

Water Gas Shift Catalysis

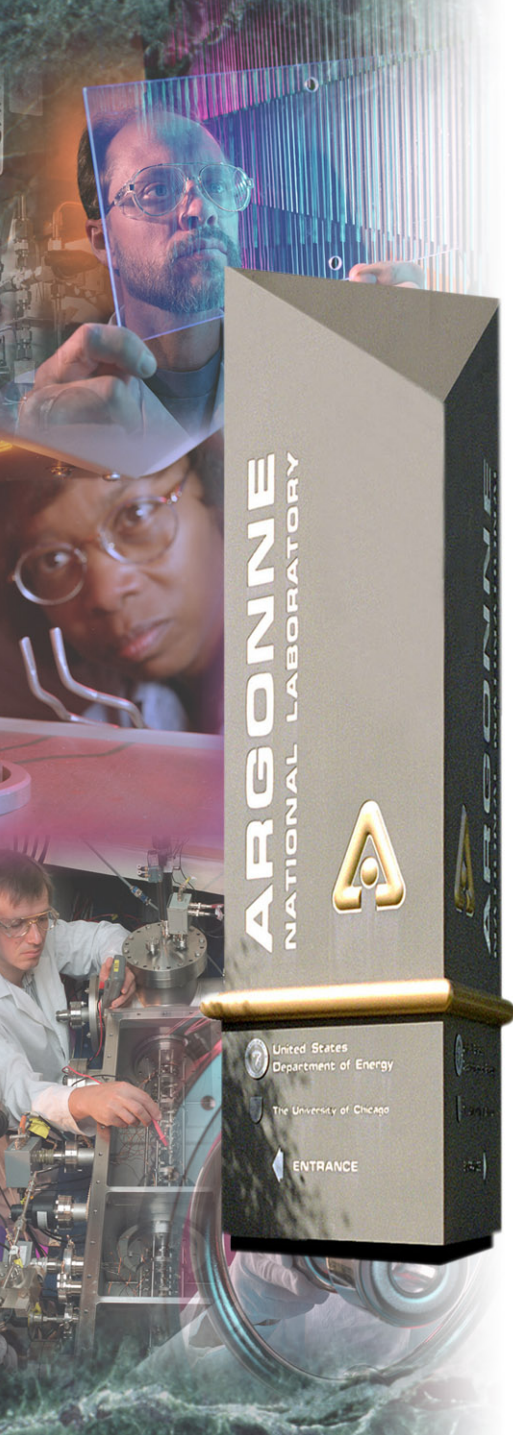
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Argonne National Laboratory

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Overview

- **Timeline**

- FY98 – Initiate catalyst development for on-board reforming of gasoline
- FY2005 – Switched focus to off-board reforming of natural gas and LPG
- FY2010 – Delivery of non-precious metal (PM) WGS catalyst

- **Budget**

- FY04 - \$600K
- FY05 - \$600K

- **Barriers**

(Distributed generation fuel processing – Task 12)

- A. Durability
- B. Cost
- F. Fuel Cell Power System Integration

- **Partners/Interactions**

- University of Alabama (Prof. Ramana Reddy)

Objectives

- **Overall**

- To develop advanced water-gas shift (WGS) catalysts that meet DOE performance requirements for distributed generation fuel processing.
- Define operating parameters (e.g., steam-to-carbon ratio, temperature, gas-hourly space velocity (GHSV),) to optimize catalyst performance and lifetime.
- Improve understanding of reaction mechanisms, catalyst deactivation, and sulfur poisoning.

- **FY05**

- Redirected focus from WGS catalysis for on-board fuel processing of gasoline to off-board processing of natural gas and liquefied petroleum gas (LPG).
- Increased emphasis on non-precious metal (PM) WGS catalysts.
- Increased catalyst durability testing.
- Improved understanding of reaction mechanism for ceria-supported catalysts.
- Initiated modeling studies to better understand reaction pathways.

Approach

- **Identify and synthesize metal and oxide combinations that**
 - promote one or more elementary reaction steps (e.g., CO oxidation, H₂O dissociation, formate/formyl decomposition) involved in the WGS reaction, and
 - inhibit undesired reactions such as methanation.
- **Conduct microreactor studies to evaluate catalyst performance (CO conversion, CO₂ and CH₄ selectivities, and durability) as a function of:**
 - catalyst composition,
 - reformat composition and sulfur content, and
 - operating parameters: H₂O:CO and H₂:CO ratios, temperature, gas-hourly space velocity (GHSV)
- **Use characterization techniques (e.g. X-ray spectroscopy, X-ray diffraction, CO and H₂ chemisorption and temperature-programmed reduction (TPR)) to identify factors needed to improve WGS activity, minimize catalyst deactivation, or inhibit methanation.**

Why focus on non-PMs for WGS catalysts for off-board fuel processing

- Base metals and non-PMs are significantly less costly than PM.
- Intrinsic reaction rates ($\text{CO} + \text{H}_2\text{O}$ in absence of H_2 and CO_2) exhibited by many non-PM metals are higher than the rates exhibited by PM.

