

# *Water gas shift catalysis*

Theodore Krause, Razima Souleimanova,  
John Krebs, and Mario Castagnola

Electrochemical Technology Program  
Argonne National Laboratory

May 24-27, 2004

**This presentation does not contain any proprietary or confidential information**

*Hydrogen, Fuel Cells, and Infrastructure Technologies  
Office of Energy Efficiency and Renewable Energy  
U.S. Department of Energy*



# Objectives

---

- **To develop advanced water-gas shift (WGS) catalysts to meet the DOE performance requirements**
  - Compared to Cu-Zn and Fe-Cr WGS catalysts, these new catalysts will be
    - more active (higher turnover rates)
    - less prone to deactivation due to temperature excursions
    - more structurally stable (able to withstand frequent cycles of vaporizing and condensing water)
    - more resistant to sulfur poisoning
  - Improve our understanding of reaction mechanisms, catalyst deactivation, and sulfur poisoning
  - Define operating parameters (e.g. steam:carbon ratios, temperature, gas hourly space velocities (GHSV), catalyst geometry) to optimize catalyst performance and lifetime



# ***Budget, technical barriers and targets***

---

- **FY04 Funding: \$600K**
- **Technical barriers**
  - A. Fuel Processor Capital Costs
  - G. Efficiency of Gasification, Pyrolysis, and Reforming Technologies
  - Z. Catalysts
  - AB. Hydrogen Separation and Purification
- **Technical targets for water gas shift catalysts**
  - gas-hourly space velocity (GHSV)  $\geq 30,000 \text{ h}^{-1}$
  - CO conversion  $\geq 90\%$  and selectivity  $\geq 99\%$
  - lifetime  $> 5000 \text{ h}$
  - cost  $< \$1/\text{kW}_e$



# Approach

---

- Identify metal(s) and oxide combinations which promote one or more elementary reaction steps (e.g. CO oxidation, H<sub>2</sub>O dissociation, formate/formyl decomposition) involved in the water-gas shift reaction
- Evaluate the water-gas shift activity of these materials in a microreactor system
- Use characterization techniques (e.g. X-ray spectroscopy, temperature-program reduction (TPR), and electron microscopy) to identify factors needed to improve WGS activity or to minimize catalyst deactivation
- Develop kinetic model to predict catalyst performance for reformer operating parameters



