NETL

NATIONAL ENERGY TECHNOLOGY LABORATORY

Structured Oxide-Based Reforming Catalyst Development

12^{th} Annual SECA Workshop, Pittsburgh, PA

July 28, 2011

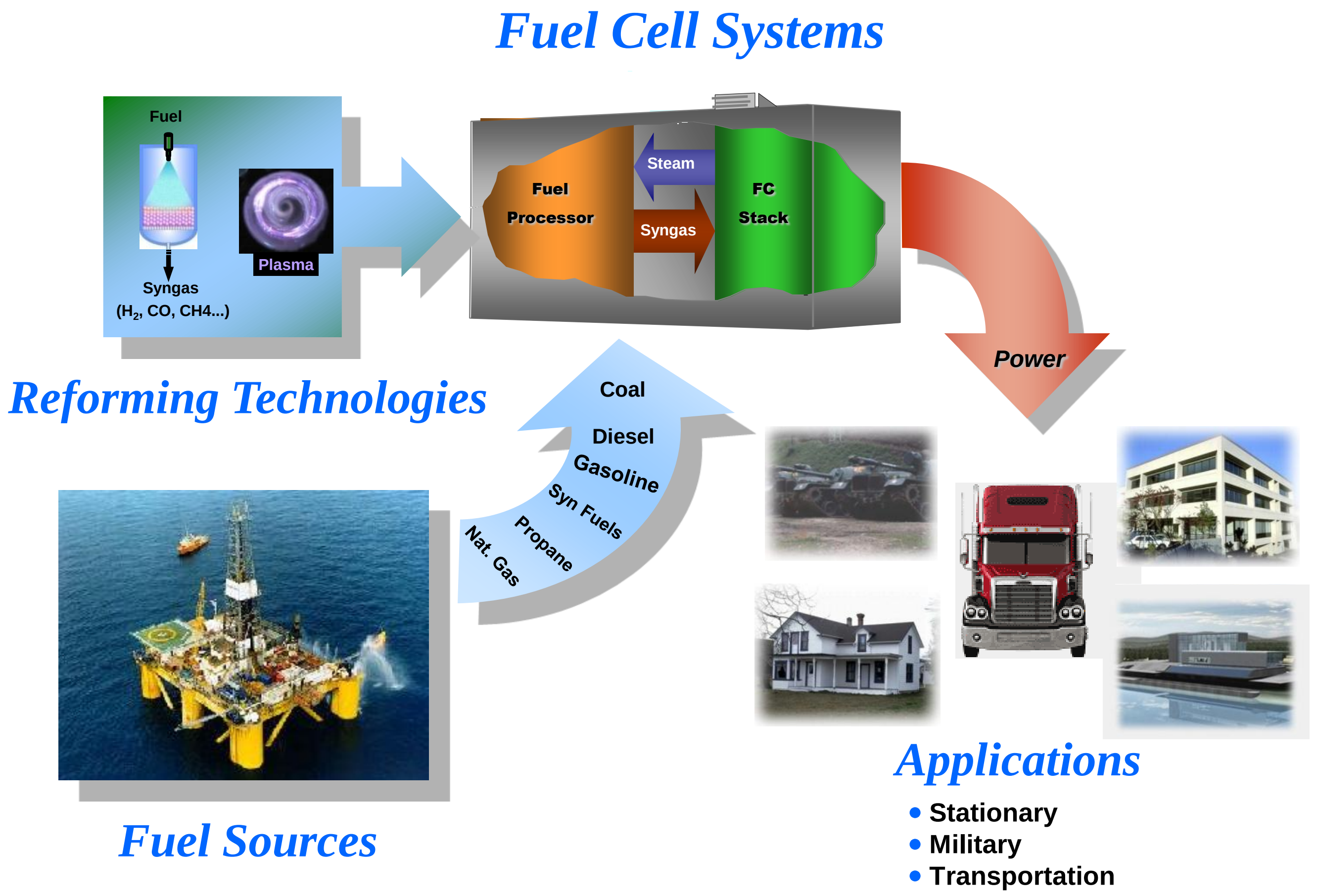
U.S. DEPARTMENT OF ENERGY

Presentation Outline

- Introduction
  - Objectives
  - Technical objectives / challenges
  - Experimental
- Pyrochlore Catalyst Development
  - Pyrochlore/Oxygen-conducting support
  - Long-term testing
- Monolith Development
  - Testing
  - Characterization
- Graded Bed Approach
- Conclusions
- Tech Transfer

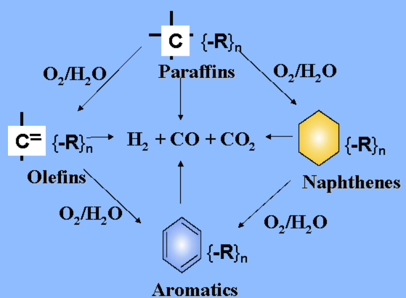
Introduction

- **Reform hydrocarbons into H_2 and CO-rich gas stream for solid oxide fuel cell (SOFC) applications**

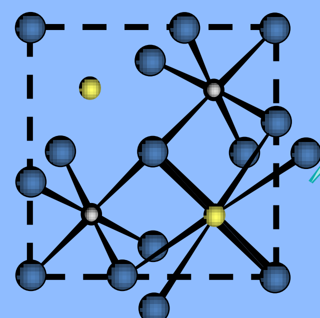


Primary Goal

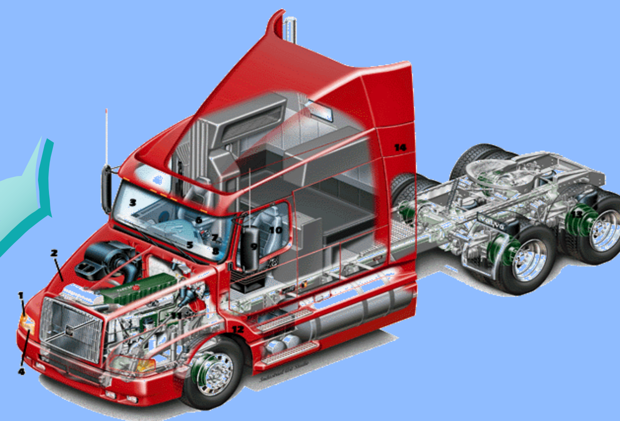
Identify, evaluate and/or develop viable hydrocarbon fuel processing technologies for high temperature solid oxide fuel cells being supported in the NETL SECA program through fundamental understanding, research, and technology demonstration.



Fuel



Technology

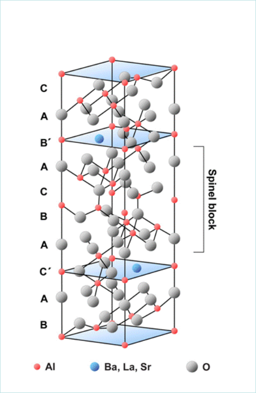


End Use

Two Project Areas

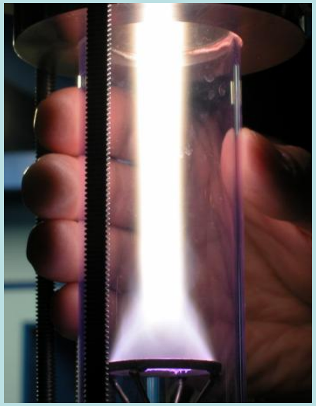
Oxide-Based Catalyst Systems:

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



Advanced Reforming Concepts:

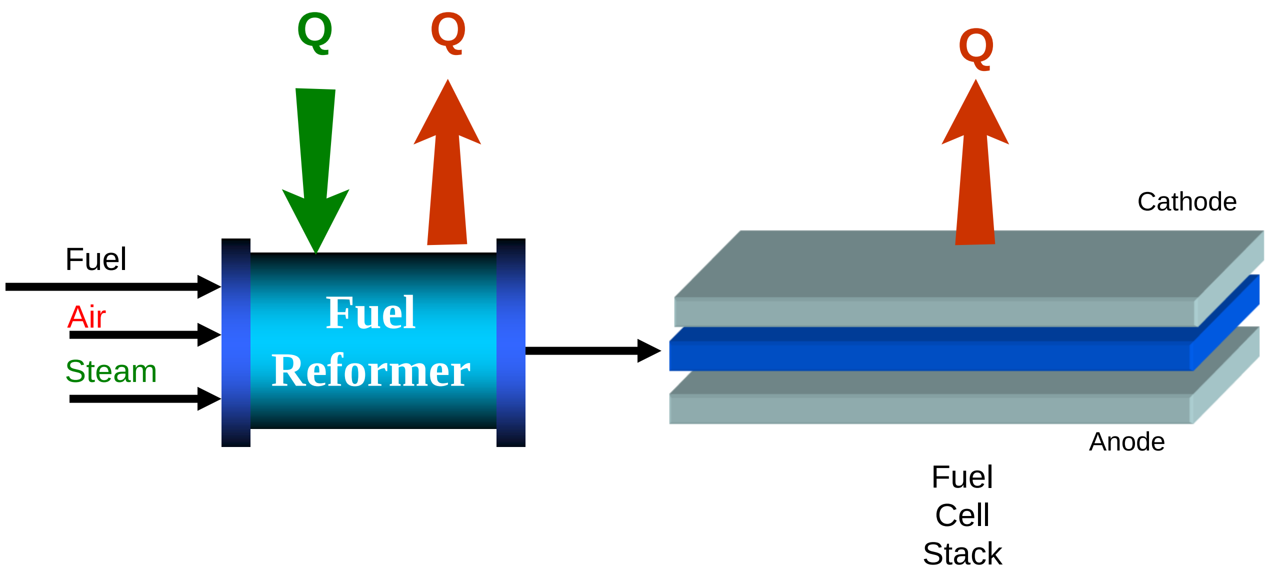
Identify and evaluate alternative non-catalytic and/or catalyst assisted processes to overcome deactivation of traditional catalytic fuel reforming of higher hydrocarbon fuel compounds.



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

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

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 require too high temperatures. 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 & naphtha.

- **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.

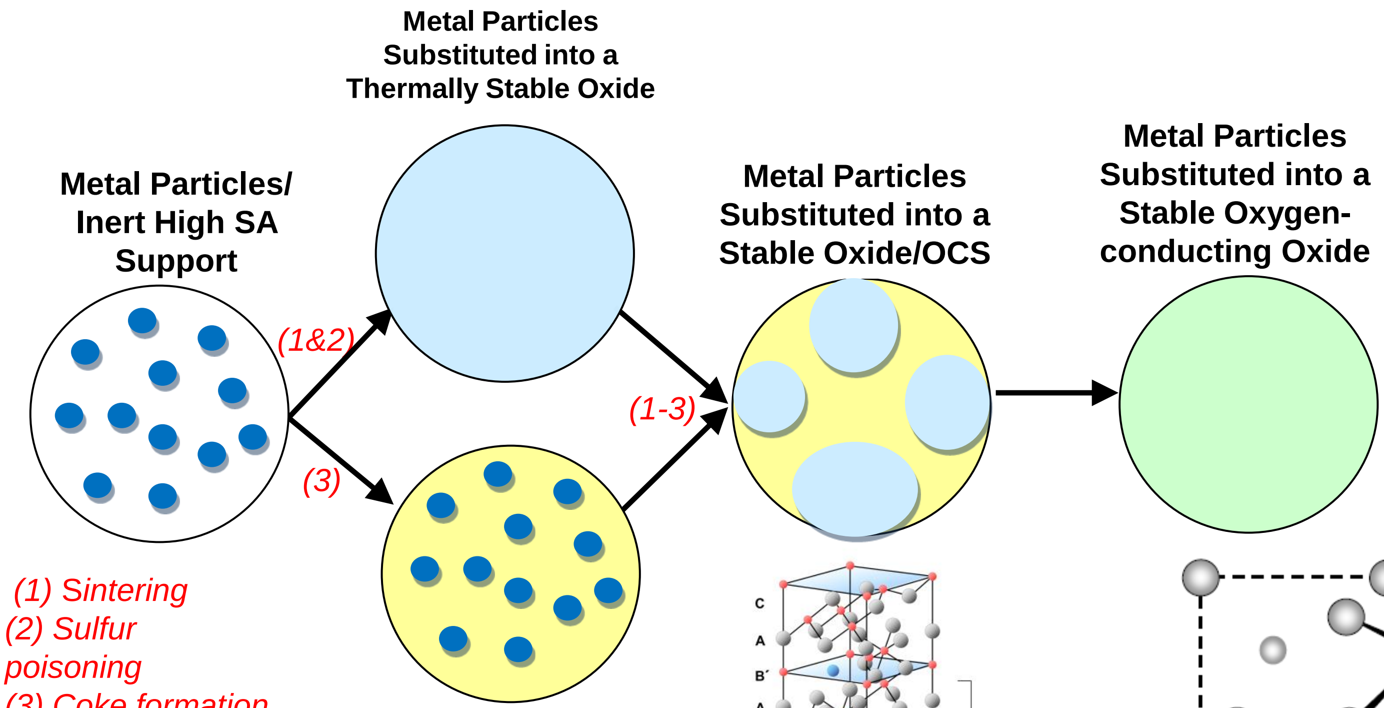
PYROCHLORE CATALYST DEVELOPMENT

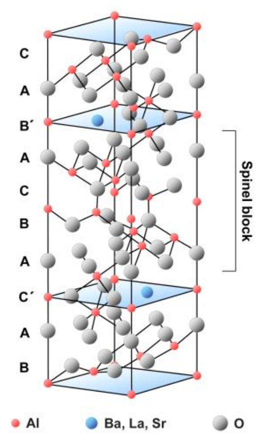
Previous Reforming Studies

What we have learned:

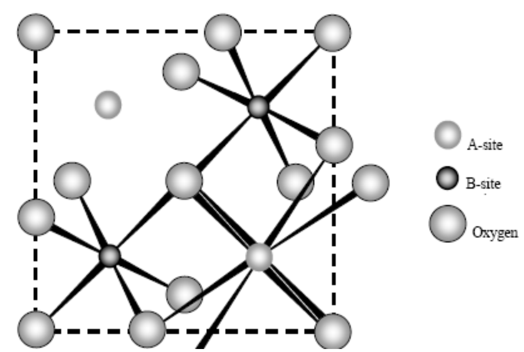
- Bulk metal deposited catalysts susceptible to carbon formation and sulfur poisoning.
- Adsorption of sulfur and carbon are structure sensitive.
- Well-dispersed active reaction sites exhibit better tolerance to sulfur and carbon deactivation.

