microlith Evaluation

Reactor Demonstration

Strategy – Conduct demo through integrated biodiesel fuel cell test @ NETL.

-Possible evaluation w/Delphi and/or other interested developers

-Planned demonstration with PCI

Biodiesel FC Demo (NETL)

PCI Reactor Evaluation

Delphi / Other Evaluation?

FY 2009 Publications

Peer Reviewed Publications

D. Shekhawat, D. A. Berry, D. J. Haynes, J. J. Spivey, Fuel Constituent Effects on Fuel Reforming Properties for Fuel Cell Applications, *Fuel,* 88 (2009) 817-825.

D. J. Haynes, A. Campos, D. A. Berry, D. Shekhawat, A. Roy, J. J. Spivey, Catalytic Partial Oxidation of a Diesel Surrogate Fuel Using an Ru-Substituted Pyrochlore *Catalysis Today* (accepted).

D. Shekhawat, D. A. Berry, J. J. Spivey, 'Preface' for the special issue of Catalysis Today about Hydrogen Production for Fuel Cell Applications (Guest Editors), *Catalysis Today*, 136 (2008) 189.

D. J. Haynes, D. A. Berry, D. Shekhawat, J.J. Spivey, Catalytic Partial Oxidation of n-Tetradecane Using Pyrochlores: Effect of Rh and Sr Substitution, *Catalysis Today*, 136 (2008) 206-213.

FY 2009 Publications cont…

Conference Presentations w/Proceedings

D. J. Haynes, D. A. Berry, D. Shekhawat, M.W. Smith, J.J. Spivey, Catalytic Partial Oxidation of Diesel Surrogate Fuel Using Optimized Ni-Catalysts International Symposium on CATALYST DEACTIVATION, The Netherlands, Delft, October 25 - 28, 2009.

M.W. Smith, D. J. Haynes, D. A. Berry, D. Shekhawat, J.J. Spivey, Effect of oxide catalysts and oxygen-conducting supports on partial oxidation of liquid hydrocarbons**,** The 237th ACS National Spring Meeting, Salt Lake City, UT, March 22-26, 2009.

J. J. Spivey, D. J. Haynes, D. A. Berry, D. Shekhawat, Fuel Processing of n-Tetradecane: Catalytic Partial Oxidation on Rh- and Ru-Substituted Metal Oxides, *7th International Workshop on Catalytic Combustion*, Lake Zurich, Switzerland, Sep 29-Oct 1, 2008.

FY 2009 Publications cont…

Conference Presentations

D. J. Haynes, D. A. Berry, D. Shekhawat, M.W. Smith, J.J. Spivey, Catalytic Partial Oxidation of a Surrogate Diesel Fuel Mixture Using Pyrochlores: Effect of Reforming Metal, 2009 AIChE Spring National Meeting, Tampa, FL, April 26-30, 2009.

M. W. Smith, D. J. Haynes, D. A. Berry, D. Shekhawat, J.J. Spivey, Effect of catalyst layer formation and character on partial oxidation of liquid hydrocarbons in the presence of oxygen-conducting supports, 2009 AIChE Spring National Meeting, Tampa, FL, April 26-30, 2009.

J. J. Spivey, D. J. Haynes, D. A. Berry, D. Shekhawat, M.W. Smith, Hydrogen Production from the Catalytic Reforming of Hydrocarbons, *2009 Gordon Research Conference on Hydrocarbon Resources*, Ventura, CA, January 11-16, 2009.

FY 2009 Publications cont…

Posters

D. J. Haynes, D. A. Berry, D. Shekhawat, M.W. Smith, J.J. Spivey, Catalytic Partial Oxidation of n-Tetradecane over Rh Substituted Pyrochlores: Effect of A-site Substitution, 21st North American Catalysis Society Meeting, June 7-12, 2009, San Francisco, CA.

M.W. Smith, D. J. Haynes, D. A. Berry, D. Shekhawat, J.J. Spivey, Reforming Liquid Hydrocarbons with Ni-substituted Barium Hexaaluminates: Effect of Oxygen-conducting Support, 21st North American Catalysis Society Meeting, June 7-12, 2009, San Francisco, CA.

FY 2009 Publications cont…

Patents

D. A. Berry, D. Shekhawat, D. J. Haynes, M.W. Smith, J. J. Spivey, Pyrochlore Materials for Chemical Reaction Systems, Patent Disclosure, April 14, 2009.

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Acknowledgements

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- Dushant Shekhawat
- Daniel Haynes
- Mark Smith
- Don Floyd
- Mike Bergen
- Jerry Spivey (LSU)