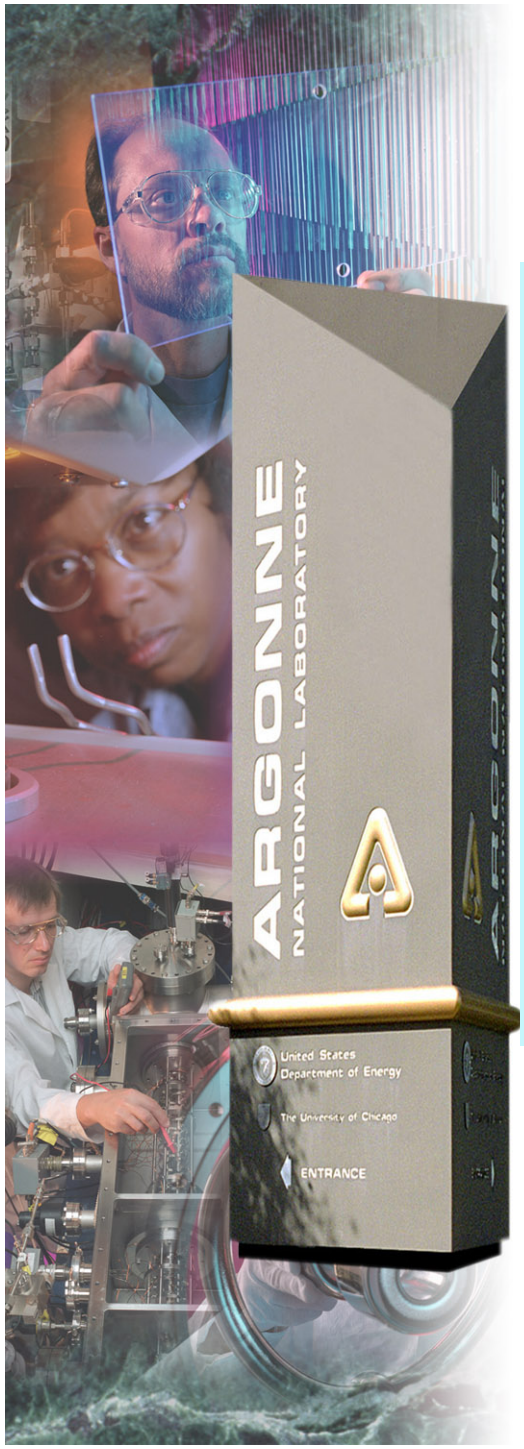

Diesel Reforming for Solid Oxide Fuel Cell Application

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

SECA Annual Workshop & Core Technology Program Peer Review Workshop
Boston, MA
May 11 – May 13, 2004

Argonne National Laboratory

Office of Science
U.S. Department of Energy

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Office of Science Laboratory
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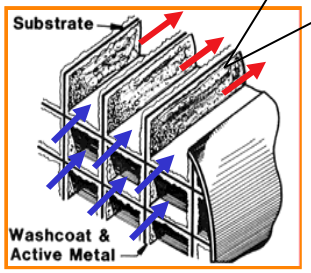
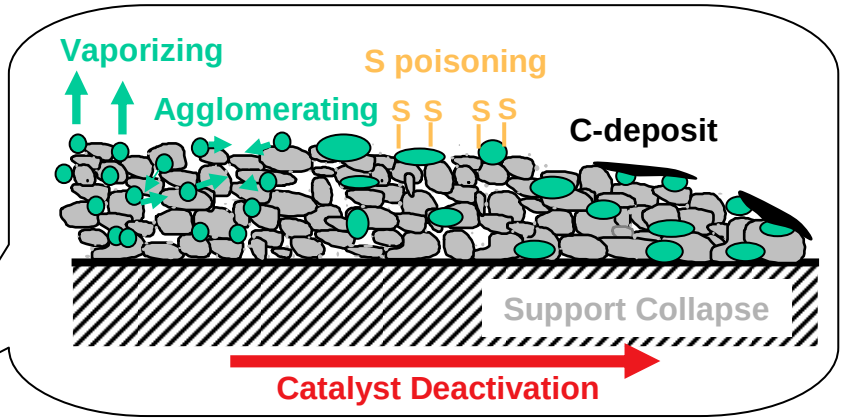
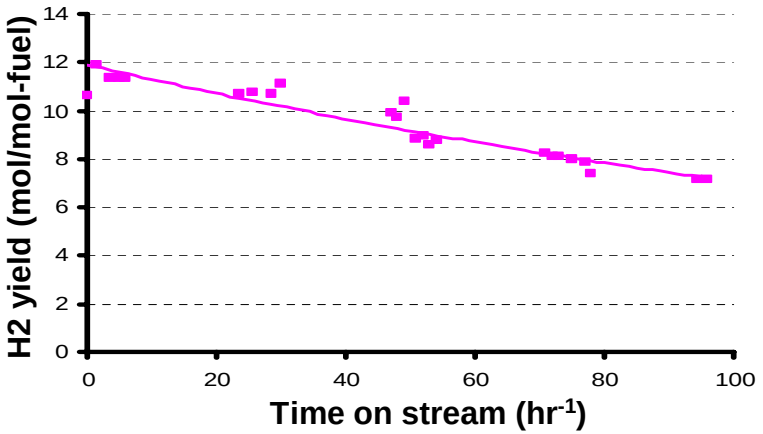
The Challenges Facing Diesel Reforming Catalyst Development

- **Cost**
  - Costly Rh usage
- **Durability**
  - Metal vaporization
  - Metal agglomeration
  - Support stability
  - Sulfur poisoning
  - Coke formation





