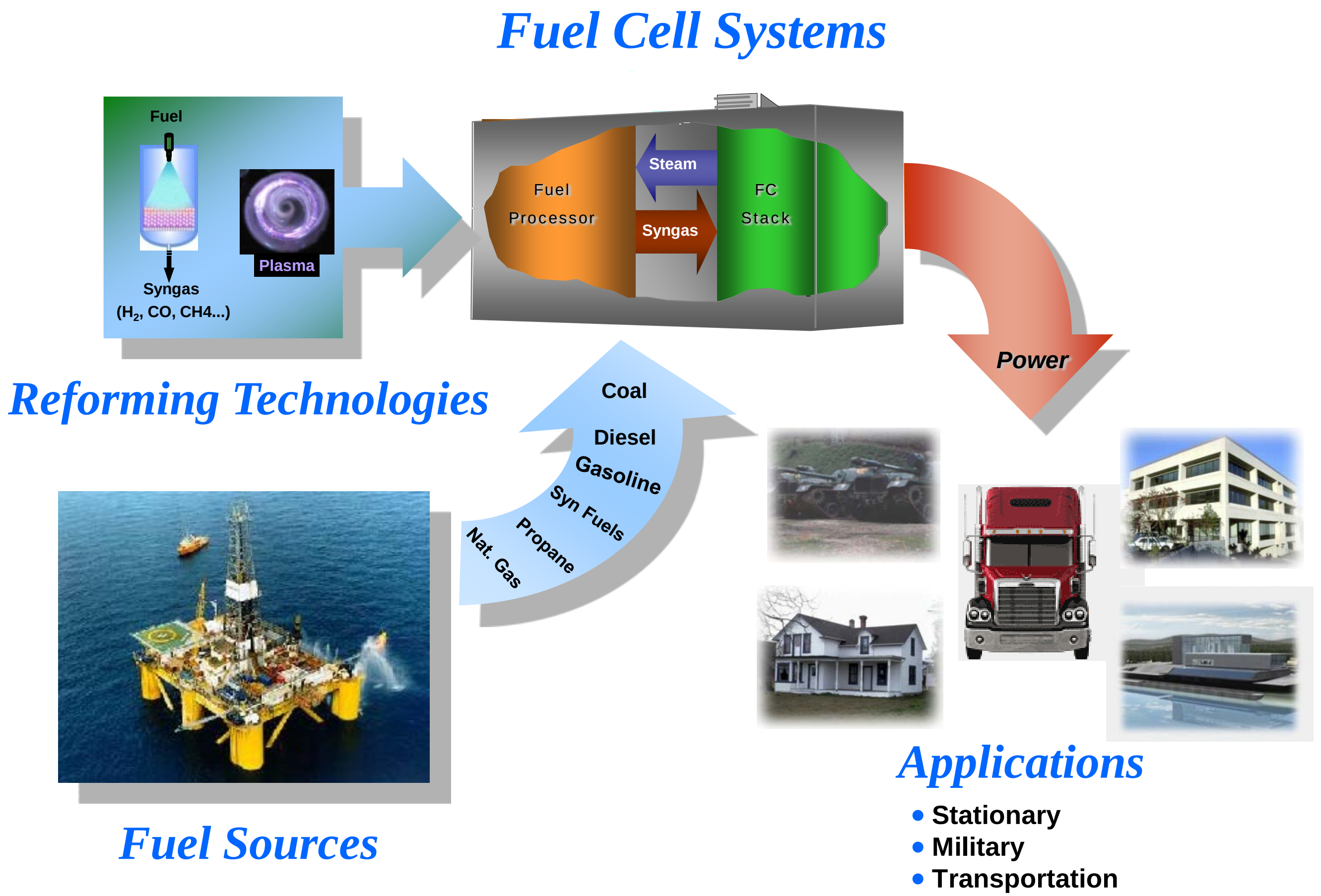
Structured Oxide-Based Reforming Catalyst Development

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

July 29, 2010

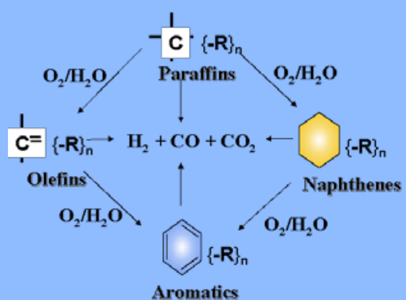
Introduction

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

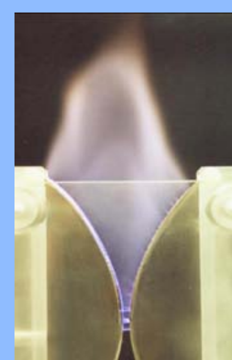


Primary Goal

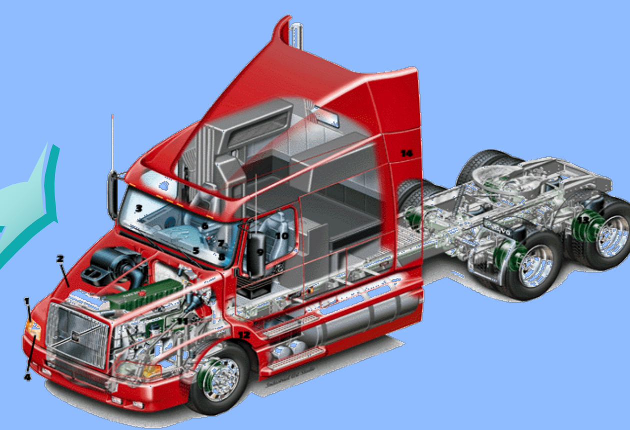
Identify, evaluate and/or develop viable hydrocarbon fuel processing technologies for high temperature solid oxide fuel cells being supported in the NETL SECA program through fundamental understanding, research, and technology demonstration.



Fuel



Technology

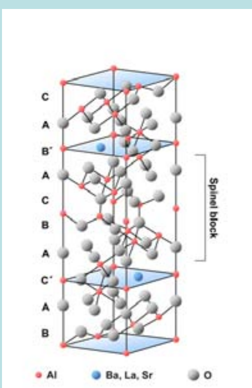


End Use

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.

