

Catalysts for Autothermal Reforming

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Objectives

- **To develop advanced fuel processing catalysts that meet DOE performance requirements**
 - Compared to Ni-based steam reforming catalysts, these new catalysts will
 - be able to process complex fuel mixtures, such as gasoline
 - process these fuels at higher rates
 - be more resistant to coking and sulfur poisoning
 - Improve our understanding of reforming reaction mechanisms, catalyst deactivation, and sulfur poisoning
 - Define operating parameters (e.g. air:fuel and steam:fuel ratios, temperature, gas hourly space velocities (GHSV), catalyst geometry) to optimize catalyst performance and lifetime



Budget, technical barriers and targets

- **FY204 Funding: \$400K**
- **Technical barriers for hydrogen production**
 - A. Fuel Processor Capital Costs
 - G. Efficiency of Gasification, Pyrolysis, and Reforming Technologies
 - Z. Catalysts
- **Technical targets for reforming catalysts**
 - gas-hourly space velocity (GHSV) $\geq 200,000 \text{ h}^{-1}$
 - conversion $\geq 99.9\%$ with H_2 selectivity $\geq 80\%$
 - lifetime $> 5000 \text{ h}$
 - cost $< \$5/\text{kWe}$



Approach

- **Building on past ANL experience, we are investigating two classes of materials**
 - transition metal(s) supported on oxide substrates
 - perovskites
- **Determine catalyst performance (H₂ yield, CO_x selectivity, hydrocarbon breakthrough, fuel conversion) and stability as a function of:**
 - catalyst composition
 - fuel composition and sulfur content
 - operating parameters: O₂:C and H₂O:C ratios, temperature, GHSV
- **Conduct catalyst characterization and mechanistic studies to identify**
 - factors influencing activity and selectivity
 - causes of deactivation
 - how sulfur affects catalyst activity