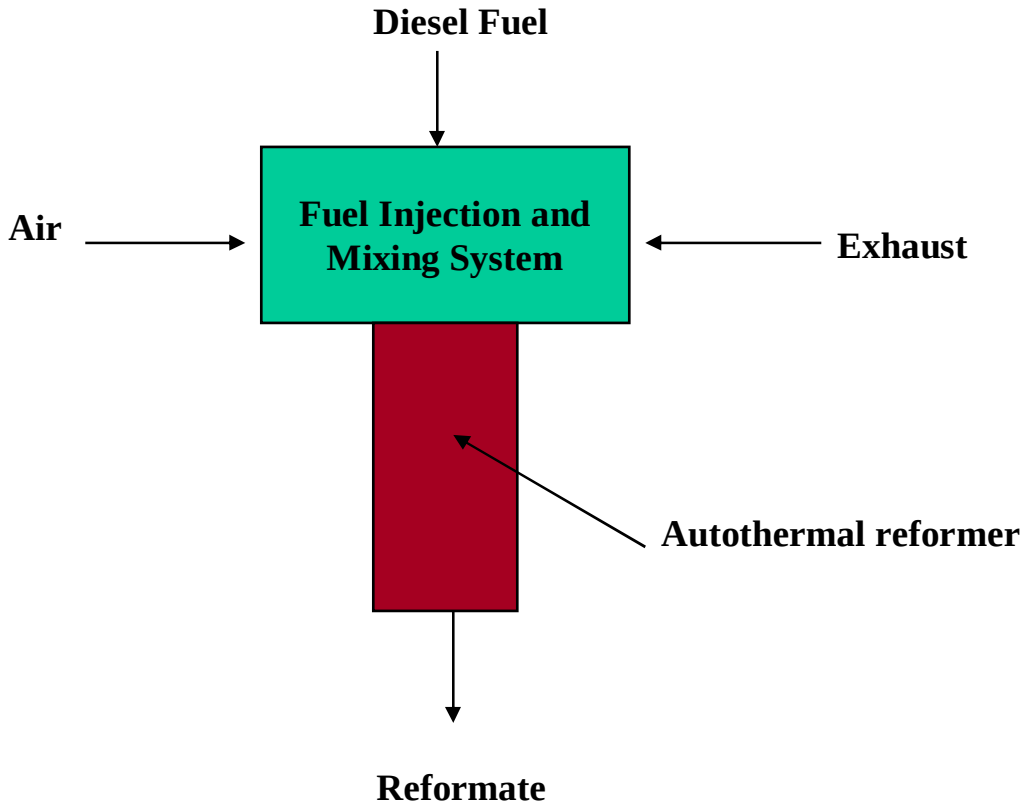
Reforming catalyst aging – an example



Catalyst activity and cost were rated as the top program need by SECA Vertical Team

The Challenges Facing Fuel Mixing

- Diesel fuel cannot be evaporated
- Incomplete mixing creates “hot spots” on the catalyst and leads to coke formation
- Pre-heating the air appears to prevent pre-ignition



Diesel Reforming Catalyst Development

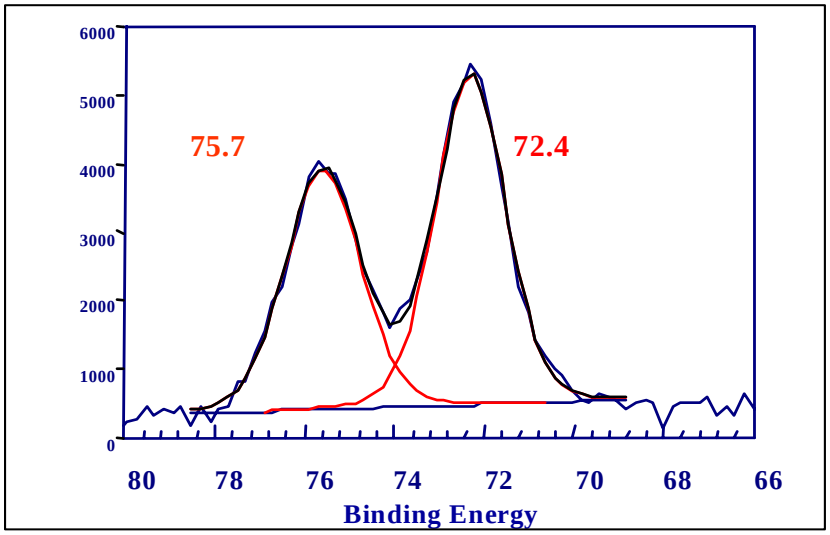
Theory: On Oxide Ion Conducting Substrates Metals Can React with Vacancies

- **Doping ceria with a trivalent rare earth element, such as Gd or Sm, introduces oxide ion vacancies.**
- **Metals on the surface can interact with the oxide ion vacancies.**

$$Pt + v^{\cdot\cdot} + \tfrac{1}{2} O_2 \leftrightarrows Pt^{2+} + O^{2-}$$

Sample	Particle Size	Comments
Pt/CeO_2	> 10Å	Pt_4 No Pt-O
Pt/CGO	< 5Å	Pt-O-Ce No Pt-Pt

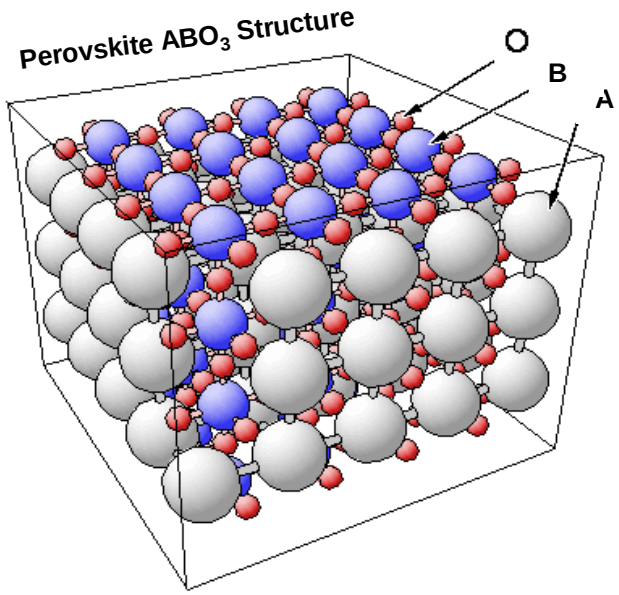
EXAFS shows Pt on a gadolinium-doped ceria (CGO) is highly dispersed