Evolution of NETL Reforming Catalyst System



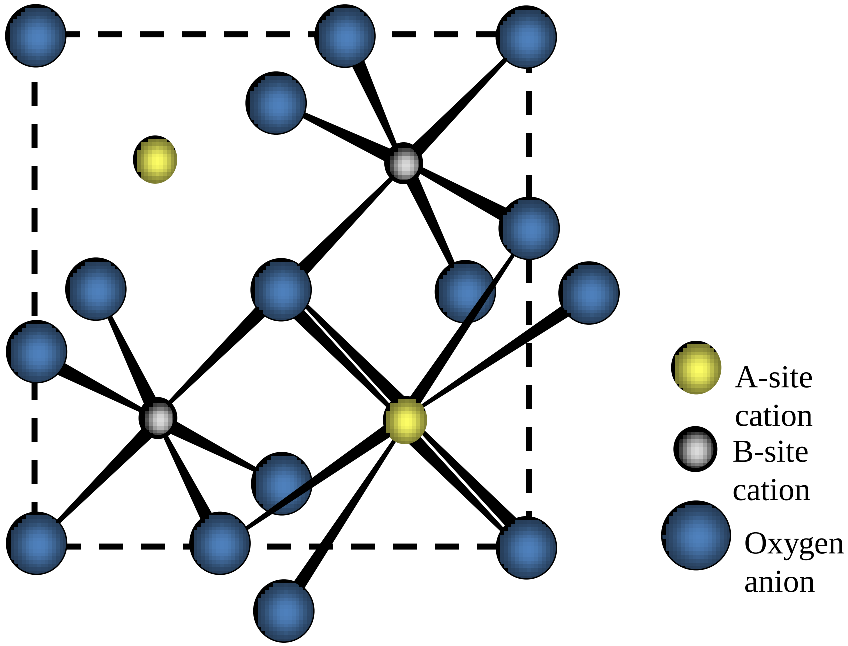


Hexaaluminate - $ABAl_{12}O_{19}$



Pyrochlore - $A_2B_2O_7$

Oxide-based Catalyst Systems (Pyrochlores)

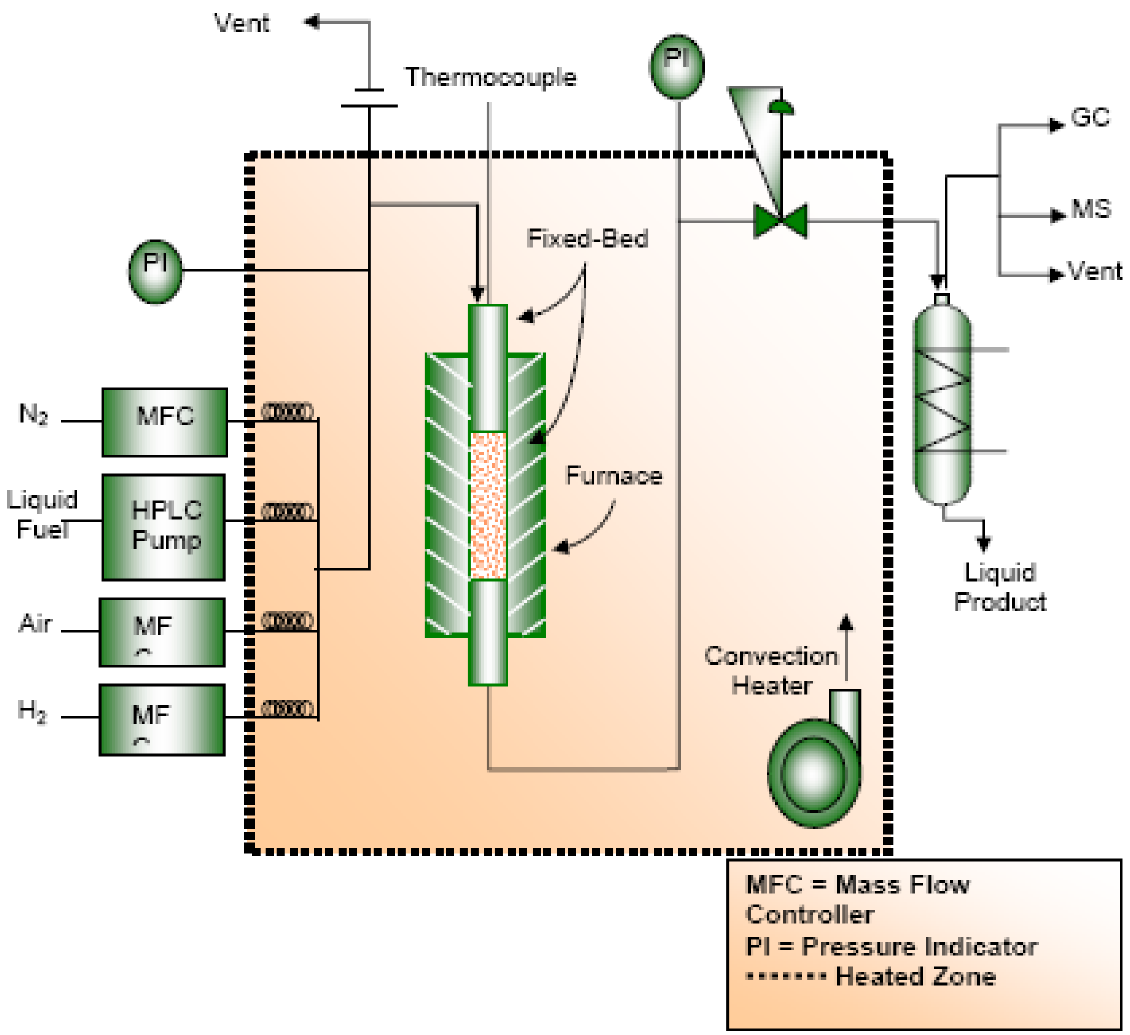


Pyrochlores ($A_2B_2O_7$) are viable reforming catalysts because they exhibit:

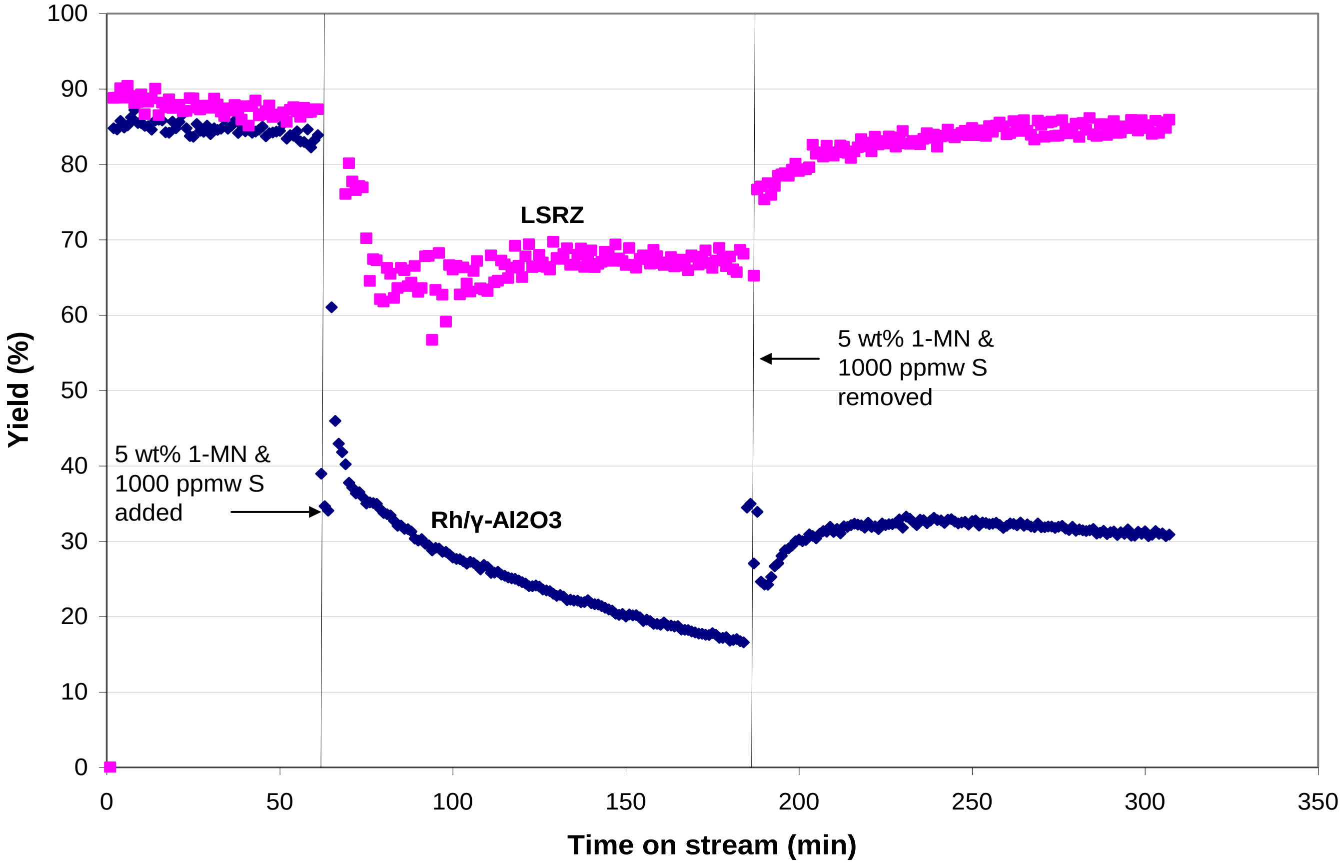
- High chemical and thermal stability [1]
- Mechanical strength to accommodate substitutions [2]
- Active metal can be substituted into B-site to improve catalytic activity
- Substitution with lower valence elements in A-site and B-site can create oxygen vacancies, which may increase lattice oxygen-ion mobility to reduce carbon formation.

[1] D. Sedmidubsky, et al., The Journal of Chemical Thermodynamics 37 (2005) 1098.
[2] H. Zhou, et al., Journal of Alloys and Compounds 438 (2007) 217