Structured Catalyst Development

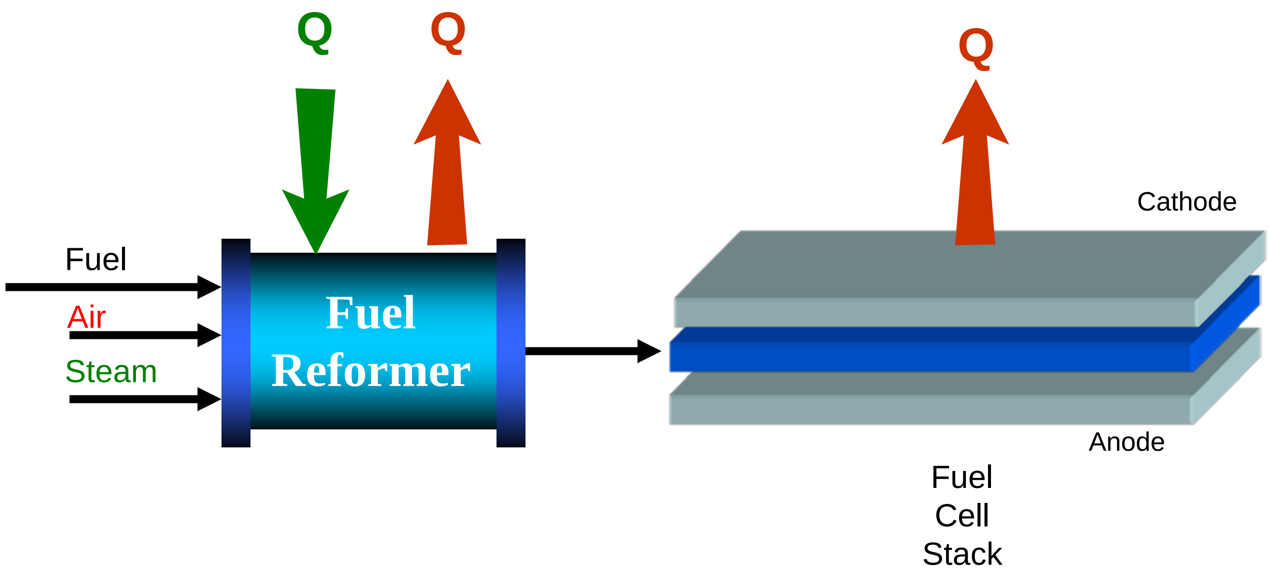
- **<u>Objective:</u> Apply fundamental understanding of fuel reforming & deactivation mechanisms into design of alternative catalyst systems for long-term, stable hydrogen-rich synthesis gas production.**

- Technical objectives / challenges
- Reforming catalyst formula development
  - Reforming studies with diesel surrogate fuel
  - Oxygen-conducting support studies
- 1000-hr OSR demonstration test on pump diesel
- Development of commercially viable catalyst structure (monolith)
  - Short-term OSR studies with diesel fuel on catalyst monolith
  - 100-hr OSR demonstration test with biodiesel in integrated fuel cell test
- Graded bed approach
- RF-assisted catalytic reforming

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

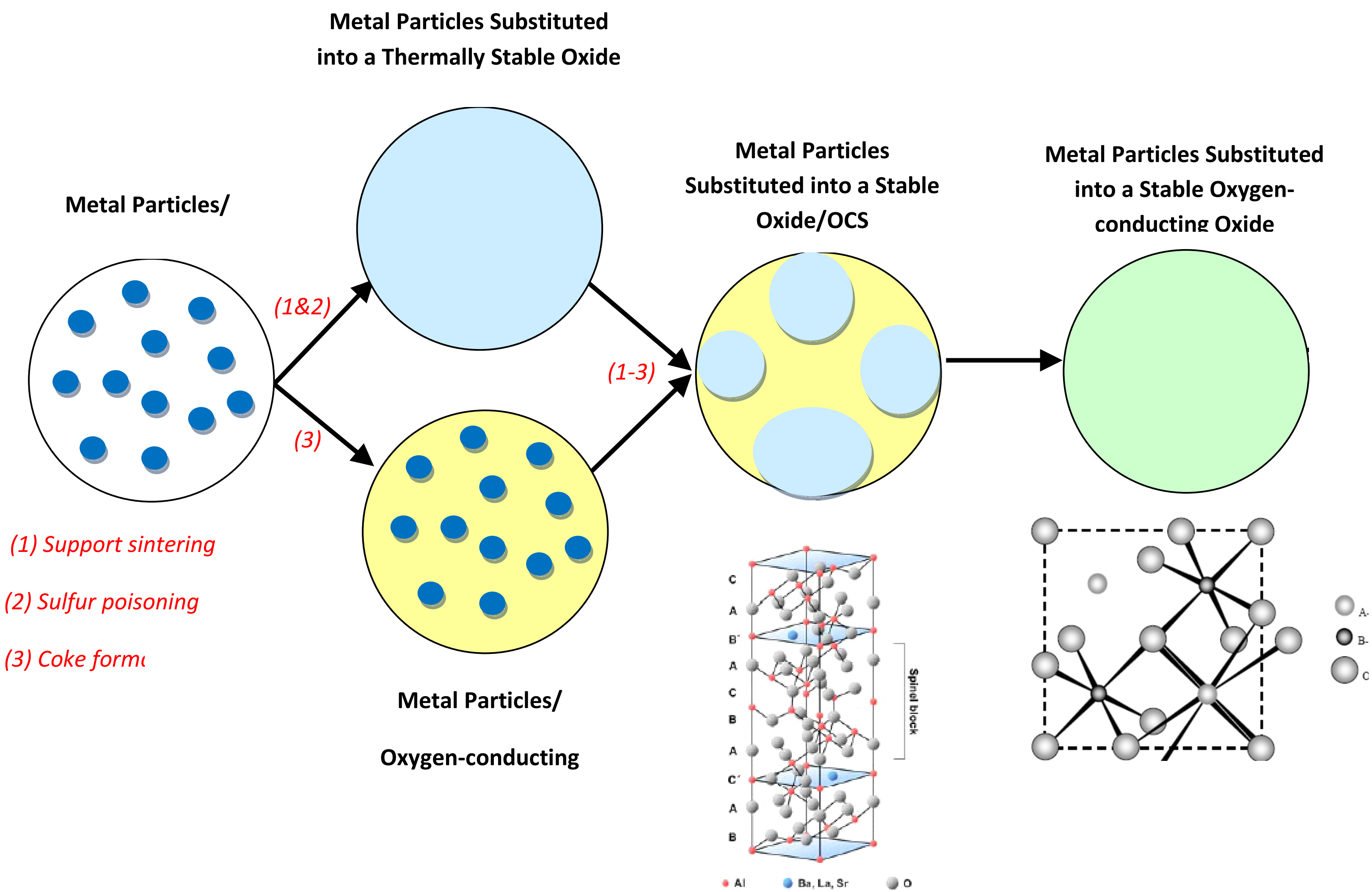
- **Desired Thermal Integration with Fuel Cell – Similar Temperature of Operation:**
  - ➢ Reduces unnecessary heat exchange and can increase system efficiency – cost & complexity savings.

    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.