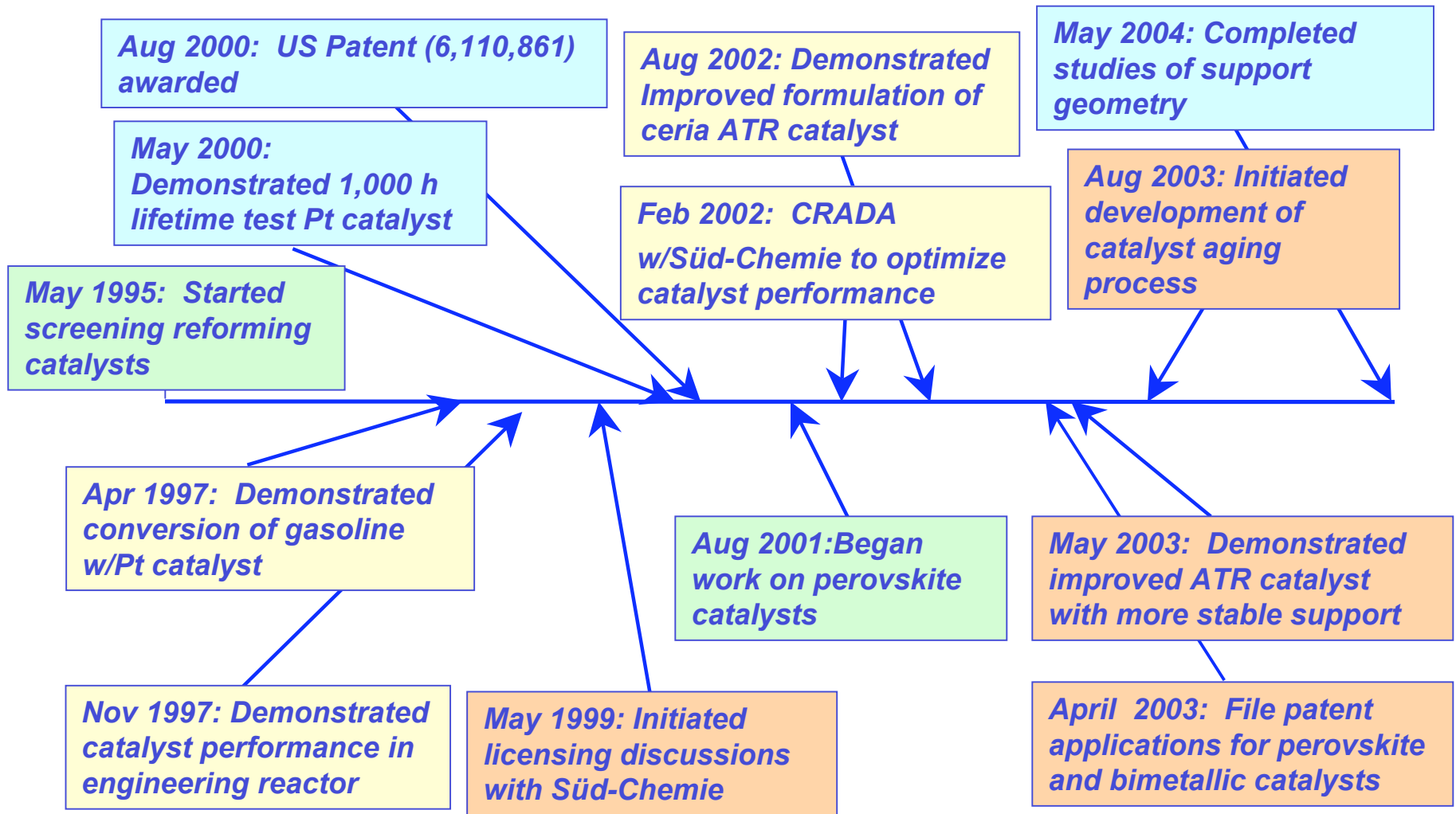


Project safety

- **Internal safety reviews are performed for all aspects of this project to address ESH issues**
 - **Catalyst synthesis**
 - Synthesis procedures are performed in fumehoods to exhaust vapors of powders and solvents
 - Waste chemicals are collected and disposed of through the Laboratory's Waste Management Operations
 - **Microreactor systems**
 - Located in fumehoods
 - Equipped with safety interlocks that shut the system down if excessive temperature or pressure is sensed or the fumehood ventilation fails
- **Safety reviews are updated and renewed annually**