Micro-Reactor Setup



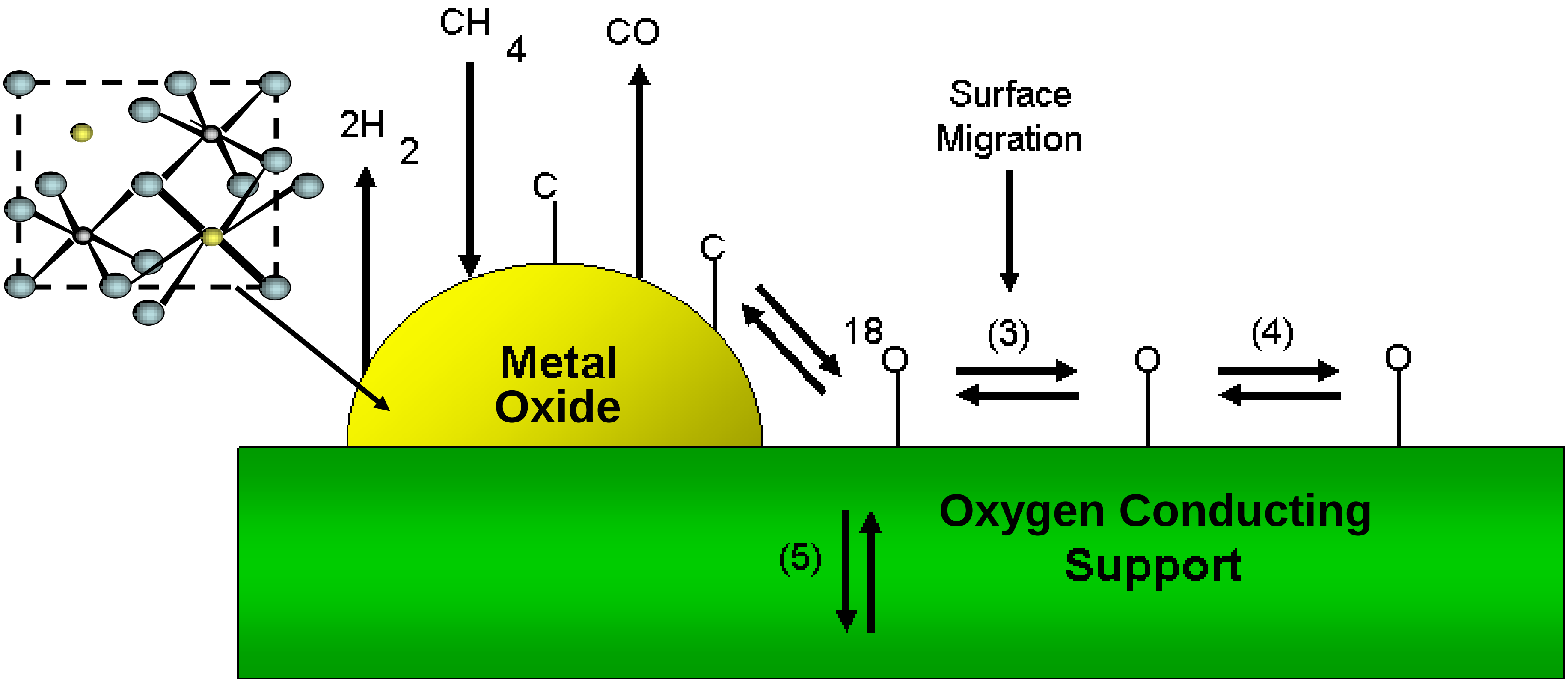
Pyrochlore for POx of Diesel Surrogate



Experimental conditions T=900 C, P= 0.25 MPa, GHSV= 50,000 sccm/g-hr

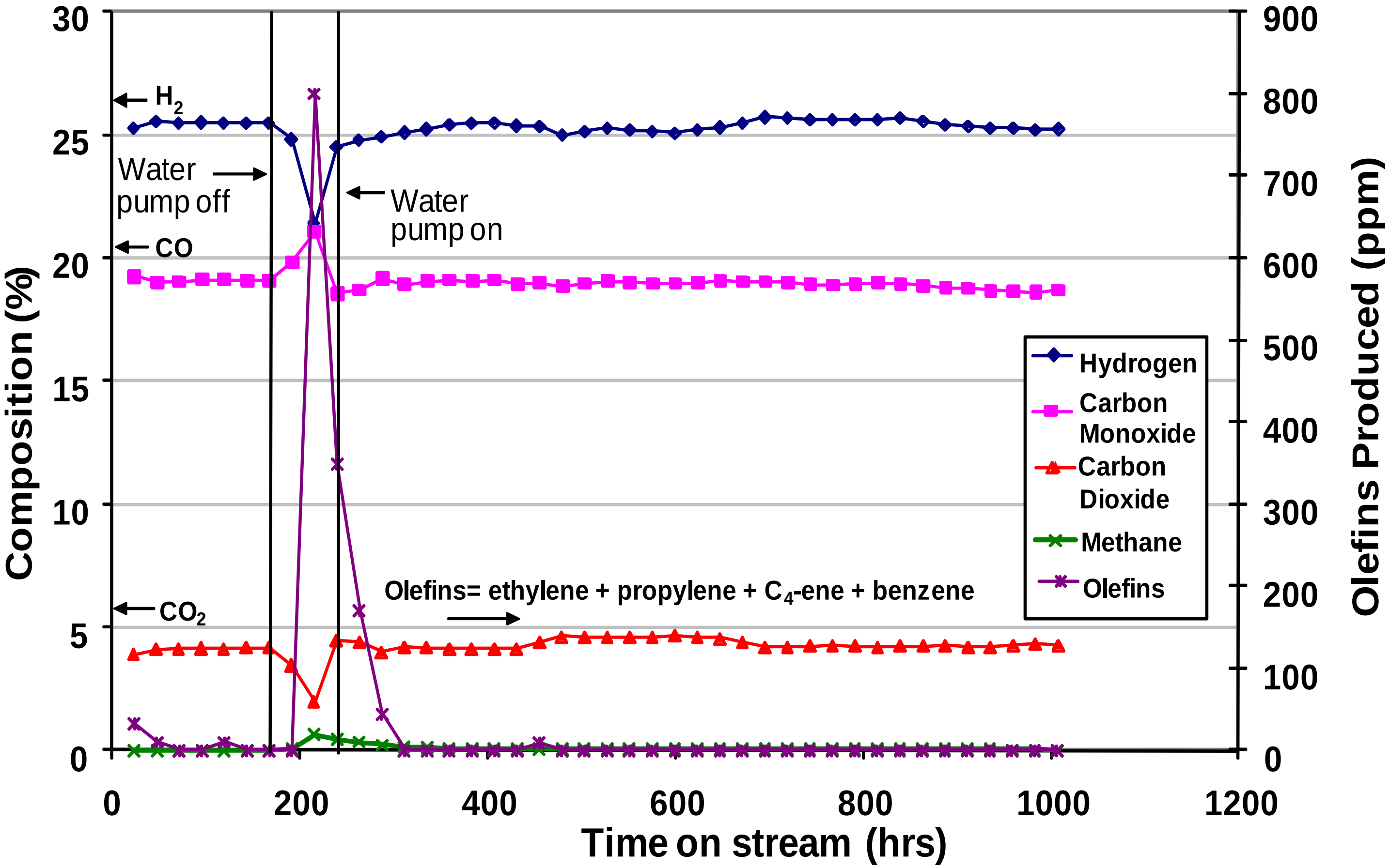
A **conductive oxide-based catalyst** was doped with 1% Rh along with a SOA Rh catalyst on alumina. After exposure to a severely carbon producing fuel compound, the oxide-based catalyst performance remained stable, while the non-conducting supported catalyst deactivated significantly.

Oxide Catalyst on Oxygen-Conducting Supports



1000-hr Demonstration of Pyrochlore Catalyst for Oxidative Steam Reforming of Pump Diesel

- ✓Fully reformed local pump diesel
- ✓ Equilibrium syngas yields achieved
- ✓Survived multiple system upsets
- ✓ O/C=1, H_2O/C=0.5, T=900 C, P= 0.25 MPa, SV= 25,000 sccm/g-hr

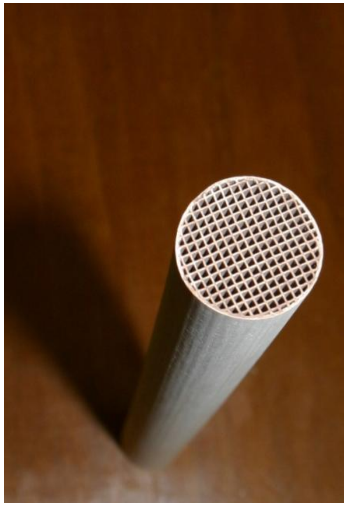


MONOLITH DEVELOPMENT

Diesel Fuel Reforming using Pyrochlore Catalyst

Collaboration with Industrial Partners

NETL's Pyrochlore Catalyst in Powder Form



Monolith Coated by NexTech

Microlith® Technology by PCI

- **Fabrication of Catalyst into a Commercially Viable Structure**
- Powder Catalyst Validation:
  - Activity tests; TPO (carbon formation)
  - Bulk characterization – ICP, XRD
  - Surface characterization – XPS, TPR, H2-chemisorption
- Characterization and Testing on Coated Monolith

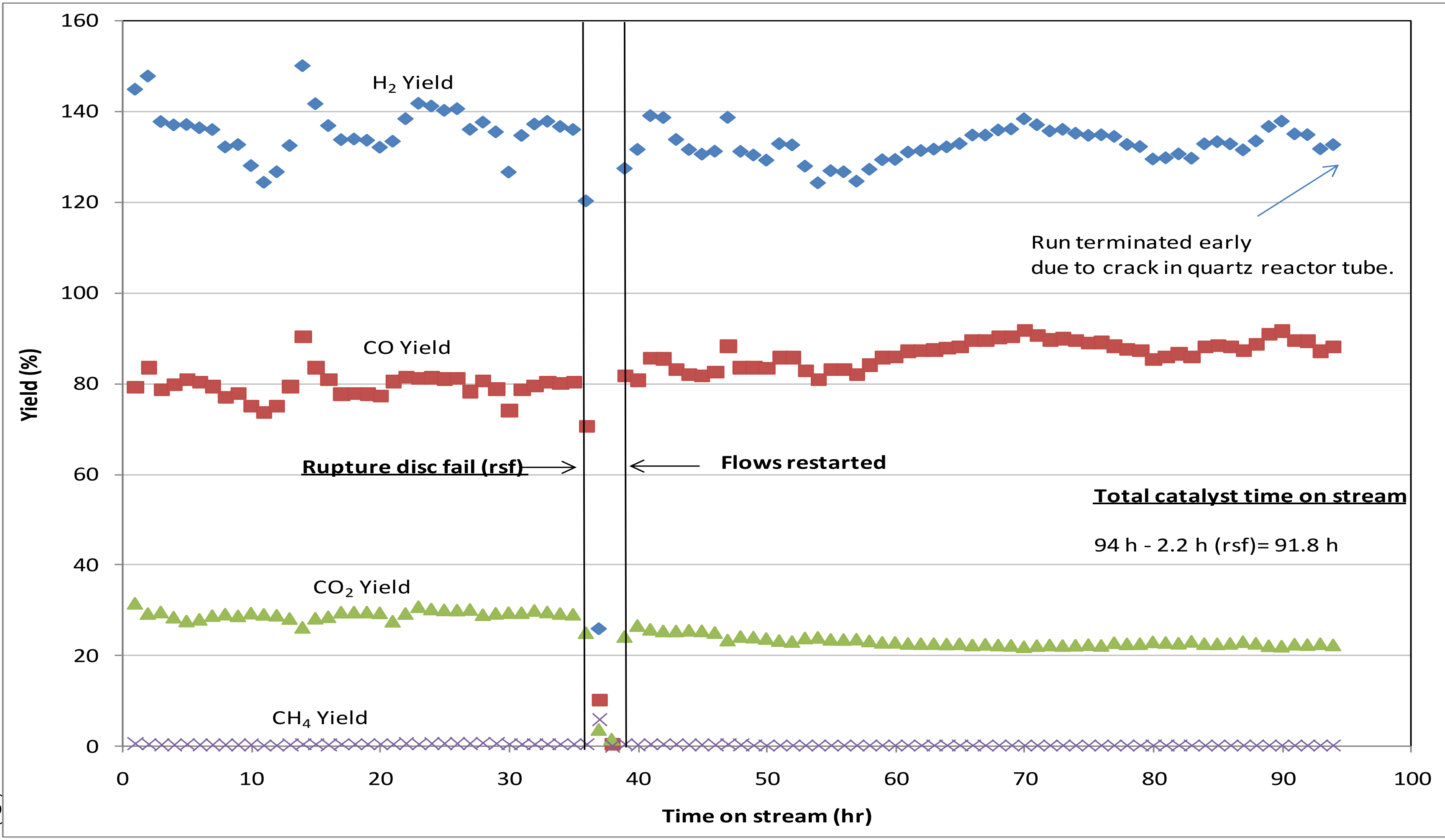
Monolith Reactor Coated with Pyrochlore Catalyst

- NETL-developed Pyrochlore catalyst deposited onto alumina monolith with oxygen-conducting interlayer
- Coated using proprietary method by Nextech Materials, Inc.