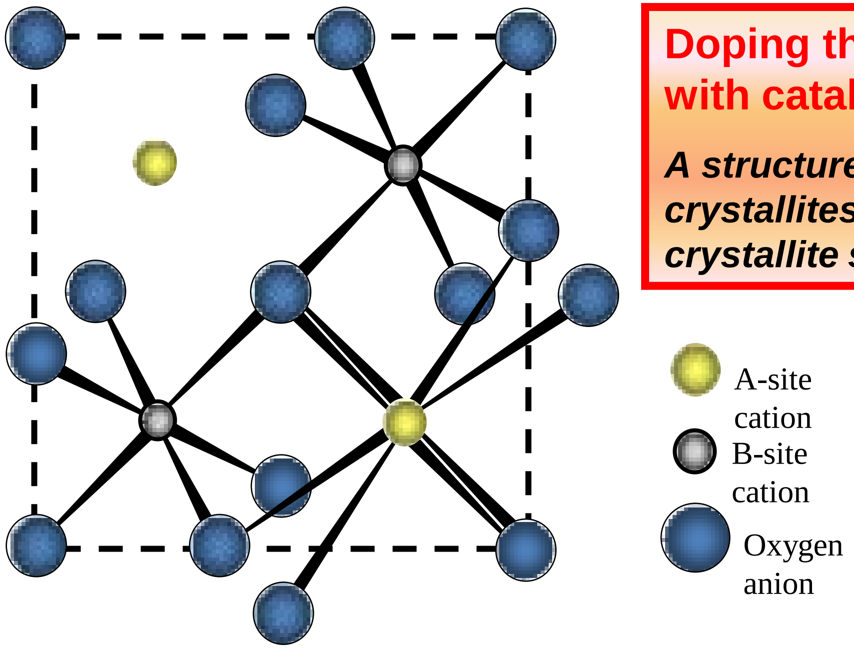
- **Possible Low or Waterless Operation:**
  - ➢ Reduces or eliminates the complexity and cost of managing water within the system. Some applications cannot consider water addition to the process.

    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.

Evolution of NETL Reforming Catalyst System



Oxide-based Catalyst Systems (Pyrochlores)



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

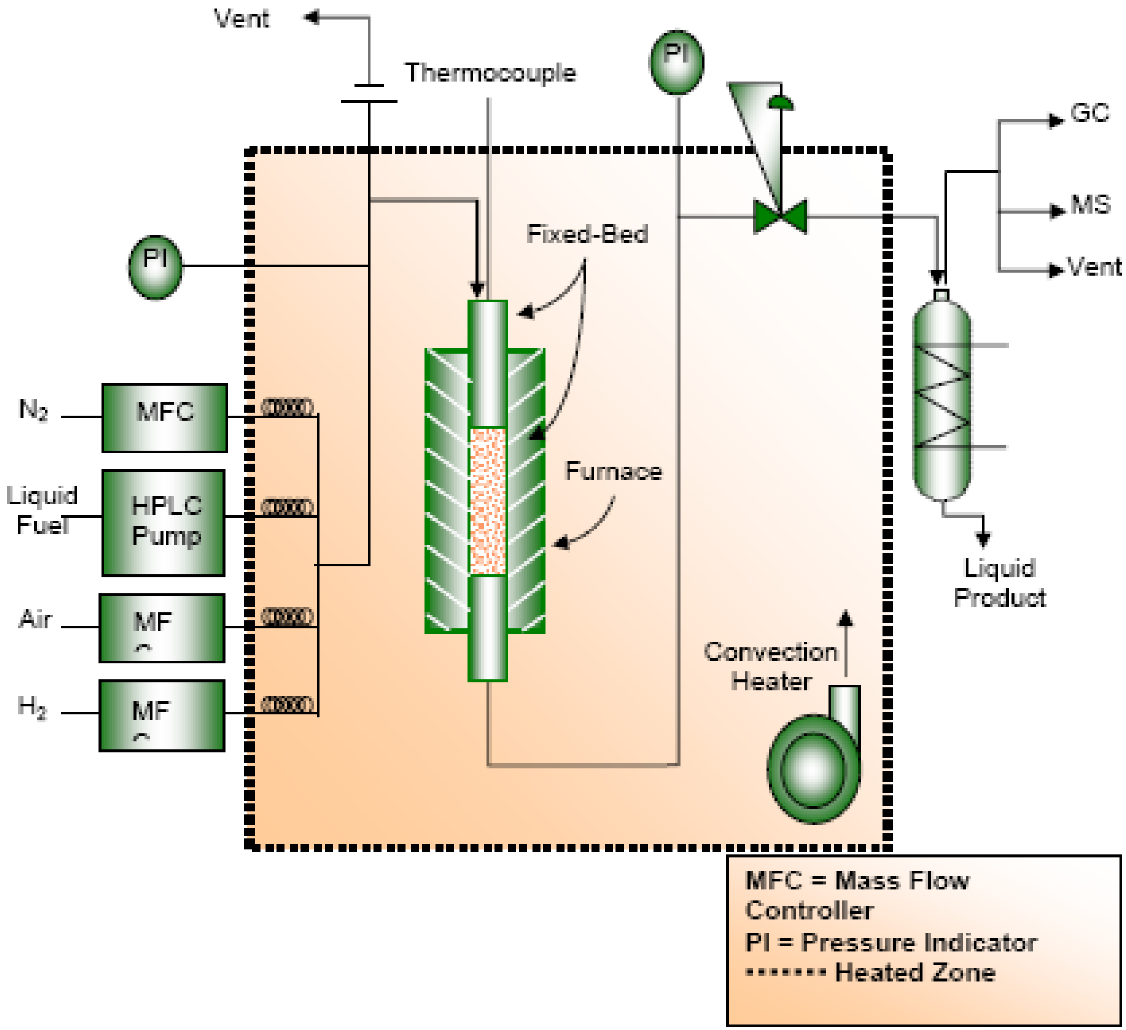
A structured catalytic surface with nano-sized metallic crystallites that serves as a template to control metallic crystallite size and dispersion.

