2004 SECA Core Technology Review

Review of Fuel Processing within the SECA Core Program and NETL On-Site Fuel Processing Activities

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by

David A. Berry

Research Team: Todd H. Gardner, Dushyant Shekhawat, (NETL) and Maria D. Salazar-Villalpando (WVU)

Fuel Processing Focus Area

Technical Issues / Challenges

- **Hydrocarbon reforming is fundamentally difficult :**
  - Deactivation of fuel reforming catalysts and fuel cell anodes via carbon deposition and sulfur poisoning are a concern.
  - Improper reactant mixing can lead to hot spots and carbon deposition.
  - More complex fuels like diesel are even more difficult (relative to methane) for their propensity to form carbon.
  - Catalyst sintering (pore closure), metal vaporization, and metal agglomeration (for catalytic processes) are issues at high temperatures.

- **System complexity and cost can be a challenge:**
  - Depending on application and technology, reformer integration with fuel cell system requires potential desulfurization, water management, and thermal considerations (high efficiency).
  - Many catalytic processes are based on potentially expensive PGM / Nobel metal catalysts.

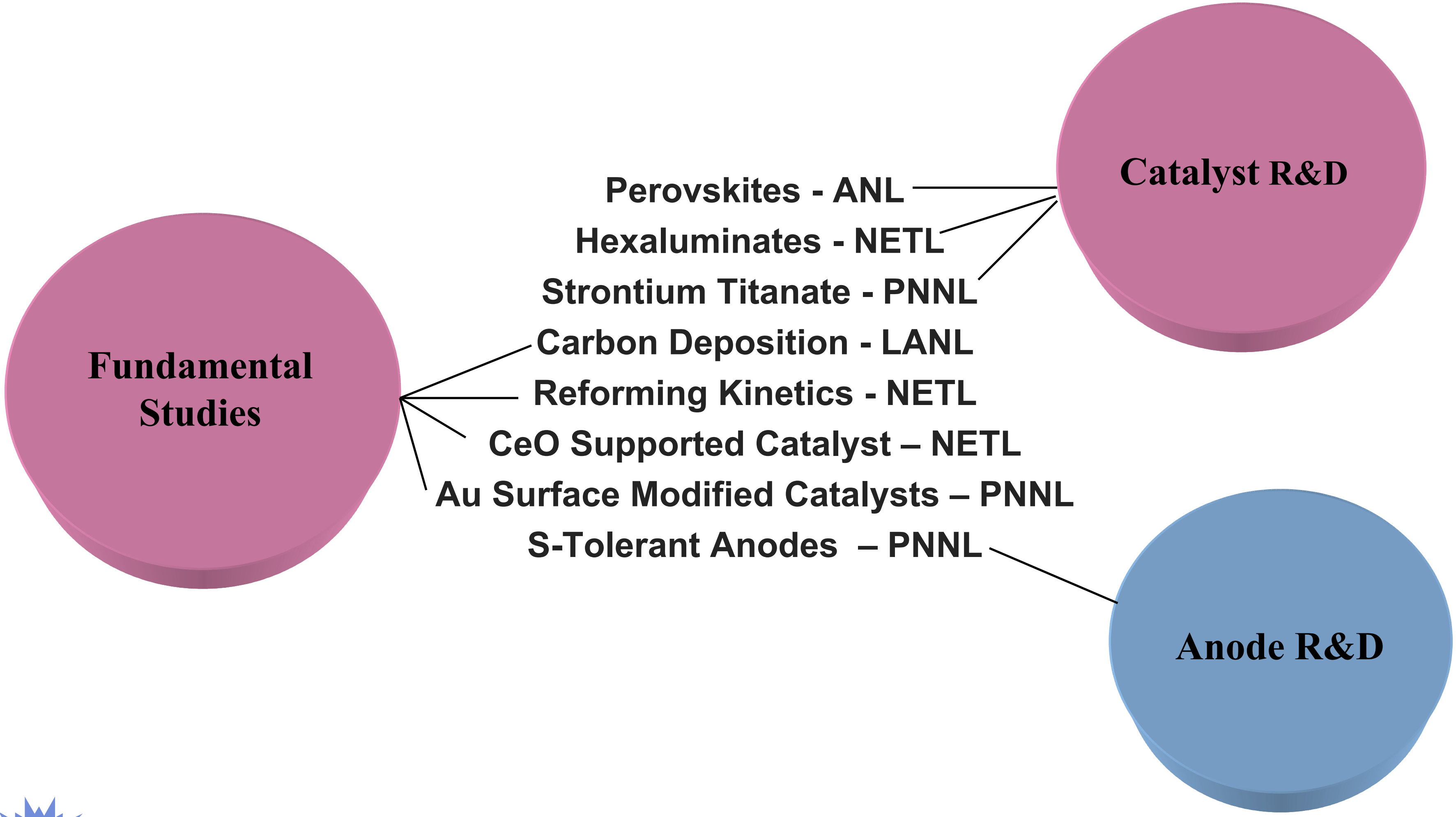
Fuel Processing Focus Area

Planning Assumptions

- **Commercial infrastructure fuels:**
  - For the foreseeable future, fuel cells will need to utilize current infrastructure fuels (natural gas, gasoline, diesel, …) as a source of hydrogen and carbon monoxide.
- **Sulfur tolerant reforming and anode catalysts :**
  - On-board or insitu sulfur removal adds a considerable cost and complexity to the fuel cell system. Most current infrastructure fuels will have very low levels of sulfur within the planning horizon of the SECA program, which should allow for a reasonable expectation of success with regard to sulfur tolerance.
- **Minimal water usage for hydrocarbon reforming:**
  - Excess water used as strategy for suppression of carbon formation. However, this increases system complexity and cost and decreases system efficiency.
  - Simplest and least cost systems utilize CPOx.
  - Use of CPOx, ATR, or steam reforming application dependent.

Fuel Processing Focus Area

Current R&D Efforts in Core Program



Catalyst R&D

Fundamental Studies

Anode R&D

Perovskites - ANL

Hexaluminates - NETL

Strontium Titanate - PNNL

Carbon Deposition - LANL

Reforming Kinetics - NETL

CeO Supported Catalyst – NETL

Au Surface Modified Catalysts – PNNL

S-Tolerant Anodes – PNNL

NETL Fuel Processing R&D

- ***Diesel Fuel Reforming Kinetics***

NETL Fuel Processing R&D

Diesel Fuel Reforming Kinetics

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).

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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.

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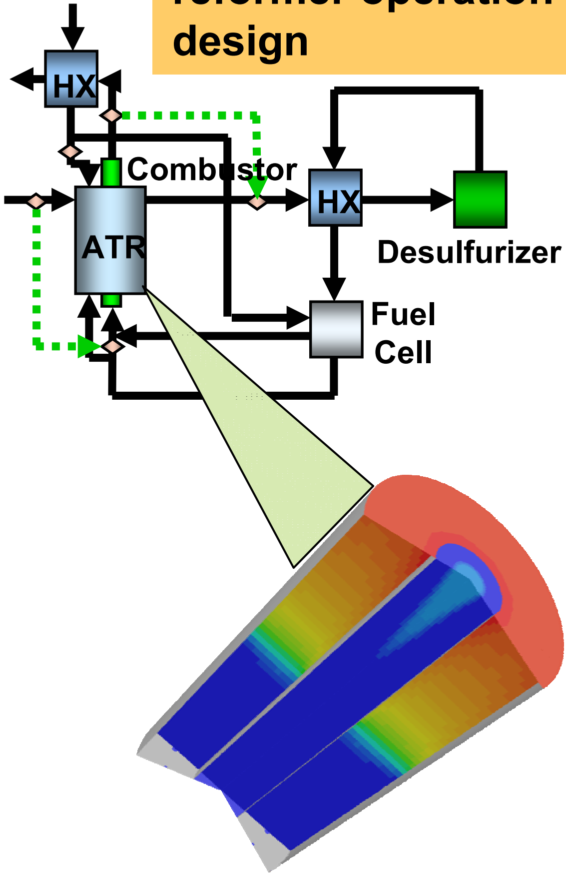
Diesel Fuel Reforming Kinetics