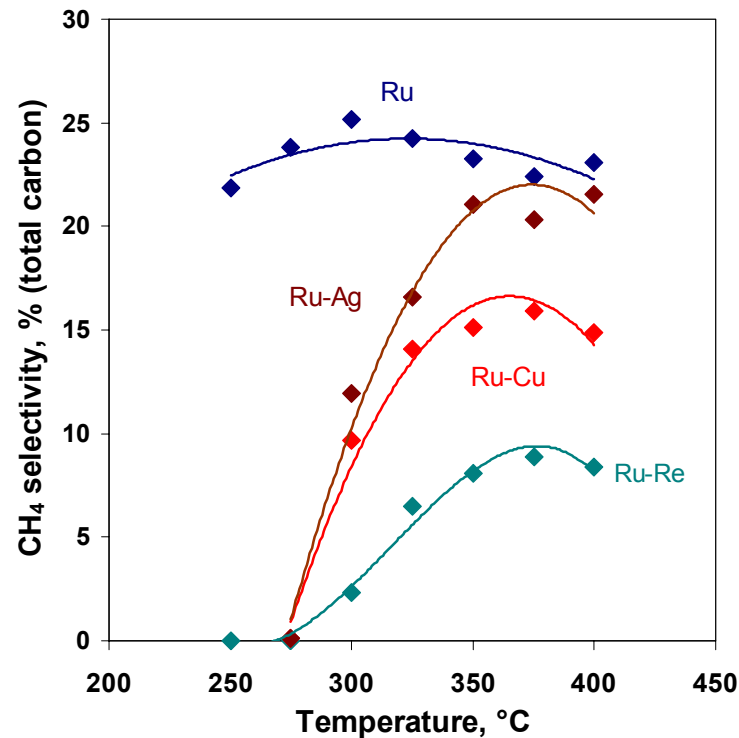
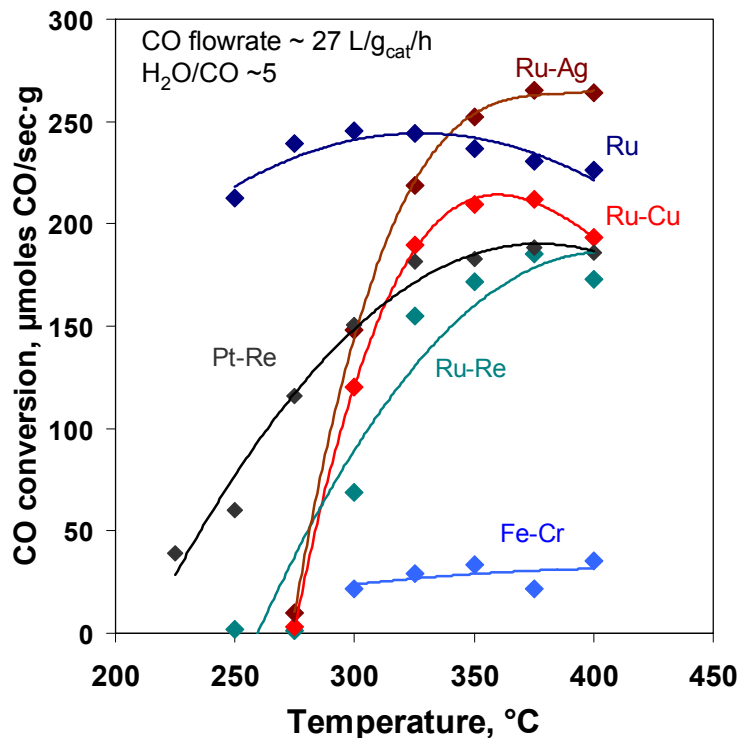
$\text{Cu} > \text{Co} > \text{Ru} > \text{Ni} > \text{Pt} > \text{Au} > \text{Fe} > \text{Pd} > \text{Rh} > \text{Ir}$

(Ref: D.C. Grenoble et al., *J. Catal.* 67, (1981) 90.)