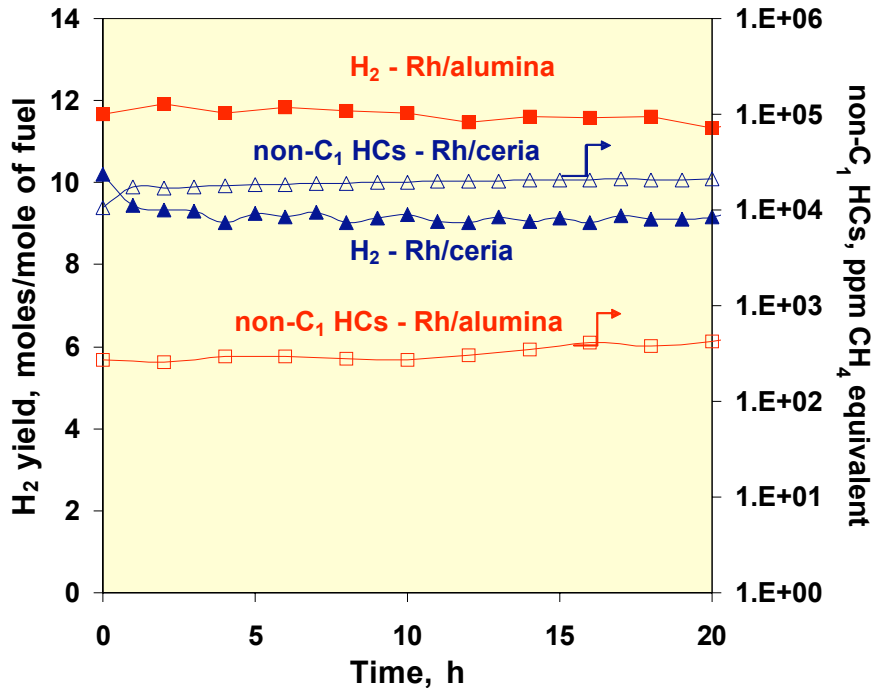


Project timeline

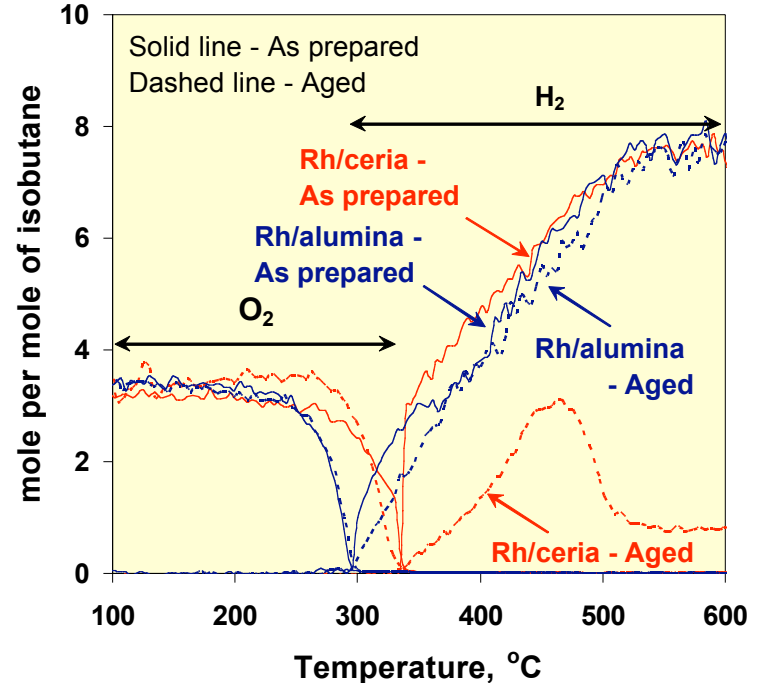


Refractory oxides provide a more stable support for Rh than reducible oxides

Higher H₂ yield and lower hydrocarbon breakthrough with Rh/alumina for gasoline ATR