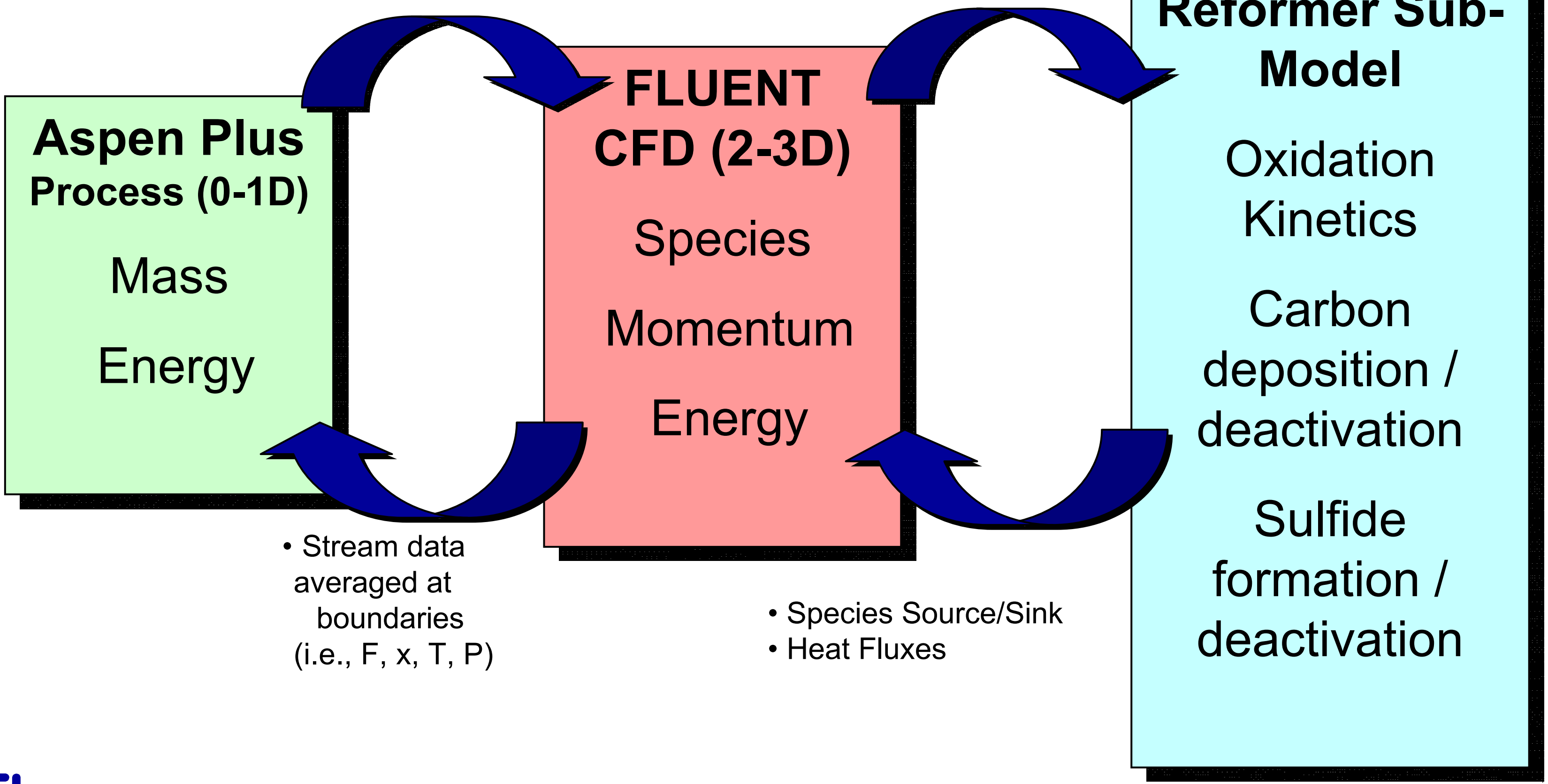
System integration & reformer operation / design



Insights for catalyst improvement & design

NETL Fuel Processing R&D

Diesel Fuel Reforming Kinetics – Model Integration



- Stream data (i.e., F, x, T, P)
- Temperature-dependent physical properties (i.e., Cp, μ, ρ, k)
- Constant properties (i.e., h0 , s0, MW)

- Local Species Concentration
- Local Temperature

Aspen Plus
Process (0-1D)

Mass

Energy

FLUENT
CFD (2-3D)

Species

Momentum

Energy

Reformer Sub-Model

Oxidation Kinetics

Carbon deposition / deactivation

Sulfide formation / deactivation

- Stream data averaged at boundaries (i.e., F, x, T, P)

- Species Source/Sink
- Heat Fluxes

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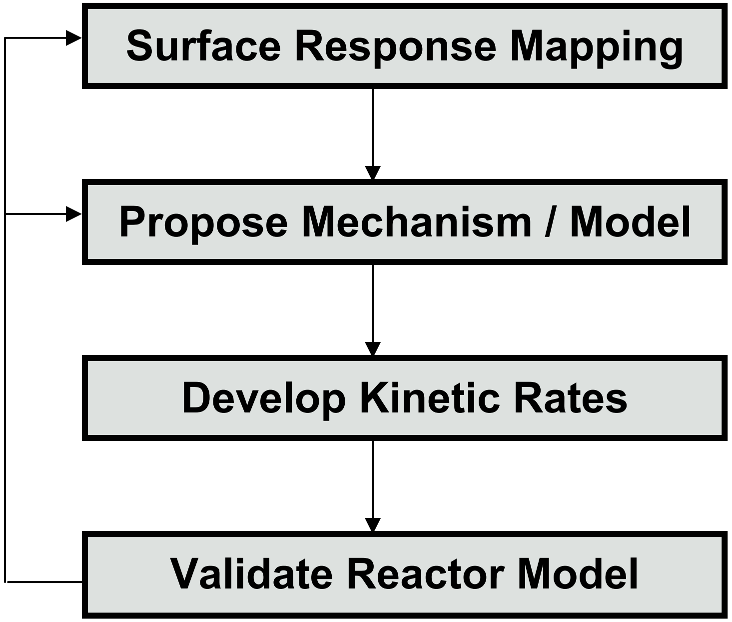
Diesel Fuel Reforming Kinetics - Methodology