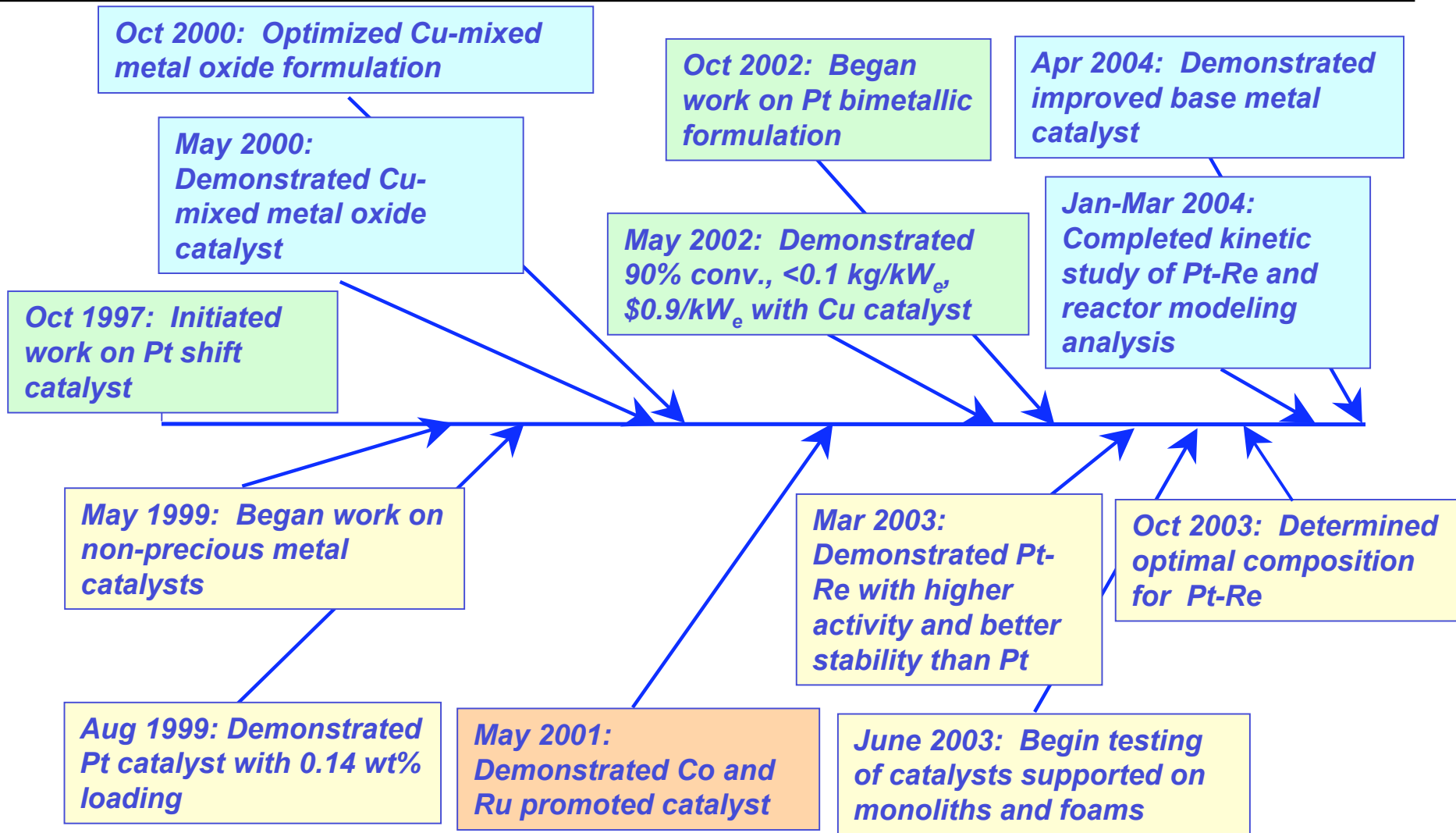
# ***Project safety***

---

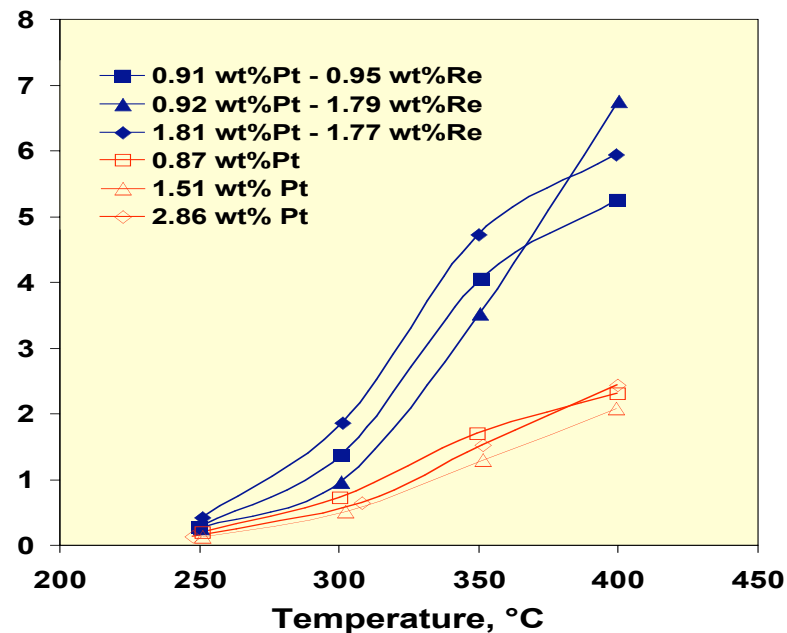
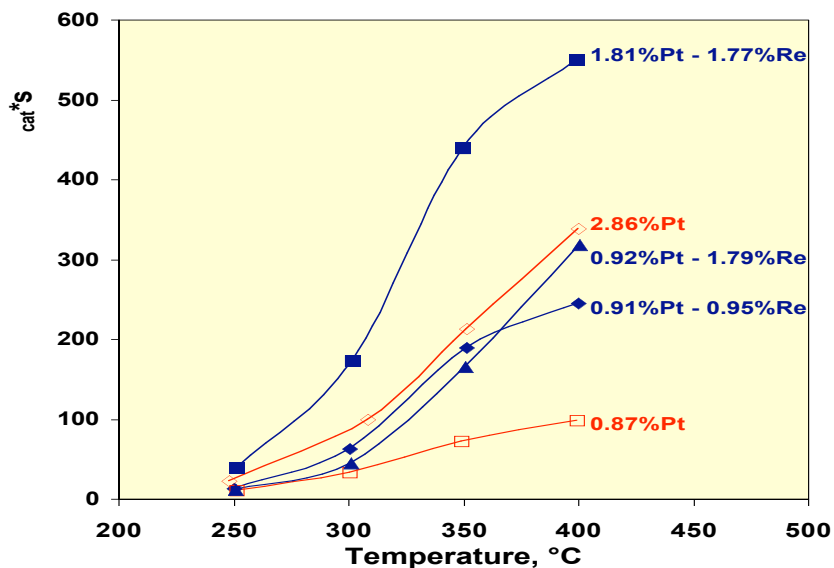
- **Internal safety reviews are performed for all aspects of this project to address ESH issues**
  - **Catalyst synthesis**
    - **Synthesis procedures are performed in fumehoods to exhaust vapors of powders and solvents**
    - **Waste chemicals are collected and disposed of through the Laboratory's 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



# Addition of Re improves performance of Pt-ceria catalyst



Rate Equation:  $\exp(-E_a/RT) \cdot \text{CO}^a \cdot \text{H}_2\text{O}^b \cdot \text{H}_2^c \cdot \text{CO}_2^d$

	$E_a$ (kcal/mol)	$a$	$b$	$c$	$d$
Pt-Re	16	0	0.40	-0.58	-0.17
Pt*	11	0	0.5	-1	-0.5