100% Pt(II) – 72.4, 75.7 eV, XPS shows Pt is oxidized

Approach: Development of Perovskite Based Catalyst

- **The Perovskite Catalyst…**
  - Has defect chemistry
  - Consists of low cost material
  - Stable under high temperature
  - Stable in strong redox environment
  - Has exchangeable *A & B* site for activity improvement
  - Has lower adsorption energy for H_2S than metals



ATR Catalytic Study: Experimental Conditions

- **Fuel**
  - Dodecane $C_{12}H_{26}$
  - Dodecane/Dibenzothiophene mixture (50 ppm S)
- **Microreactor**
  - Catalyst loading: ~ 0.5 to 1 gram catalyst diluted in inert alumina.
  - Temperature: 600 °C to 725 °C
  - Preheating: 200 °C
  - GC analysis for reformate product
- **Reforming Input Mixture**
  - **ATR: O_2/C = 0.3 ~0.5, H_2O/C = 1 ~ 3**
- **Space Velocity**
  - **Fuel Flow Rate = 2.8x10^{-3} gfuel/gCat•sec**
  - **GHSV = 50 K ~ 100 K hr^{-1}**

Diesel ATR Catalyst Development – H_2 Yield and COx Selectivity of Some Representative Samples

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

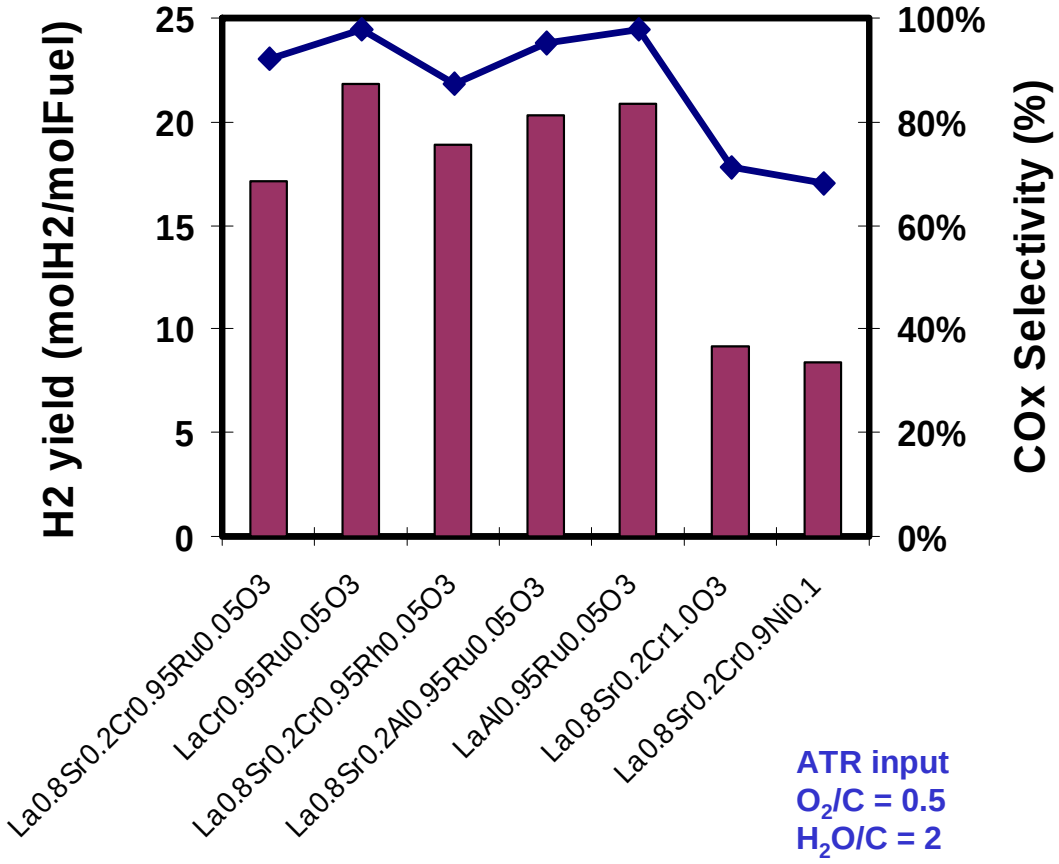
Definition:

