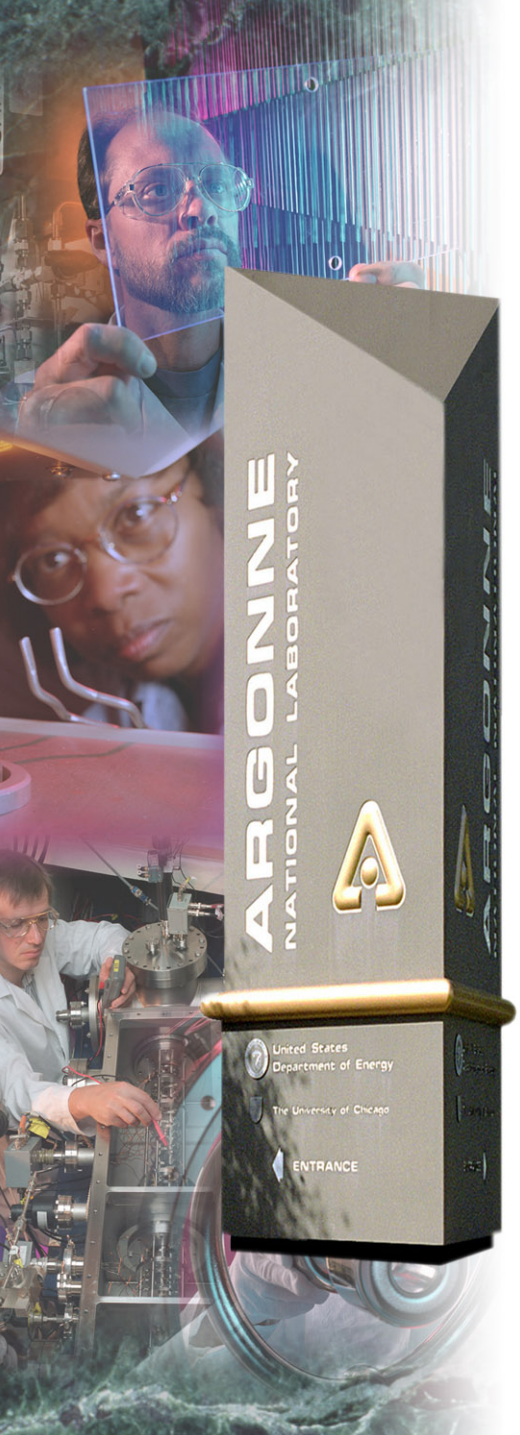


Diesel Reforming for Solid Oxide Fuel Cell Application

Di-Jia Liu, Shuh-Haw Sheen,
& Michael Krumpelt

SECA Core Technology Peer Review Workshop
Tampa, FL
January 27 - 28, 2005

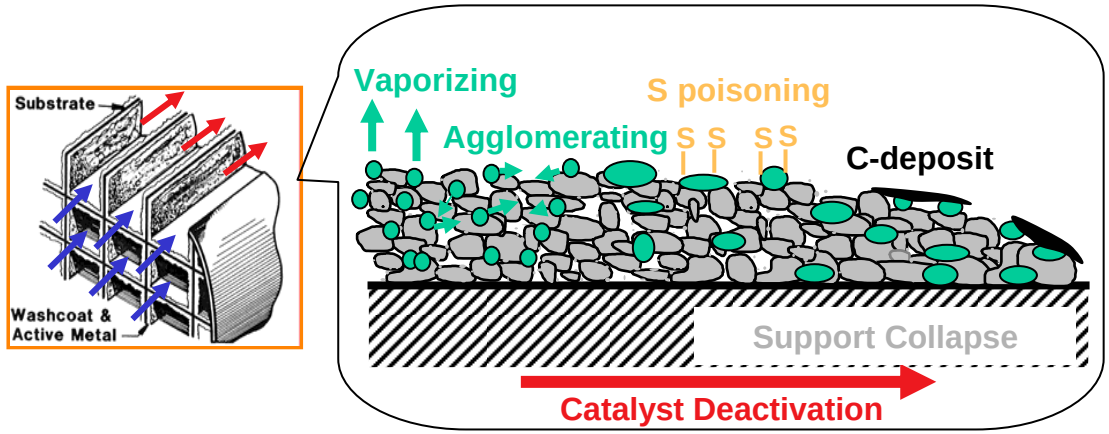
Argonne National Laboratory

A U.S. Department of Energy
Laboratory Operated by
The University of Chicago

The Critical Issues in Diesel Reforming Catalyst & Catalytic System Development

Catalyst

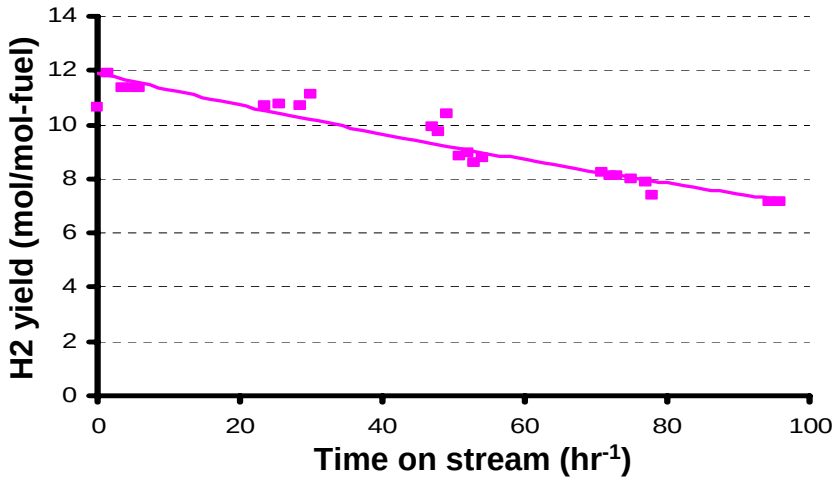
- **Cost**
  - **Costly Rh usage**
- **Activity**
  - **Efficiency & Selectivity**
  - **Fuel property & chemistry**
- **Durability**
  - **Metal vaporization & agglomeration**
  - **Support stability**
  - **Sulfur poisoning**
  - **Coke formation**



System

- **Fuel injection & mixing**
- **System integration**

Reforming catalyst aging – an example



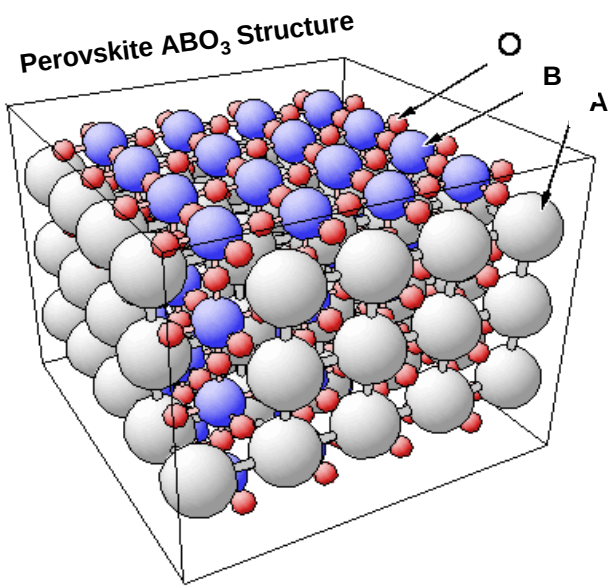
Diesel Reforming Catalyst Development

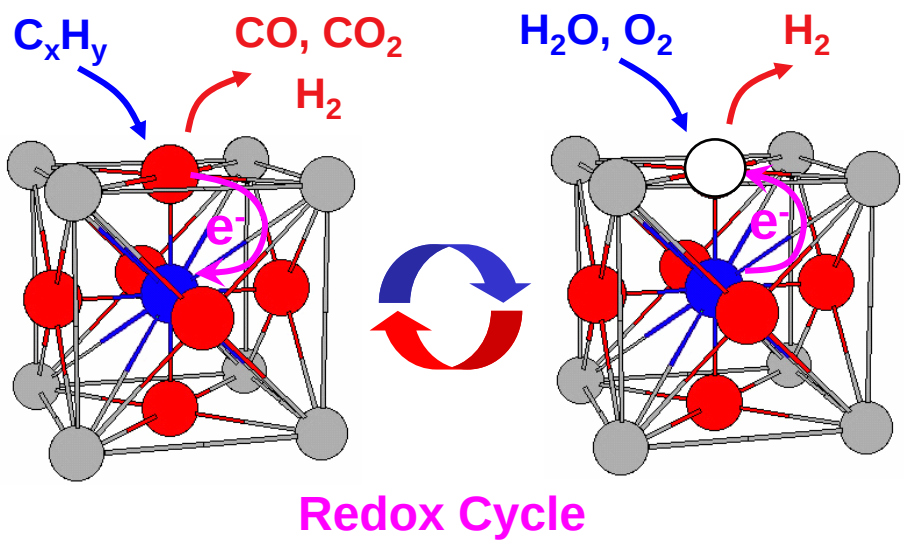
What Constitutes an Ideal Diesel Reforming Catalyst?