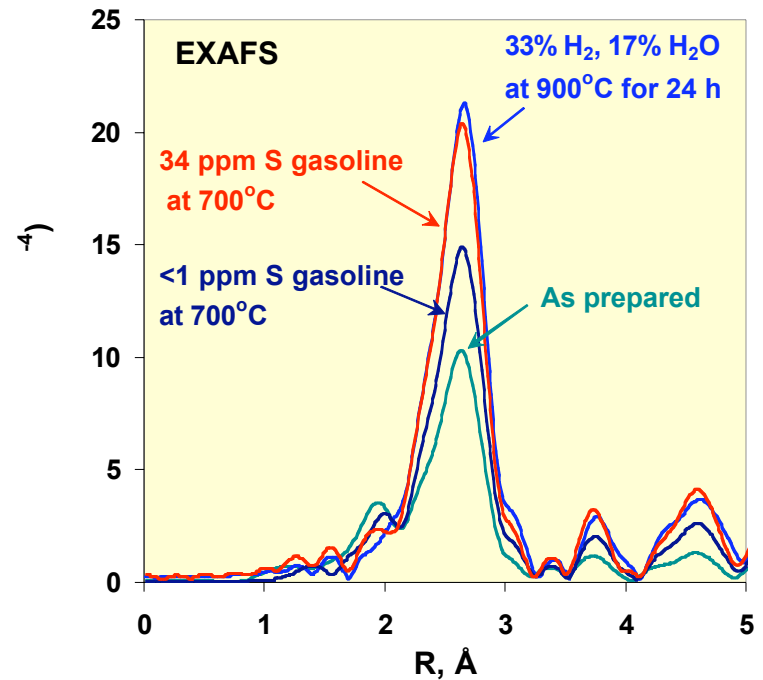
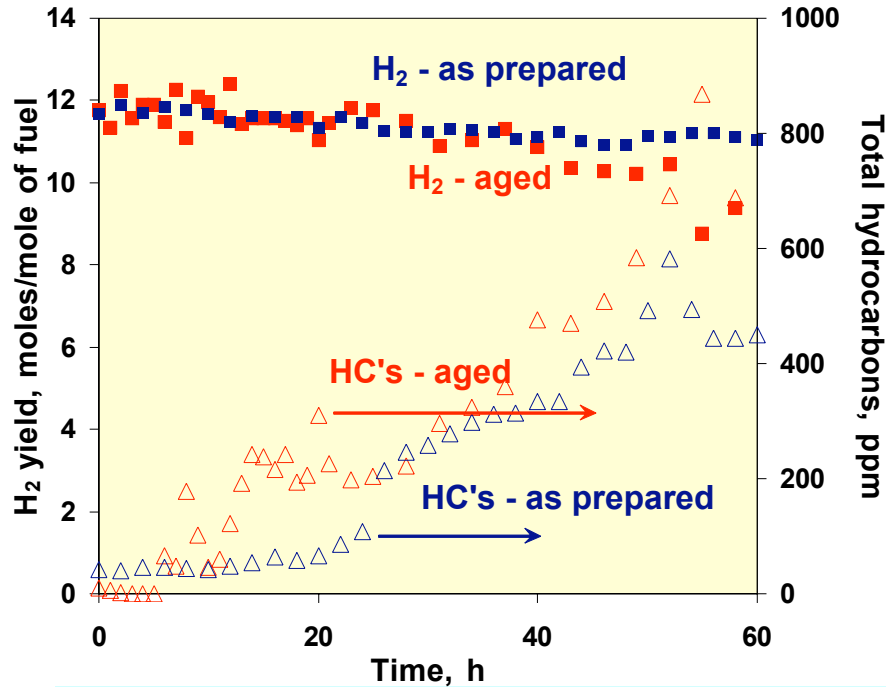
Significant decrease in H₂ yield with Rh/ceria but not with Rh/alumina after aging* for isobutane ATR



	Surface Area, m ² /g		Rh dispersion, %	
	Fresh	Aged*	Fresh	Aged*
Rh/alumina	130	105	81	31
Rh/ceria	36	3	21	1

* - treated at 900°C in H₂/H₂O for 24 h

We are working to develop an aging process to simulate effects of long-term operation