- **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



Surface Response Mapping

Propose Mechanism / Model

Develop Kinetic Rates

Validate Reactor Model

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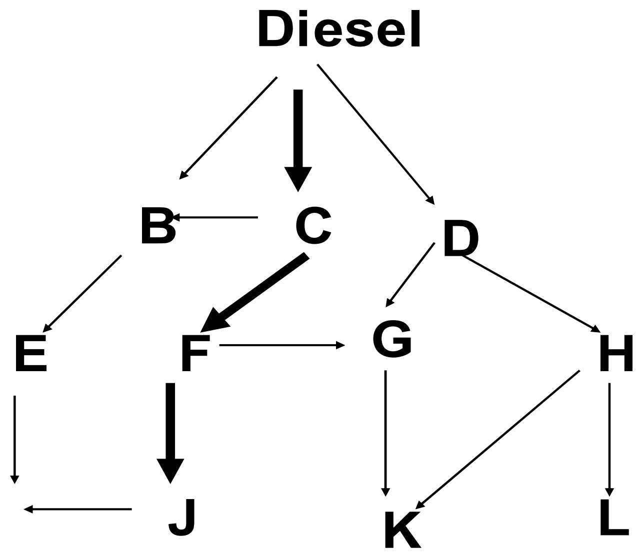
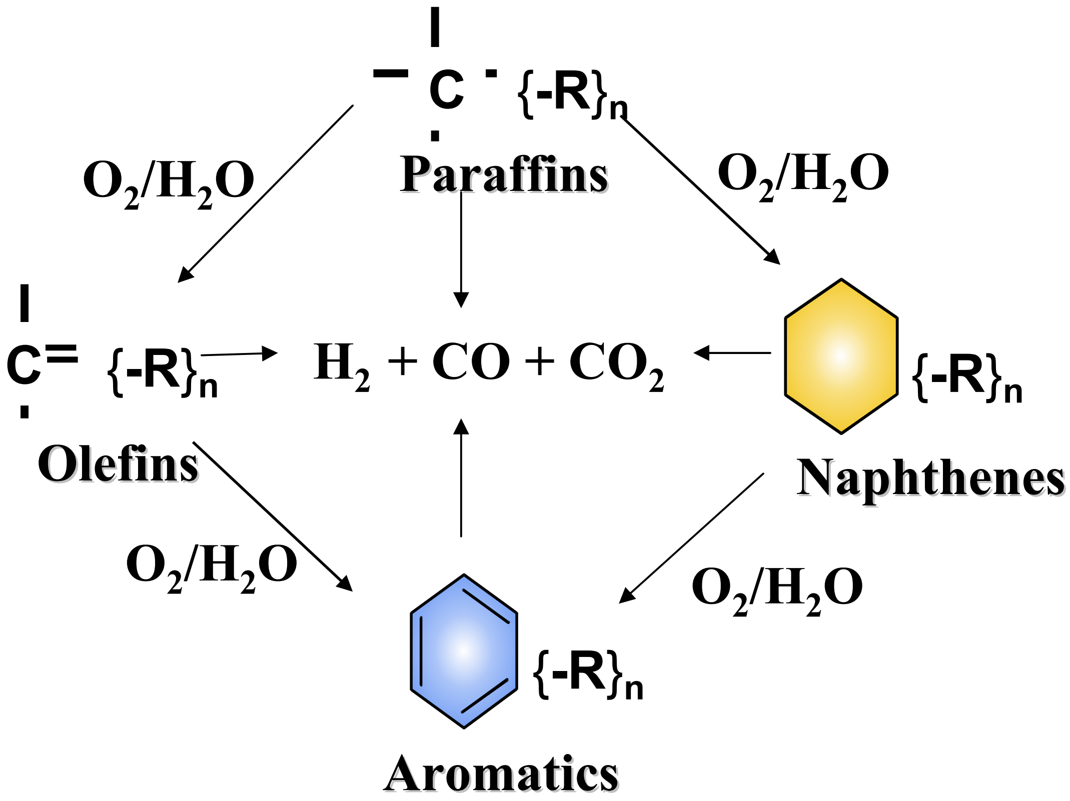
Diesel Fuel Reforming Kinetics – Rxn Pathways

Dominant reaction pathways to be elucidated

Assessment of kinetic parameters





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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-1st order
- Psuedo-homogeneous phase
- Easy to develop, inexpensive
- Suitable for process simulators, e.g. ASPEN, ChemCad
- Predicts transient response and hydrocarbon slip

Level 2
Mechanism Based Lumping

- Psuedo-homogeneous phase
- Based on psuedo-species 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

Level 3
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

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Diesel Fuel Reforming Kinetics – Rxn Pathways

- **Different reaction schemes for each class proposed based on RSM studies**
- **Each of the proposed schemes evaluated with respect to the experimental results obtained with each of the model compounds**
- **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.

Analysis of Kinetic Scheme

- **Paraffin Steam Reforming**

$$\mathrm{P} \xrightarrow{k_1} \mathrm{LP}$$

$$\mathrm{LP} \xrightarrow{k_2} \mathrm{OL}$$

$$\mathrm{P} \xrightarrow{k_3} \mathrm{OL}$$

$$\mathrm{OL} \underset{k_5}{\overset{k_4}{\rightleftarrows}} \mathrm{AR}$$

$$\mathrm{P} + \mathrm{H_2O} \xrightarrow{k_6} \mathrm{Syngas}$$

$$\mathrm{LP} + \mathrm{H_2O} \xrightarrow{k_7} \mathrm{Syngas}$$

$$\mathrm{OL} + \mathrm{H_2O} \xrightarrow{k_8} \mathrm{Syngas}$$

$$\mathrm{AR} + \mathrm{H_2O} \xrightarrow{k_9} \mathrm{Syngas}$$

P = Paraffins
LP = Lower Paraffins
OL = Olefins
AR = Aromatics

Analysis of Kinetic Scheme

- **Naphthenes Steam Reforming**

$$N \xrightarrow{k_1} LP$$

$$LP \xrightarrow{k_2} OL$$

$$N \xrightarrow{k_3} OL$$

$$N \underset{k_5}{\overset{k_4}{\rightleftarrows}} AR$$

$$N + H_2O \xrightarrow{k_6} \text{Syngas}$$

$$LP + H_2O \xrightarrow{k_7} \text{Syngas}$$

$$OL + H_2O \xrightarrow{k_8} \text{Syngas}$$

$$AR + H_2O \xrightarrow{k_9} \text{Syngas}$$

P = Paraffins
LP = Lower Paraffins
OL = Olefins
AR = Aromatics
N = Naphthenes

Analysis of Kinetic Scheme

- **Aromatics Steam Reforming**

$$AR \xrightarrow{k_1} CH_4$$

$$AR \underset{k_3}{\overset{k_2}{\rightleftharpoons}} OL$$

$$AR + H_2O \xrightarrow{k_6} \text{Syngas}$$

$$CH_4 + H_2O \xrightarrow{k_7} \text{Syngas}$$

$$OL + H_2O \xrightarrow{k_8} \text{Syngas}$$

P = Paraffins
LP = Lower Paraffins
OL = Olefins
AR = Aromatics

NETL Fuel Processing R&D

Diesel Fuel Reforming Kinetics – FY 03 Accomplishments

- Developed lumped “power law” model for diesel autothermal reforming
- Tested three model compounds from the major representative functional groups in diesel fuel
- Developed surface response maps for steam reforming, partial oxidation and ATR over Pt catalysts for single component fuels
- Built liquid hydrocarbon characterization capability

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Diesel Fuel Reforming Kinetics – Exp. Conditions

	ATR	**SR**	**POX**
O/C	0.6	0.0	1.0
H_2O/C	1.5	3.0	0.0
T (°C)	750 – 850	750 – 850	750 – 850
GHSV (h^{-1})	50,000 - 150,000 (20,000-65,000)*	50,000 - 150,000 (20,000-65,000)*	50,000 - 150,000 (20,000-65,000)*