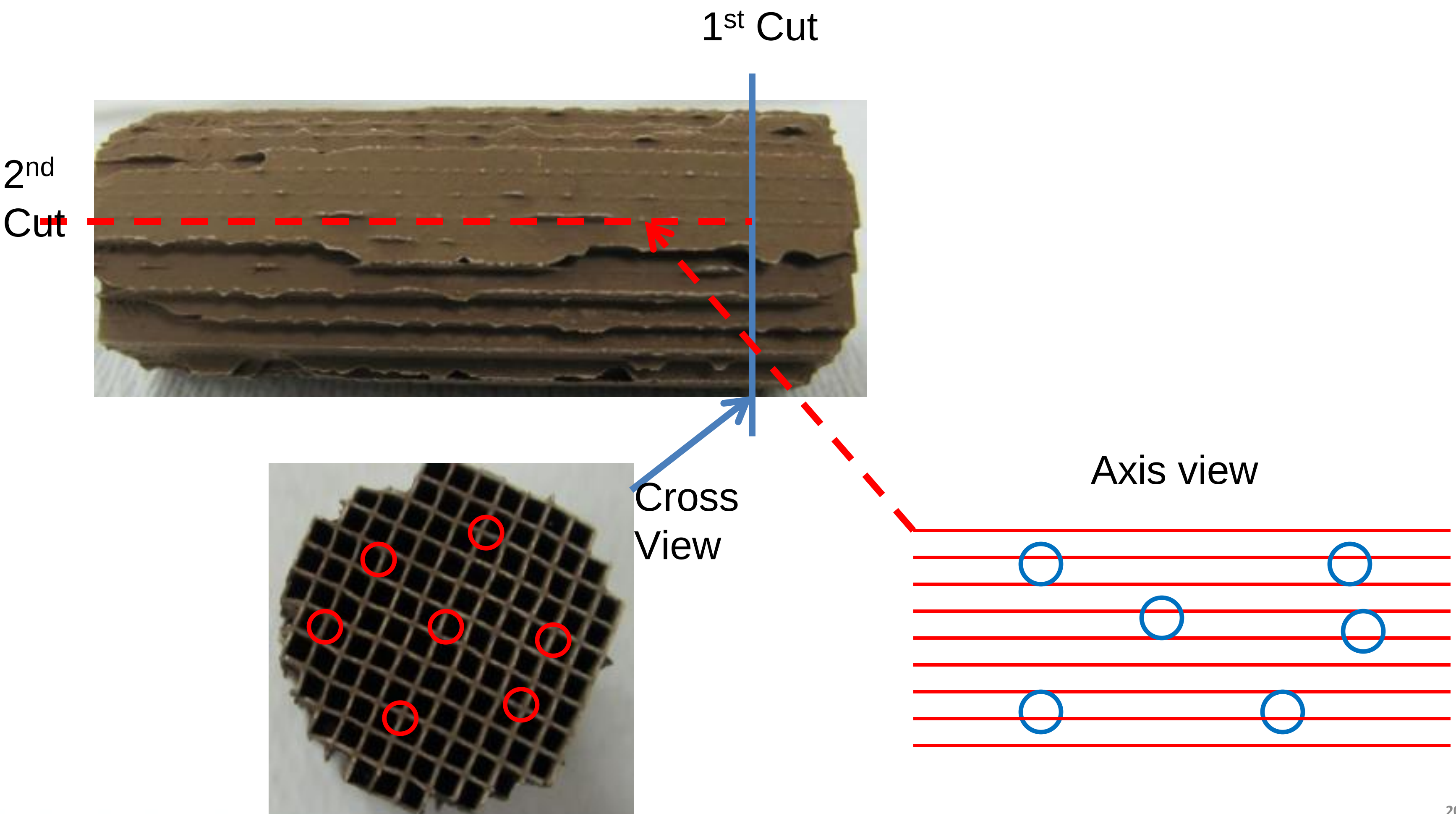
Recent Monolith 100 hr Test

Oxidative Steam Reforming of Commercial Diesel

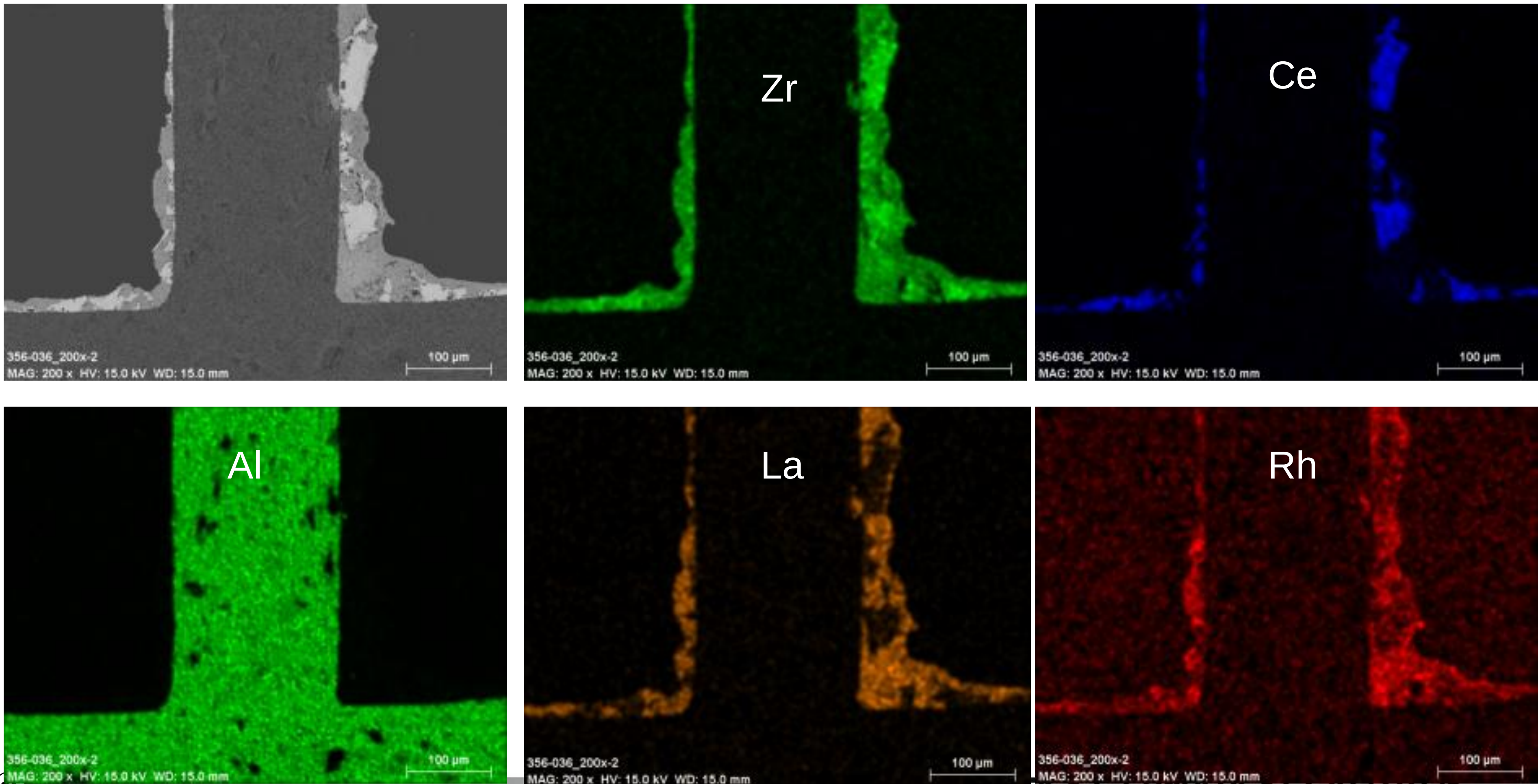
O/C=1, H_2O/C=0.5, T=900 C, P= 0.25 MPa, SV= 20,000 sccm/g-hr



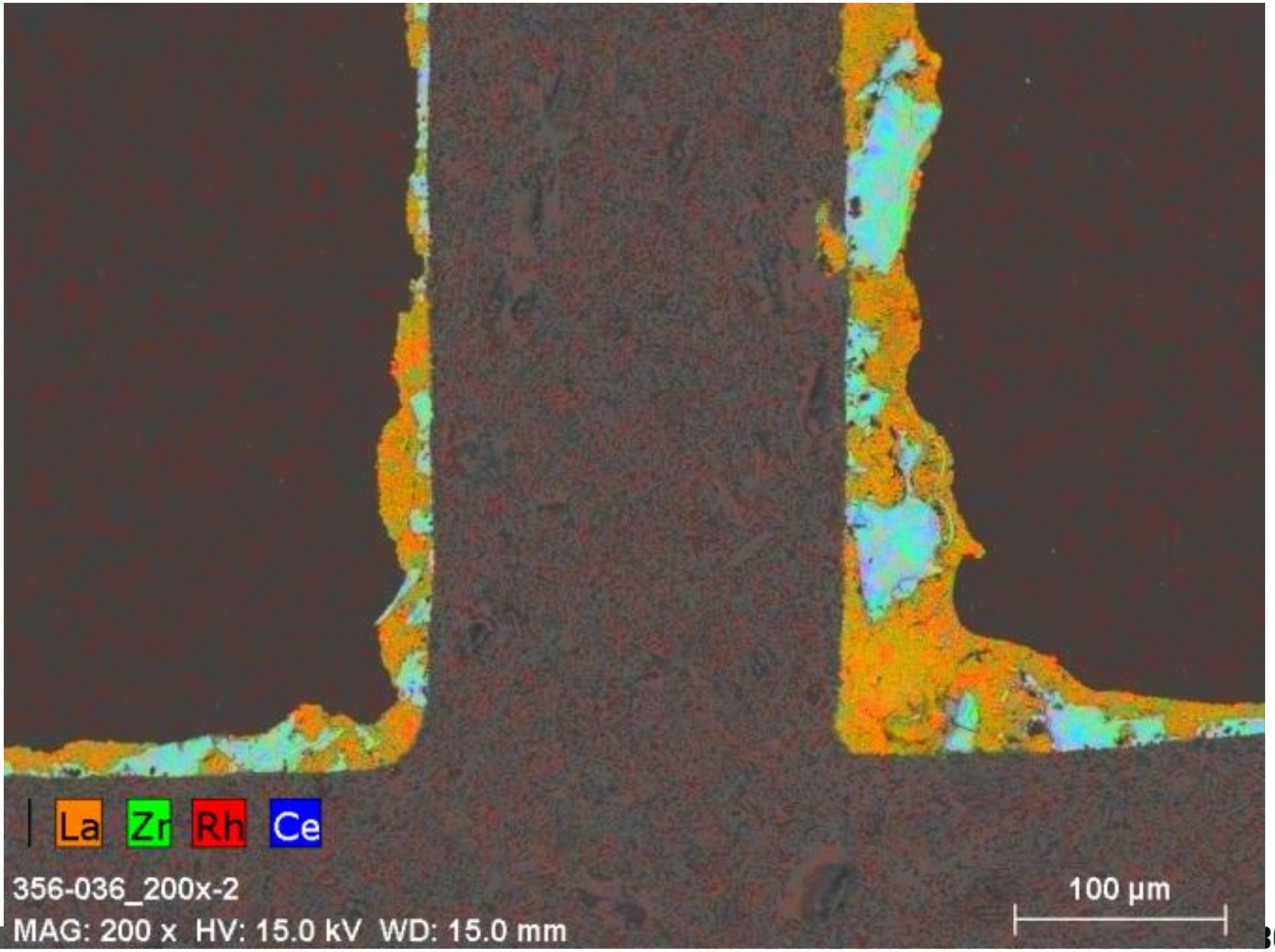
Monolith Characterization
Monolith Cutting



Monolith Characterization
Dot Map Analysis

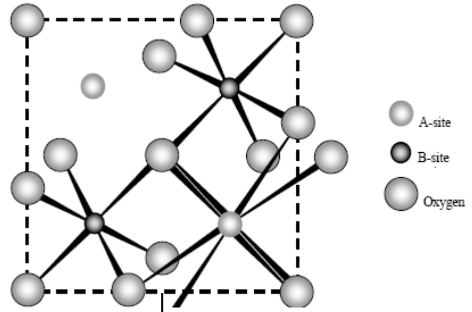


Monolith Characterization
Dot Map Analysis



COMMERCIALIZATION: SYNTHESIS METHOD DEVELOPMENT

Pyrochlore Synthesis Methods



Pyrochlore - $A_2B_2O_7$

Pechini (NETL)

•Good for small scale (lab)

•Results in well-mixed, uniform catalyst

•Most active material (1000 hr catalyst)

• Economic scale-up?

Hydrothermal

•Can produce larger batch size.

•Not able to get Rh into pyrochlore structure.

•Activity not as good as Pechini.

Solid State Mixing

• Economical for large batches.

•Requires high temperatures and long firing times to form pyrochlore.

•Catalyst uniformity a potential issue.

Combustion Method

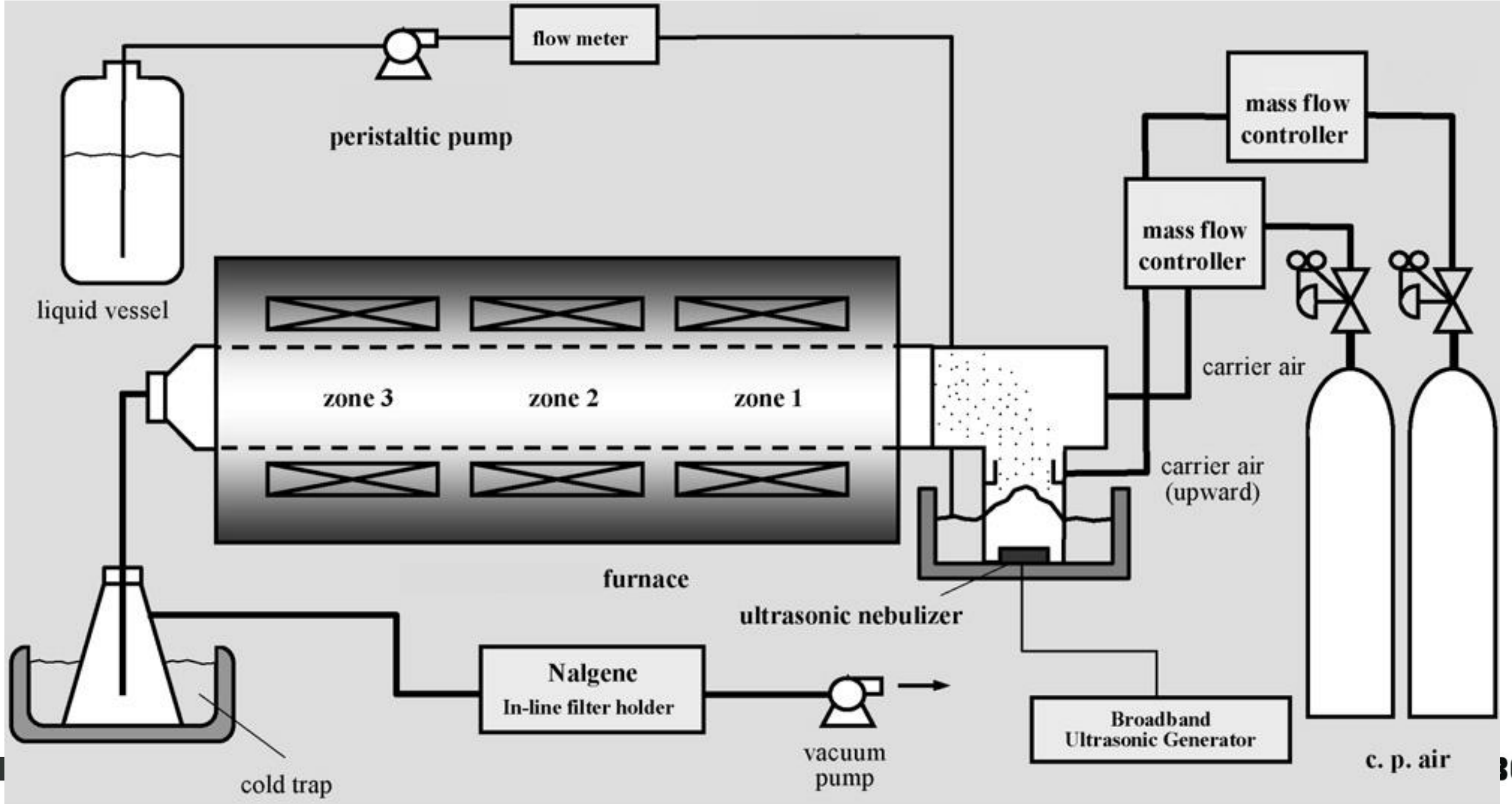
•Potential for continuous high throughput.

•Material produced should be similar to Pechini.

•Under development

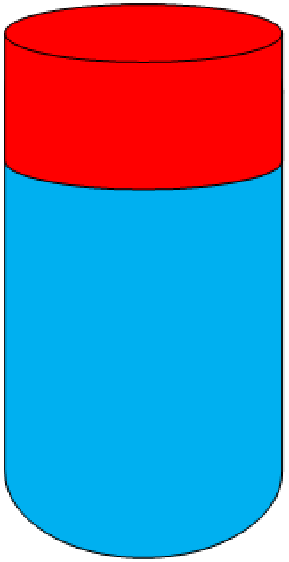
Combustion Synthesis Method

- Produces fine powders
  - Inexpensive
  - Potentially Continuous
  - Operates at atmospheric pressure
- Precursor drops undergo **three major steps**
  - **(1)** drop size shrinkage due to evaporation,
  - **(2)** conversion of precursor into oxides
  - **(3)** solid particle formation.