- **Atomically dispersed active site.**
- **Stably anchored over the support surface.**
- **Effectively cleaving C-H, C-C & C=C bonds through oxidative process.**
- **Competitively releasing hydrogen over oxidation to H_2O.**
- **Competitively oxidizing surface carbon over C=C bond growth.**
- **Minimum chemical binding energy with sulfur.**

Objective: Developing Perovskite Based ATR Catalyst

- **The Perovskite Catalyst…**
  - Low cost material.
  - Stable under high temperature & redox environment.
  - Exchangeable *A & B* sites lead to ionic dispersion & improve catalytic activity.



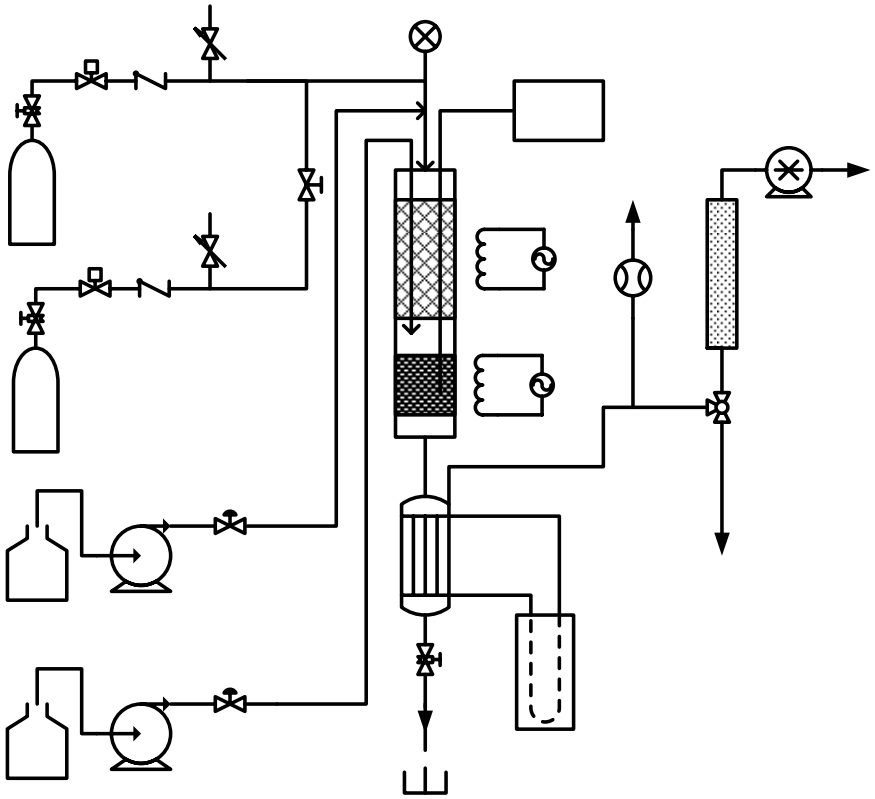


Conductivities of both e^- and $V_O^{\cdot\cdot}$ of perovskite enhance catalytic active site through electron & oxygen vacancy transfers in a redox process.

Approach: ANL Perovskite Catalyst Materials

- **Perovskites include chromite, aluminite, manganite, ferrite, …**
- **Self-combustion synthesis (Pechini method)**
- **B-site doped with Ru, Rh, etc…**
- **A-site exchanged with La, Sr, Ba, Gd, Ce, Pr, …**

Catalyst Activity Study: Test Apparatus & Conditions



Diesel Reforming Catalyst Test Plant

- **Fuel**
  - **Alkane surrogate - $C_{12}H_{26}$**
  - **Organic sulfur - Dibenzothiophene (50 ppm S)**
  - **Other HC surrogates – Monoaromatics, Polyaromatics, Cycloparffins …**
- **Temperature**
  - **Reactor: 700 °C to 800 °C**
  - **Preheating: 200 °C.**
- **Input Mixture**
  - **ATR: O_2/C = 0.3 ~0.5, H_2O/C = 1 ~ 3**
- **Space Velocity**
  - **Fuel Flow Rate = 2.8~5.0x10^{-3} gfuel/gCat•sec**
  - **GHSV = 50K ~ 100K hr^{-1}**