Rh dispersion, %

Catalyst

As prepared

33% H₂, 17% H₂O at 900°C - 24 h

<1 ppm S gasoline at 700°C - 100 h

34 ppm S gasoline at 700°C - 100 h

Initial

81

31

24

3

Reoxidized

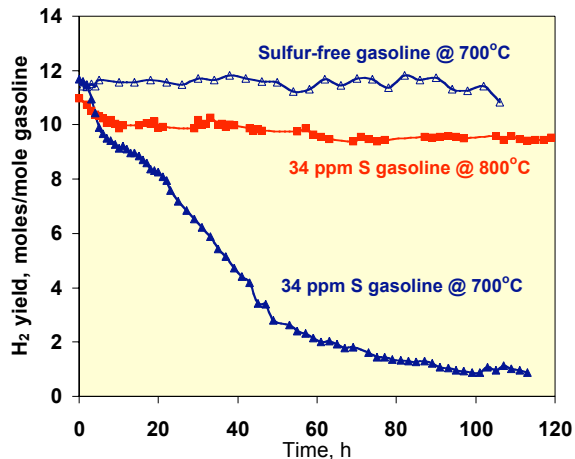
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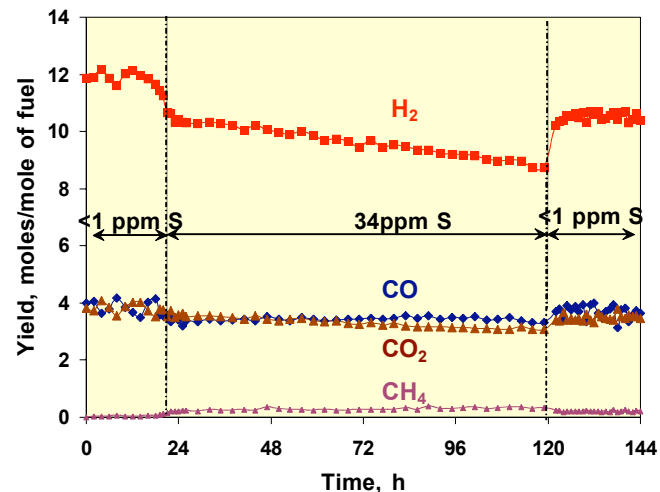


Reversible adsorption of sulfur appears to be the primary cause of sulfur poisoning with Rh

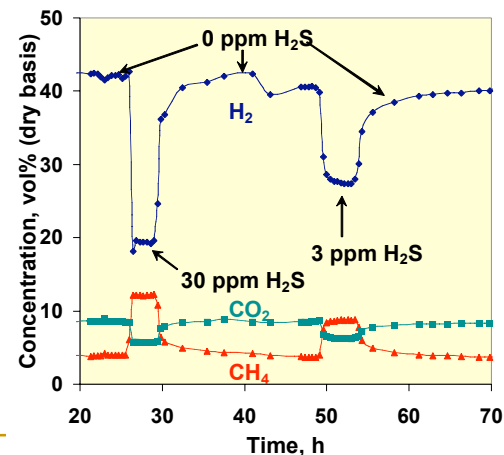
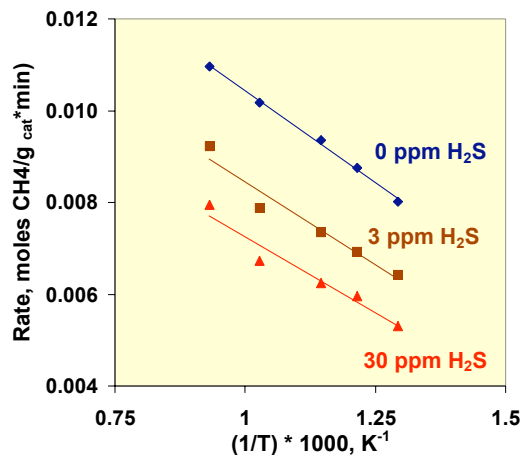
- Effect of sulfur poisoning decreases with increasing temperature



- Most of the activity is recovered in ~1-2 h after sulfur is removed from feedstock