GRADED-BED APPROACH

CPOX Indirect Mechanism



$$CH_4 + O_2 \rightarrow xCO_2 + 2xH_2O + (1-x)CH_4; \Delta H < 0$$

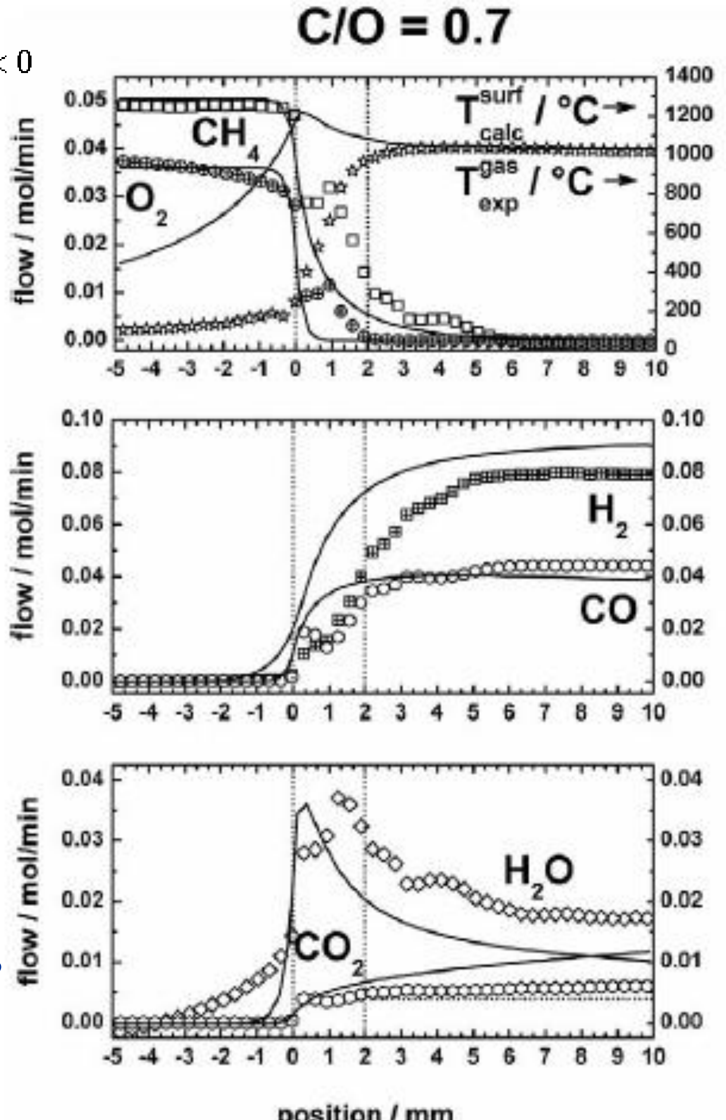
Total Oxidation

$$CH_4 + H_2O \rightarrow CO + 3H_2; \Delta H > 0$$

Steam Reforming

$$CH_4 + CO_2 \rightarrow CO + H_2; \Delta H > 0$$

CO_2 Reforming



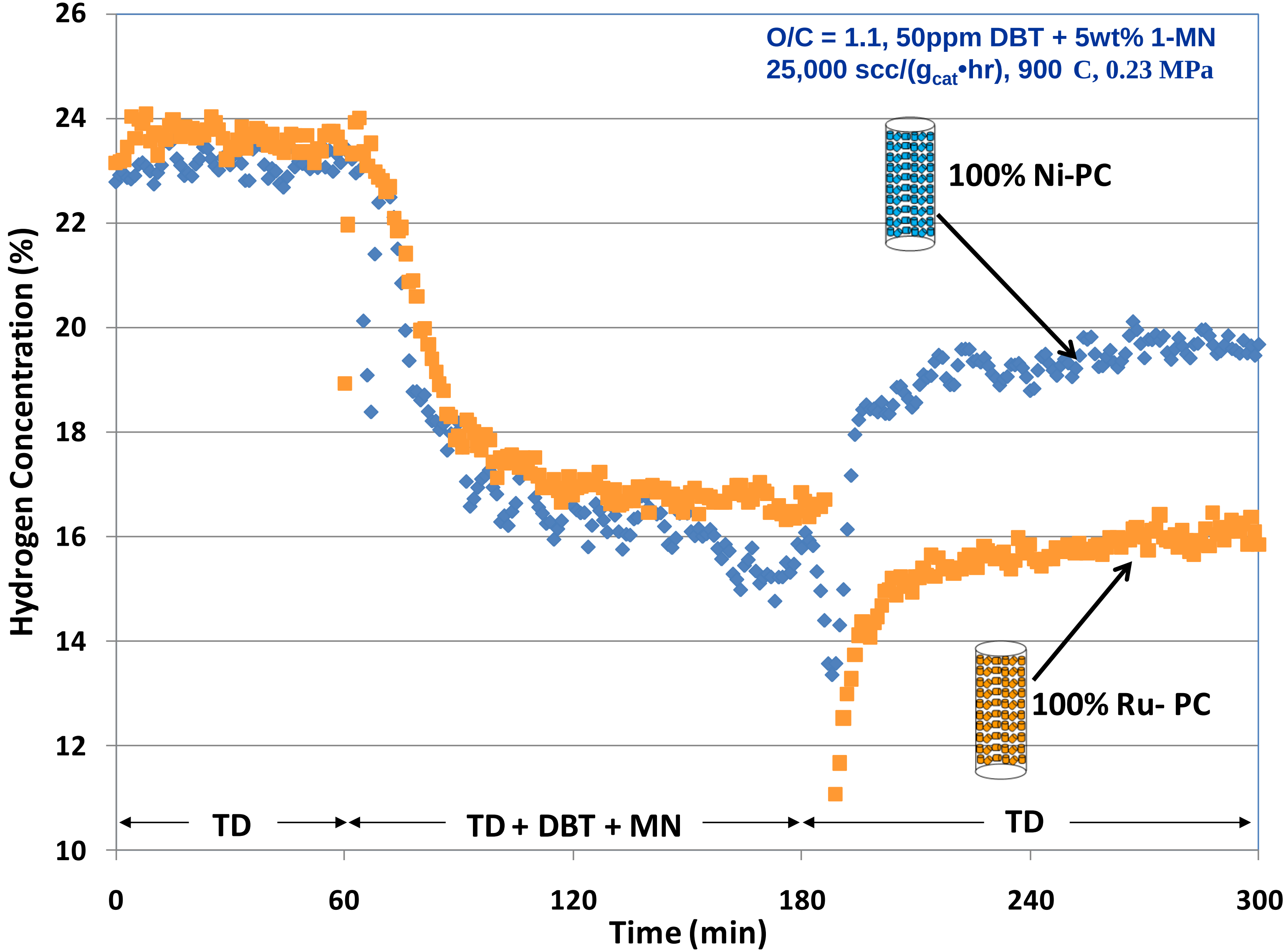
M.W. Smith, D. Shekhawat, Catalytic partial oxidation, Fuel Cells: Technologies for Fuel Processing, Chapter 5, p. 73-128, Elsevier, Amsterdam, June 2011.

R. Horn et al., Journal of Catalysis 242 (2006) 92–102.

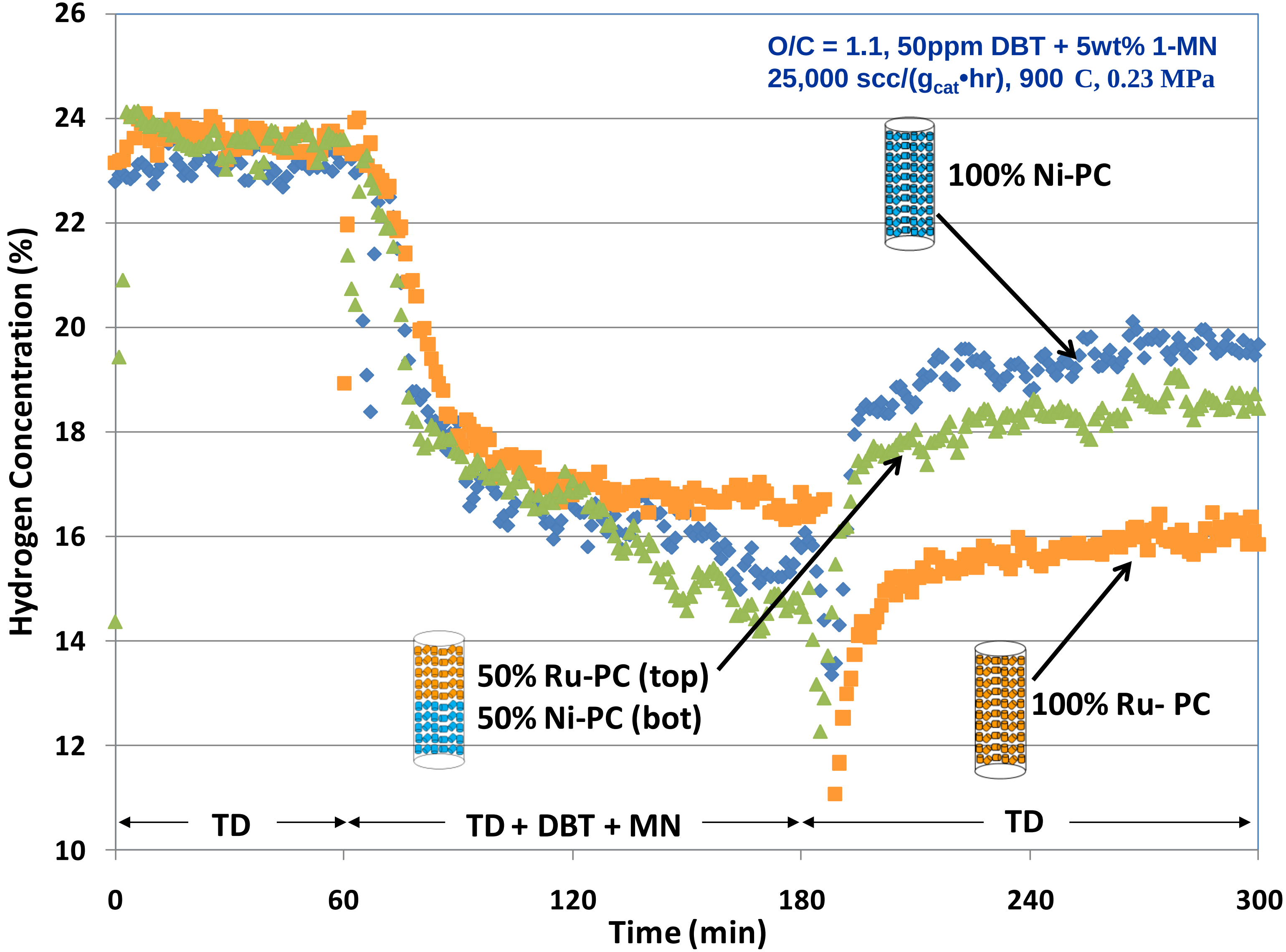
Reforming Catalyst Study

- **Partial oxidation of *n*-tetradecane (TD) in presence of sulfur and aromatics**
  - 1hr pure TD
  - 2hrs TD + 50ppmw S as DBT + 10%wt. 1-MN
  - 2hr pure TD
- **Total bed carbon (TBC) formation study**
  - Temperature Programmed Oxidation (TPO)
  - 200 C to 900 C at ramp of 1 C/min