***If 1-methylnaphthalene is in feed**

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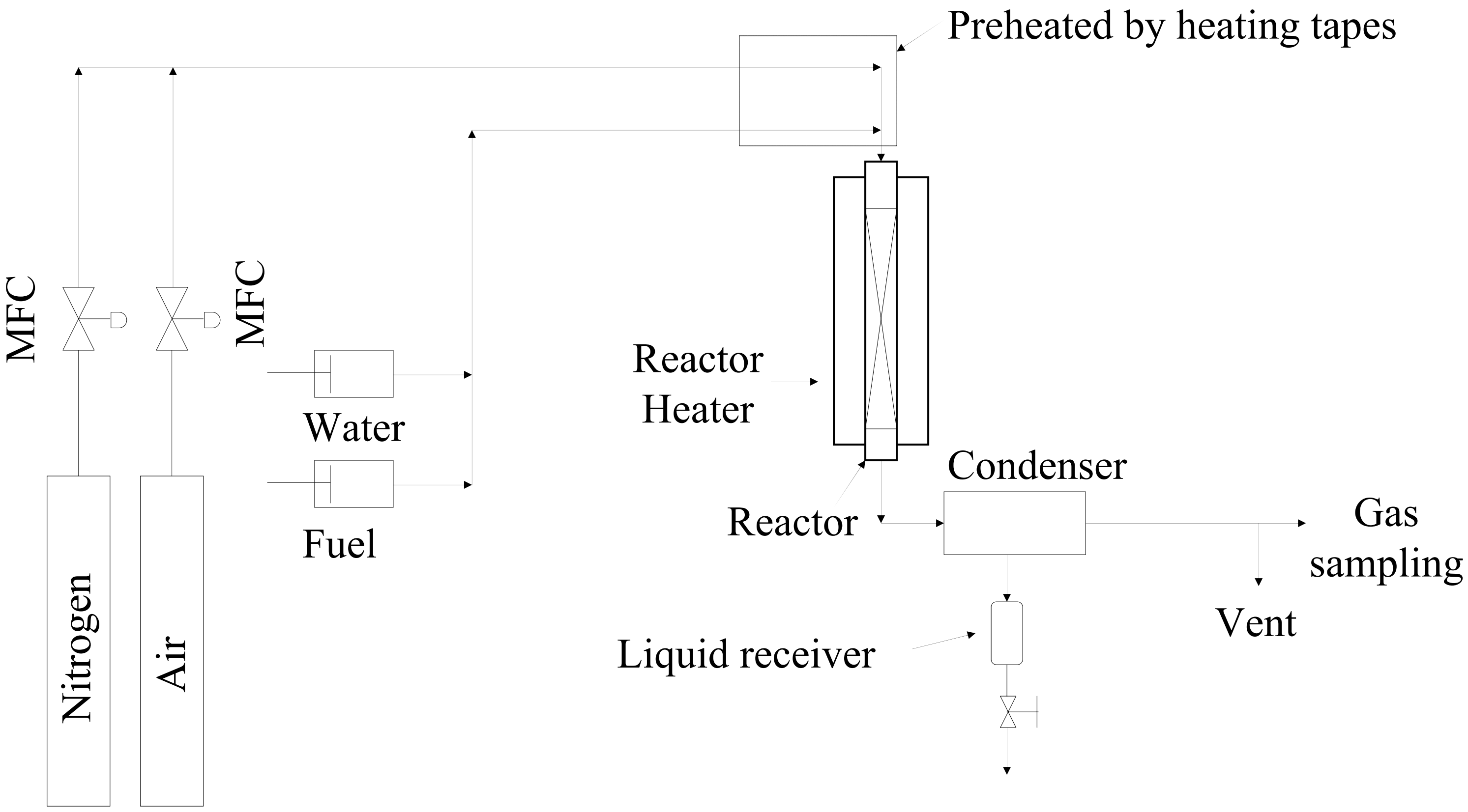
Diesel Fuel Reforming Kinetics – Exp. Setup



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Diesel Fuel Reforming Kinetics – Binary Components

Conducted combinatorial fuel reforming studies

N-Tetradecane and Decalin (50wt% each)

Decalin and 1-methylnaphthalene (50wt% each)

1-Methylnaphthalene and n-tetradecane (50wt% each)

Production of specie k is defined as

= Moles of k formed per mole of carbon in the feed x 100.

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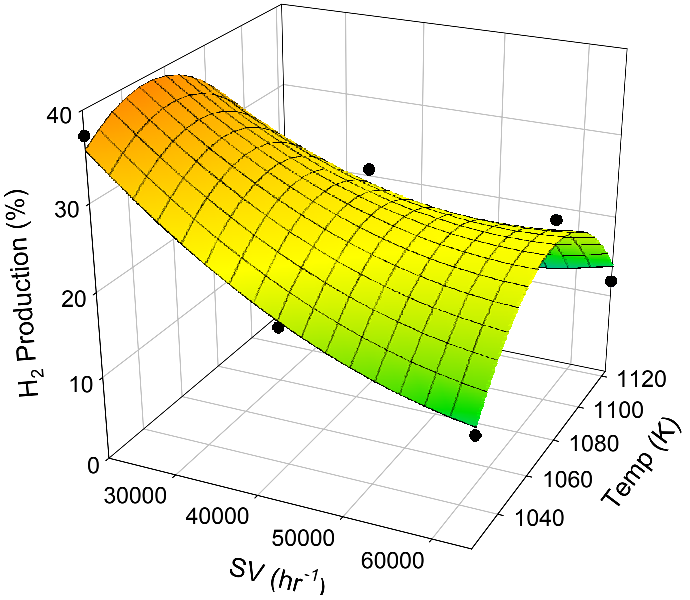
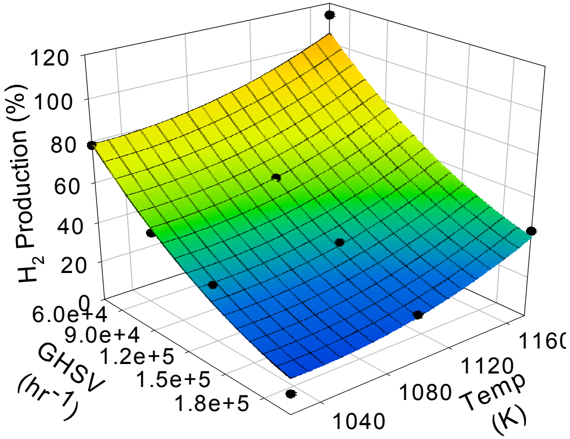
Diesel Fuel Reforming Kinetics

ATR, Pt/Al_2O_3, S/C=1.5, and O_2/C=0.3

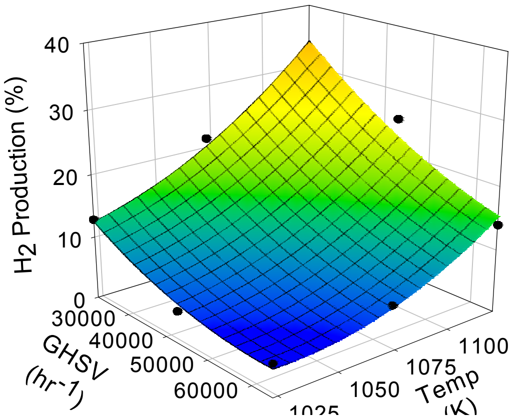
H_2 Production from TD and MN



H_2 Production from TD



H_2 Production from MN

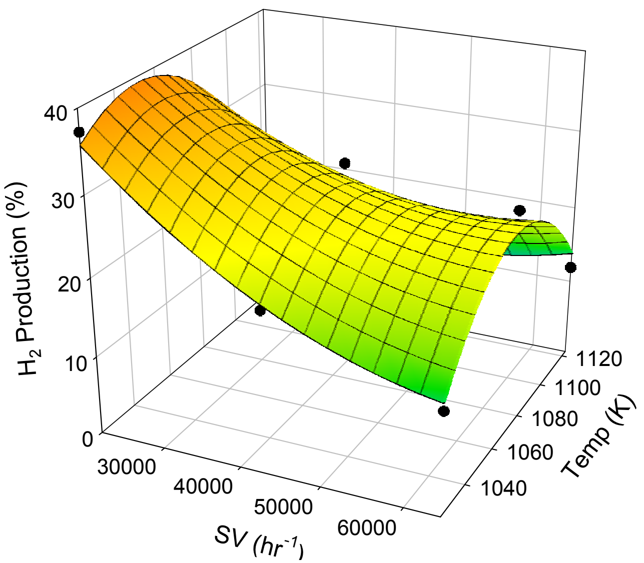


- **Overall yields are not additive of yields from individual fuel components**
- **Relative reactivity of one fuel component considerably affects the conversion pattern of other**
  - More the difference in relative reactivity; larger the effect
- **Conversion of highly reactive fuel component proceeds towards completion**