H_2 yield =

Mole H_2 produced/Mole of input fuel

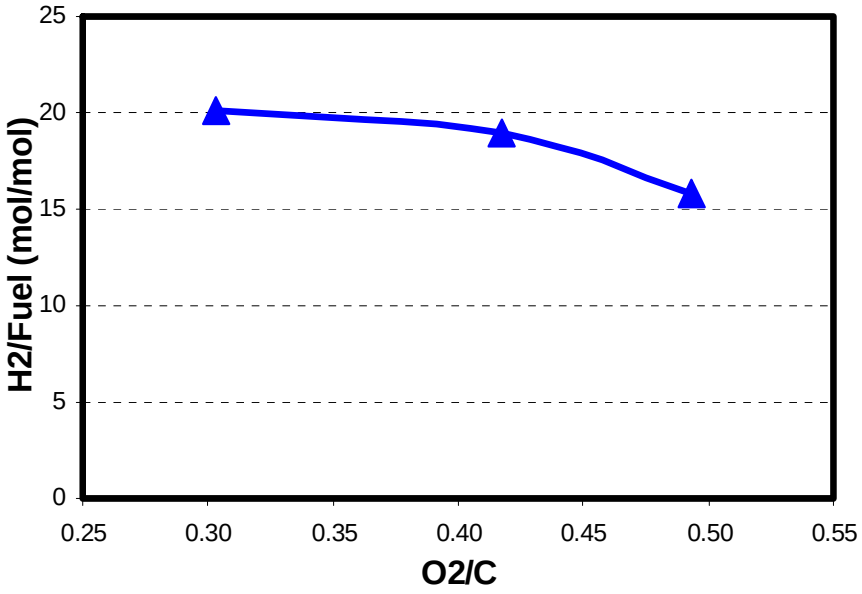
COx selectivity =

Mole ($CO + CO_2$) in reformate/Mole C in fuel

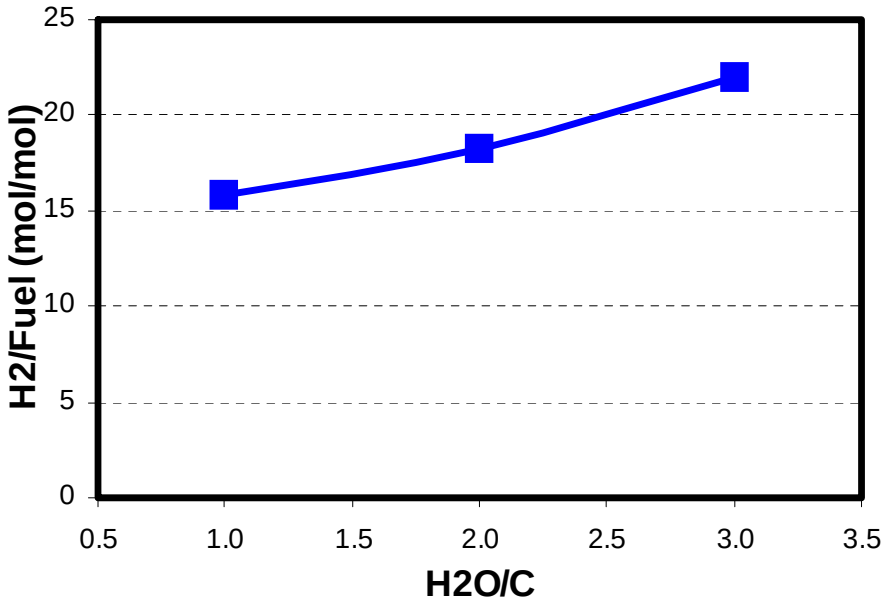


Diesel ATR Catalyst Development – H_2 Yield as Function of O_2/C and H_2O/C

The hydrogen yield as the function of O_2/C during the reforming over $La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$, H_2O/C = 1.0



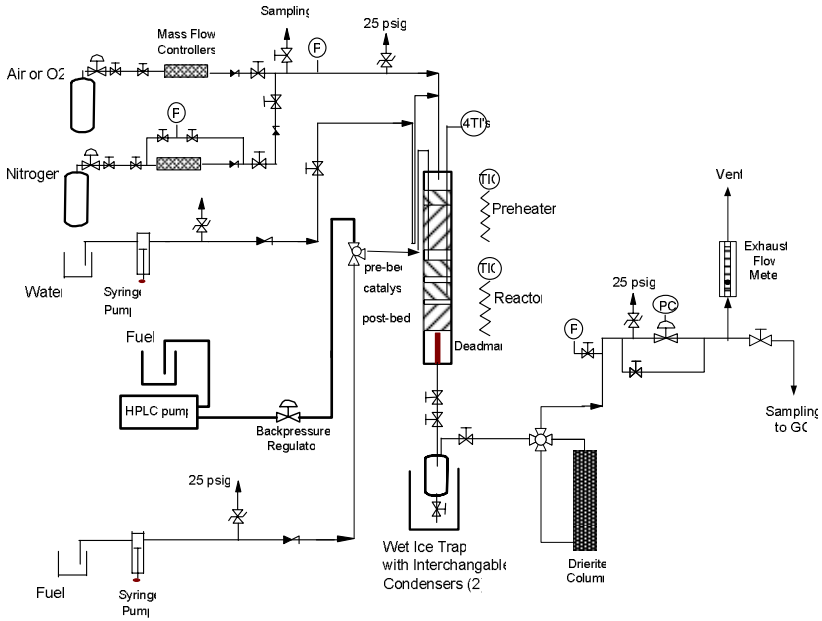
The hydrogen yield as the function of H_2O/C during the reforming over $La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$, O_2/C = 0.5



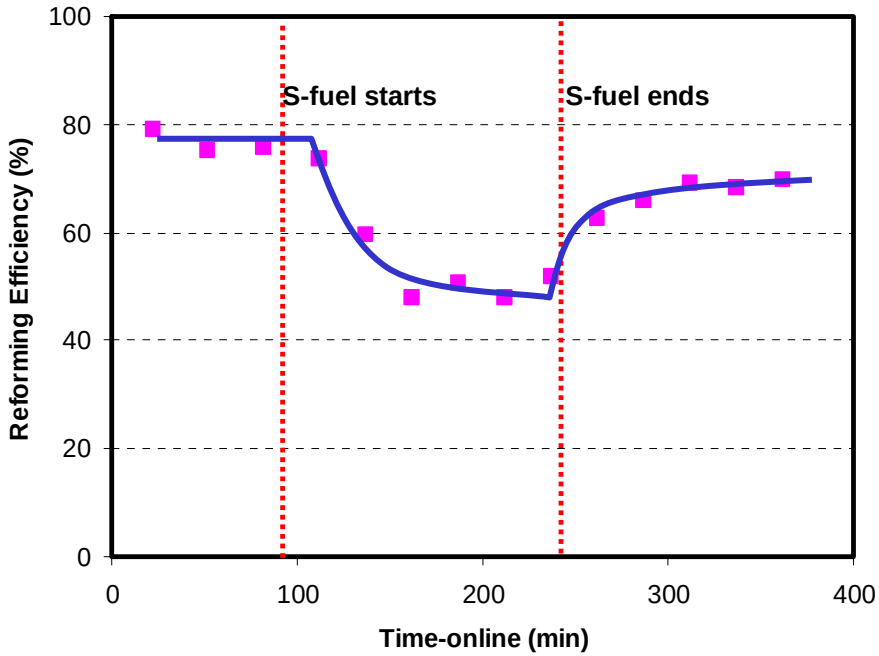
Hydrogen yield and reforming efficiency can be affected by oxygen and steam contents