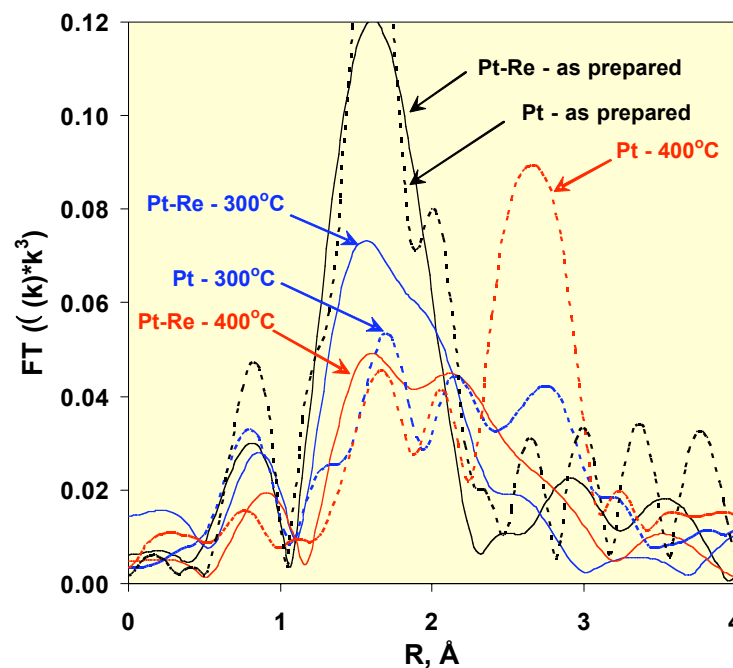
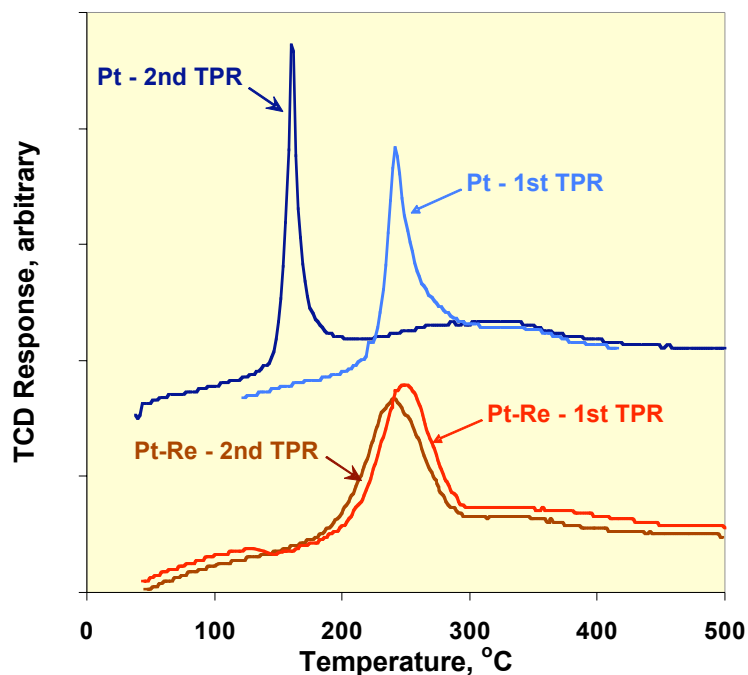
\*Ref: T. Bunluesin et al. Appl. Catal. B, 15 (1998) 107-114.

DOE/EE/HFCIT Program



# *TPR and extended X-ray absorption fine structure (EXAFS) analysis suggests that Re stabilizes Pt*

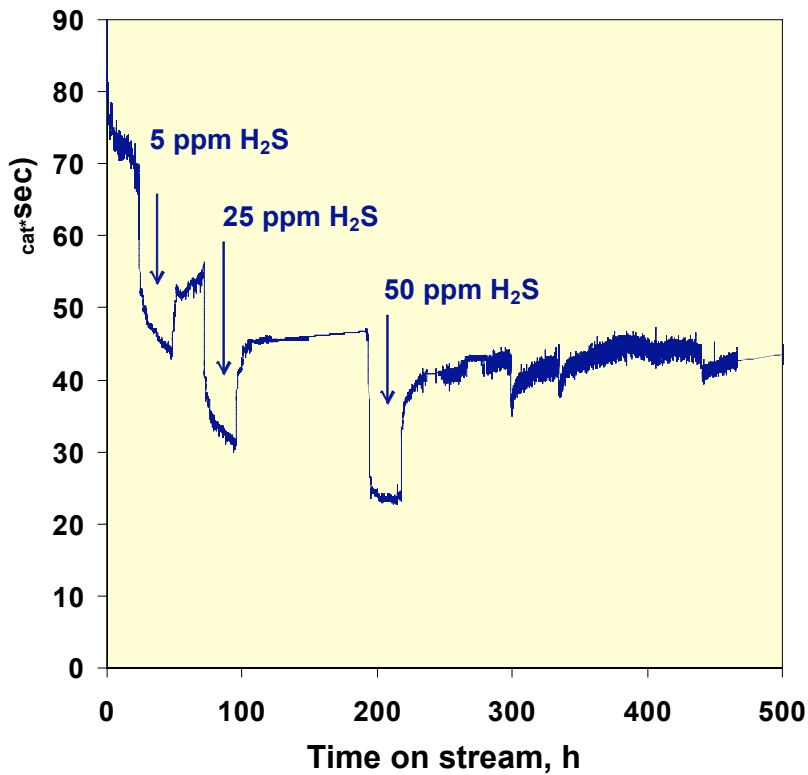
- For Pt, shift in reduction peak to lower temperature is indicative of particle growth
- For Pt-Re, no change in reduction profile
- More Pt-Pt bond formation in Pt than Pt-Re after 100+ h on stream at 400°C