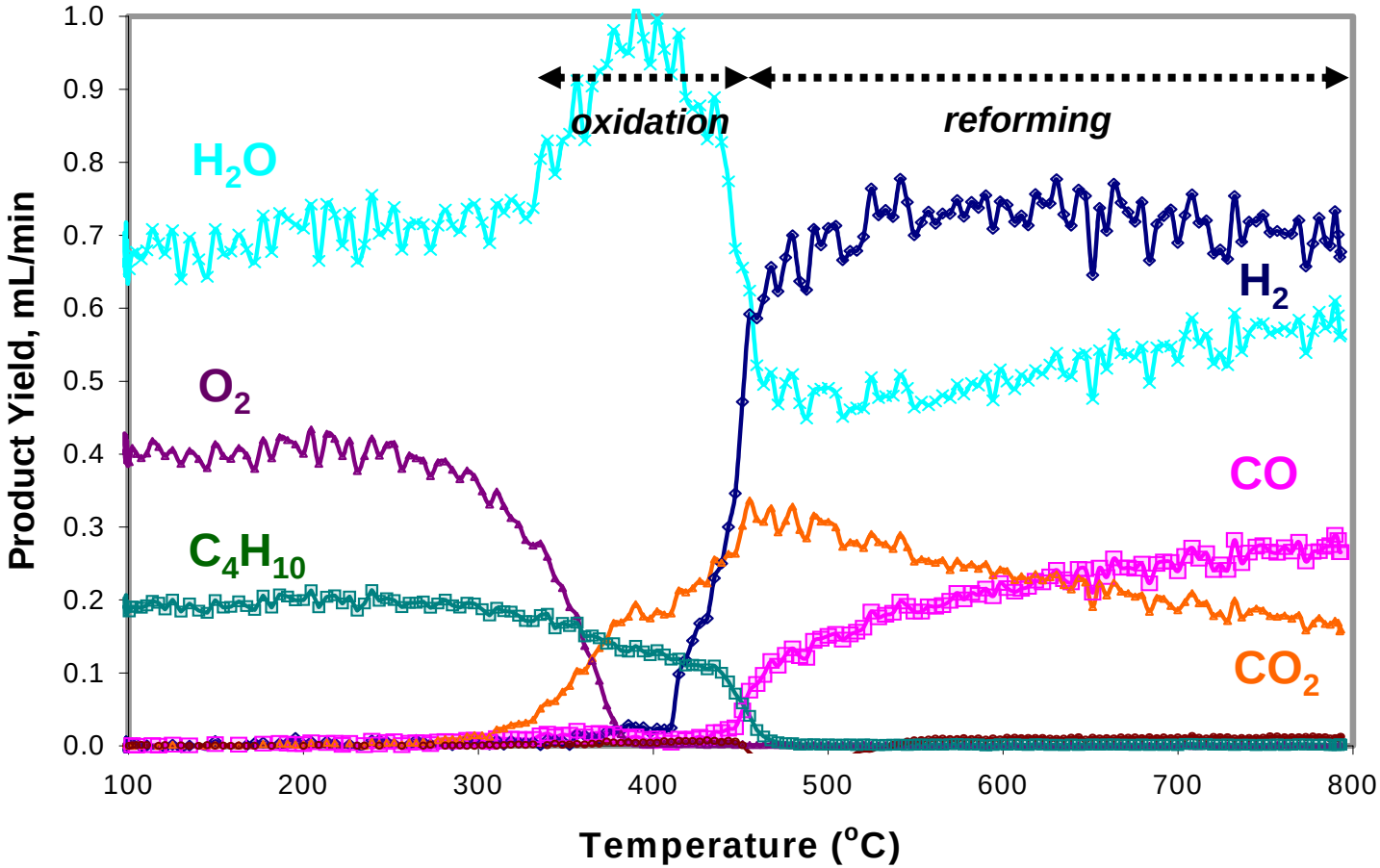
Overhead

Pressure

Flow

Catalyst Activity Study: Test Plant

Catalyst Activity Study: Investigation on ATR Catalytic Light-Off for Perovskite Material



Ru doped perovskites demonstrate low light-off temperature for hydrogen production suitable for SOFC application

Catalyst Activity Study: Basic Performance Parameters in Catalytic ATR Reforming

Chemical Reactions in Diesel ATR Reforming:

$$C_nH_m + xO_2 + yH_2O = nCO_2 + (m/2 + 2n - 2x)H_2 + (y + 2x - 2n)H_2O$$

An example: $C_{12}H_{26} + 6O_2 + 12H_2O = 12CO_2 + 25H_2$

Definition of Reforming Performance:

$$H_2 \text{ yield} = C_{H2} / C_{fuel}$$

$$\text{Reforming efficiency} = \{C_{H2}\Delta Hc_{H2} + C_{CO}\Delta Hc_{CO}\} / C_{fuel}\Delta Hc_{fuel}$$

$$\text{COx selectivity} = \{C_{CO2} + C_{CO}\} / nC_{fuel}$$

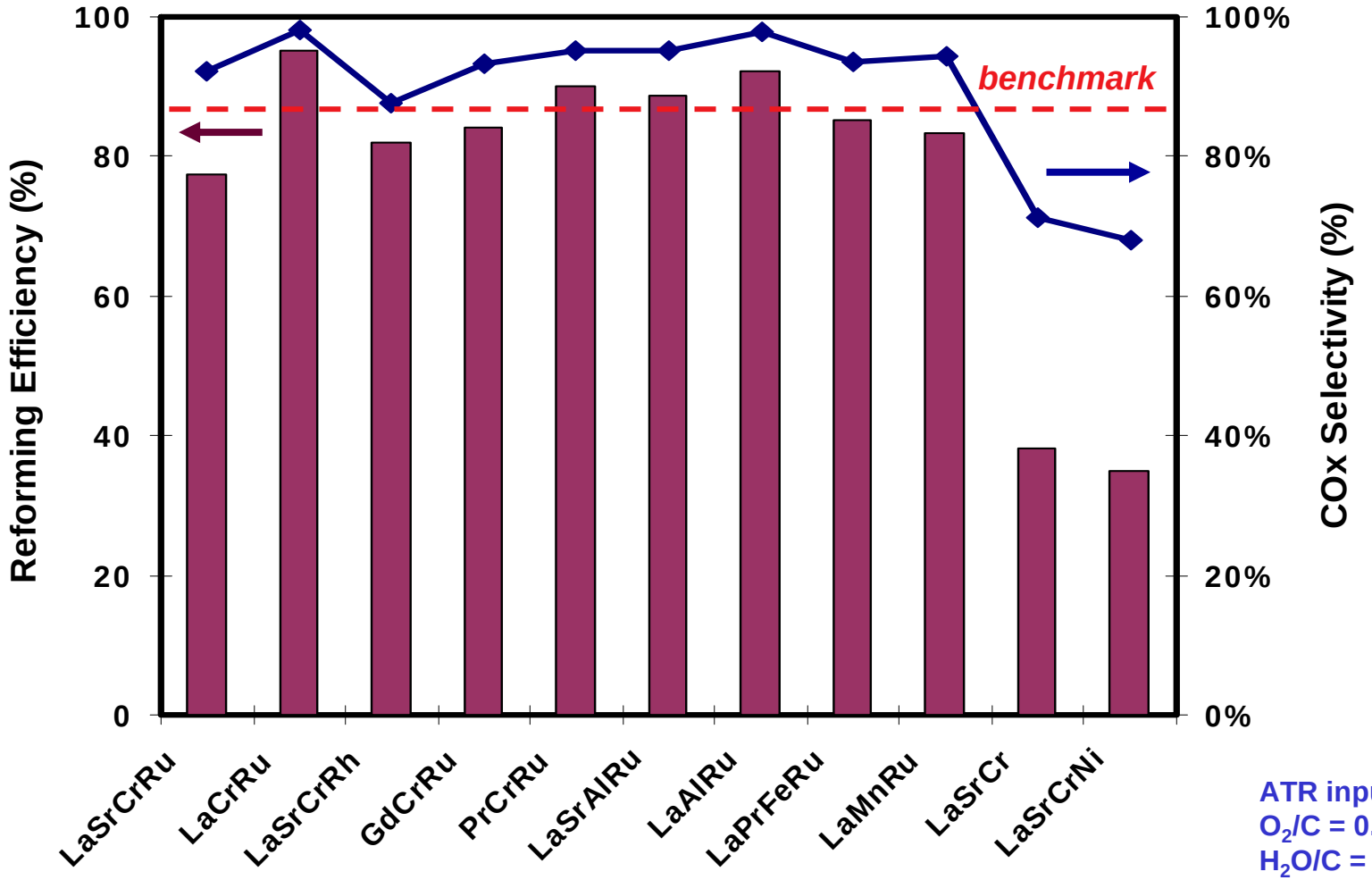
C_i = Molar flow of *i*,

ΔHc_i = Heat of combustion of *i*,

n = Number of C in fuel molecule

Catalyst Activity Study: Benchmarking New Perovskite Materials with Rh-Based Catalyst

Performance of a selected group of perovskites

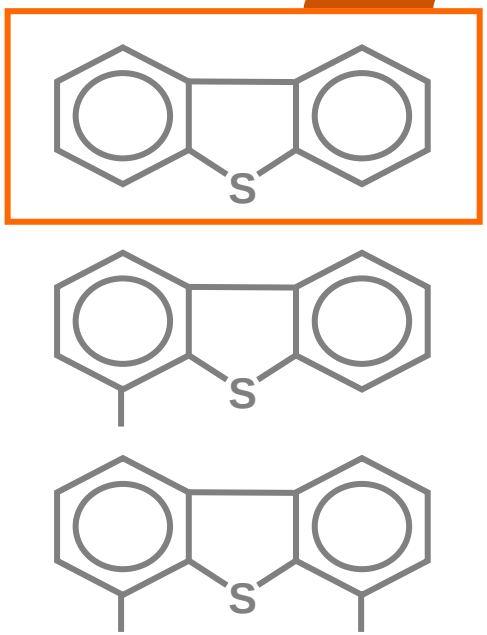


ATR input
$O_2/C = 0.5$
$H_2O/C = 2$

Sulfur Tolerance Study: Recoverable Activity over Perovskite Materials

Dibenzothiophene (DBT) and its derivatives are difficult to be removed from diesel through HDS process …