Diesel ATR Catalyst Development – Sulfur Tolerance Experiment

Fuel switching capability in microreactor allows the study of S impact under identical conditions



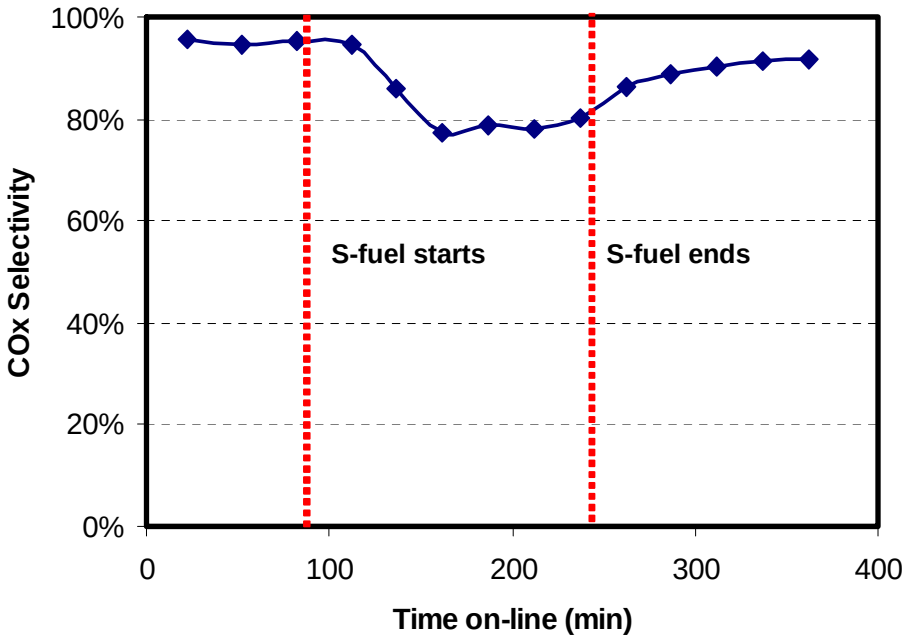
Reforming efficiency decreases when fuel is replaced by DBT/dodecane mixture.



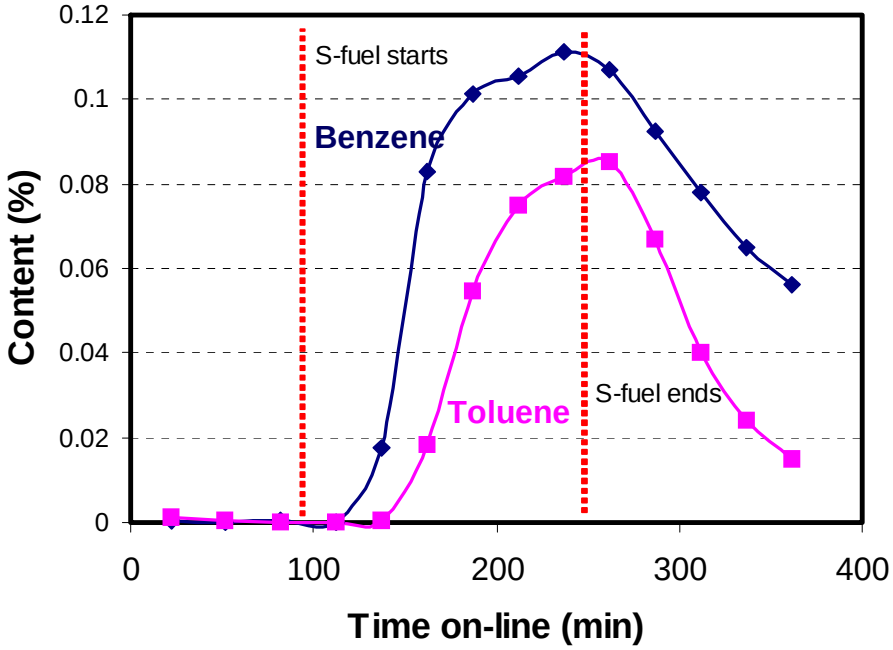
Sulfur contaminated fuel (DBT with 50 ppm S) results in catalyst deactivation. Catalyst re-activates after S is removed from fuel.

Diesel ATR Catalyst Development – Sulfur Impact on COx Selectivity & Aromatics Formation