- Performance requirements for WGS reactors in off-board fuel processing may be less demanding than for on-board fuel processing.
- The challenge is to inhibit dissociative CO adsorption leading to methane formation.

| | Associative | Dissociative | |
|----|--|--|------------------------------------|
| | $\frac{\text{CO}_{(g)} \rightarrow \text{CO}_{(s)}}{}$ | $\frac{\text{CO}_{(g)} \rightarrow \text{C}_{(s)} + \text{O}_{(s)}}{}$ | (All energies are in eV) |
| Cu | -0.62 | 1.77 | |
| Pt | -1.89 | 0.37 | (Ref: T. Bligaard et al., |
| Co | -1.50 | -1.51 | <i>J. Catal.</i> 224, (2004) 206.) |

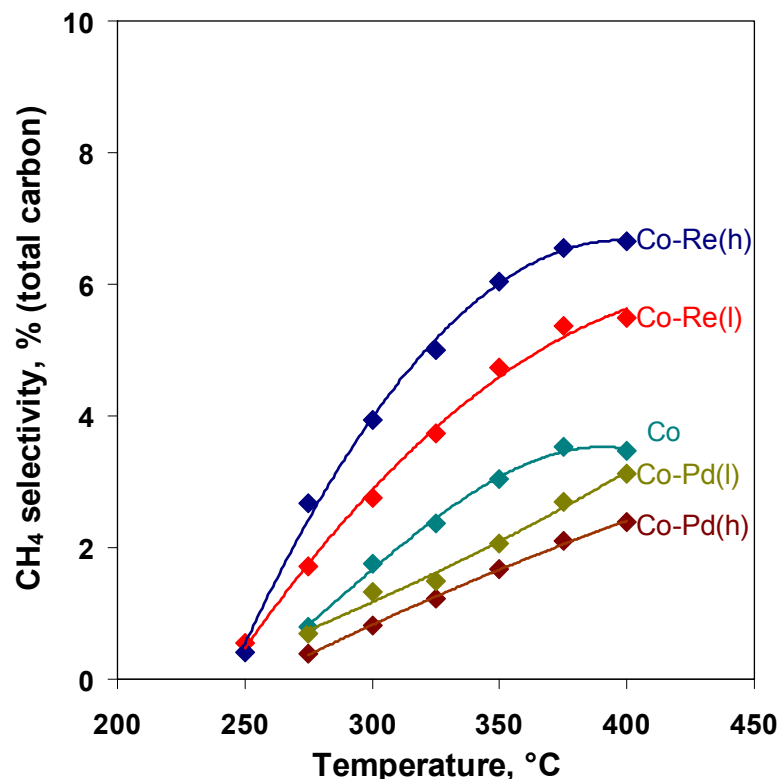
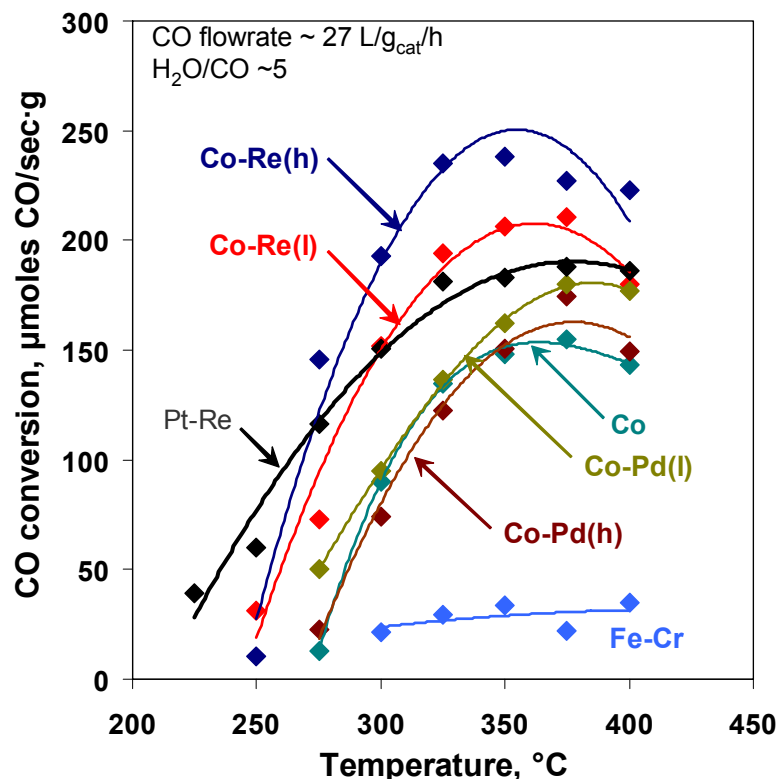
Addition of Re to Ru significantly reduces the methane selectivity