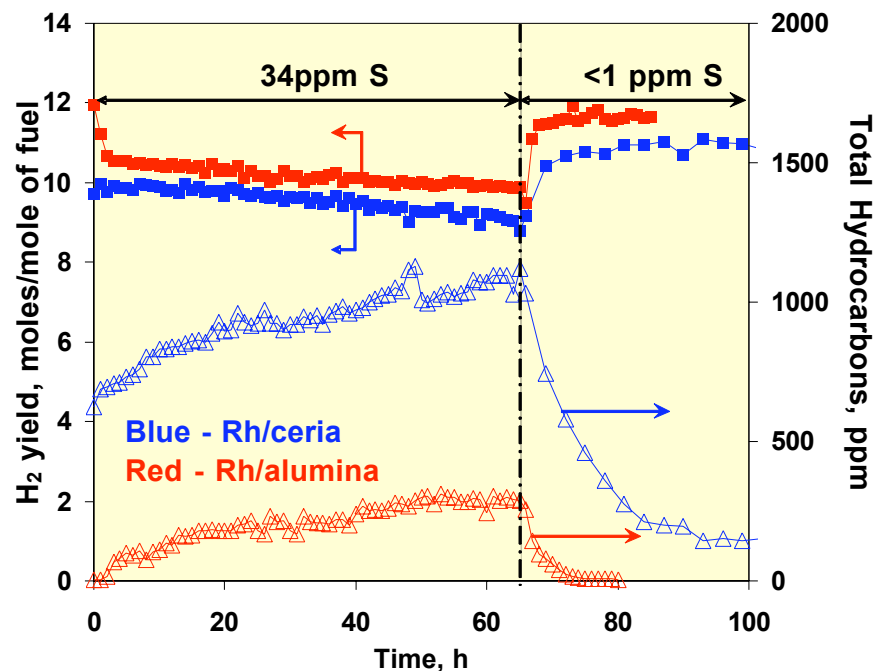
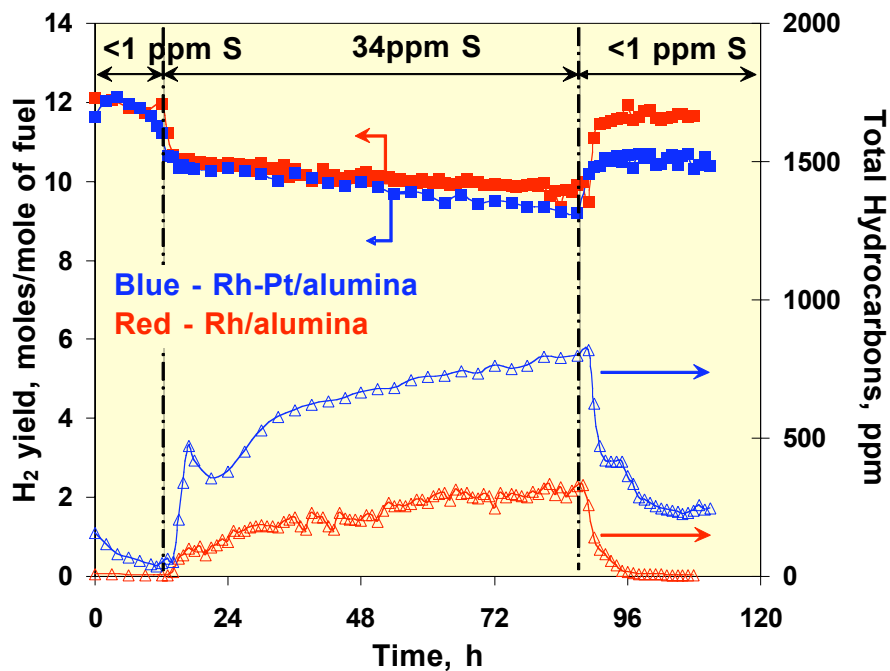


- Loss in activity increases as H₂S concentration increases



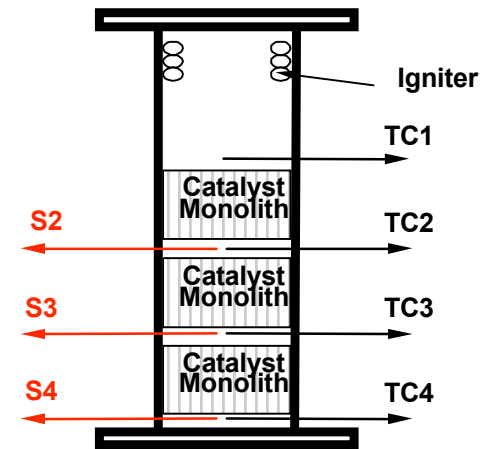
Use of bimetallic formulations or sulfur-adsorbing supports has not improved the sulfur tolerance of Rh