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

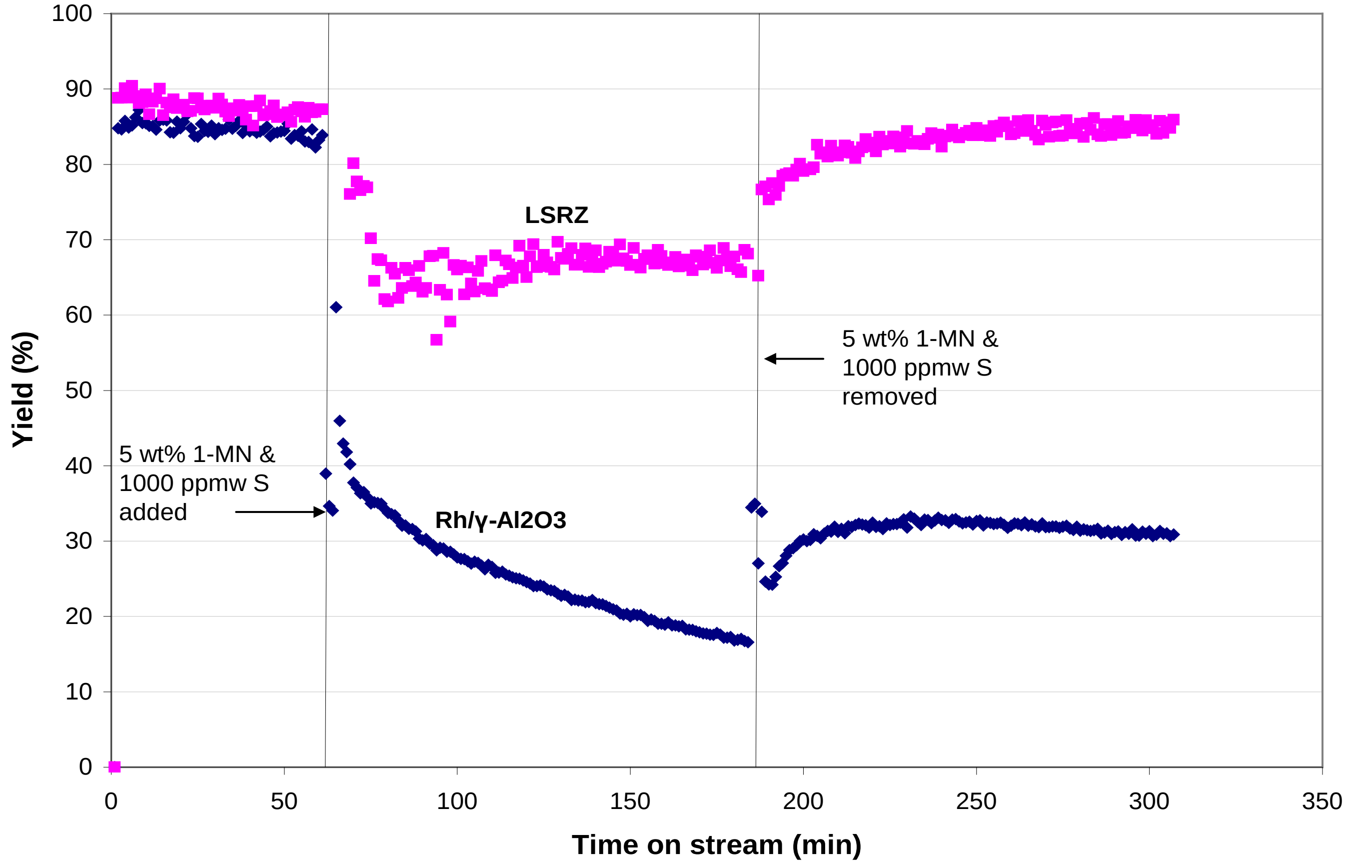
- High chemical and thermal stability [1]
- Mechanical strength to accommodate substitutions [2]
- Active metal can be substituted into B-site to improve catalytic activity
- Substitution with lower valence elements in A-site and B-site can create oxygen vacancies, which may increase lattice oxygen-ion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



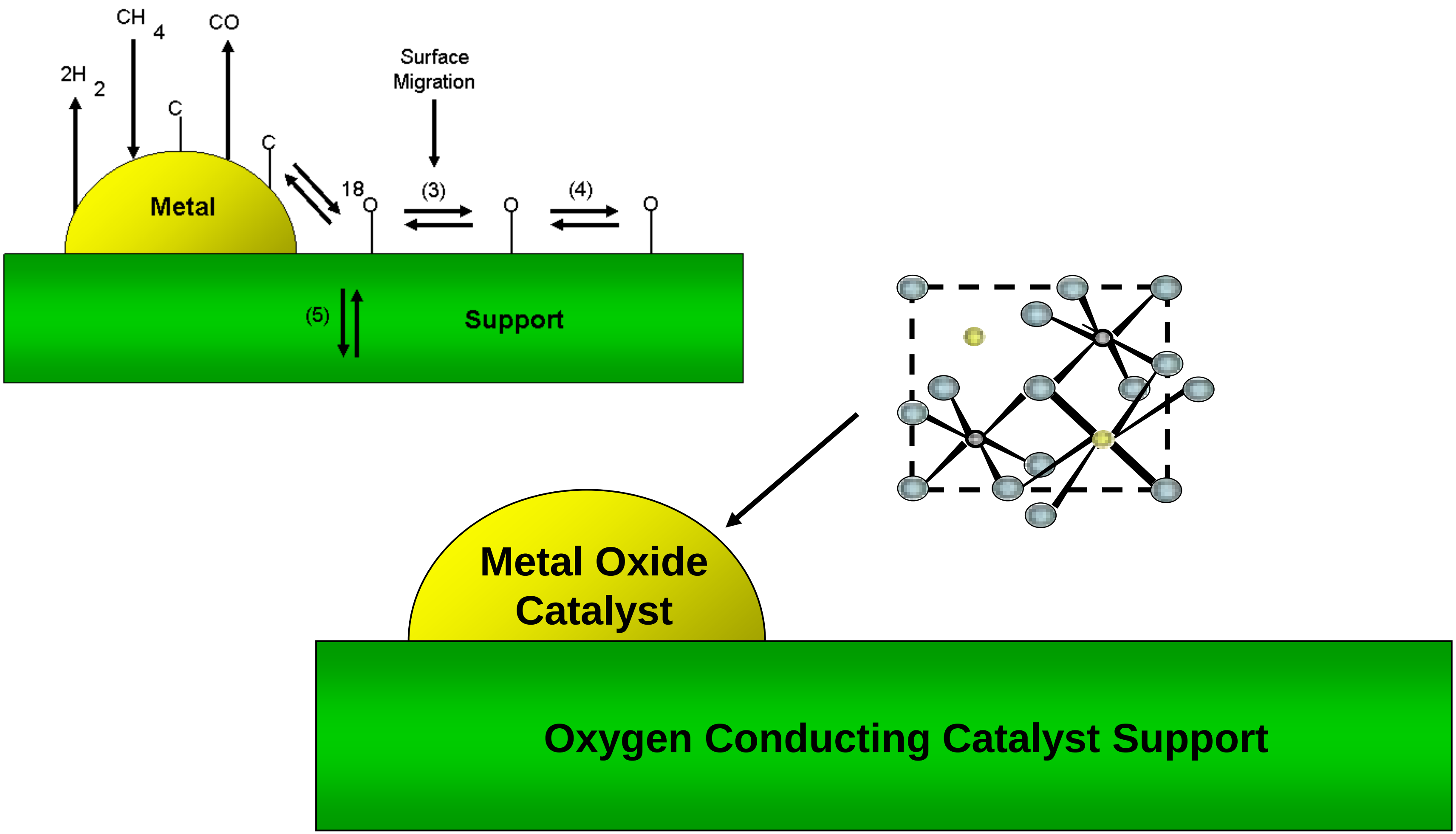
Pyrochlore for POx of Diesel Surrogate



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

Composition (%): 30, 25, 20, 15, 10, 5, 0

Olefins Produced (ppm): 900, 800, 700, 600, 500, 400, 300, 200, 100, 0

H_2

Water pump off

CO

Water pump on

CO_2

Olefins= ethylene + propylene + C_4-ene + benzene

Hydrogen
Carbon Monoxide
Carbon Dioxide
Methane
Olefins

0 200 400 600 800 1000 1200

Time on stream (hrs)

Diesel Fuel Reforming using Pyrochlore Catalyst

Collaboration with Industrial Partners

NETL's Pyrochlore Catalyst in Powder Form

- **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
- Preliminary Tests on Coated Monolith