COx selectivity drops as the impact of sulfur from DBT in the input mixture…

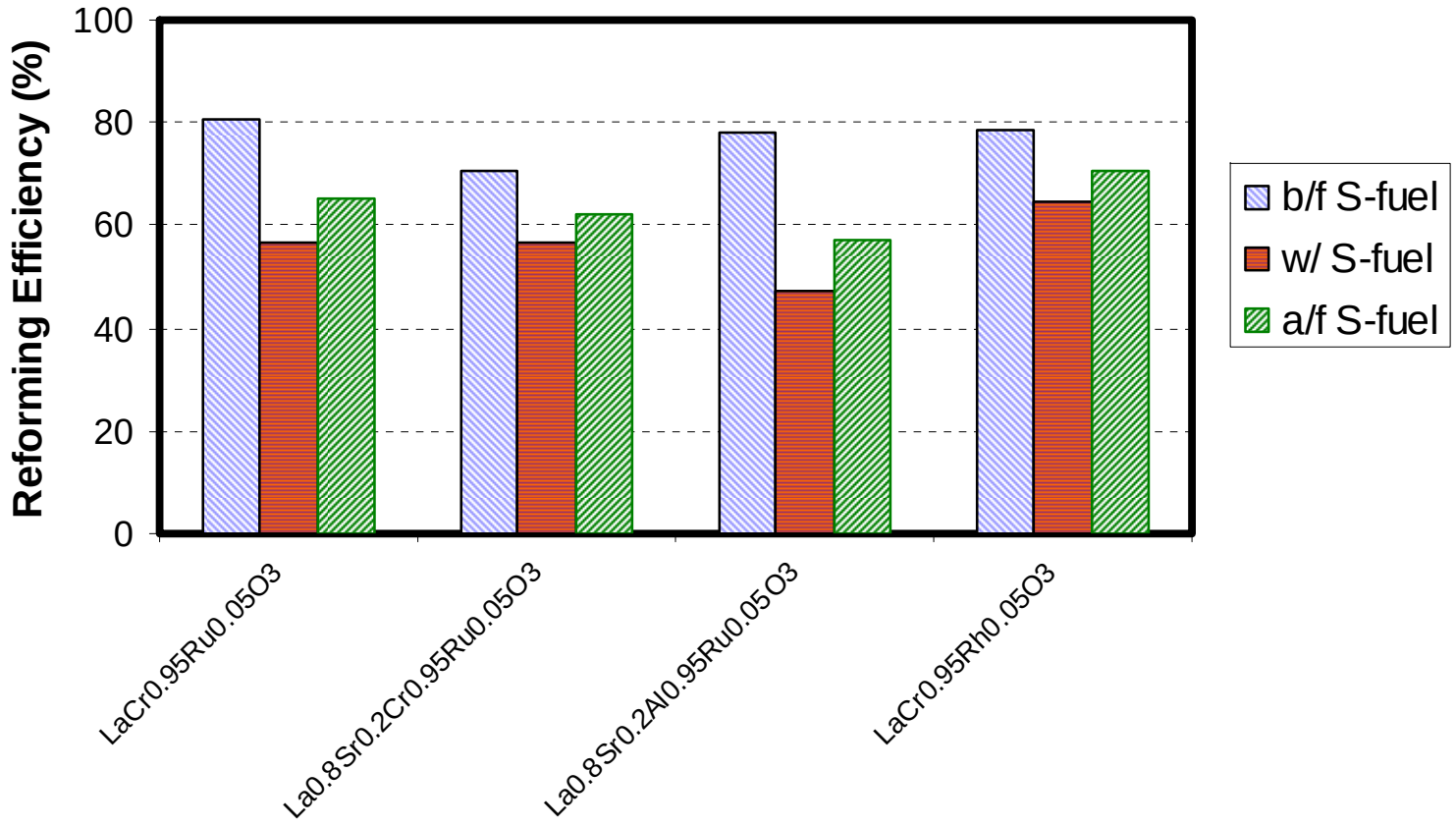


… while benzene and toluene production increased significantly



Sulfur slows down the conversion of hydrocarbons to COx and enhances the production of aromatics

Diesel ATR Catalyst Development – Change of Reforming Efficiency Before & After S-Poisoning

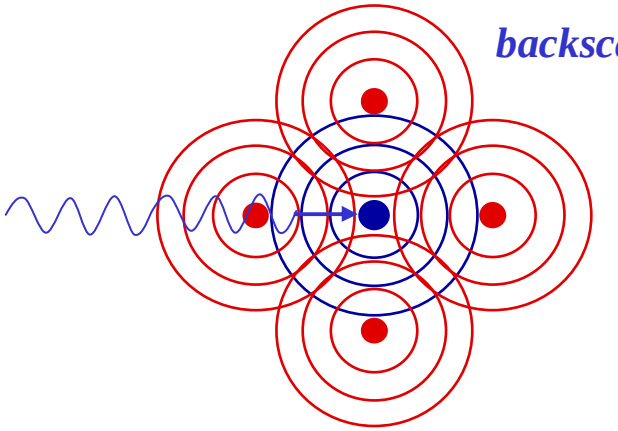


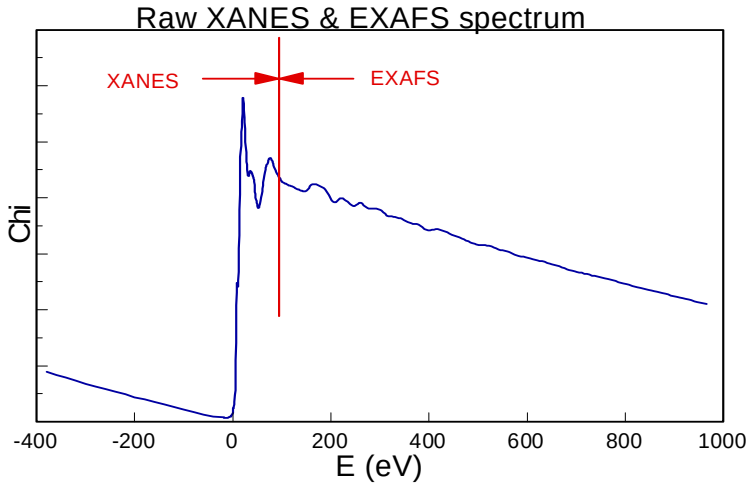
Fuel reforming efficiency to H_2 + CO = $\{c_{t,H2}\Delta H_{c,H2} + c_{t,CO}\Delta H_{c,CO}\}/c_{t,fuel}\Delta H_{c,fuel}$