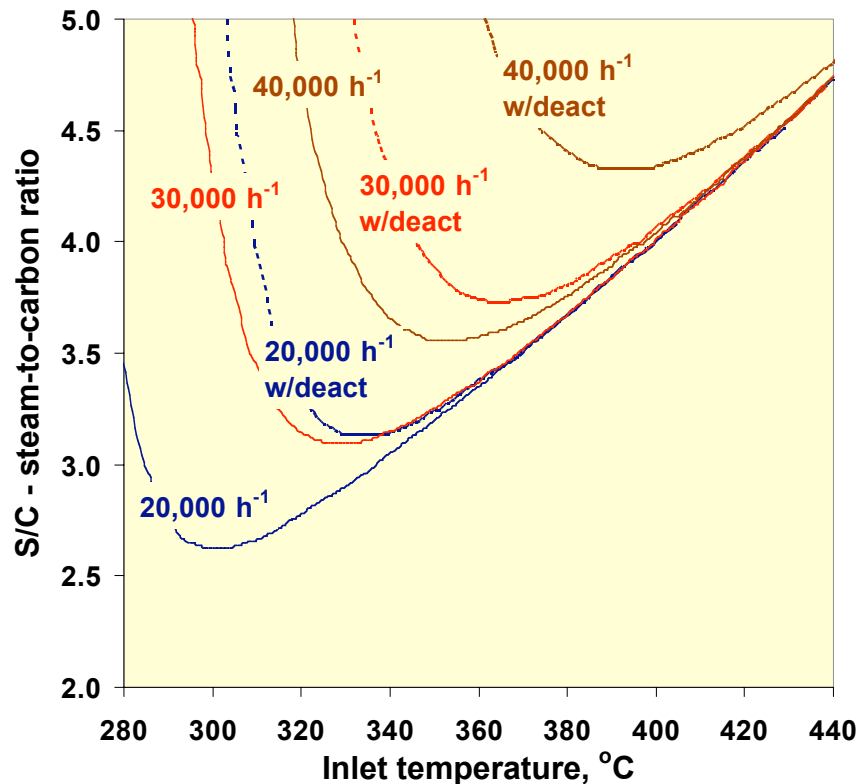


# Even with deactivation, Pt-Re catalyst should be able to meet GHSV target

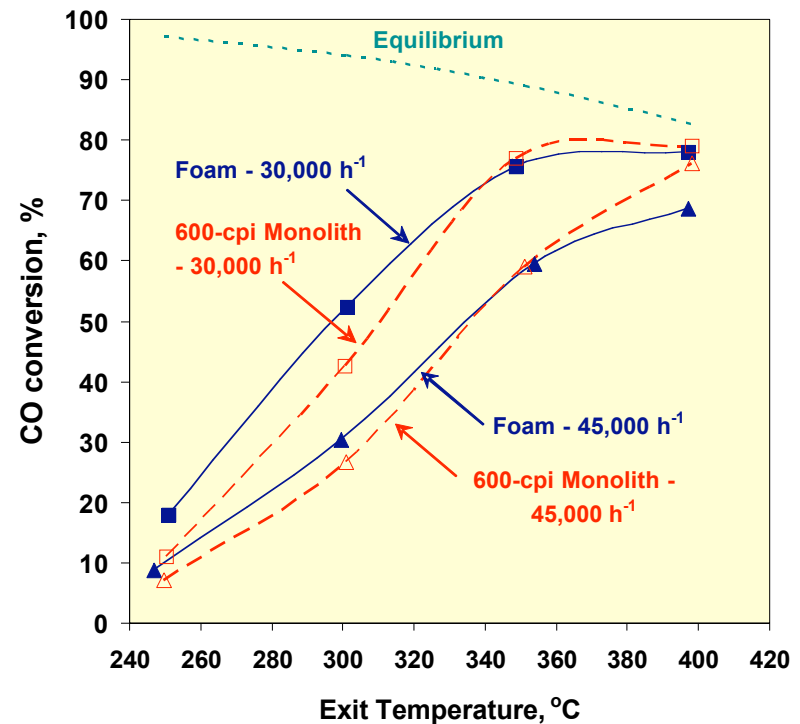
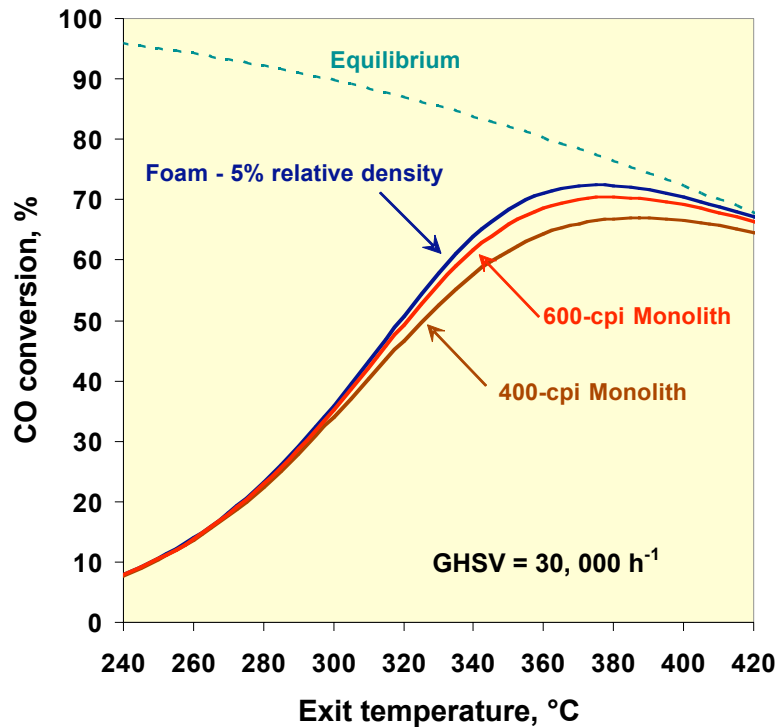
- Pt-Re lost about 50% of its initial activity during the first 250 hours, but the activity then stabilized



- Modeling study shows that 1% CO can be achieved even with deactivation if the temperature and S/C ratio are increased