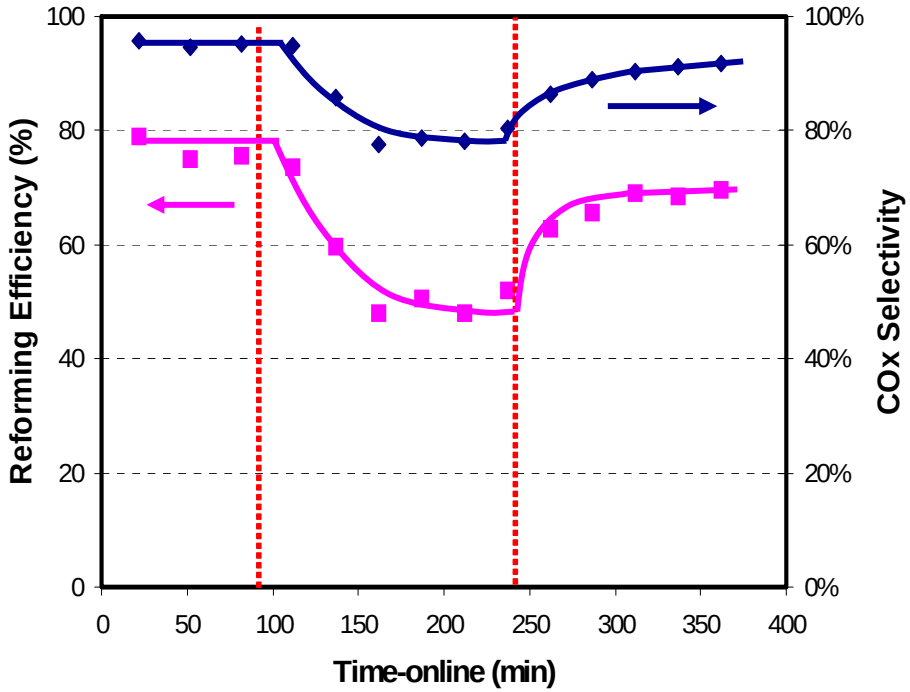
Introducing 50 ppm sulfur in the form of DBT temporarily suppress reforming efficiency and COx selectivity.



DBT

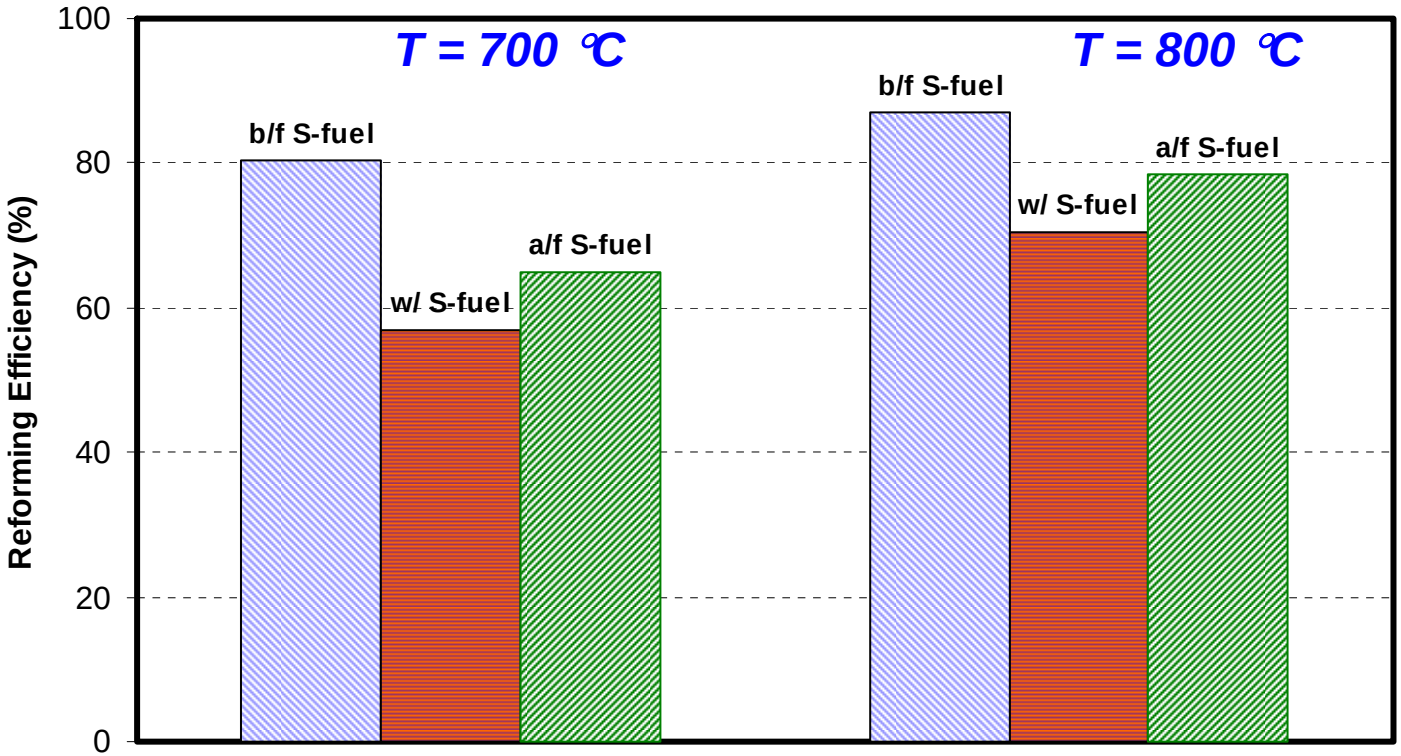
4-MDBT

4,6-DMDBT



Catalyst re-activates after S is removed from fuel.

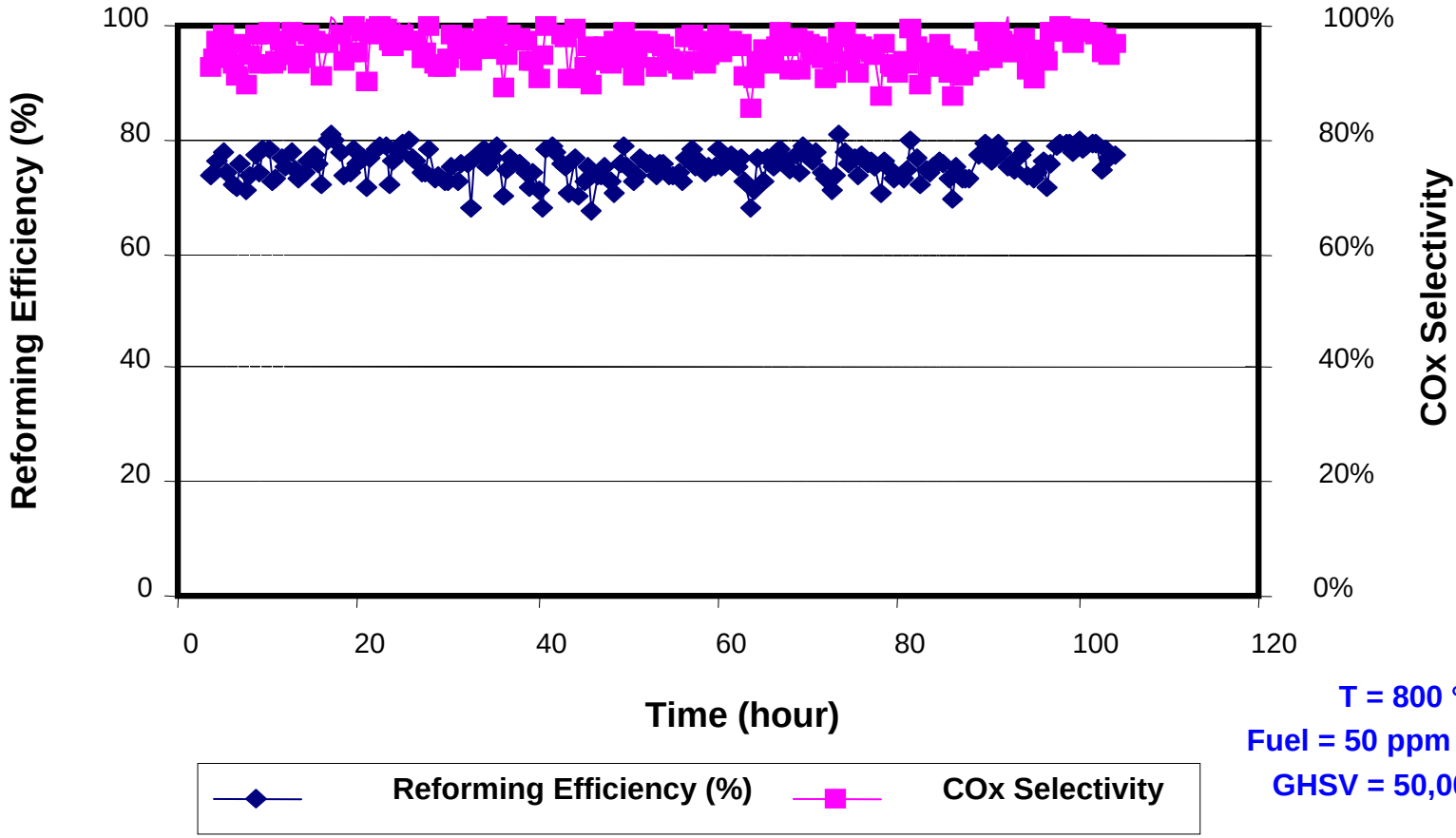
Sulfur Tolerance Study: Resistance to Poisoning Improves at Higher Operating Temperature