Ct,i = Molar flow rate of I, $\Delta Hc,i$ = Heat of combustion of i

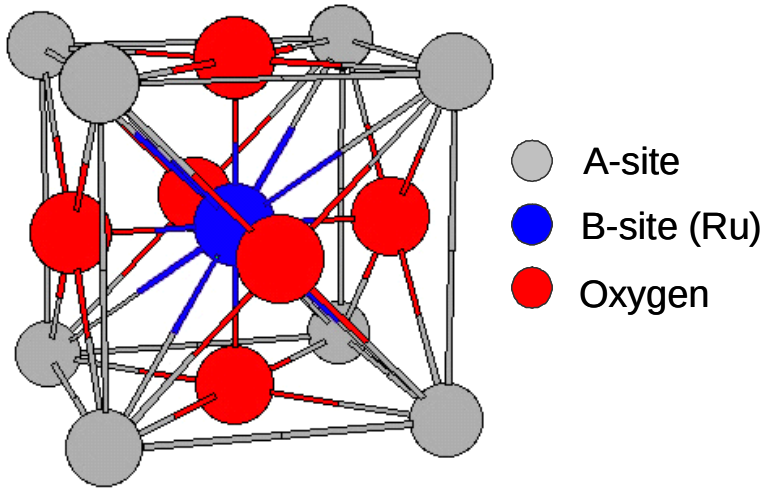
Diesel ATR Catalyst Development – Advanced Catalyst Characterization

EXAFS & XANES





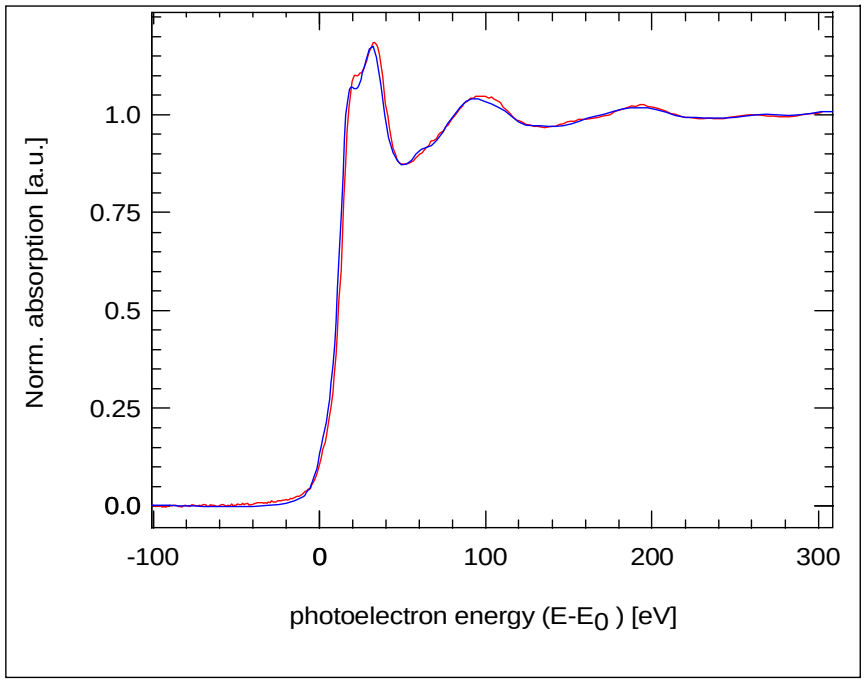
Lattice Structure of a Single Cell in Perovskite



Diesel ATR Catalyst Development – Preliminary EXAFS & XANES Studies

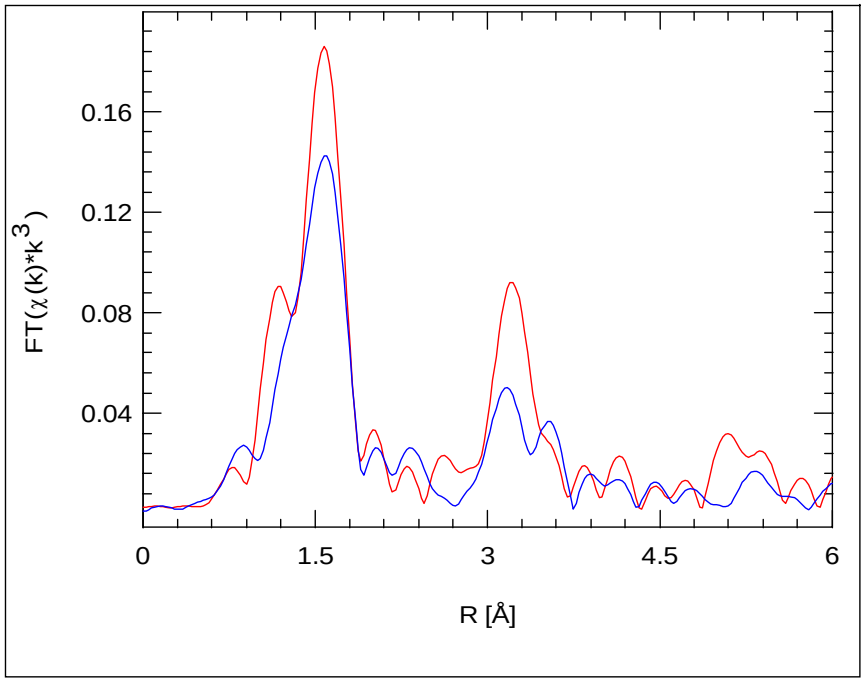
- **Initiated Ru K-edge EXAFS and XANES studies for B-site doped perovskites using Advanced Photon Source at Argonne.**

XANES comparison between $LaCr_{0.95}Ru_{0.05}O_3$ & $LaAl_{0.95}Ru_{0.05}O_3$



Doped Ru in both perovskite is mostly likely in +3 oxidation state when prepared.