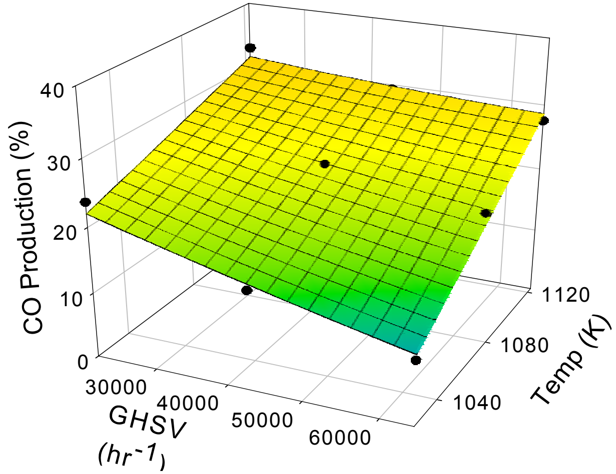
NETL Fuel Processing R&D

Diesel Fuel Reforming Kinetics – Rxn Pathways

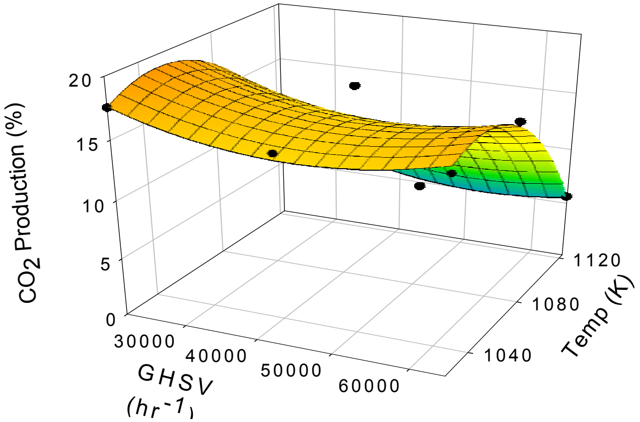
ATR, Pt/Al_2O_3, S/C=1.5, and O_2/C=0.3



H_2 Production from TD and MN



CO Production from TD and MN



CO_2 Production from TD and MN

- **Reverse of water gas shift reaction dominates at high temperatures**

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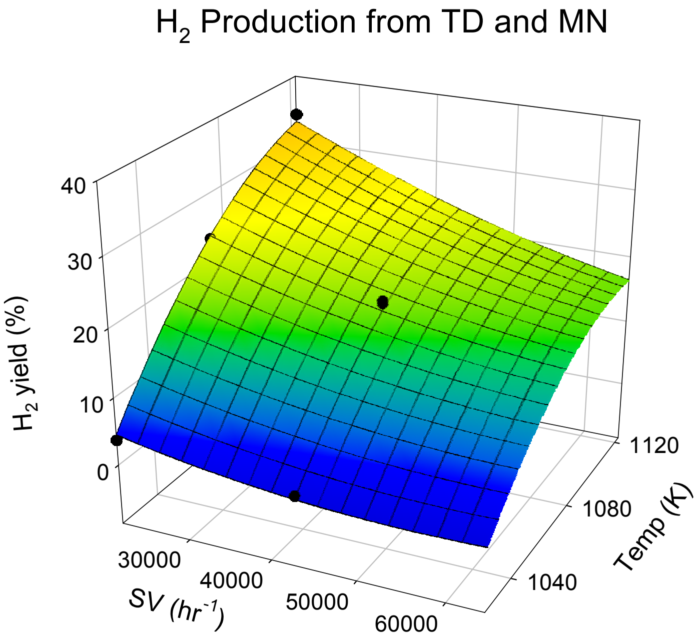
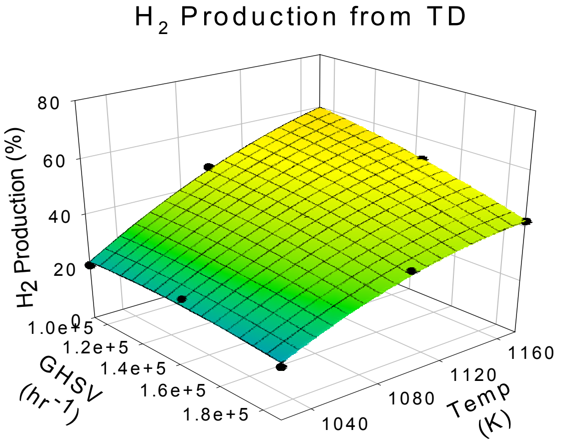
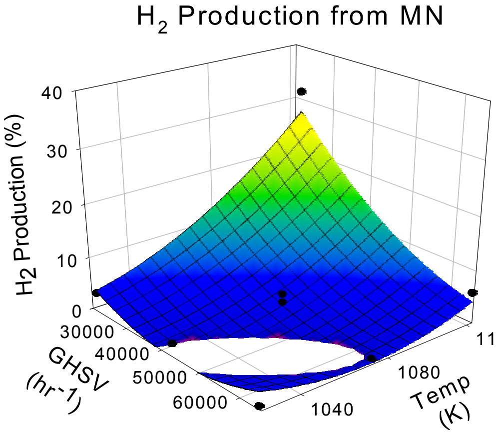
Diesel Fuel Reforming Kinetics – Rxn Pathways

Pt/Al_2O_3, POX, and O_2/C=0.5


H_2 Production from TD and MN


H_2 Production from TD


H_2 Production from MN

- **Partial oxidation reforming affected significantly by the difference in reactivity of fuel components**
  - Highly reactive component consumes available O_2
    - Produces combustion products
- **O_2 not spared for the less reactive component**
  - Pyrolysis reaction dominates

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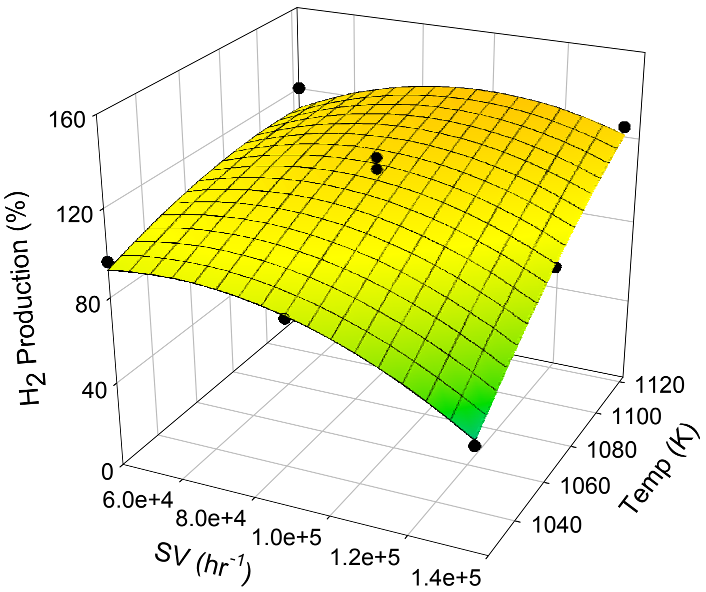
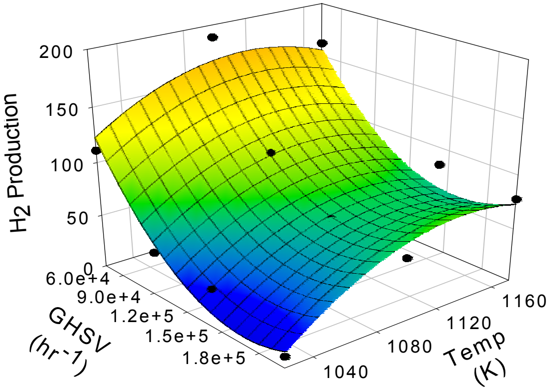
Diesel Fuel Reforming Kinetics – Rxn Pathways