Monolith Coated by NexTech

Microlith® Technology by PCI

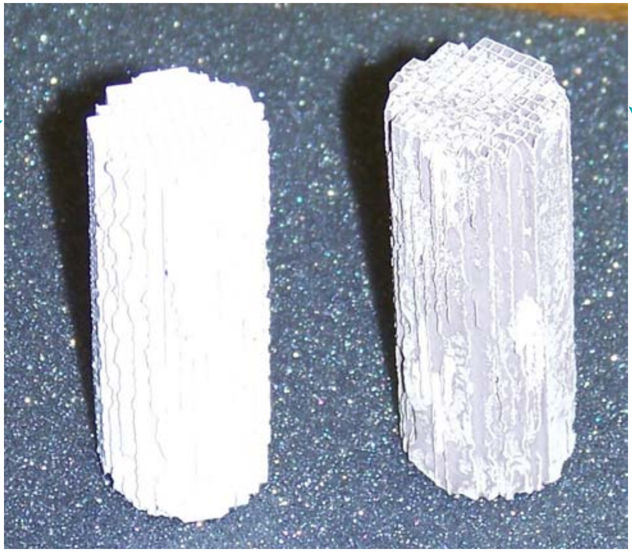
Monolith Reactor Coated with Pyrochlore Catalyst

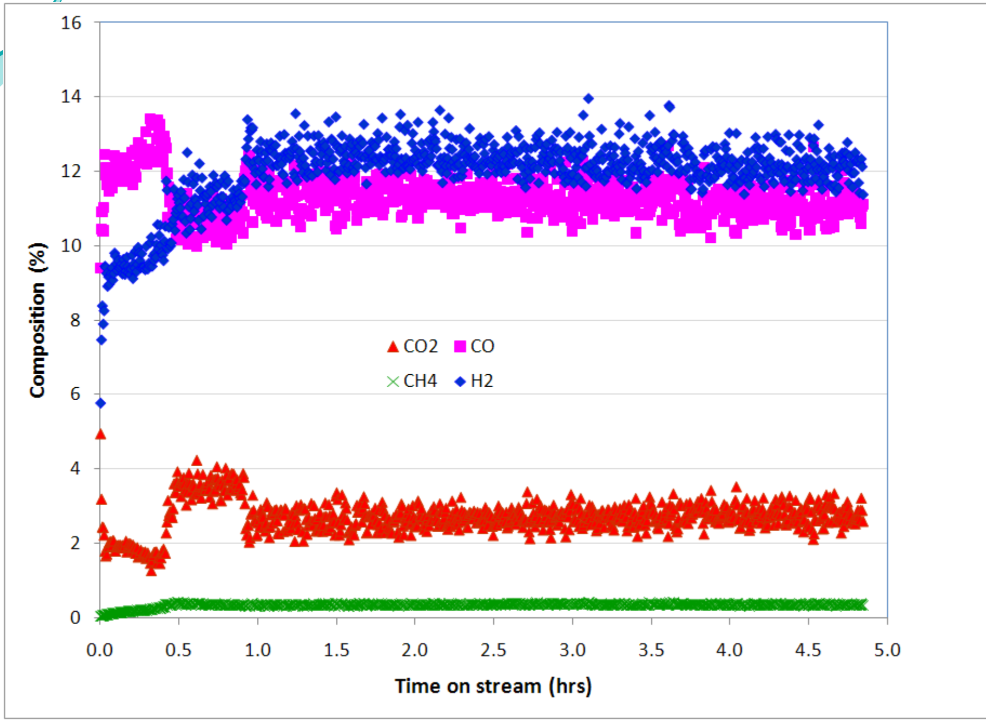
- NETL-developed Pyrochlore catalyst deposited onto alumina monolith with oxygen-conducting interlayer
- Coated using proprietary method by Nextech Materials, Inc.

Coated Monoliths from NexTech

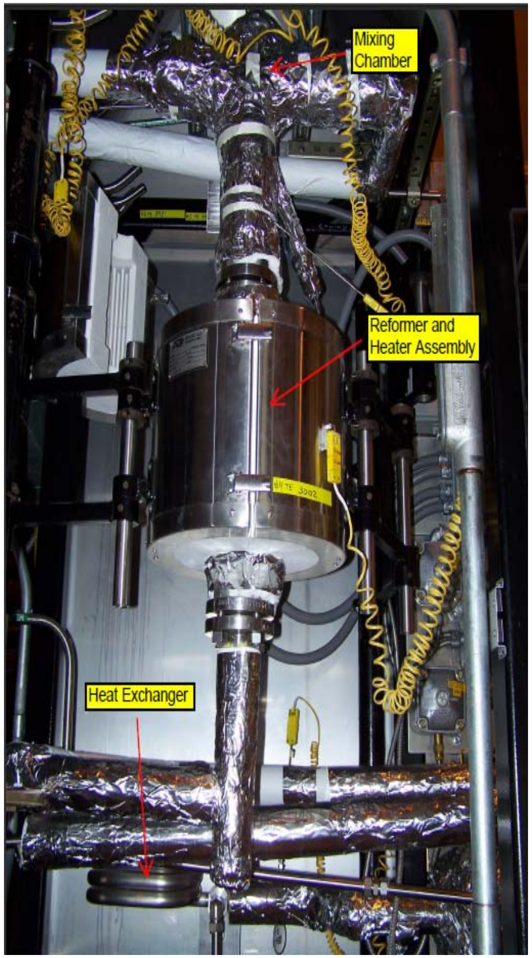
<u>Base Support</u>: 400 cpi alumina-based