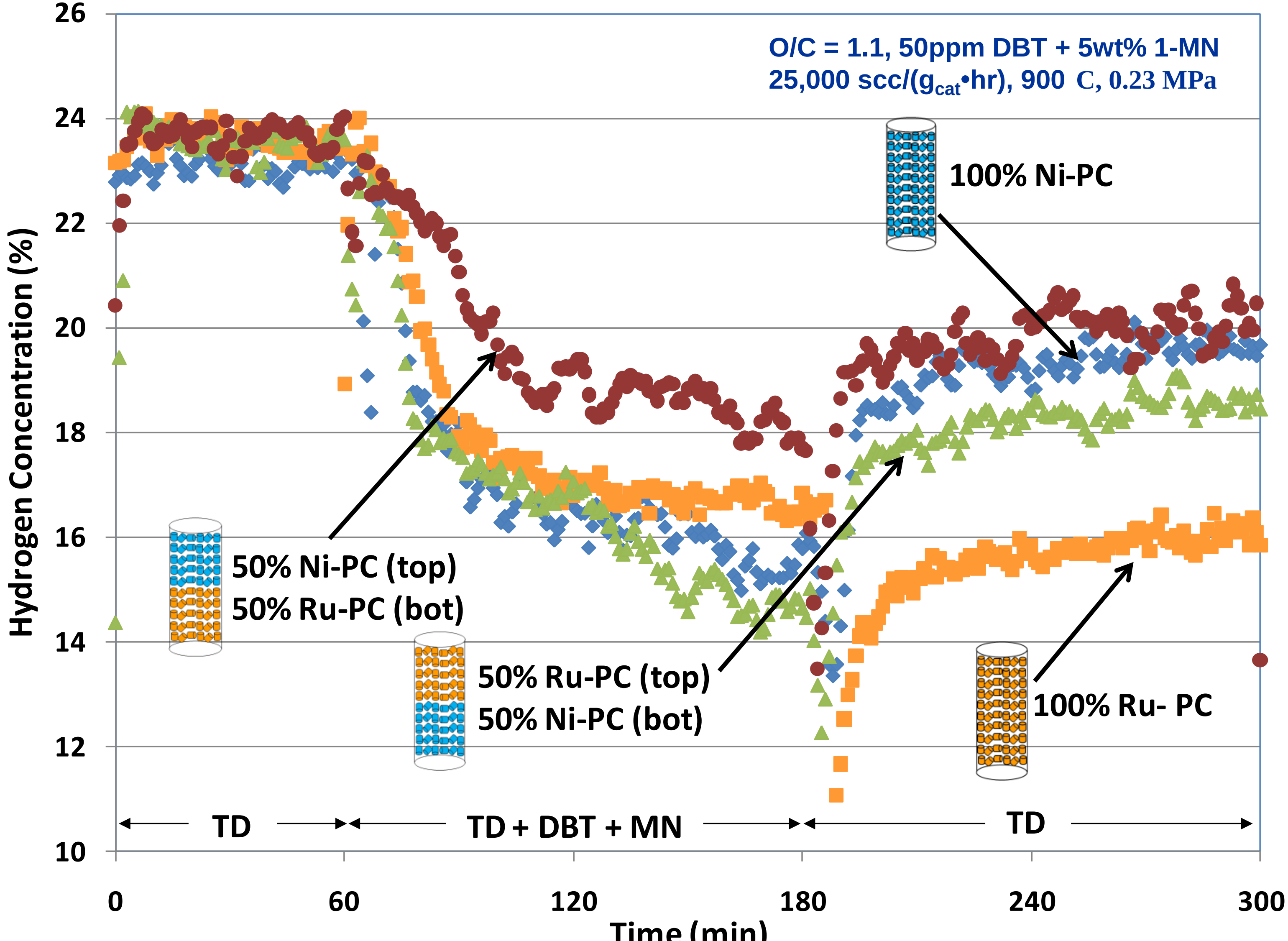
Results: Ni3-PC:Ru1-PC



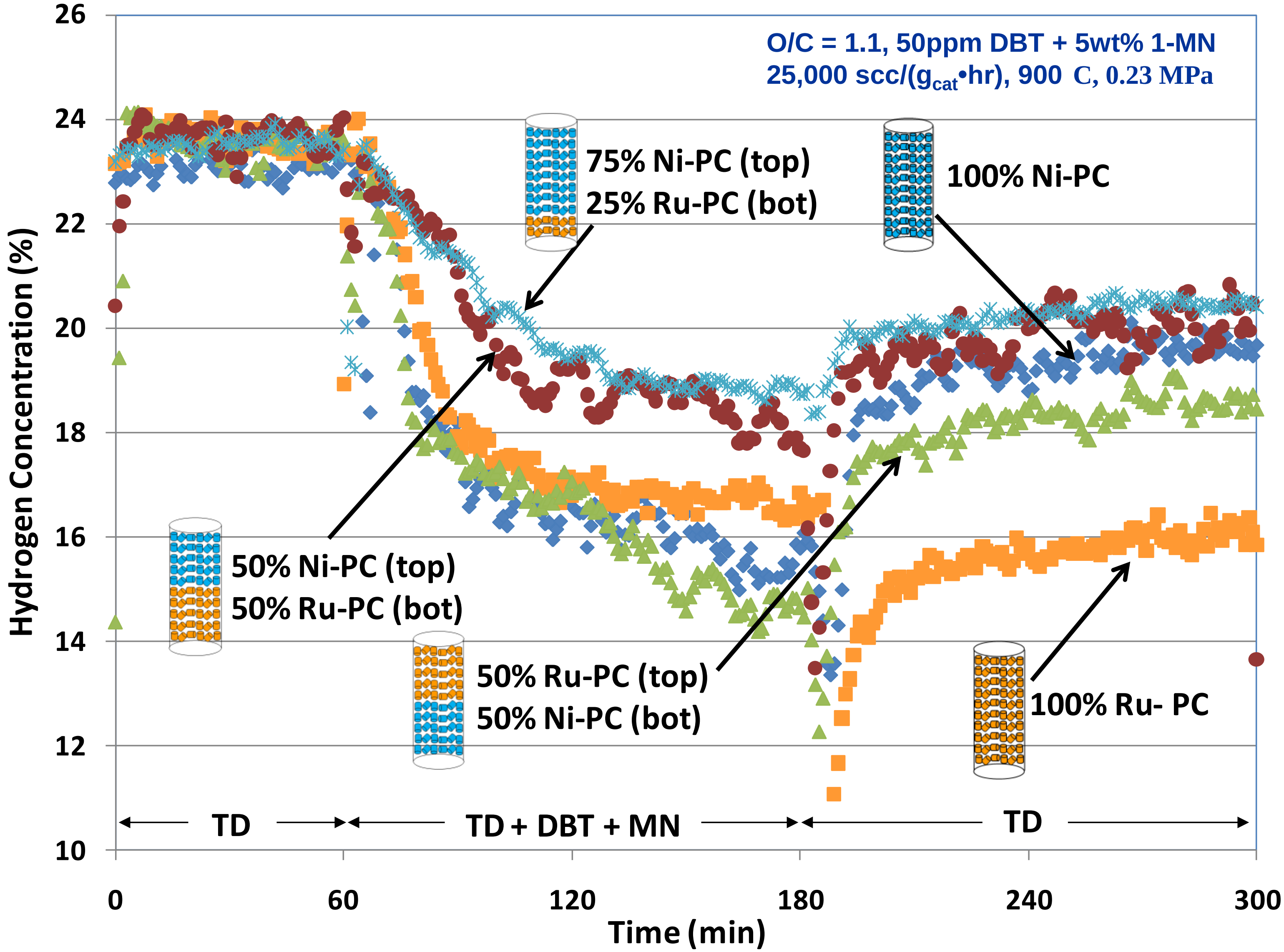
Results: Ni3-PC:Ru1-PC



Results: Ni3-PC:Ru1-PC



Results: Ni3-PC:Ru1-PC



Results: Ni3-PC:Ru1-PC
Carbon Formation

Top (%) / Bottom (%)	Total Carbon (g)	Predicted* Carbon (g)
100% Ni3-PC	1.12	--
100% Ru1-PC	0.59	--
50% Ru1-PC/ 50% Ni3-PC	0.75	0.86
50% Ni3-PC/ 50% Ru1-PC	0.82	0.86
75% Ni3-PC/ 25% Ru1-PC	0.72	0.99

***Calculated from Total Carbon measured for 100%Ni-PC and Ru-PC**

Predicted value calculated from TPO of single-composition bed runs:
Total Carbon Predicted = $Weight_{Cat1}$ X Total $Carbon_{Cat1}$ + $Weight_{Cat2}$ X Total $Carbon_{Cat2}$

Summary/Conclusions

- **SOFC-based APUs for commercial diesel trucks is an excellent market entry technology**
  - Reforming catalyst with long-term stability and performance is critical for successful demonstration of transportation application
- **Optimized pyrochlore catalyst applied to commercially representative structured supports**
  - Preliminary performance of catalyst monolith was demonstrated on pump diesel under oxidative steam reforming condtions
- **Characterization of the monolith revealed channel coating is not uniform or evenly distributed.**
  - Catalyst was covered by ZDC and vice versa (not exposed to gas phase)
- **Noble metal (Rh) content may be reduced using the graded catalyst bed approach**
- **Ni-based catalysts deactivate more rapidly in the bottom region of the catalyst bed**
- **Best combination of catalysts may be Ni- and Rh-substituted pyrochlores, to be examined next**

Acknowledgements

- SECA
- NexTech Materials
- Pyrochem Catalyst Corp.
- Precision Combustion Inc.

Pyrochem Catalyst Company

- Pyrochem Catalyst Company (PCC) formed to commercialize novel NETL catalyst – 1st spin-off company of NETL generated IP.
- PCC holds an exclusive worldwide license to two NETL patents applications
- Company objective is to further develop and commercialize the NETL pyrochlore catalyst.
- Starting to work with end users (fuel cell & reformer companies) to understand customer needs
- Interfacing with catalyst companies for manufacture of the technology.
- Experienced management team in place with cleantech, catalyst and materials science domain expertise

Founders/Management Team

- **Steve Gallo – Chairman and CEO**
  - Electronic materials/component industry depth
  - Fuel cell domain / industry experience
- **Jeffery Harrison – President and COO**
  - 17 years in the energy industry
  - Oil, gas and biomass catalytic conversions
  - Expertise in start-ups (RightStart Business Enterprises)
- **Dave Berry – NETL Scientist**
  - Lead Inventor of catalyst technology
  - 25 years in energy-related R&D
  - Division Research Director at NETL/DOE
  - Specialization in fuel cells and catalysis

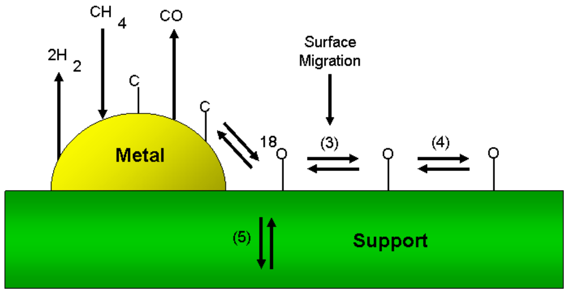
Contact: sgallo@pyrochemcatalyst.com
jbharrison@pyrochemcatalyst.com

Other Slides

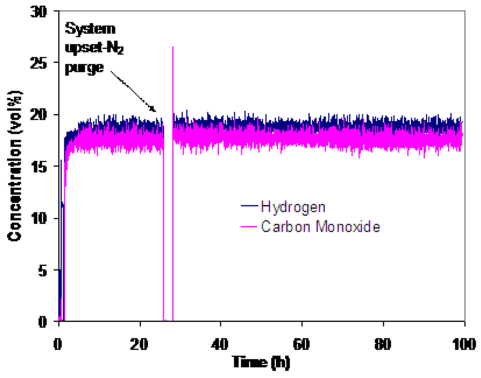
- - Company objective is to further develop and commercial the NETL pyrochlore catalyst.
- - Starting to work with end users (fuel cell & reformer companies) to understand customer needs
- - Interfacing with catalyst companies for manufacture of the technology.
- - Assessing applications (transportation, stationary, DOD...) for support and development opportunities

Project Objectives - Approach

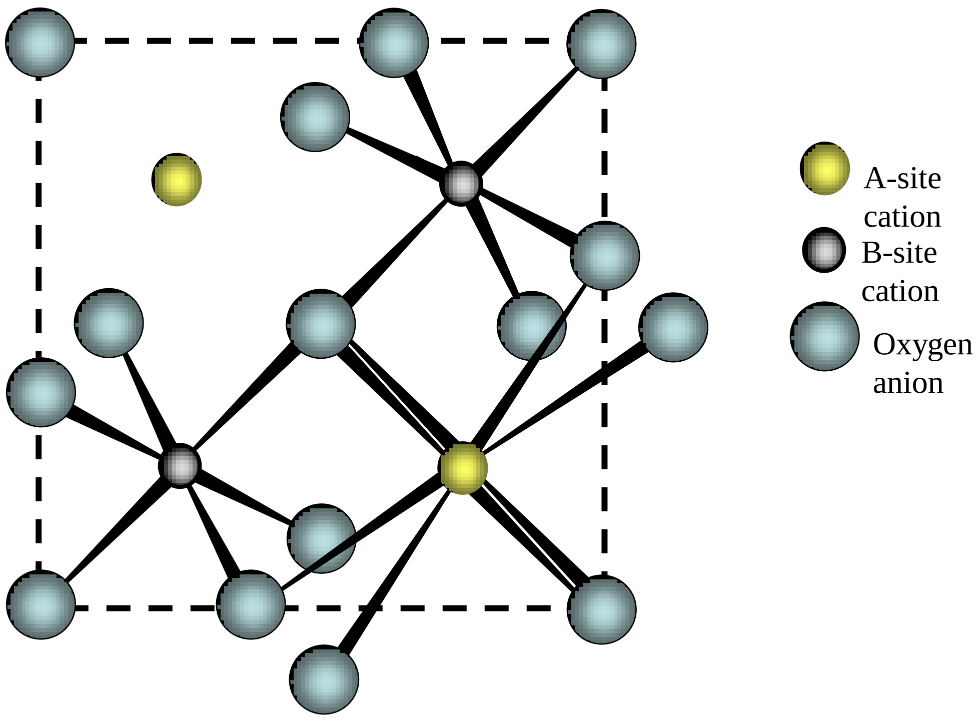
- **Gain a fundamental understanding of catalyst function and mechanism of deactivation.**