# Optimal geometric support for WGS catalyst - foam or monolith?

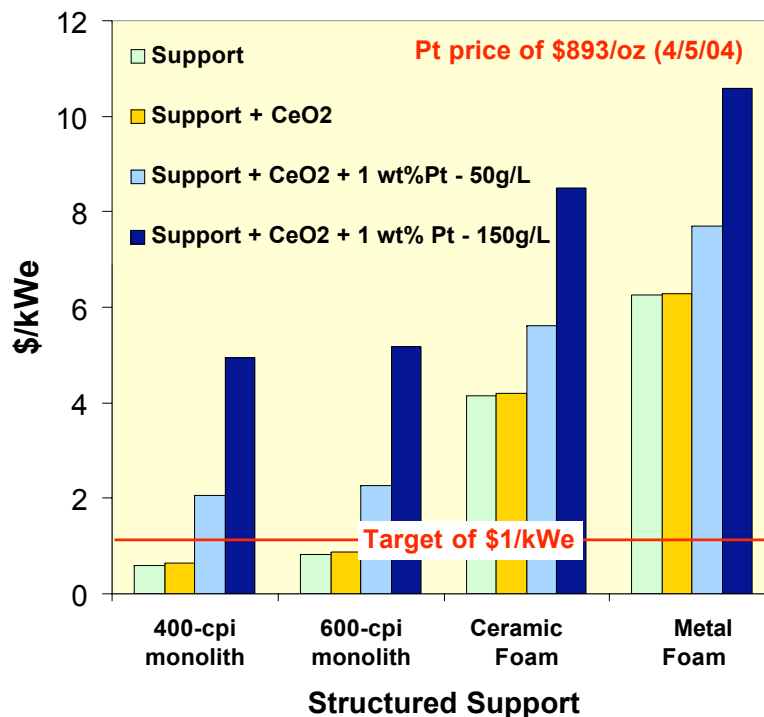
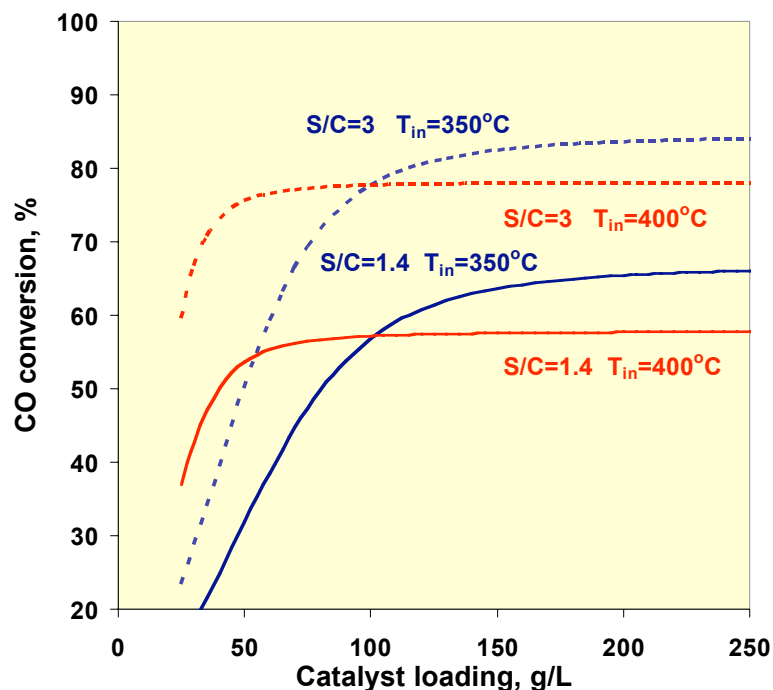


- Both modeling and experimental studies show that there may be a slight benefit to using a foam as a support
- However, the monolith is the preferred support based on cost and production capacity



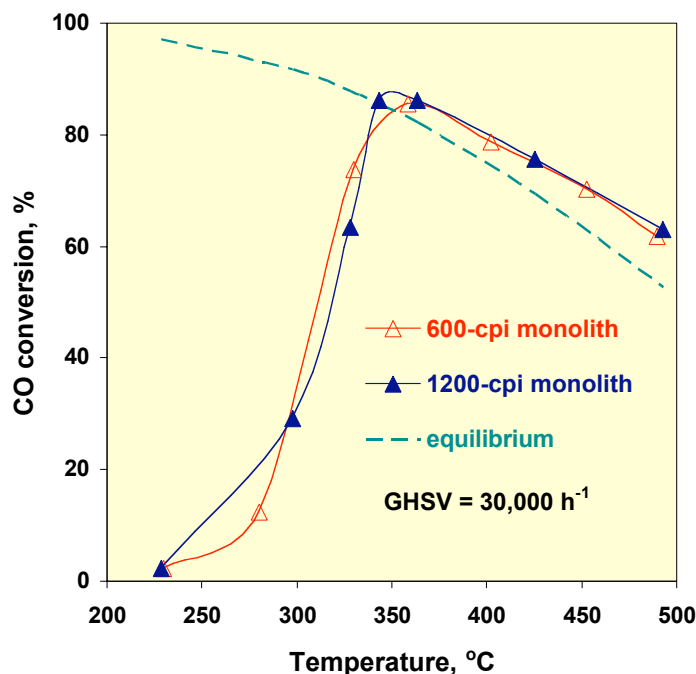
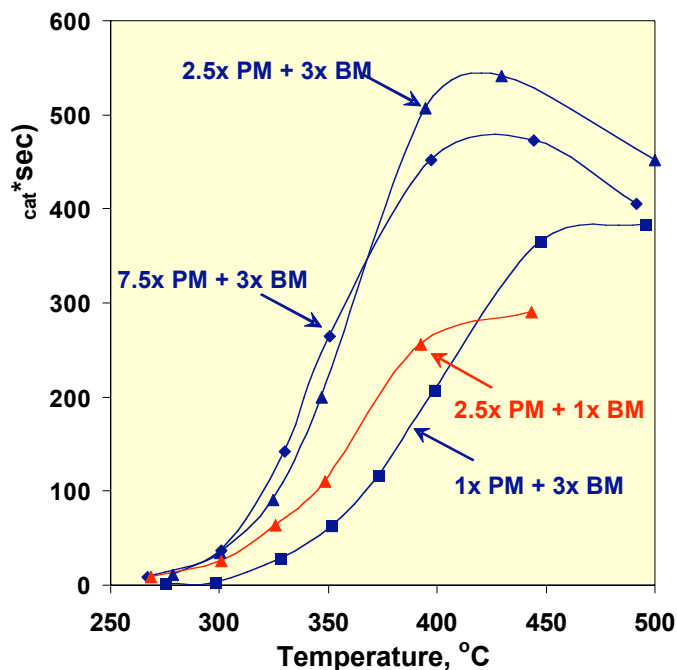
# Even with the higher activity of the Pt-Re, still higher activity is needed to meet the cost targets