Radial distribution functions obtained from EXAFS of $LaCr_{0.95}Ru_{0.05}O_3$ & $LaAl_{0.95}Ru_{0.05}O_3$



Ru-O and Ru-La shell structure is tentatively assigned. Small crystallite in chromite leads to less oxygen coordination.

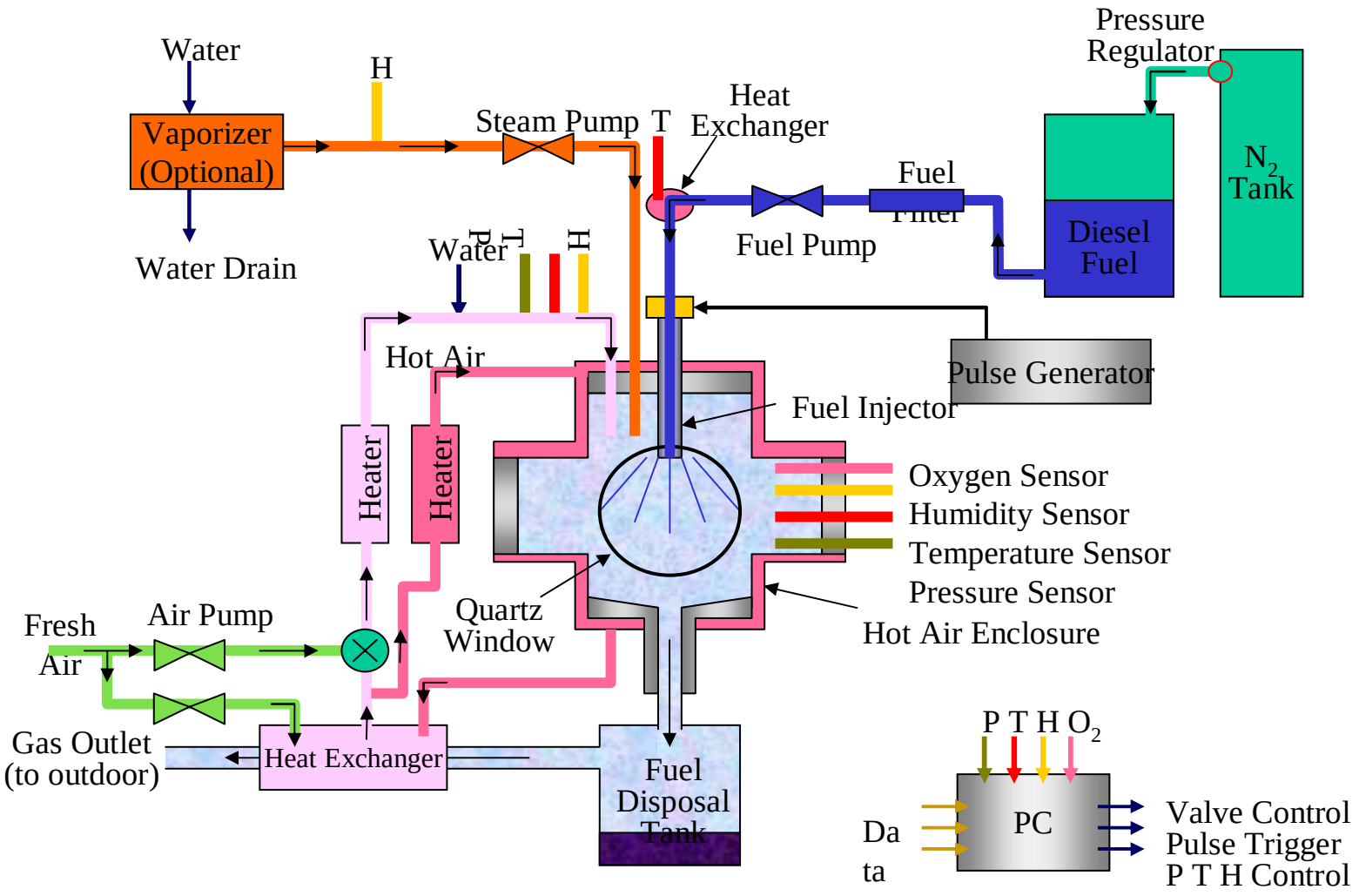
Diesel Fuel Mixing Study

Approach to Mixing Challenge

- Joint effort between ANL and International Truck and Engine Corporation (ITEC)

  - ITEC will provide diesel-fuel injectors and fuel-injection control system
  - ANL will establish a test facility, develop a fuel/exhaust-gas mixing system, and conduct tests to evaluate the ANL autothermal reforming process.

Fuel-air-steam Mixing Facility



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 Torque: 105 mm^3/stroke at 240 bar and 600 rpm
  - Idle Single Shot 9.2 mm^3/stroke at 45 bar and 600 rpm

Fuel Injection Test Chamber

Test Matrix

- **Test variables**
  - Exhaust-gas-fuel ratio (O/C : 0.4, Steam/C : 1.0)
  - Exhaust-gas temperature (300 deg. C)
  - Exhaust-gas water content (10%)
  - Mixing configuration
- **Proposed measurements**
  - Flow rates (exhaust gas and fuel)
  - Temperatures (fuel, exhaust-gas, and mixing region)
  - Fuel mist characterization
  - Carbon deposit
  - Humidity
  - Pressure

Summary

- **Perovskite catalysts show good catalytic activity for reforming dodecane and are relatively tolerant to sulfur**

- **A test facility to address fuel mixing issues will soon be operational**

Acknowledgements

- **We would like to thank the U.S. Department of Energy, Office of Fossil Energy, Solid State Energy Conversion Alliance (SECA) Program, Office of FreedomCar and Vehicle Technologies for funding this research under Contract W-31-109-ENG-38.**

- **Program Managers Norman Holcombe and Sid Diamond**