Pt/Al_2O_3, SR, and S/C=3.0

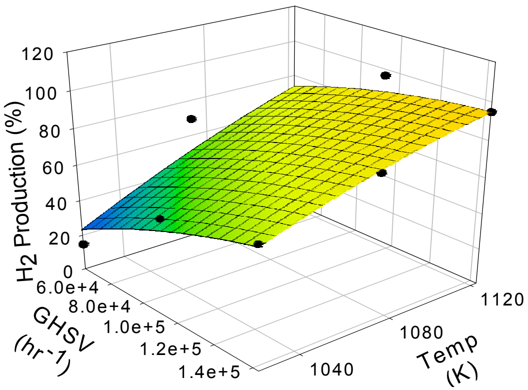
H_2 Production from TD and DHN



H_2 Production from TD



H_2 Production from DHN



- **Steam reforming not affected much from the difference in reactivity of fuel components**

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Diesel Fuel Reforming Kinetics – Conclusions

- Conducted binary fuel compound studies
- Developed surface response maps for steam reforming, partial oxidation and ATR over Pt catalysts for binary fuel mixtures
- Quadratic fit of data from RSM was excellent (>90%)
- Overall yields are not additive of yields 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
- Proposed probable kinetic schemes for different hydrocarbons

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Diesel Fuel Reforming Kinetics – Conclusions cont.

- **Conversion of highly reactive fuel component proceeds towards completion**
- **Side reactions specific to one component plays important role**
  - Aromatics more coking prone
- **Catalyst surface-component interaction also important**
  - Aromatics may occupy catalyst active sites for longer time
- **Product distribution also changed**

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Diesel Fuel Reforming Kinetics – Future Plans

- **Continue Surface Response Mapping :**
  - Evaluate other fuel compounds within a classification to examine if similar reforming behavior exists
  - Conduct tertiary fuel compound studies
  - Continue evaluation of carbon formation
- **Develop Kinetic Submodels**
  - Develop intuitive kinetic models for individual model compounds and benchmark fuel for particular catalyst types
  - Continue collaboration with Las Alamos National Laboratory (LANL) to provide carbon deactivation kinetics
  - Obtain experimental reactor performance data to validate reaction models from other program participants.
- **Technology Transfer**
  - Continue dissemination of results through publications and FE SECA program reviews to principle developers such as Acumentrics, Cummings/McDermott, Delphi Automotive, FCE, GE/Honeywell, Siemens-Westinghouse.

NETL Fuel Processing R&D

- ***Investigation of Oxygen Conducting Catalyst Supports***

NETL Fuel Processing R&D

O2 Conducting Supports – Objective

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.

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O2 Conducting Supports – Carbon Formation

- **Boudouard Reaction**
  - $CO + H_2 = C + H_2O$
  - $2CO = C + CO_2$
- **Polymerization Reaction (Encapsulating Carbon)**
  - C_nH_m => olefins => polymers => coke
- **Pyrolytic Reaction**
  - $CH_4 = C + 2H_2$
  - $(\text{-}CH_2\text{-})_n \Rightarrow nC + nH_2$
- **Whisker Carbon Formation**

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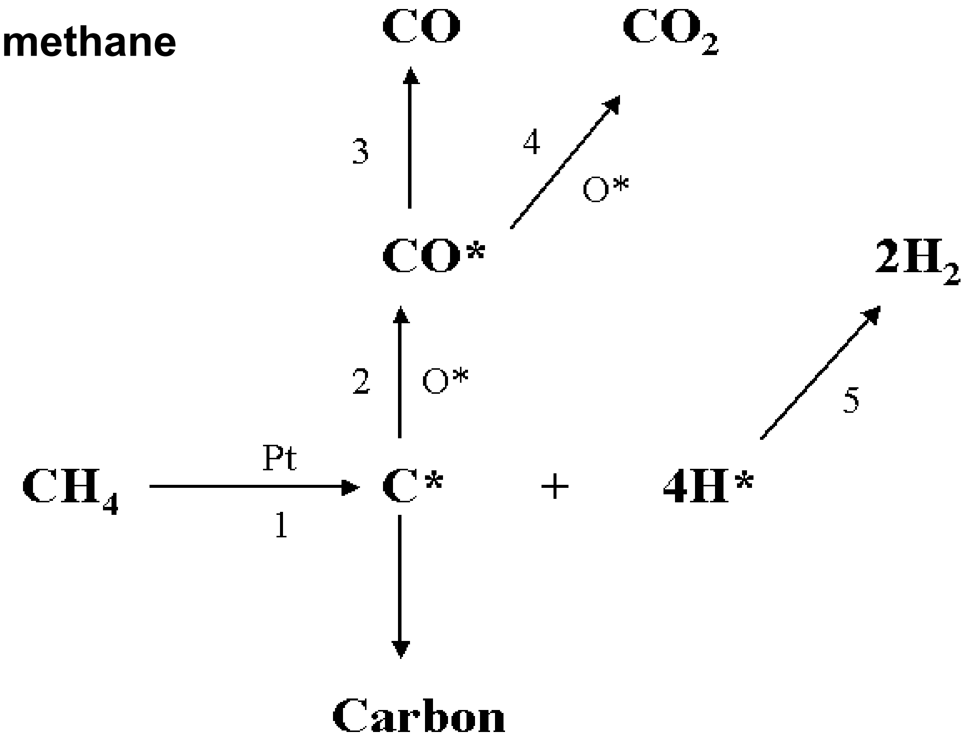
O2 Conducting Supports – Rxn Network for CH4

Suggested reaction network for methane oxidation
(stars indicate surface species)