- Modeling studies suggest that the optimal catalyst loading on the structured support is 50-150 g/L
- The \$1/kW<sub>e</sub> target is tough to achieve



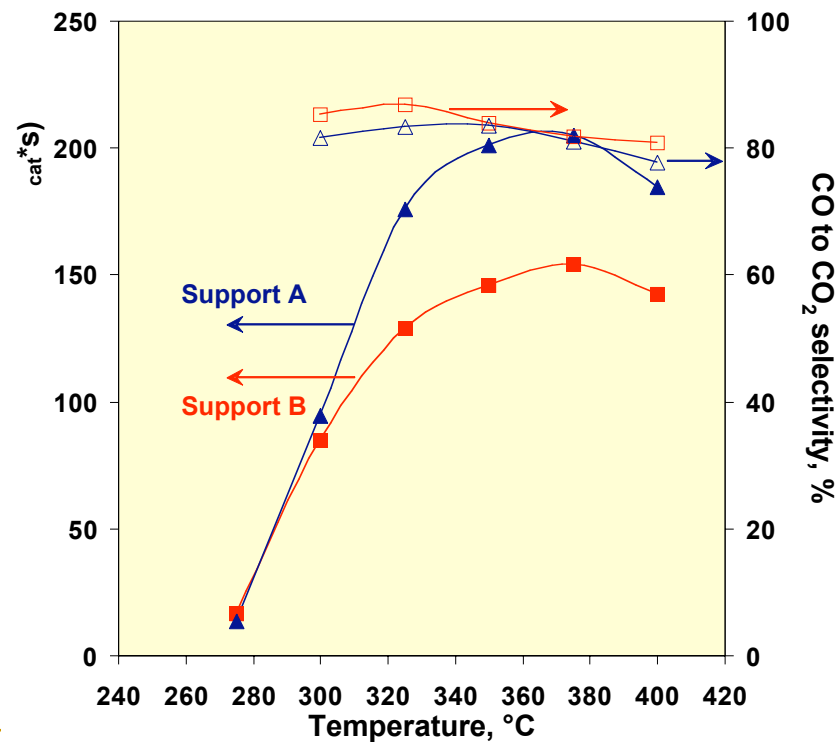
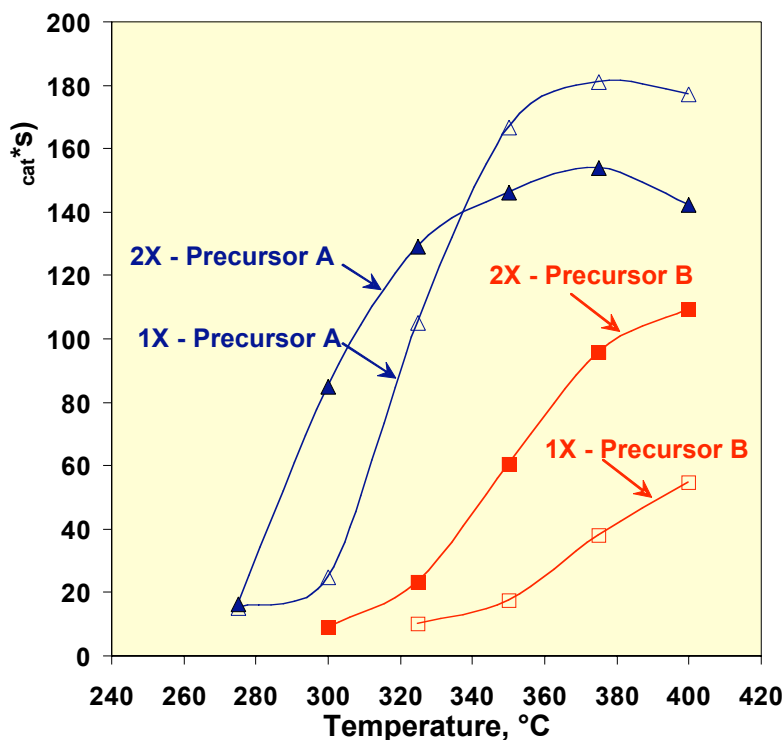
# We are investigating less-costly precious metal bimetallic catalysts

- A combination of a precious metal (PM)-base metal (BM) has been identified that exhibits higher WGS activity than either the PM or BM
- The equilibrium-predicted CO conversion is achieved at a GHSV of 30,000 h<sup>-1</sup> at >340°C
- Long-term stability is yet to be verified