Catalyst = LCR-800, O_2/C = 0.5, H_2O/C = 1.0, GHSV = 130,000 hr^{-1}

Increase reaction temperature by 100 °C significantly improved catalytic performance in the presence of sulfur

Sulfur Tolerance Study: Stable Reforming Observed during 100-Hr Aging Test with 50 ppm S in DBT



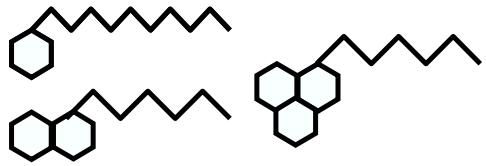
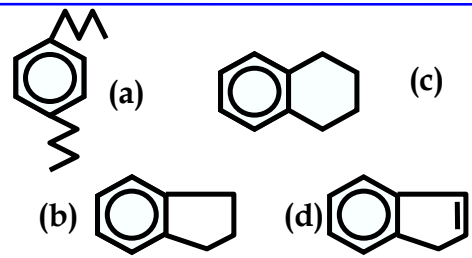
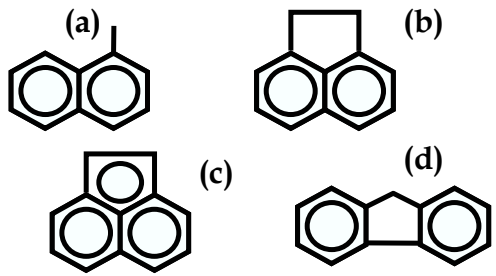
T = 800 °C

Fuel = 50 ppm S/$C_{12}H_{26}$

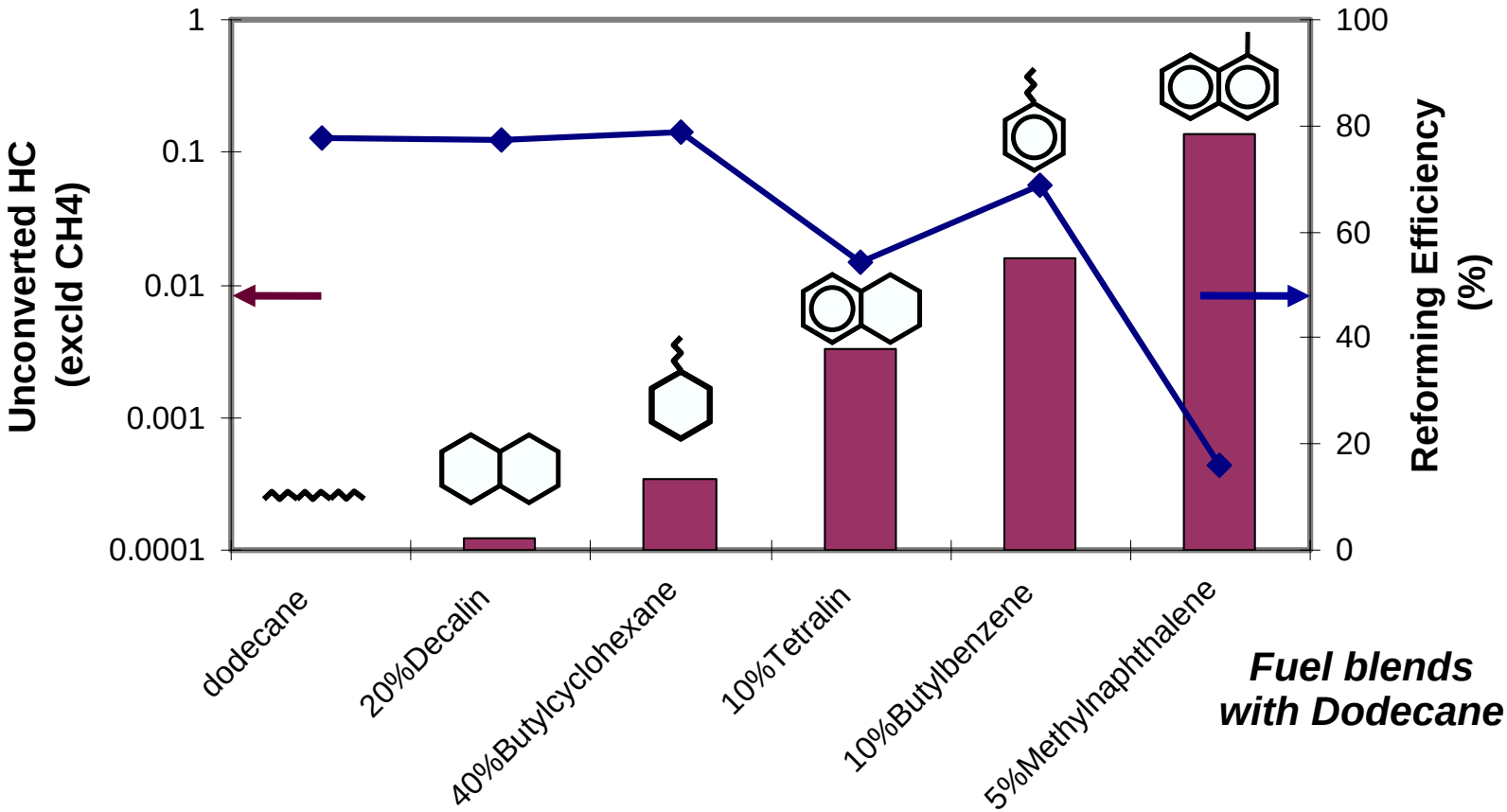
GHSV = 50,000 hr-1

Excellent catalytic stability was observed during 100 hour aging test with S contaminated fuel

Coking Prevention Study: Issues with Heavy Hydrocarbon Components in Diesel

Compound Type	Wt% Analysis, ANL	Wt% Analysis, Exxon	Ave. or Ref. Formula (ANL)	Representative Molecular Structures
Paraffins	38.7	39.7	$C_{16}H_{34}$	
Cycloparaffins 1-ring cycloparaffins 2-ring cycloparaffins 3-ring cycloparaffins	 29.6 11.5 4	 23.6 20.6 6.5	 $C_{10}H_{21}$ $C_{16}H_{32}$ $C_{22}H_{38}$	
Mono-aromatics Alkyl benzenes (a) Naphthenebenzenes (Indans (b) + Tetralins (c) + Indens (d))	 7.3 3.2	 3.2 0.9	 C_8H_8 $C_{12}H_{16}$	
Di-aromatics Alkylnaphthalenes (a) Acenaphthenes (b)/Biphenyls Acephthalenes (c)/Fluorenes (d)	 1.8 3.5 0.3	 1.6 2.2 1.7	 $C_{13}H_{14}$ C_9H_{12} $C_{13}H_{10}$	