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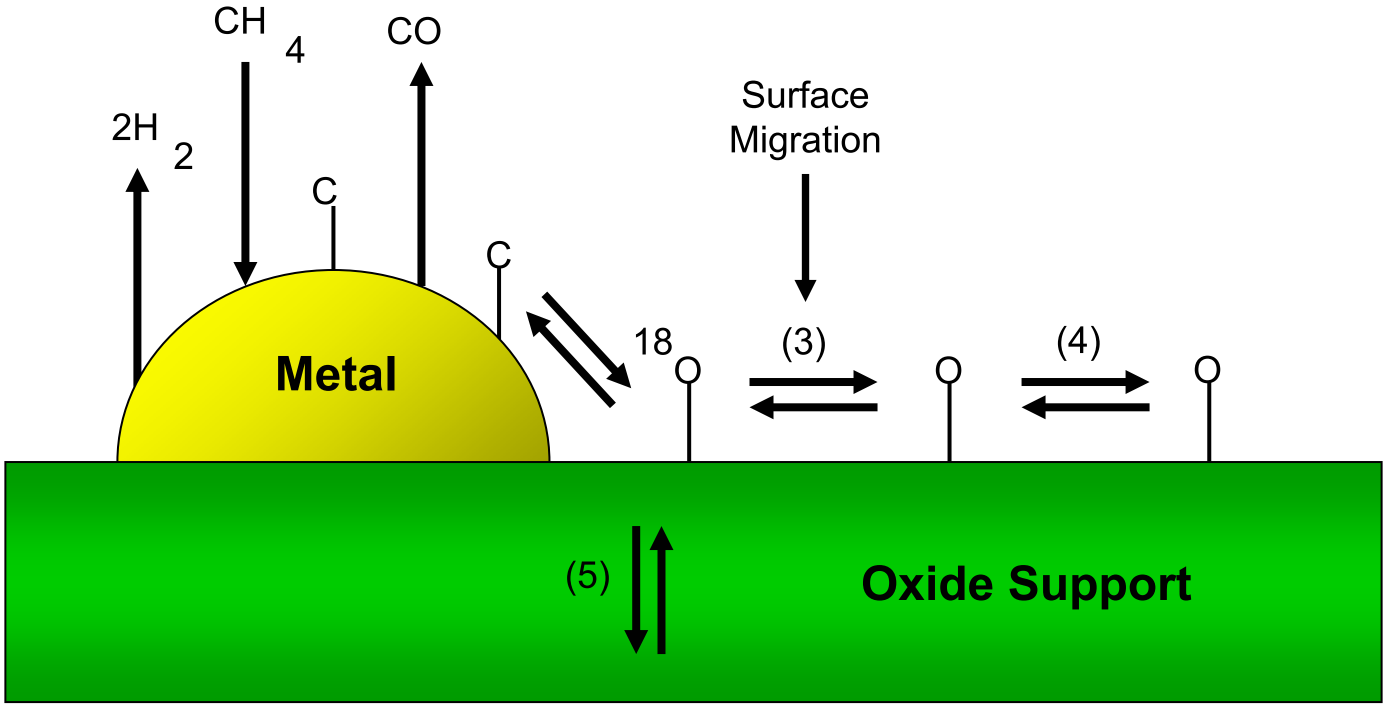
O2 Conducting Supports – Rxn Network for CH4



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O2 Conducting Supports – Approach

- **Conduct reforming tests to elucidate effects of:**
  - -Support type (O2 conducting vs non-conducting)
  - -Ionic conductivity
  - -Dopant type (La, Gd)
  - -Dopant concentration
  - -Oxygen storage capacity vs ionic conductivity
  - -Catalyst type (Pt, Ni, Rh)

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O2 Conducting Supports – Sample Matrix

$Ce_{.9}Gd_{.1}O_2$		200nm	4g
$Ce_{.9}Gd_{.1}O_2$	1% Rh	200nm	4g
$Ce_{.9}Gd_{.1}O_2$	1% Ni	200nm	4g
$Ce_{.9}Gd_{.1}O_2$	1% Pt	200nm	4g
***$Ce_xLa_{1-x}O_2$**		200nm	4g
***$Ce_xLa_{1-x}O_2$**	1% Rh	200nm	4g
***$Ce_xLa_{1-x}O_2$**	1% Ni	200nm	4g
***$Ce_xLa_{1-x}O_2$**	1% Pt	200nm	4g
$Ce_{.5}Zr_{.5}O_2$		200nm	4g
$Ce_{.5}Zr_{.5}O_2$	1% Rh	200nm	4g
$Ce_{.5}Zr_{.5}O_2$	1% Ni	200nm	4g
$Ce_{.5}Zr_{.5}O_2$	1% Pt	200nm	4g

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O2 Conducting Supports – Accomplishments

- Preliminary studies initiated to characterize product distribution as function of temperature during the partial oxidation of methane on Rh/Al2O3.
- Completed an accepted review paper entitled "Synthesis gas partial oxidation and the role of oxygen-conducting supports: A review" to be presented at the Second International Conference on Fuel Cell Science, Engineering and Technology.
- Temperature Programmed Oxidation was conducted to determine the amount of carbon formed on the catalyst.

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O2 Conducting Supports – Future Activities

- Doped ceria based catalysts and alumina with different dispersed metals such as Pt, Rh and Ni will be characterized for performance and carbon formation during methane cPOx.

- Post analysis of the catalysts will be performed to determine changes in the BET surface area, crystalline phase and redox state. Selected samples will be analyzed by scanning electron microscopy (SEM) and other techniques to investigate the types of carbon formed.

- Mechanistic studies will be carried out by isotopic exchange experiments. Lattice oxygen in the support will be exchanged by oxygen in the gas phase during the methane conversion to Syn-gas.

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Hexaaluminate Reforming Catalysts

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Hexaaluminate Reforming Catalysts – Objective

Objectives:

- Assess activity and selectivity of active transition metals dispersed within **thermally stable** hexaaluminate
  - Hexaaluminate ($AB_yAl_{12-y}O_{19-z}$)
    - A-site: alkali, rare earth (e.g., Ba, Ca, La)
    - B-site: transition metal (e.g., Ni, Co, Fe, Pt)
  - Model fuel compounds
    - n-tetradecane
    - 1-methylnaphthalene

- Minimize use of expensive PGM's
  - Examine activity levels at various levels of B-site substitution

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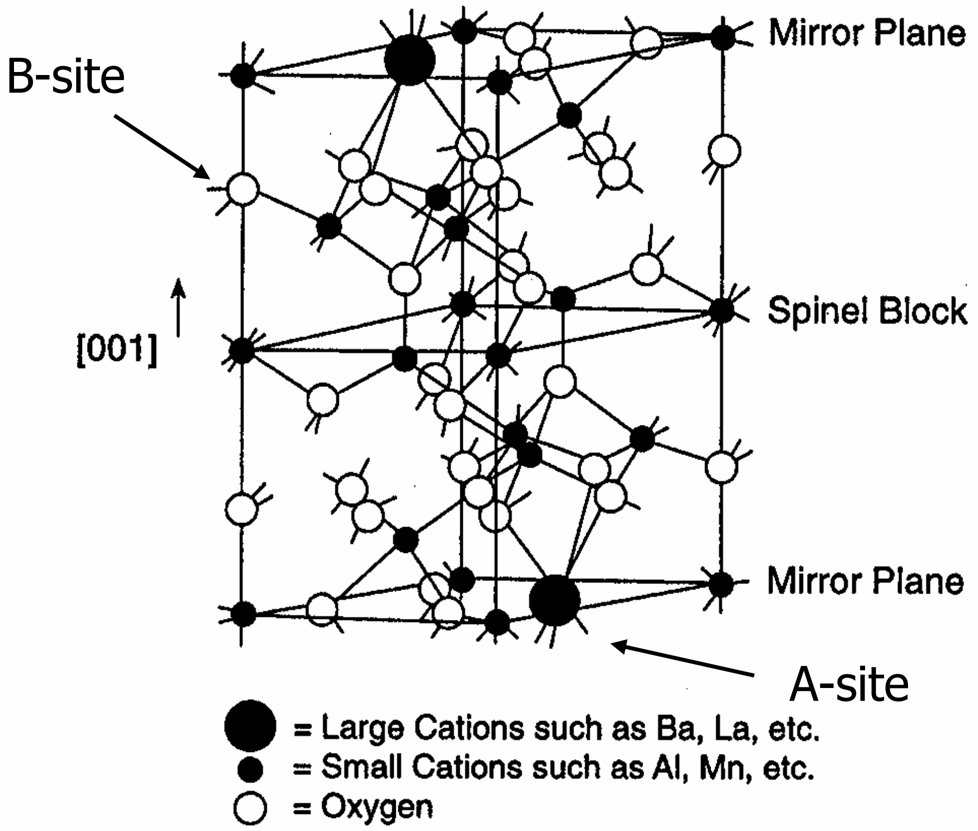
Hexaaluminate Reforming Catalysts – Properties