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

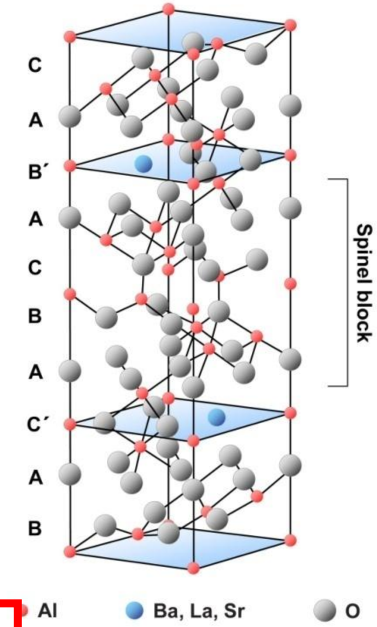


Oxide-based Catalyst Systems



General Formula

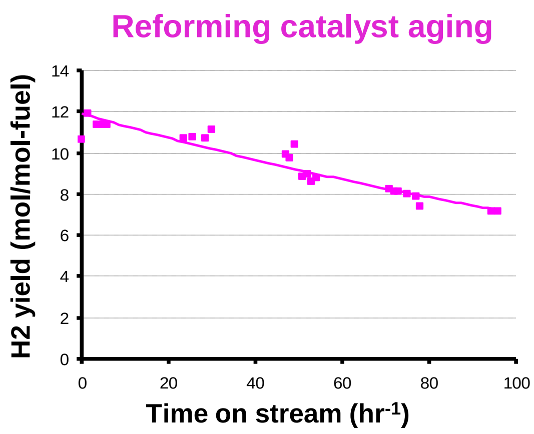
ABO

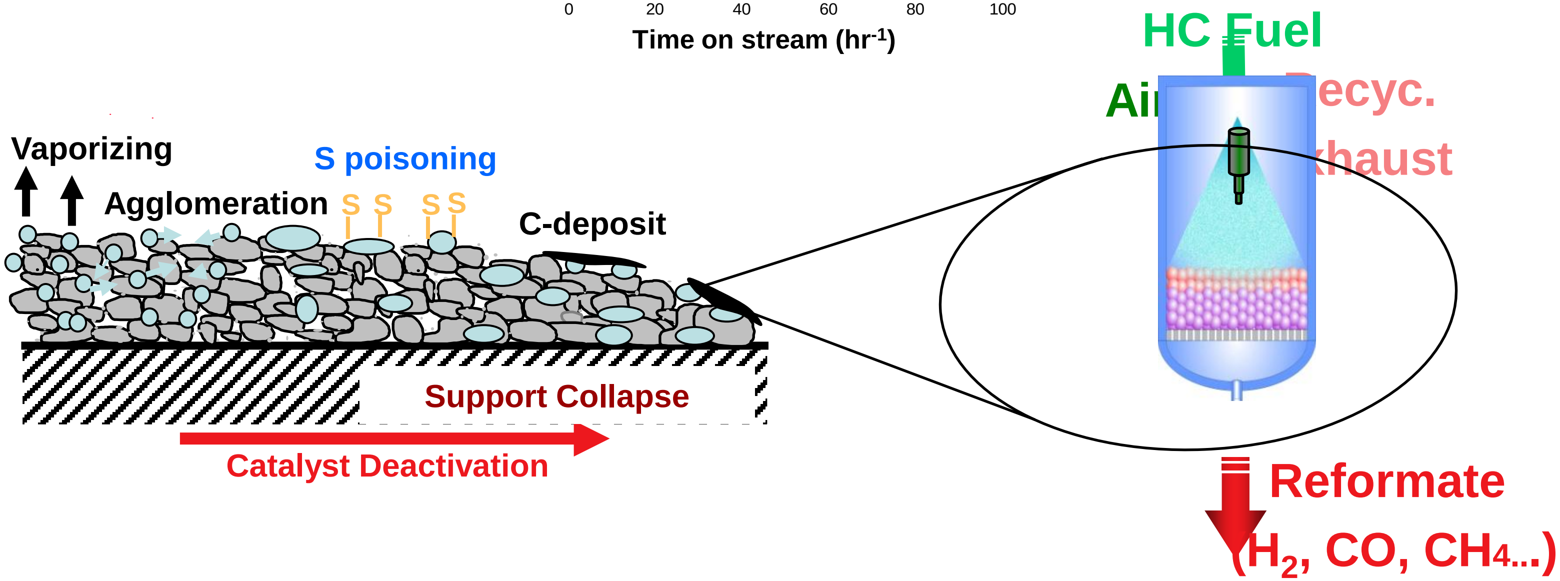


Doping the lattice of certain oxide-based compounds with catalytic metals results in…

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

Deactivation Issues – Why?



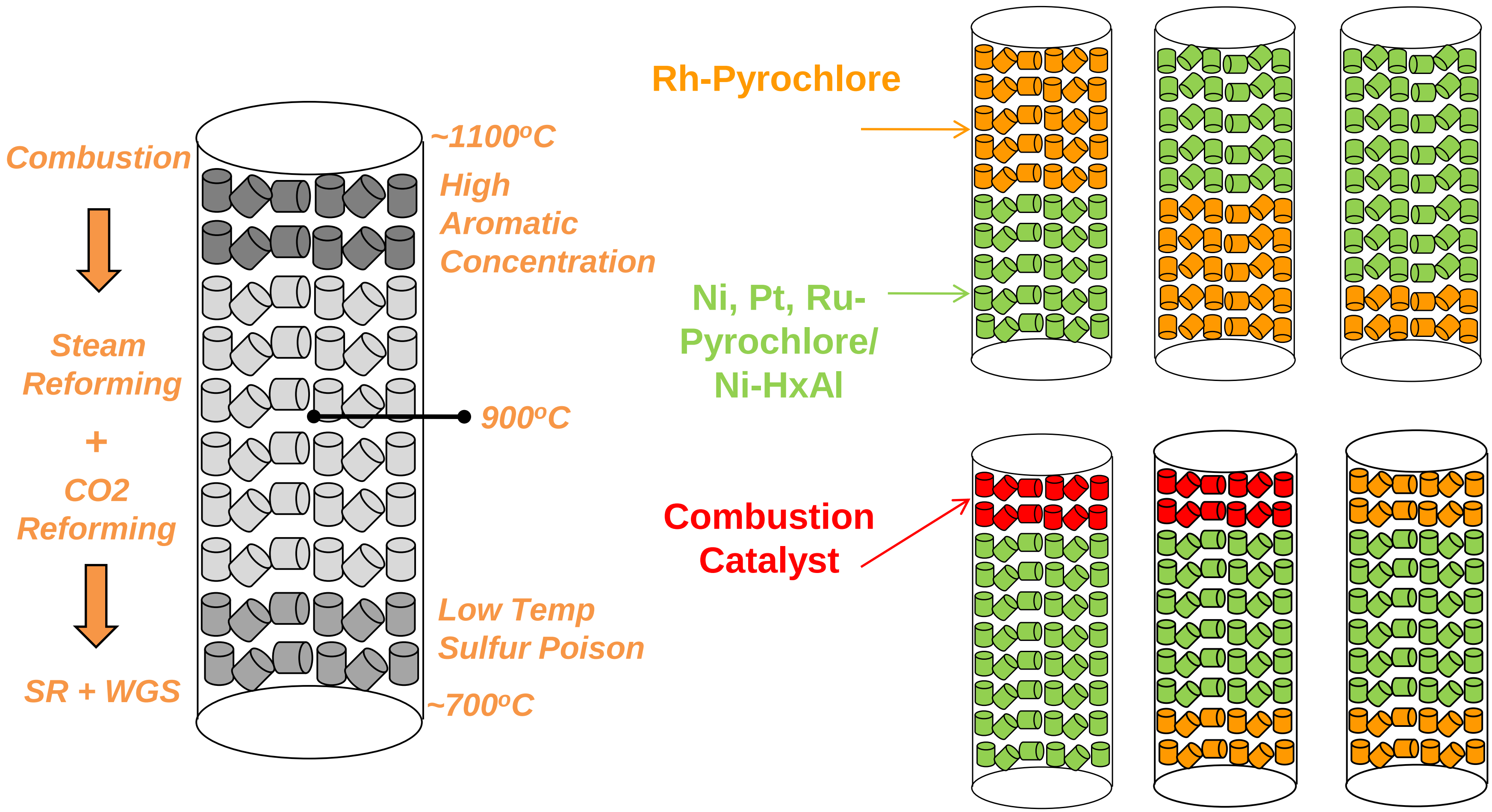


R&D Studies Indicated….

- Bulk metal deposited catalysts susceptible to carbon formation and sulfur poisoning
- Small "atomically dispersed" 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?

Graded Catalyst Bed Approach

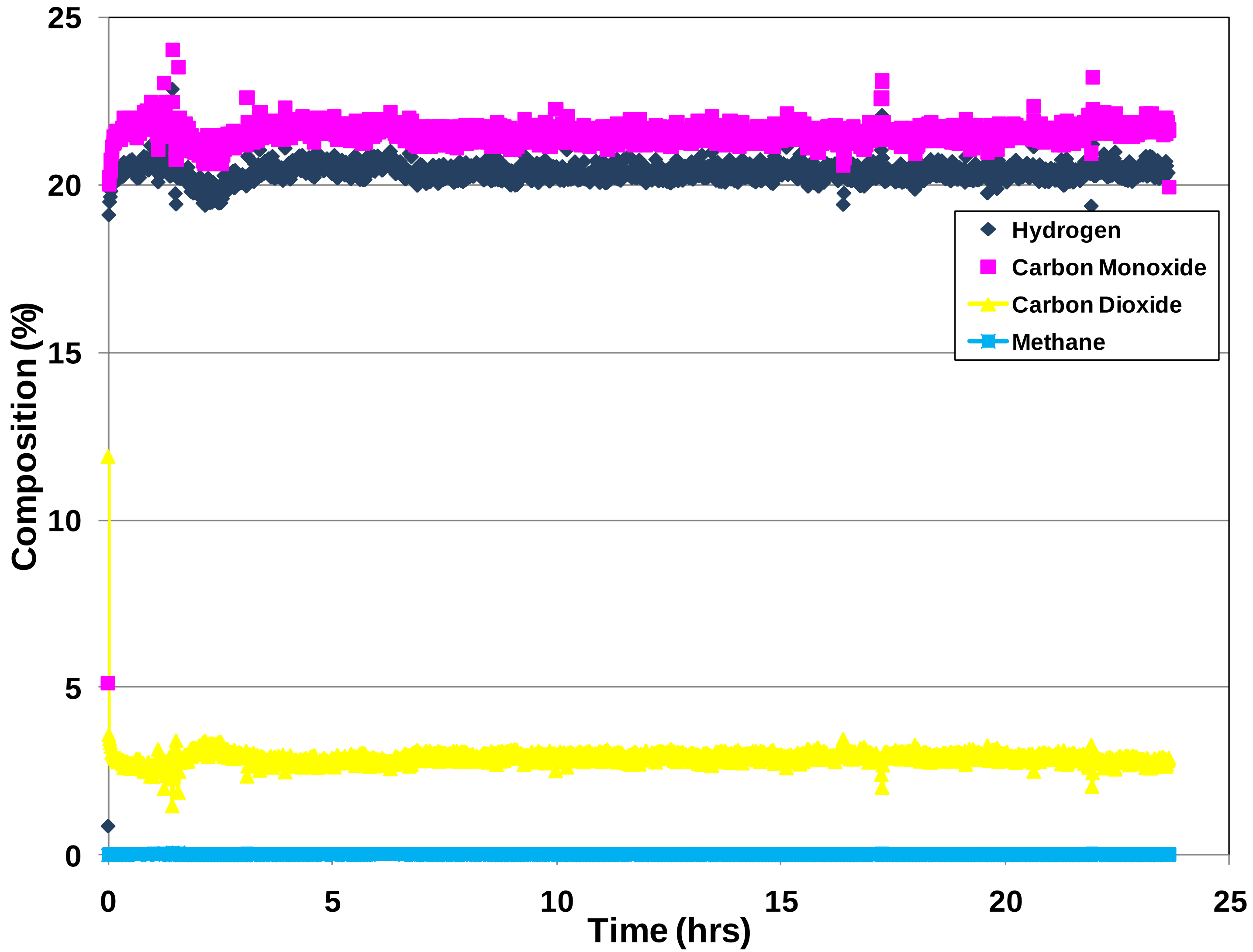


Experimental Conditions

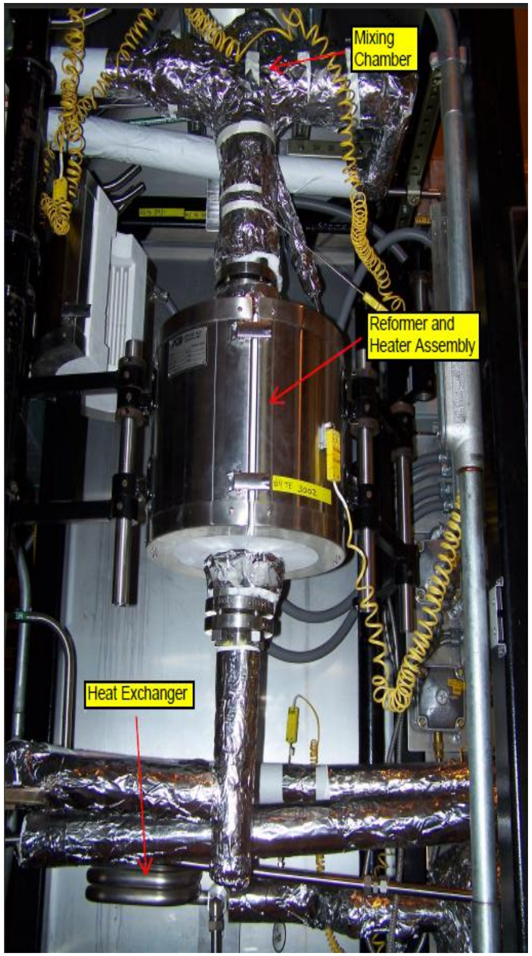
Reaction Conditions	
Overall O/C ratio	1.5
O/C from air	1.0
S/C ratio	0.5
GHSV (scc gcat^{-1} h^{-1})	25,000
Bed Temperature (°C)	900
Catalyst Bed (g)	9.6
Pressure (MPa)	0.23

O/C – oxygen to carbon ratio
S/C – steam to carbon ration
GSHV – gas hourly space velocity