- The addition of a second metal is known to improve the sulfur tolerance of some catalysts, such as the addition of Pd to Pt catalysts used in petroleum refining
- Some supports, such as ceria, form a stable sulfide in the temperature range of ATR, which could serve as a potential “sink” for sulfur

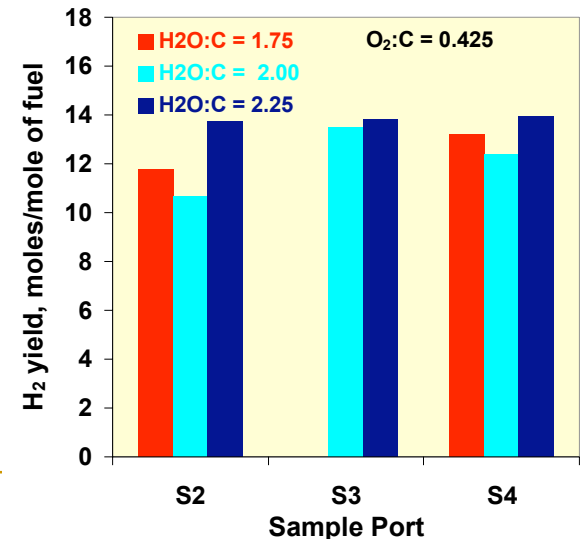


Proper selection of the structured support is critical for optimizing catalyst performance

- Performance of a Rh catalyst loaded onto 600-, 900-, and 1200-cpi monoliths and a 40-ppi metal foam for reforming gasoline is being evaluated to determine optimal support geometry
- Some preliminary observations
 - The highest temperature is observed at the exit of the first monolith
 - Nearly all of the H_2 is produced in the first monolith
 - CH_4 yield increases from the first to last monolith suggesting that methanation may be occurring as temperature decreases
- Data are being used to generate a reaction model



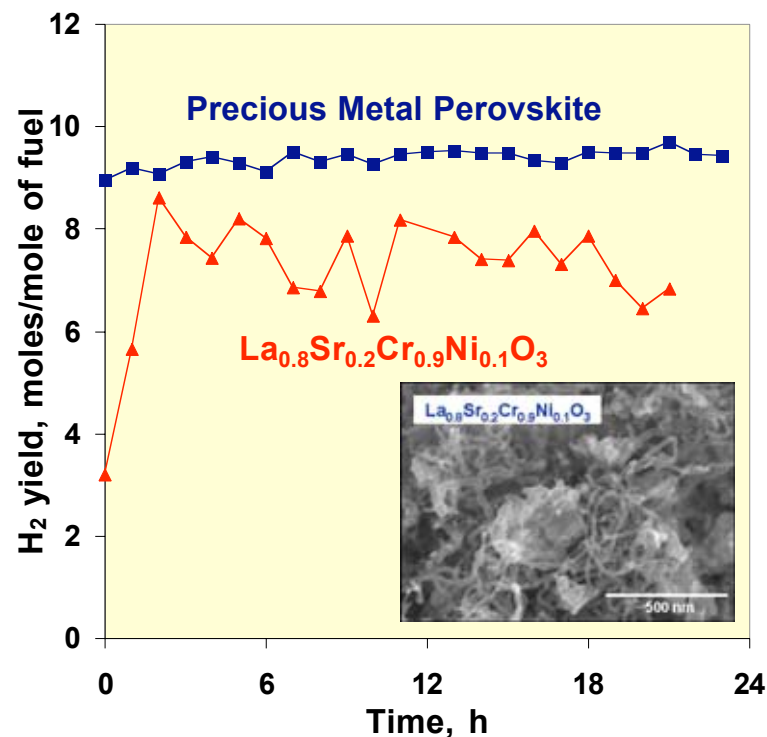
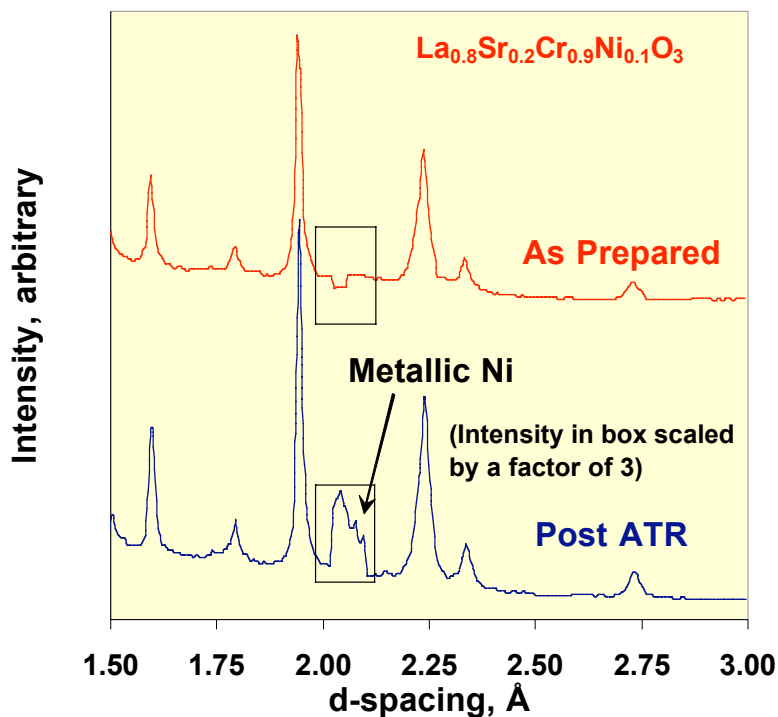
kW_e Reactor System