<u>Coated Monolith</u>: Incorporates NETL pyrochlore catalyst system



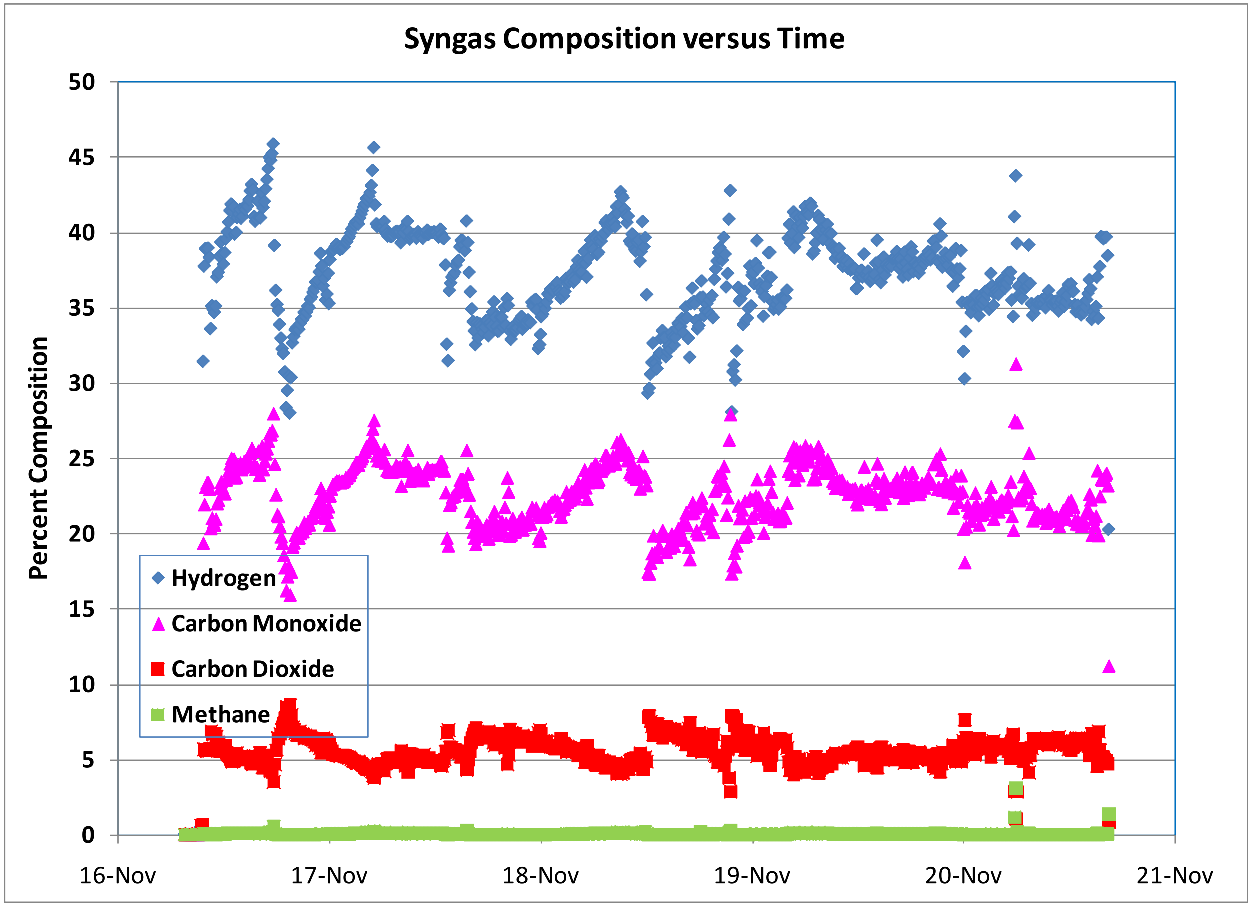


Successful Operation of a Solid Oxide Fuel Cell Fueled with Syngas from Biodiesel Reforming