- Hexaaluminate structure: magnetoplumbite
- Structural formula: AByAl12-yO19-z
- Thermal stability: Layered Al-O structure results in anisotropic crystal growth and mass diffusion that is suppressed in the [001] direction
- Strong interactions with neighboring atoms suppress active metal mobility, growth and aggregation
- Smaller active metal crystals are less susceptible toward carbon formation



From: Jang et al., Cat. Today 47 (1999) 103

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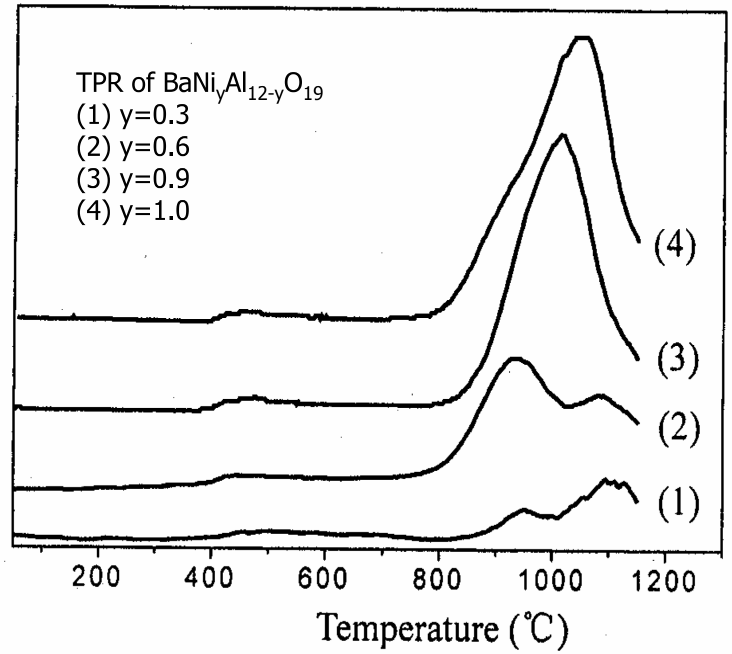
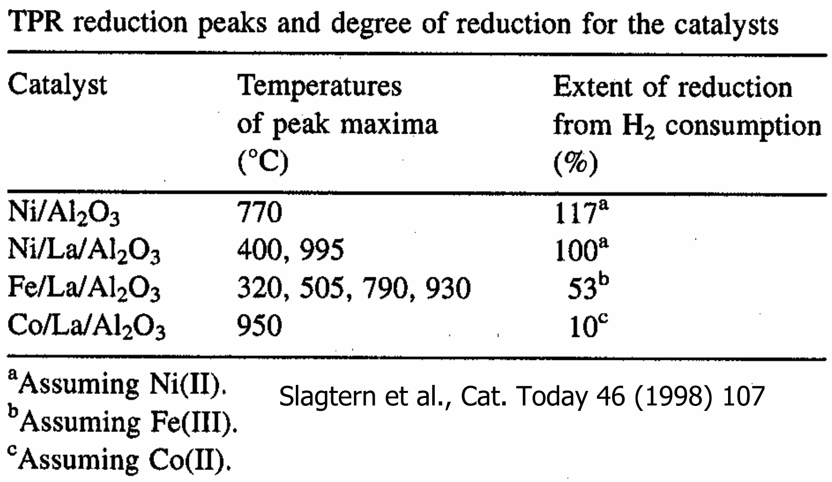
Hexaaluminate Reforming Catalysts – Properties



From: Chu et al., Appl. Cat. A 235 (2002) 39

In (1) and (2) the first reduction peak is due to the presence of other Ni-aluminum containing phases that are less stable



TPR reduction peaks and degree of reduction for the catalysts

Catalyst	Temperatures of peak maxima (°C)	Extent of reduction from H_2 consumption (%)
Ni/Al_2O_3	770	117[a]
$Ni/La/Al_2O_3$	400, 995	100[a]
$Fe/La/Al_2O_3$	320, 505, 790, 930	53[b]
$Co/La/Al_2O_3$	950	10[c]

[a] Assuming Ni(II).
[b] Assuming Fe(III).
[c] Assuming Co(II).

Slagtern et al., Cat. Today 46 (1998) 107

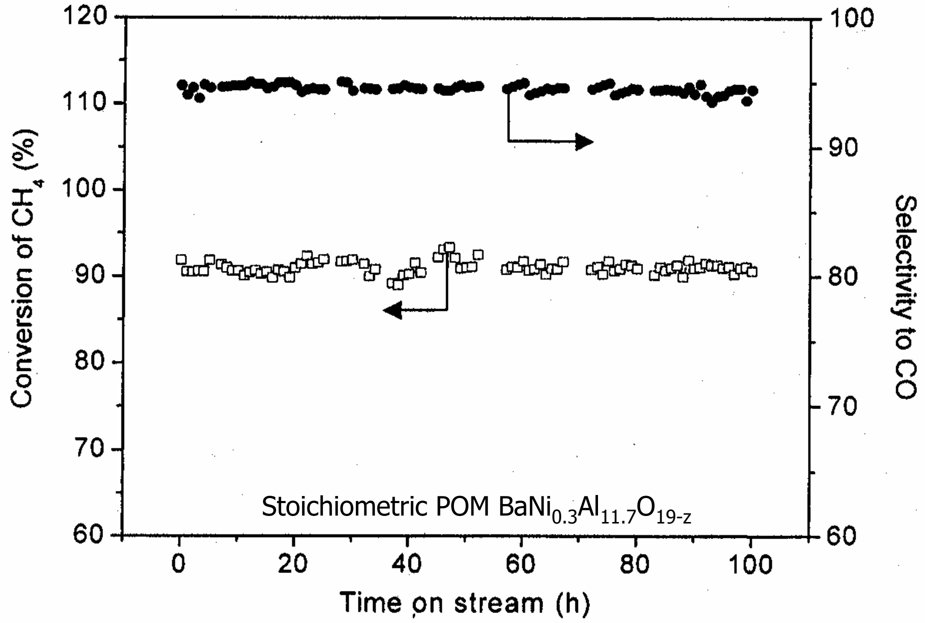
- ➢Ni dispersed within hexaaluminate posses greater resistance to reduction than Ni supported on Al2O3 and La/Al2O3

NETL Fuel Processing R&D

Hexaaluminate Reforming Catalysts – Activity & Carbon Resistance

<u>Ni hexaaluminate POM performance</u>
CO selectivity: 95%
CH4 conversion: 92%
Carbon formation: 0.8 wt%

- BaNi0.3Al11.7O19-z showed excellent resistance to carbon deposition over 100 hrs
- High levels of conversion and CO selectivity were obtained at 1.2x104 cm3/gcat h



From: Chu et al., Appl. Cat. A 235 (2002) 39

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Hexaaluminate Reforming Catalysts – Accomplishments

- **Completed detailed review of relevant literature**
- **Synthesis completed**
  - $LaCoAl_{11}O_{19-z}$
  - $LaFeAl_{11}O_{19-z}$
  - $LaNiAl_{11}O_{19-z}$
- **Currently undergoing characterization**

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Hexaaluminate Reforming Catalysts – Future Work

- **Identify the effect of alkali A-site doping on coking propensity**
- **Identify the effect of B-site substitution level on activity and selectivity**
- **Examine B-site substitution with PGM's**