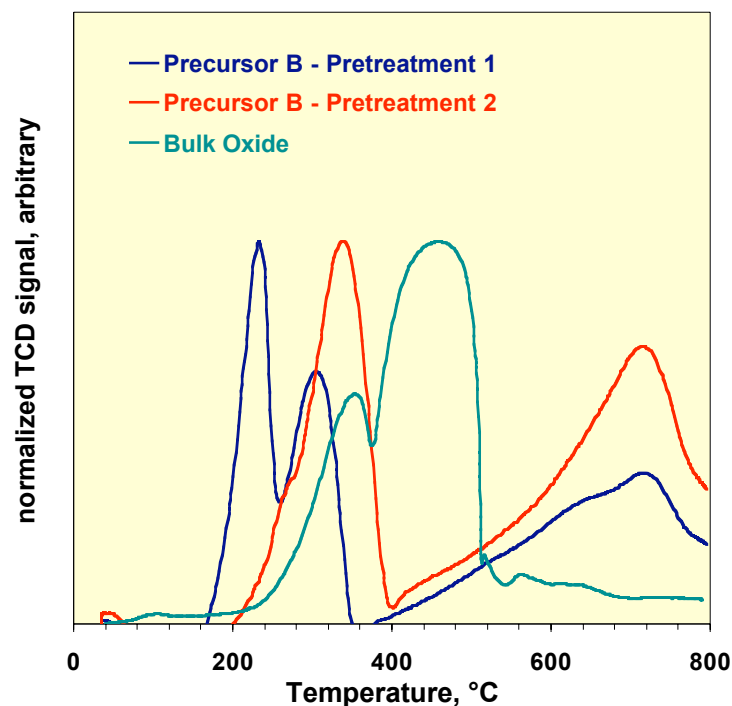
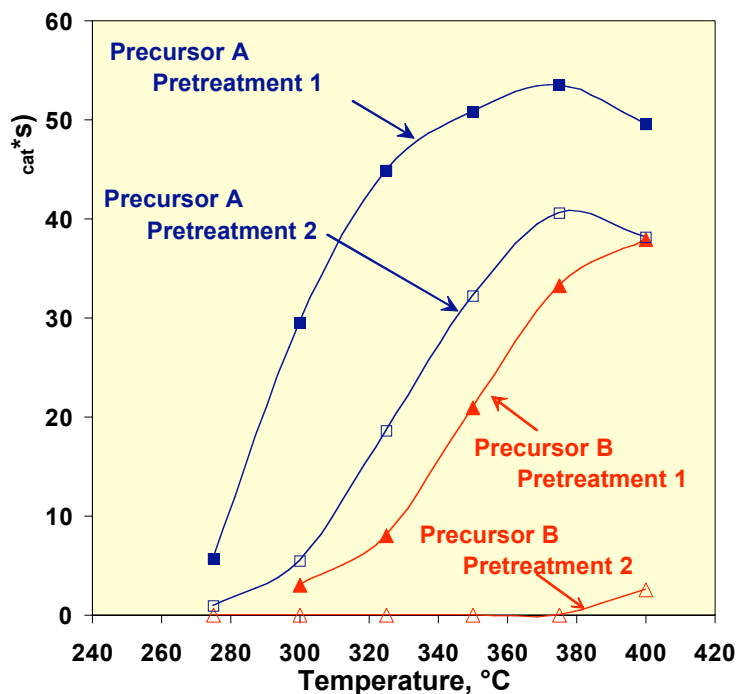
# Base metal WGS catalysts may also be possible

- The choice of precursor and oxide support were critical factors for optimizing activity
- The catalyst promotes methanation; however,
- The selectivity of CO to CO<sub>2</sub> does not depend on the precursor or support



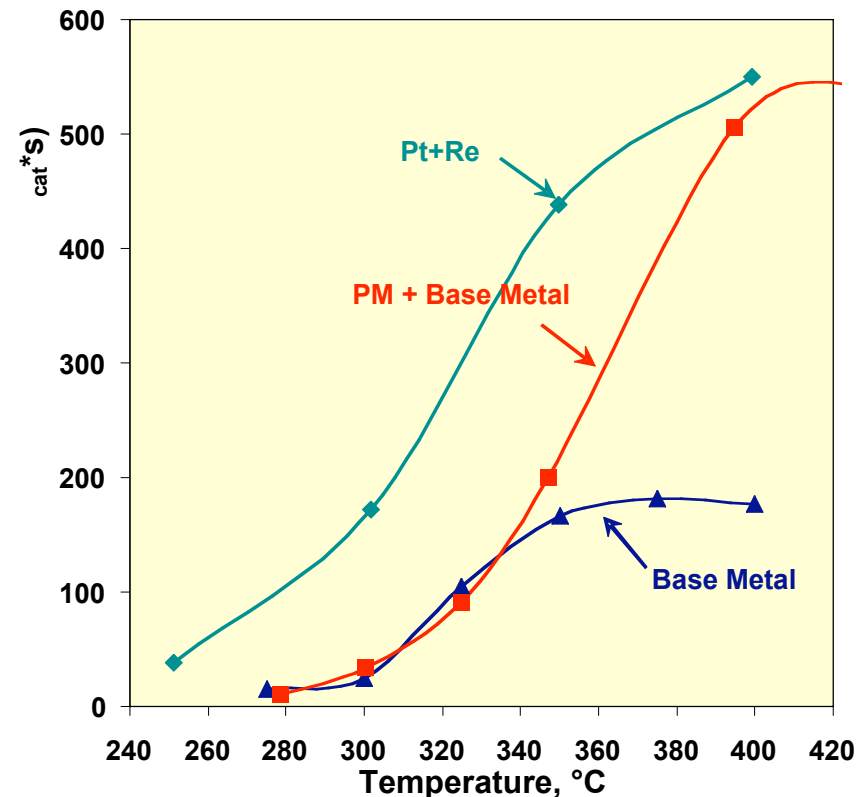
# A critical factor for the base metal catalyst is to prevent formation of the oxide and surface interactions

- Pretreatment has a significant influence on catalyst activity
- The most active catalysts have a reduction peak at  $\sim 200^{\circ}\text{C}$
- The reduction peak at  $\sim 700^{\circ}\text{C}$  is indicative of metal-support interaction