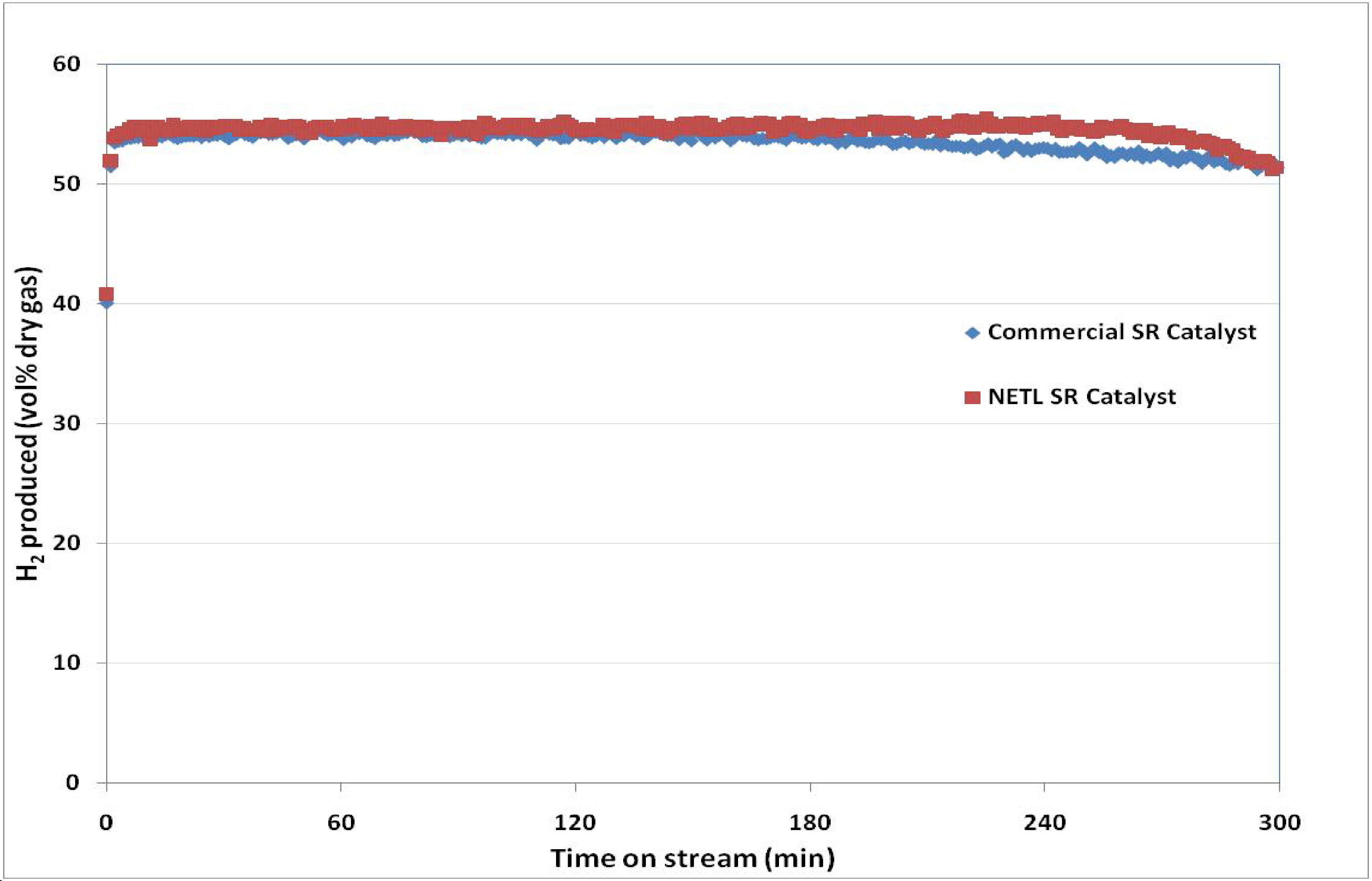
Biodiesel Reformer

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

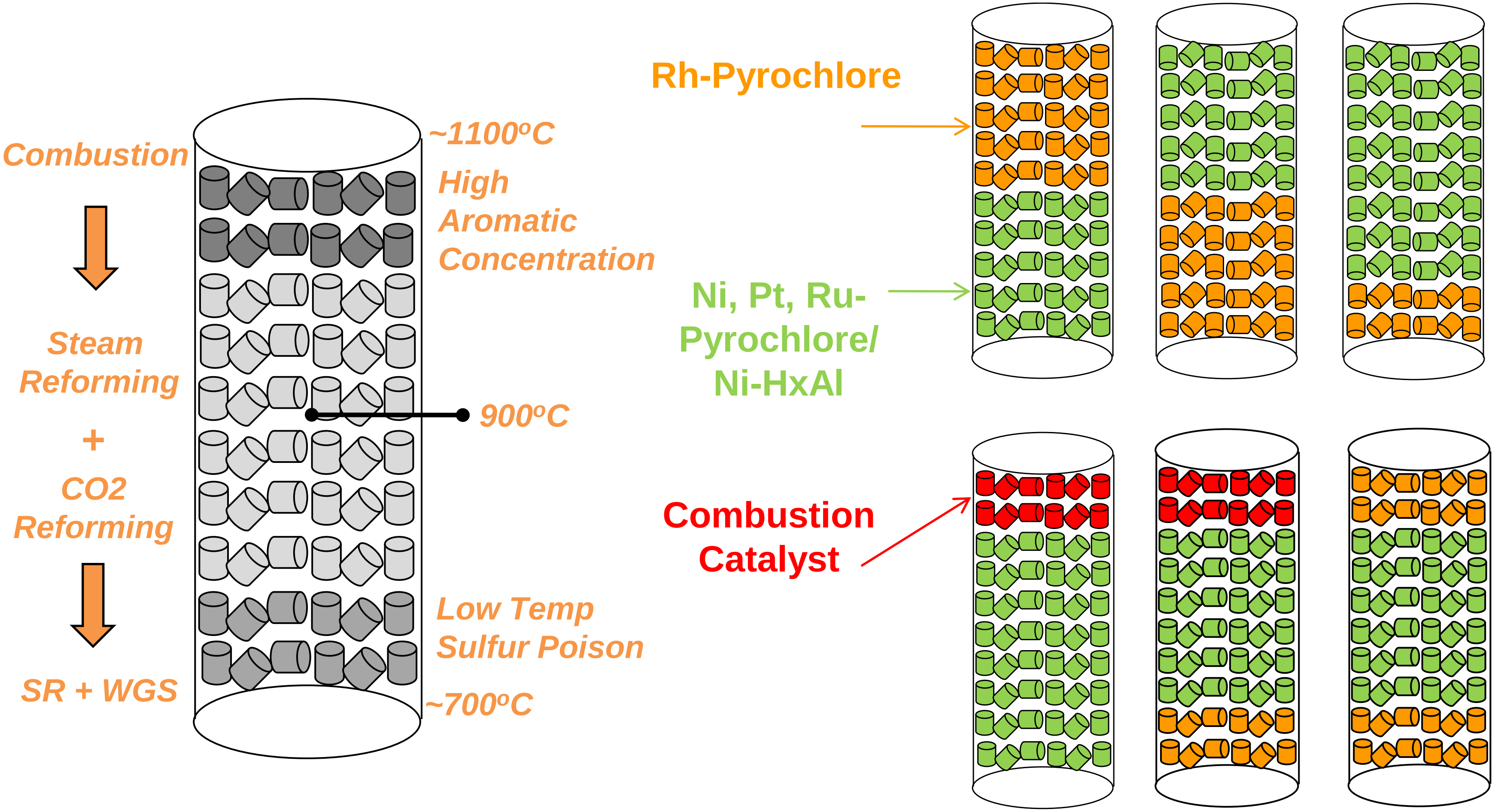


Pyrochlore for Natural Gas Steam Reforming

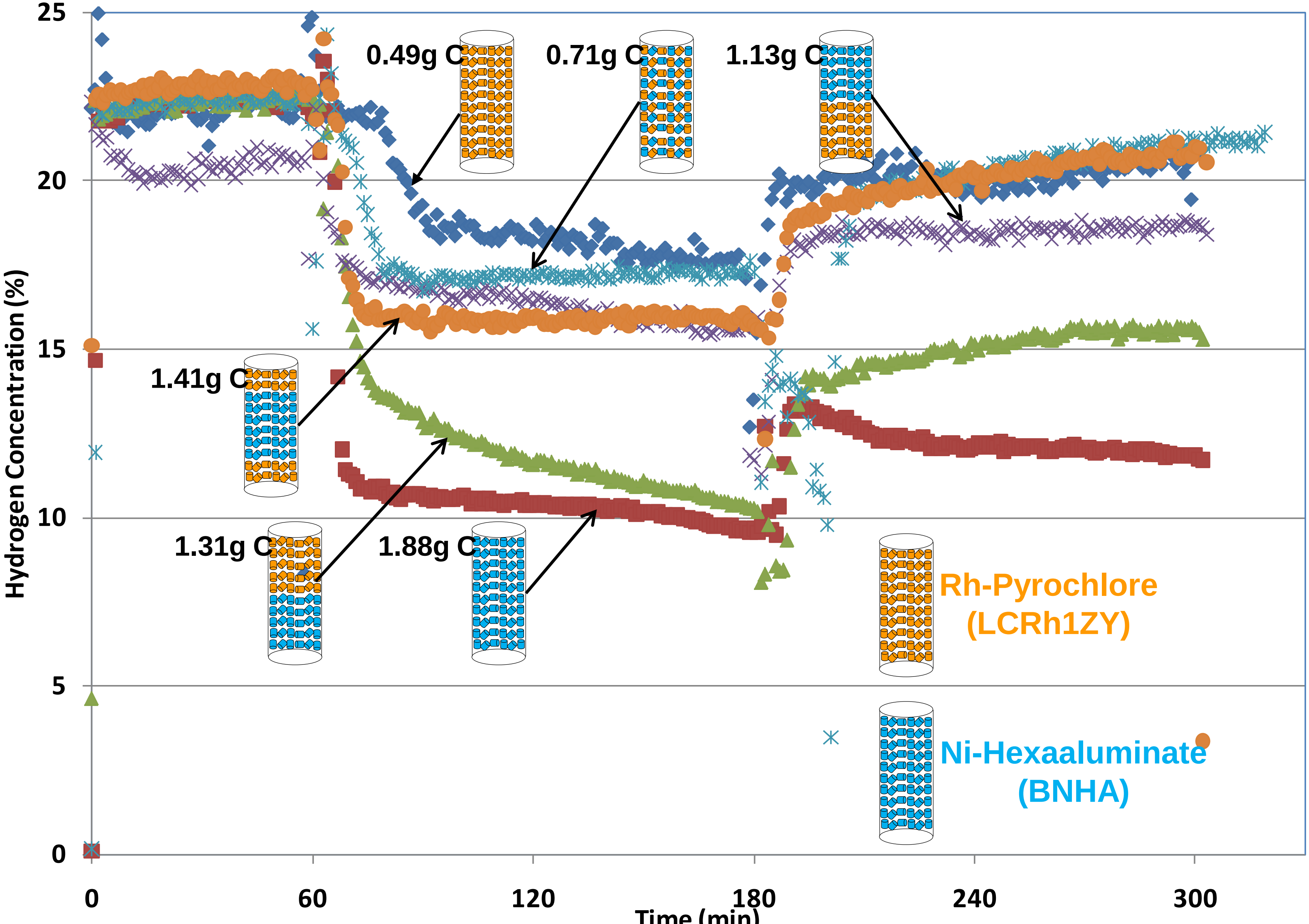
S/C = 0.9; T_{RXR} = 700 C; GHSV = 25,000 scc/g_{cat}•hr