Results: POx of Biodiesel with NETL Pyrochlore Catalyst

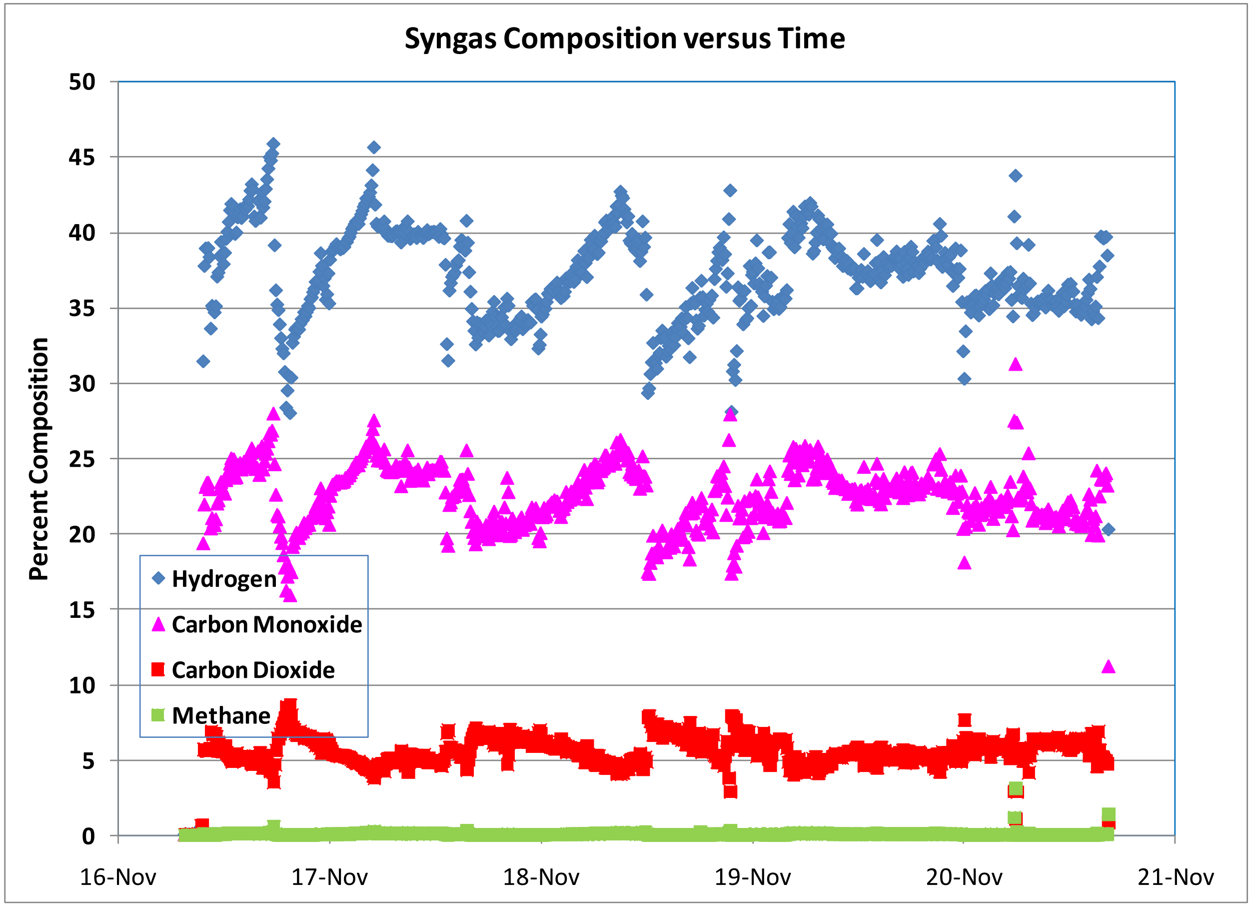


Successful Operation of a Solid Oxide Fuel Cell Fueled with Syngas from Biodiesel Reforming



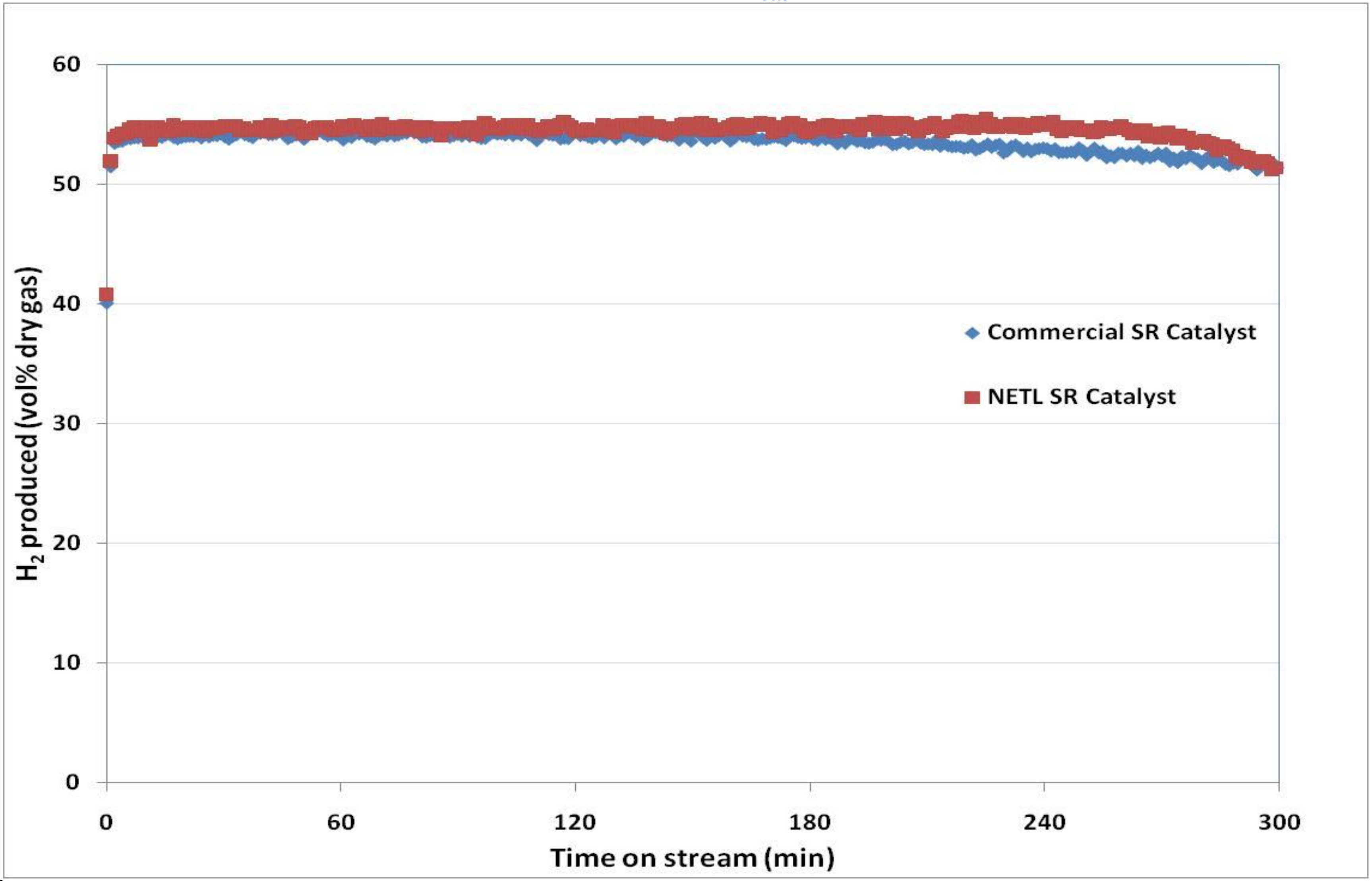
Biodiesel Reformer

- Biodiesel was reformed for 100 hrs on a pyrochlore catalyst supported on a monolith



Pyrochlore for Natural Gas Steam Reforming

S/C = 0.9; T_{RXR} = 700 C; GHSV = 25,000 scc/g_{cat}•hr



Alternative Reforming Concepts
Plasma Reforming: Objective and Goal

Objective:

Evaluate the use of plasma energy to reform heavy hydrocarbons into hydrogen-rich synthesis gas for fuel cells for use by high-temperature fuel cells being developed in the SECA program. Demonstrate/ develop a plasma diesel fuel reformer with 100% fuel conversion to < C3 hydrocarbons with minimal carbon formation / performance decline, and parasitic power consumption of < 5%.

Project Goal:

Identify/develop technology for fuel cell systems integrated with coal or diesel applications for ultimate commercial use.

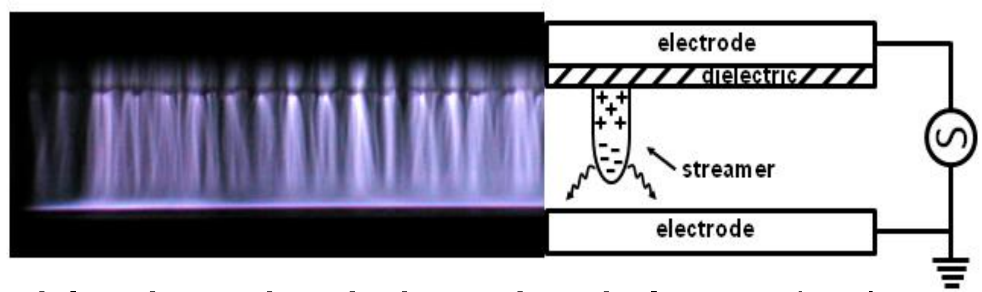
Advanced Reforming Concepts
Summary

- Plasma processes have been demonstrated in recent experimental reforming efforts and relevant related industrial applications.
  - NETL is scheduled to receive the Drexel Vortex Plasma reformer by Summer 2009 for evaluation.
- Relevant RF processes in prior project demonstrated as promising for reforming applications.
  - NETL is constructing facilities for RF installation by Fall 2009.

Alternative Reforming Concepts
Plasma: Thermal vs. Non-thermal

Non-thermal plasma

- Very high electron temperature but low gas temperature (T_g=300K)
- High chemical selectivity possible because high electron energy stimulates the creation of active chemical agents (radicals, excited species)
- Low power density



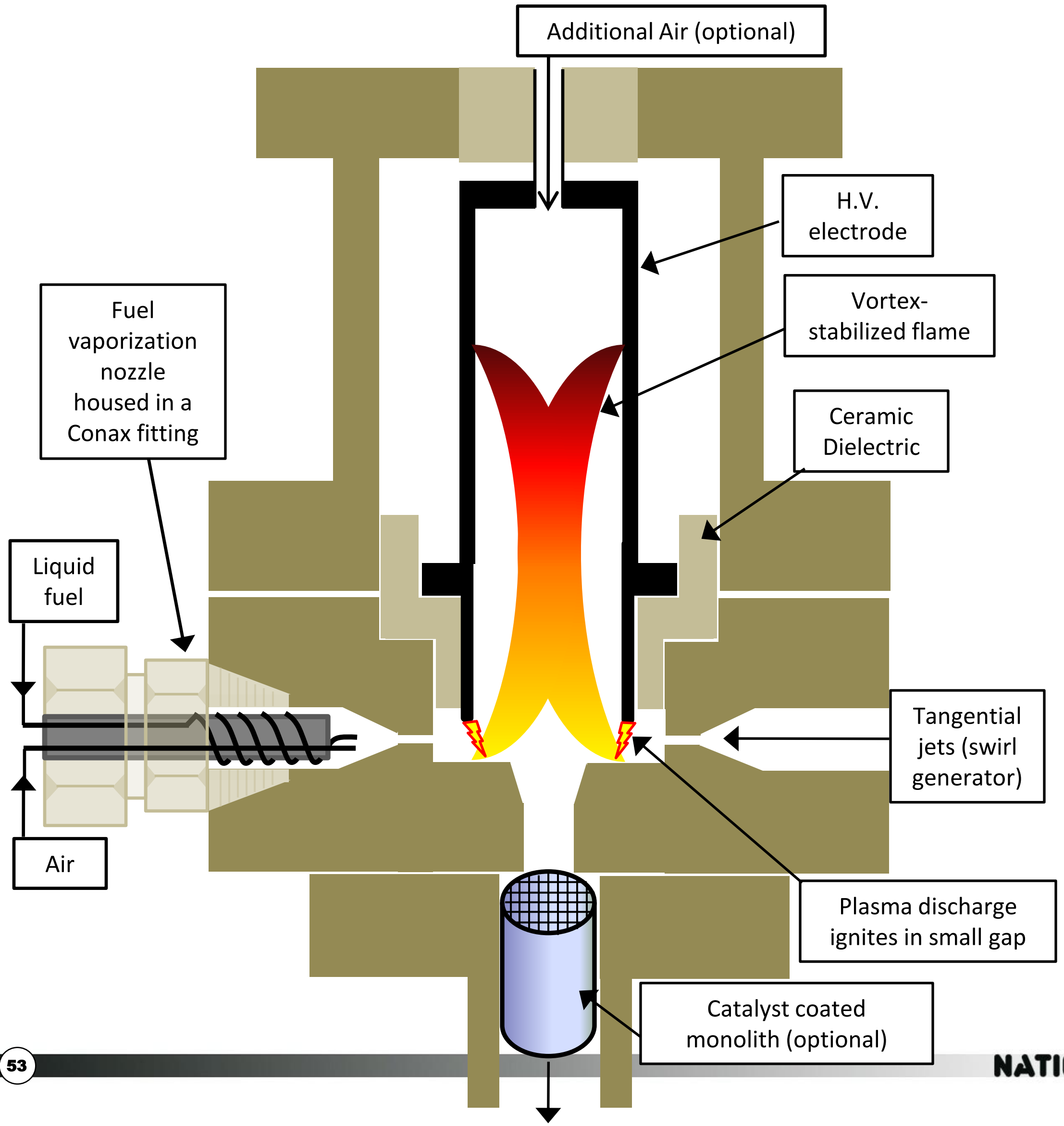
Dielectric Barrier Discharge (DBD) plasma – has lower power density compared to thermal plasma, but higher energy electrons, which induce formation of active chemical agents

Thermal Plasma – conventional technology

- All species are in thermal equilibrium – high gas temperature (T_g=10,000K)
- Very high plasma power and density
- Little chemical selectivity can be obtained, energy is only spent for gas heating (including inert nitrogen)

Thermal plasma torches – used in cutting applications, gas temperatures > 10,000K

Alternative Reforming Concepts
Gliding Arc Plasma Reformer



- DC Gliding Arc plasma stabilized in reverse vortex (tornado) flow – to convert diesel/JP-8 into syngas
- Utilizes new prototype fuel vaporization nozzle
    - Provides accurate control of reactant temperatures
    - Avoids fuel cracking prior to exposure to plasma
- Reactor has capability to attach a catalytic monolith to exhaust to investigate synergistic combination of plasma + catalytic reforming

Gliding arc Plasma discharge (top view)