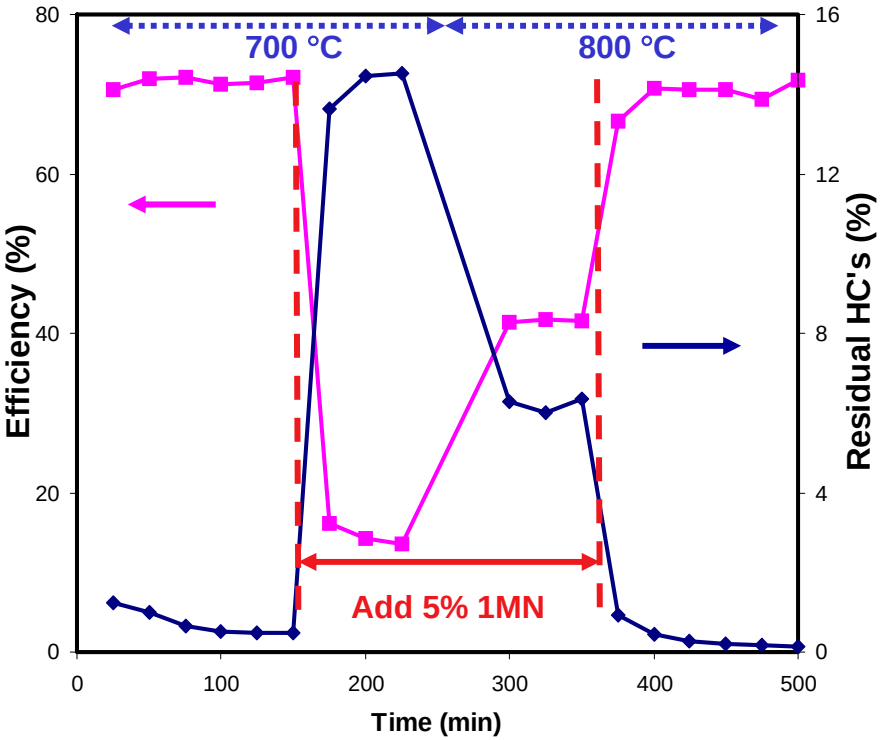
Coking Prevention Study: Correlation b/w Efficiency & Residual HC's Formation from Diesel Components



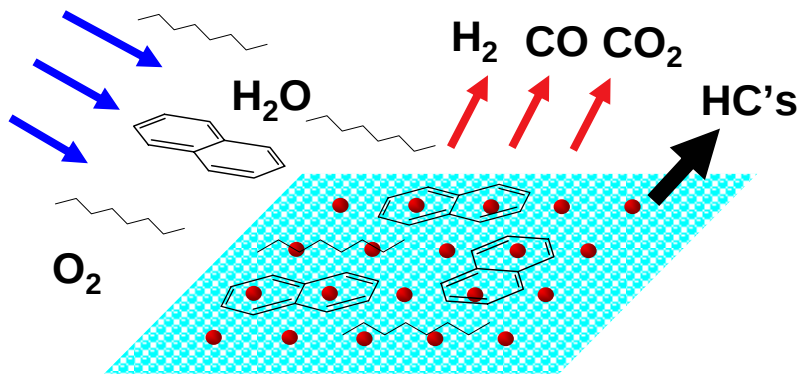
Coking is affected by Temperature, O_2/C, H_2O/C, Catalyst & ***CATALYSIS CHEMISTRY of HYDROCARBONS***.

Coking Prevention Study: Deactivation Mechanism & Coke Formation by Polyaromatics

- **Impact on ATR reforming by 1-methylnaphthalene (1MN)**



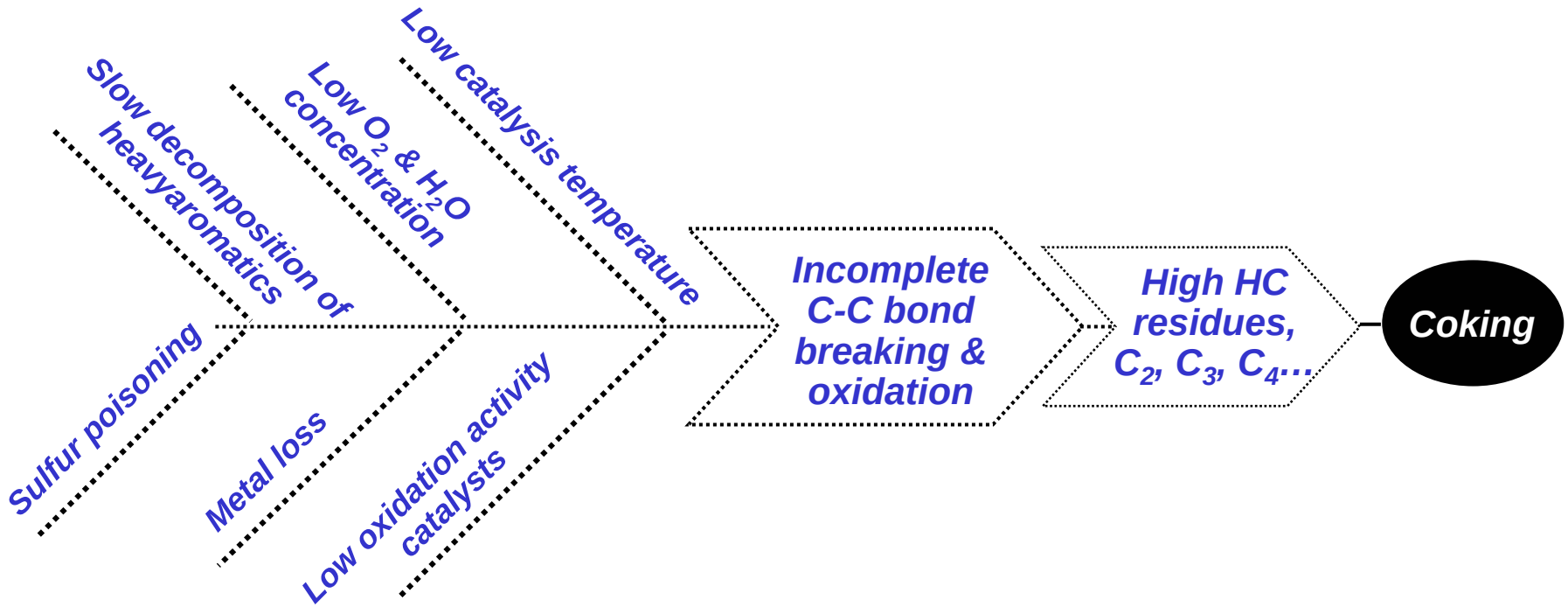
- **Proposed Model of PAH impact on Reforming and C-formation**
  - **Low cetane# / high Tig make them hard to oxidize.**
  - **Competition b/w oxidation vs. C growth**



- **1MN tentatively deactivates reforming.**
- **Activity recoverable after 1MN removal.**
- **Performance improves a higher T.**
- **O_2/C & H_2O/C have limited impact.**

Long resident time and slow decomposition of PAH over active site reduce reforming rate & increase residual HC's & coke formation!