Graded Catalyst Bed Approach



Preliminary Results: BNHA/LCRh1ZY



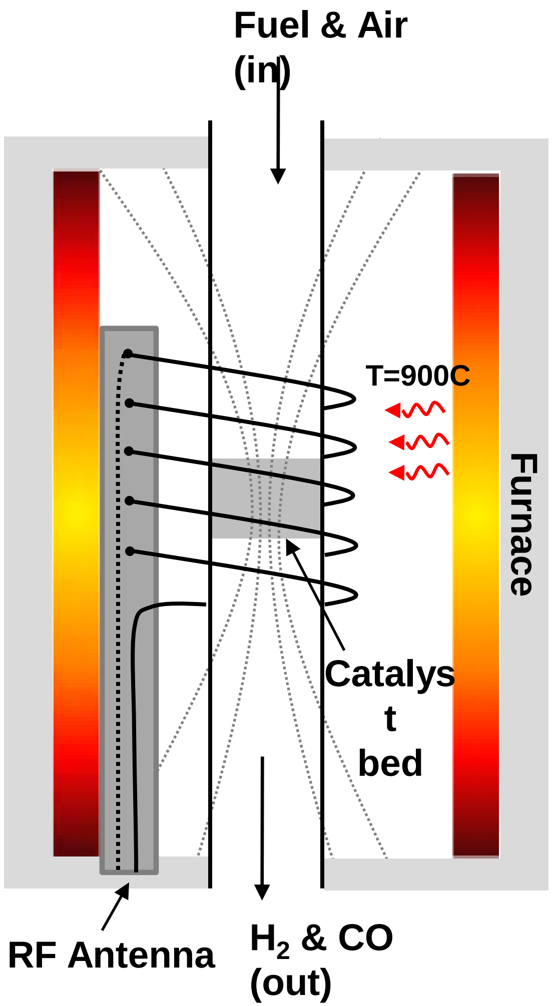
Alternative Reforming Concepts
Radio-Frequency Enhanced Reaction Concept

Energy bands of atoms or molecules absorb the RF energy

Localized heating of the material at the rxn site with higher dielectric loss index and excitation of valence electrons

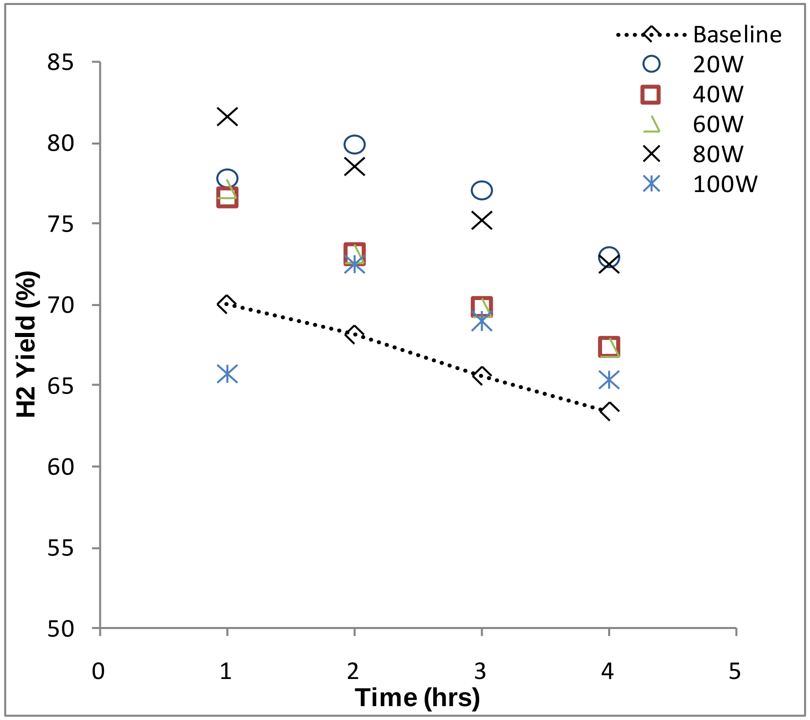
Lowers the activation energy required for desired chemical reactions

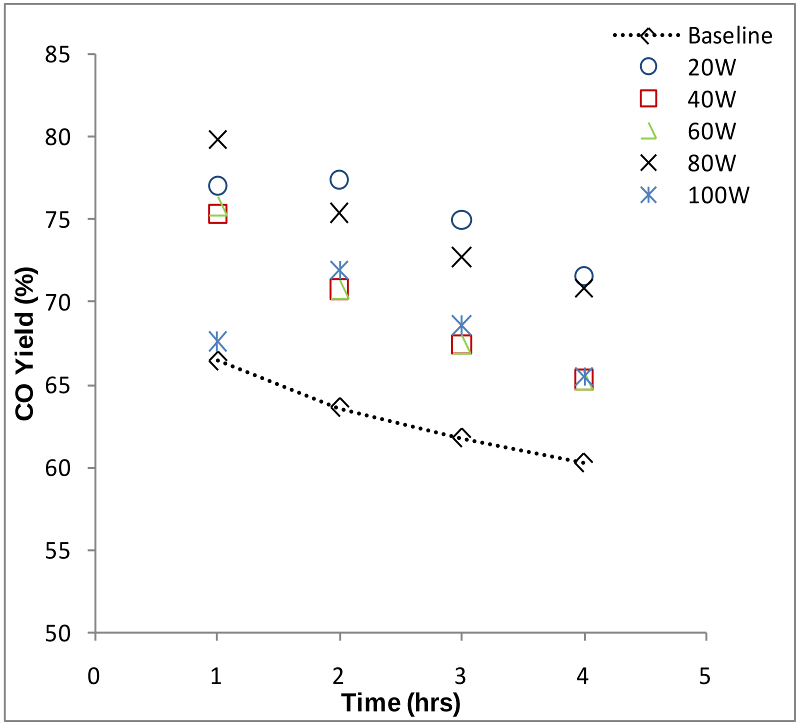
Functions as an enhanced catalyst



Alternative Reforming Concepts

Radio-Frequency Enhanced Reaction Concept





- **Effect of RF power on Syngas yields at fixed frequency (13.6 MHz)**
- **Preliminary results suggest that applied RF field has a positive influence on reforming**
- **Also see a slight reduction in carbon (coke) formation on the catalyst bed when RF field is applied**
- **Further testing in underway to repeat these findings and understand the underlying mechanism of enhanced catalyst activity**

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
- **Pyrochlore catalyst on oxygen-conducting support successfully reformed pump diesel for 1000-hr**
- **Optimized pyrochlore catalyst applied to commercially representative structured supports**
  - Preliminary performance of catalyst monolith demonstrated on pump diesel and biodiesel fuels under oxidative steam reforming
- **Preliminary RF experiments have shown some evidence of reduced carbon formation and enhanced catalyst activity**

NETL Fuel Processing Team

- David Berry
- Dushyant Shekhawat
- Nick Siefert
- Dan Haynes
- Mark Smith
- Mike Gallagher
- Don Floyd
- Mike Bergen
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