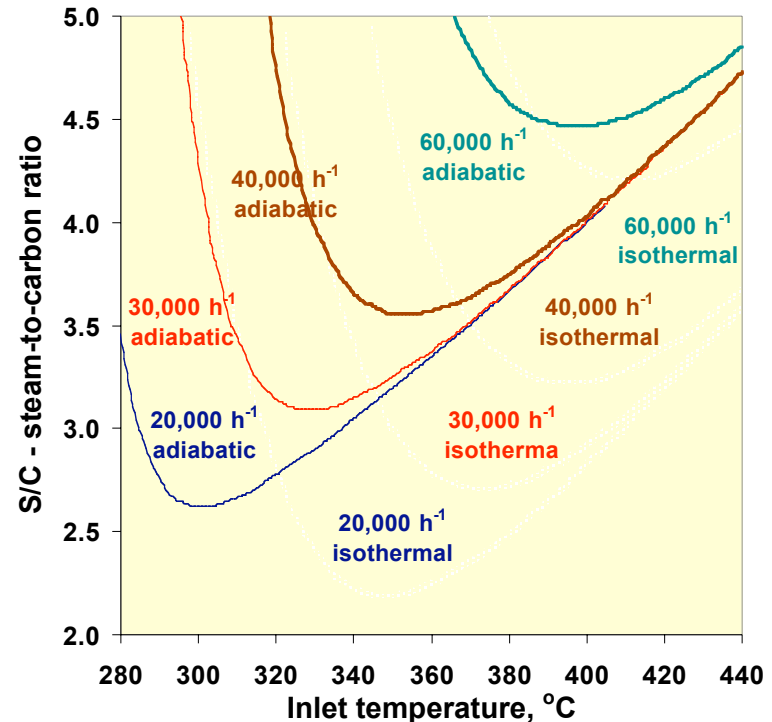
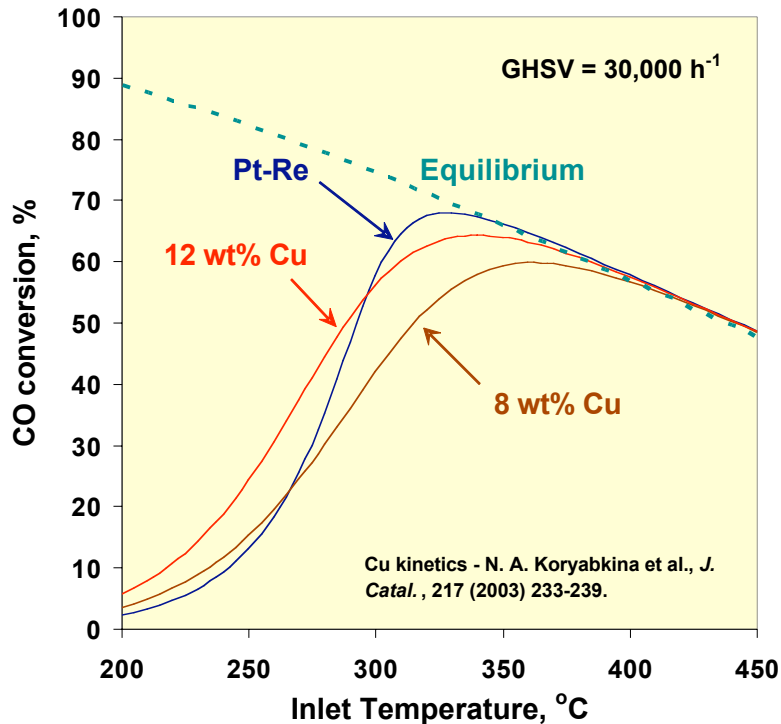
# Comparing the three types of WGS catalysts

- **Pt-Re**
  - Very active shift catalyst
  - Good stability
  - High Cost
- **PM + Base Metal**
  - Good shift activity
  - Less costly than Pt-Re
  - Stability not yet established
- **Base Metal**
  - Less active than both Pt-Re and PM + Base metal catalysts
  - Methanation and stability are yet to be addressed
  - Lowest cost



# Can we avoid low temperature shift for on-board reforming?

- Modeling studies show that the activity of Pt and Cu catalysts decreases significantly below 300°C
- Pt-Re can achieve 1% CO at >300°C at GHSV  $\geq 30,000 \text{ h}^{-1}$





# *Interactions and collaborations*

---

- **University of Alabama (Prof. Ramana Reddy) to characterize shift catalysts using SEM, TEM, and XPS**
- **Non-disclosure agreement (NDA) with Catalytica Energy Systems to evaluate new shift catalysts**
- **Provided samples for evaluation**
  - **Toyota**
  - **Nissan**
  - **Süd-Chemie, Inc.**



# ***Response to reviewers' comments from FY03***

---

- **Monolith work should be given priority**
- **Improve durability (longer-term endurance testing is needed)**
- **Better performance from non-precious metal catalysts**
- **Are low temperature catalysts feasible for on-board fuel processing?**



# Milestones

---

<u>Milestone</u>	<u>Date</u>
Determine the optimal operating conditions for the water-gas shift reactor	01/04
Determine the optimal bimetallic formulation for the Pt-based shift catalyst	05/04
Complete the assessment of the feasibility of a low temperature non-precious metal catalyst to meet the DOE targets	05/04
Demonstrate $\leq 1\%$ CO out using structured catalyst(s) for $>500$ h	09/04



# Future work

---

- **For bimetallic precious metal-base metal and base metal catalysts**
  - Optimize formulation to increase activity and minimize methanation
  - Improve our understanding of reaction mechanisms
- **To improve catalyst durability and minimize deactivation**
  - Conduct characterization studies of spent catalysts to further understand deactivation mechanisms
  - Conduct long-term tests of improved catalyst formulations
- **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 kinetic models