Coking Prevention Study: Fishbone Analysis on Root Cause of Coking

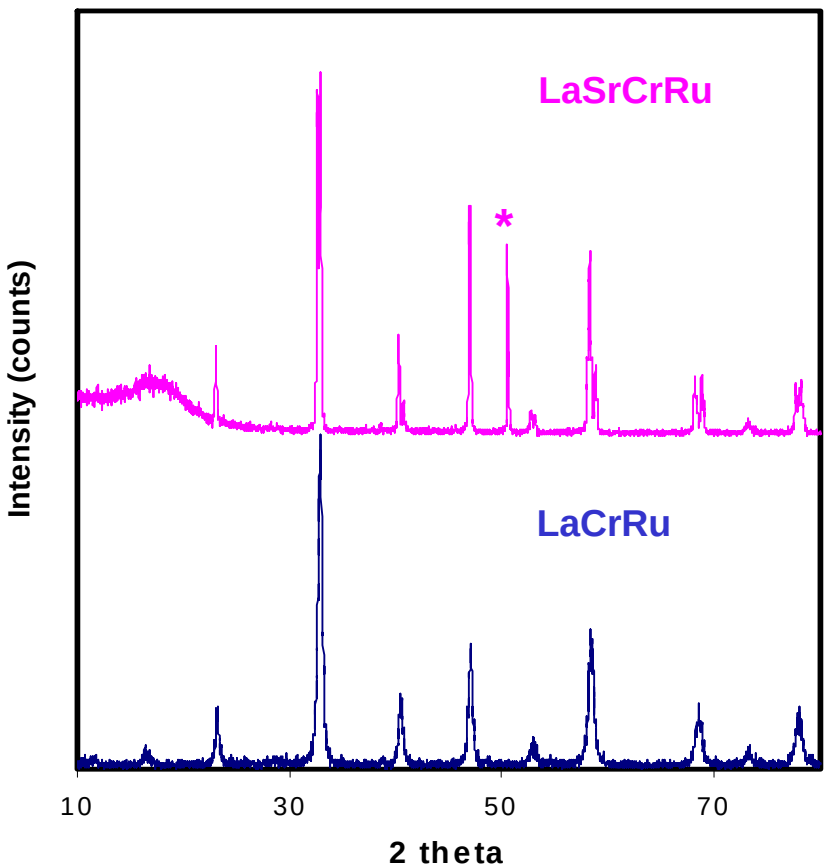


We are currently working on coking reduction through both catalyst & engineering improvements

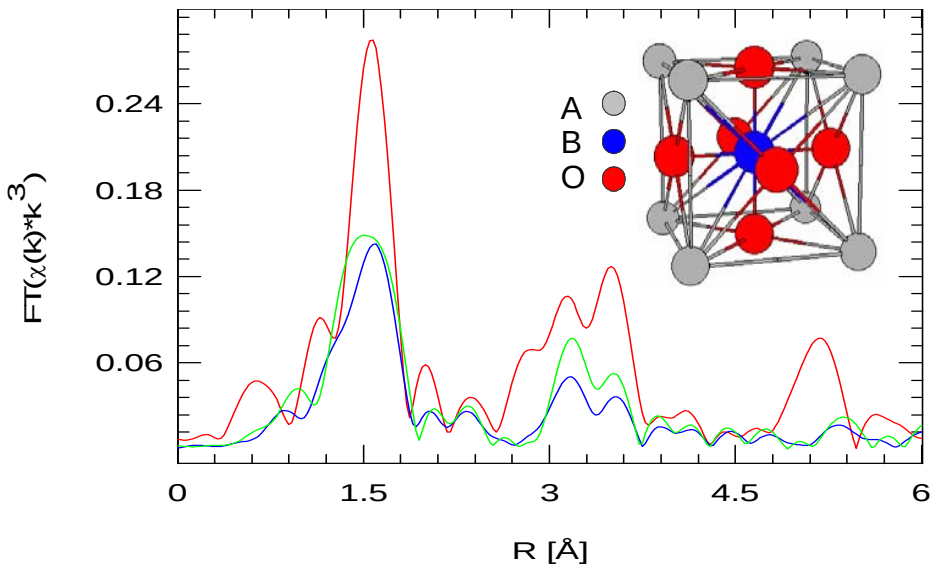
Catalyst Characterization: Identifying Perovskite Structure & Ru Active Site

Conventional (XRD, SEM, ICP, TPR, BET…) and Advanced (EXAFS, XANES) characterization methods were used to study structure-activity relationship

XRD confirms perovskite structure



EXAFS reveals Ru embedded in perovskite



	N	*R (Å)*	σ^2
LCSR1200	6.0	1.943	2.5×10^{-5}
LCSR800	4.7	1.953	2.5×10^{-5}
LCR800	4.3	1.962	1.0×10^{-5}

Summary: Knowledge Gained on Perovskite Catalyst & Its Applicability to SECA

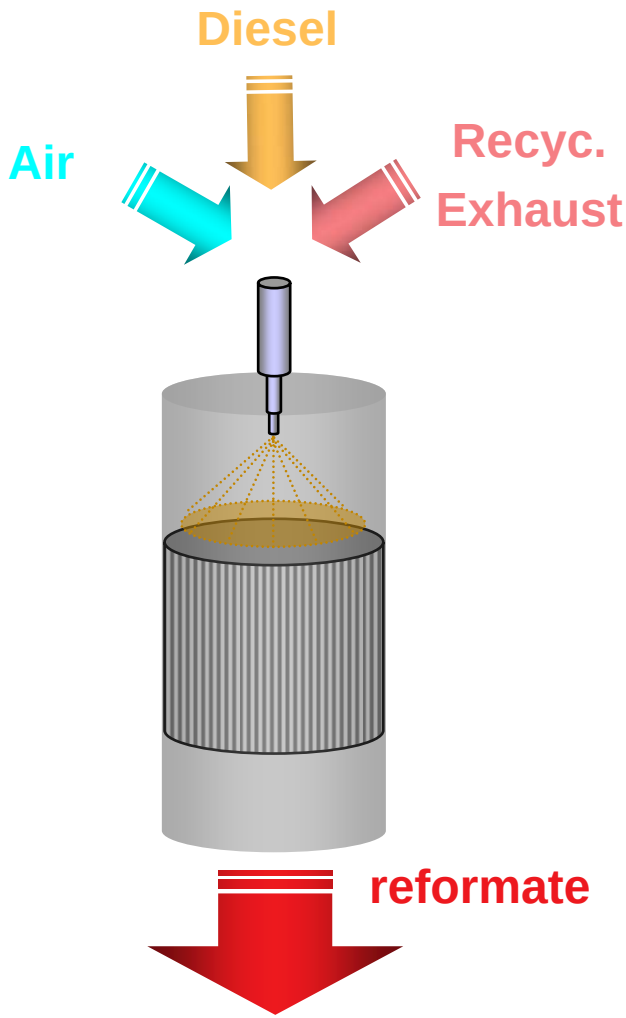
- **Ru doped perovskites demonstrated excellent catalytic reforming activities comparing with Rh based catalysts.**
- **Active catalysts are the perovskites containing Ru at B site with oxygen vacancy and high surface area.**
- **Improved sulfur tolerance and perovskite stability were demonstrated through 100-hr aging at higher operating temperature.**
- **Root cause of catalyst deactivation through coking by aromatics was identified. Improvement through catalyst material refinement and new reactor engineering approach is underway.**

Perovskite ATR catalysts provide new low-cost alternatives in fuel reforming for SECA.

Diesel Fuel Mixing & Cool Flame Study

Critical Issues in Fuel Mixing

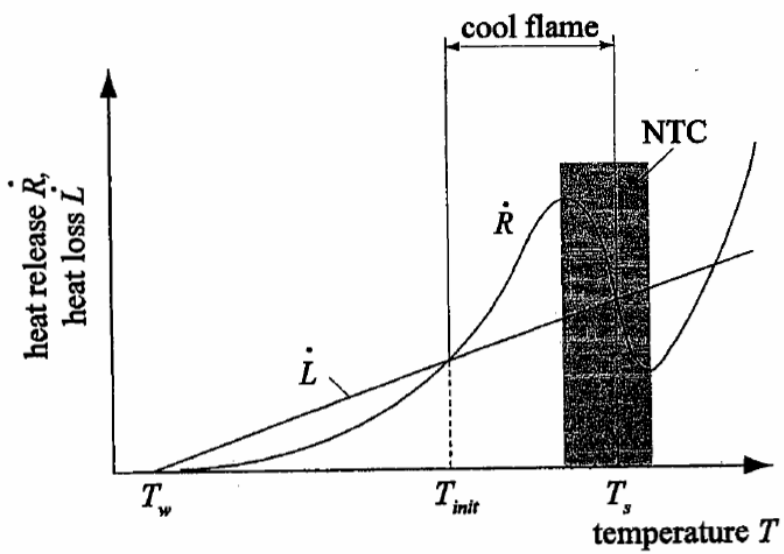
- **Completed vaporized fuel is essential for catalytic reforming.**
- **Diesel fuel cannot be evaporated without fractioning.**
- **Incomplete mixing creates “hot spots” on the catalyst and leads to sintering & coke formation.**