Less focus on perovskite catalysts

- Stability of Ni perovskite during ATR is an issue
- Results from electron microscopy and X-ray diffraction were inconclusive
- Neutron spectroscopy showed that metallic Ni particles was present

- Ni perovskites were active for gasoline ATR but the H₂ yield was low and decreased with time due to coking
- Substituting a precious metal for Ni produced a higher and more stable H₂ yield



Interactions and collaborations

- **University and industrial interactions**
 - University of Alabama (Prof. Ramana Reddy) to characterize ATR catalysts using SEM, TEM, and XPS
 - University of Alabama (Prof. Alan Lane) to develop more sulfur tolerant ATR catalysts
 - University of Puerto Rico, Mayagüez (Prof. José Colucci) to determine operating parameters for reforming gasoline and biodiesel
 - Participant in a proposal with General Electric and University of Minnesota submitted in response to the Hydrogen Production and Delivery Research Solicitation
 - Süd-Chemie, Inc., monolith and foam studies



Response to reviewers' comments from FY03

- **More emphasis on sulfur tolerance**
- **Need more fundamental understanding of reaction and deactivation mechanisms**
- **What criteria can be used to decide when a catalyst is “good enough”**
- **Interaction with reforming work in the Hydrogen Program**



Milestones

<u>Milestone</u>	<u>Date</u>
Determine the optimal support structure (monolith vs. foam) to minimize mass transfer effects	01/04 (05/04)
Complete benchmarking of the ANL ATR catalyst against other reforming catalysts under development	05/04
Complete 1000 h test with best catalyst formulation supported on structured support using 30 ppm sulfur gasoline	09/04



Future work

- **Improve catalyst durability and minimize deactivation**
 - Conduct characterization studies of spent catalysts to further understanding of deactivation mechanisms
 - Validate catalyst aging process
 - Conduct long-term testing of improved catalyst formulations
- **Improve sulfur tolerance of catalysts by increasing our understanding of sulfur poisoning mechanisms**
- **Mechanistic studies to increase our understanding of reaction pathways**
- **Address catalyst issues identified in “FASTER” Program**
 - Catalyst deactivation and structural stability issues (i.e., effect of frequent and rapid startup)
 - Obtain performance data as a function of operating parameters to develop ATR/SR reaction models