ANL Approach: Diesel Injection Technology Improvement & Pre-reforming through Cool Flame

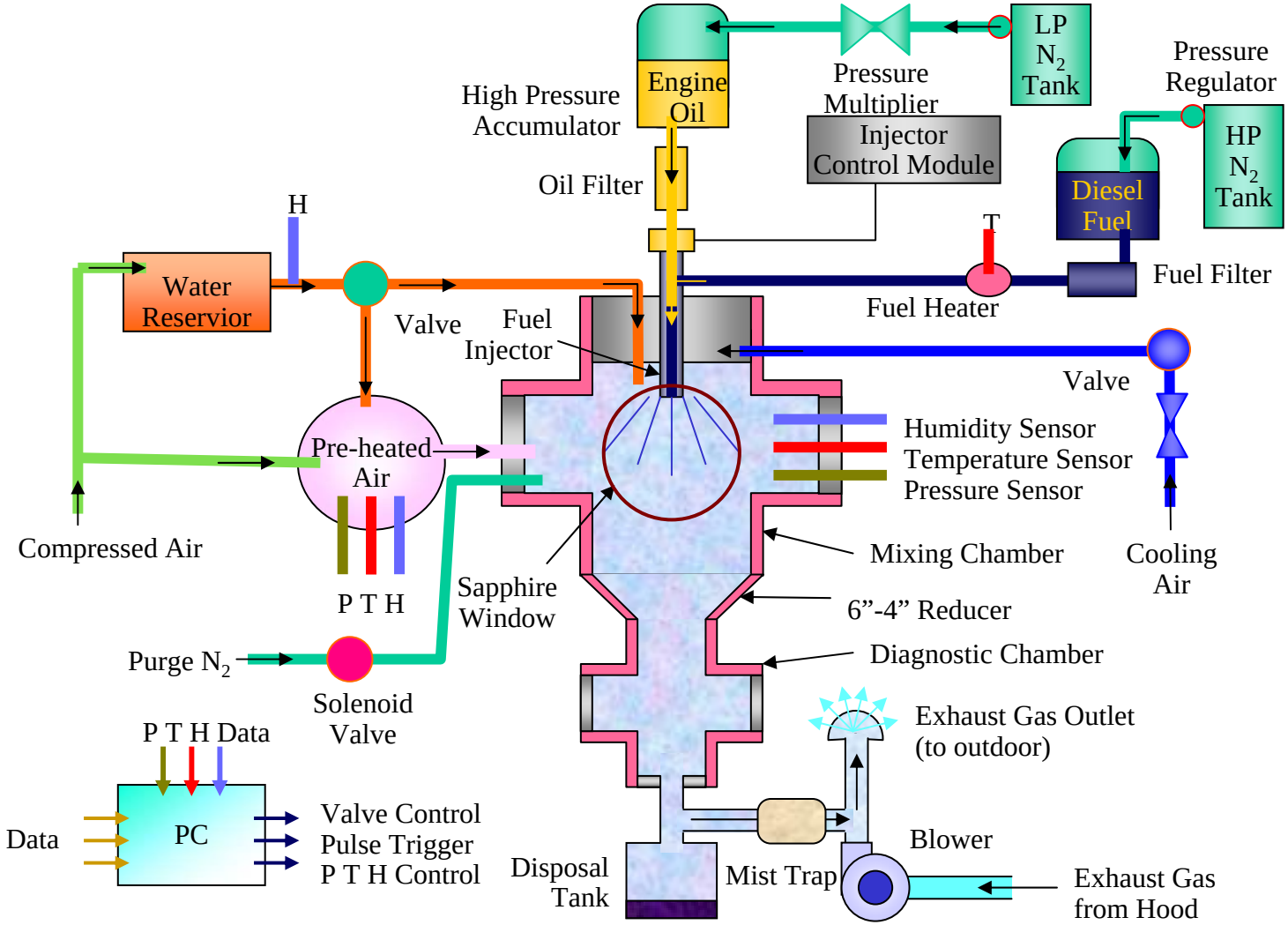
- **Diesel Injection – A joint effort between ANL and International Truck and Engine Corporation (ITEC)**
  - ANL is currently building a test facility for air-steam-fuel-exhaust gas mixing study with catalyst testing capability for ANL autothermal reforming process.
  - ITEC provides diesel-fuel injectors and fuel-injection control system

- **Cool Flame – An alternative method to further improve fuel mixing and pre-reforming.**
  - What is cool flame?
  - How it may benefit SECA fuel reforming effort?
  - Our approach – Investigating operating condition and gas composition in cool flame.



L. Hartmann, K. Lucka, and H. Kohne, 2003

Diesel Mixing Study: Fuel-Air-Steam Mixing Facility Under Construction



Diesel Mixing Study: ITEC Diesel Fuel Injector

- Pulsed injection with pulse rate of

  10 ~ 70 Hz (500 ~ 4000 rpm for 4-cylinder engine)
- Injection duration

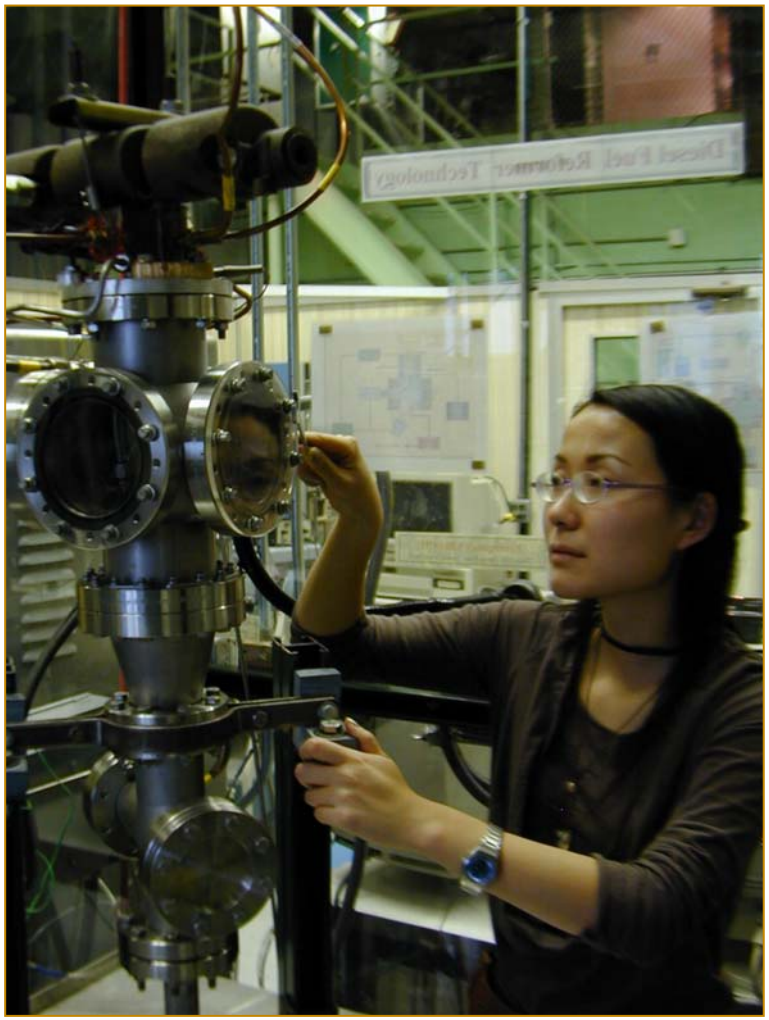
  Below 1 ms at idle to 20 ms at high load
- Injection nozzles

  6 holes around
- Fuel injection rate

  Peak : 105 mm^3/stroke at 240 bar and 600 rpm

  Idle : 9.2 mm^3/stroke at 45 bar and 600 rpm

Diesel Mixing Study: Demonstration of Fuel Injection Test Chamber



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