- **Rationale behind choice of additive**

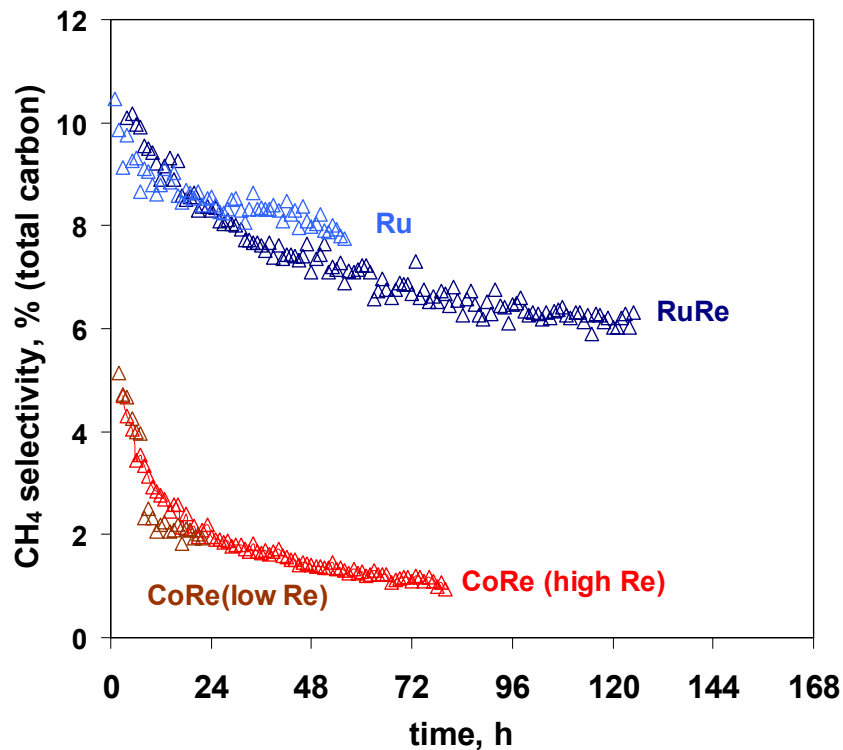
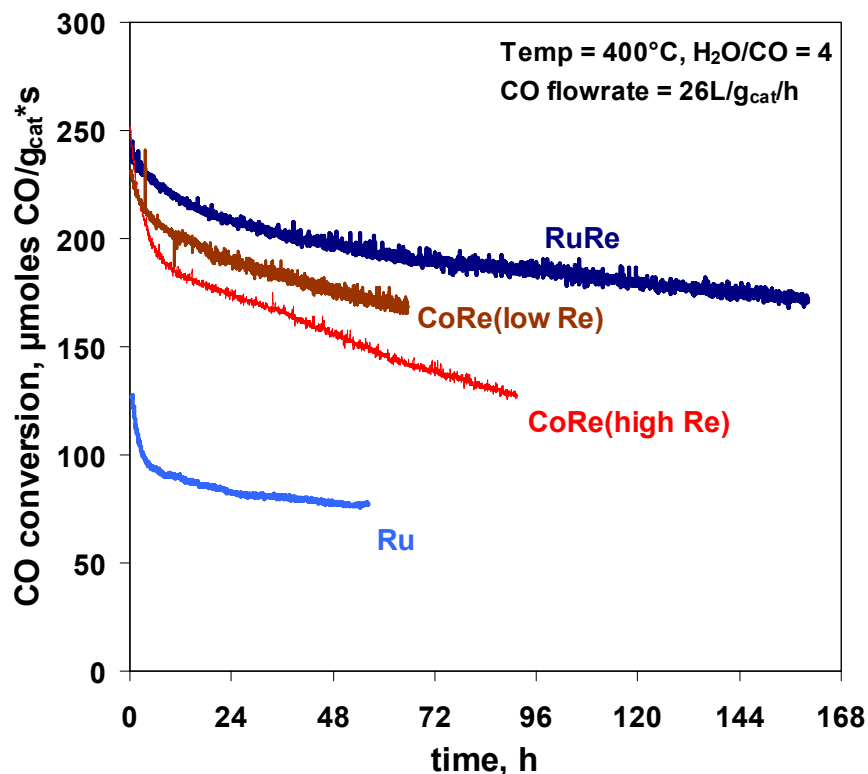
- **Block dissociative adsorption of CO - Cu and Ag occupy edge, corner, or defect sites (highly active for CO dissociation) on Ru**
- **Reduce H₂ adsorption – Ag shown to decrease rate of H₂ adsorption**
- **Promote oxidation of C or CO – Re?**

Co-Re catalysts exhibit activity comparable to Ru catalysts but with lower methane selectivity



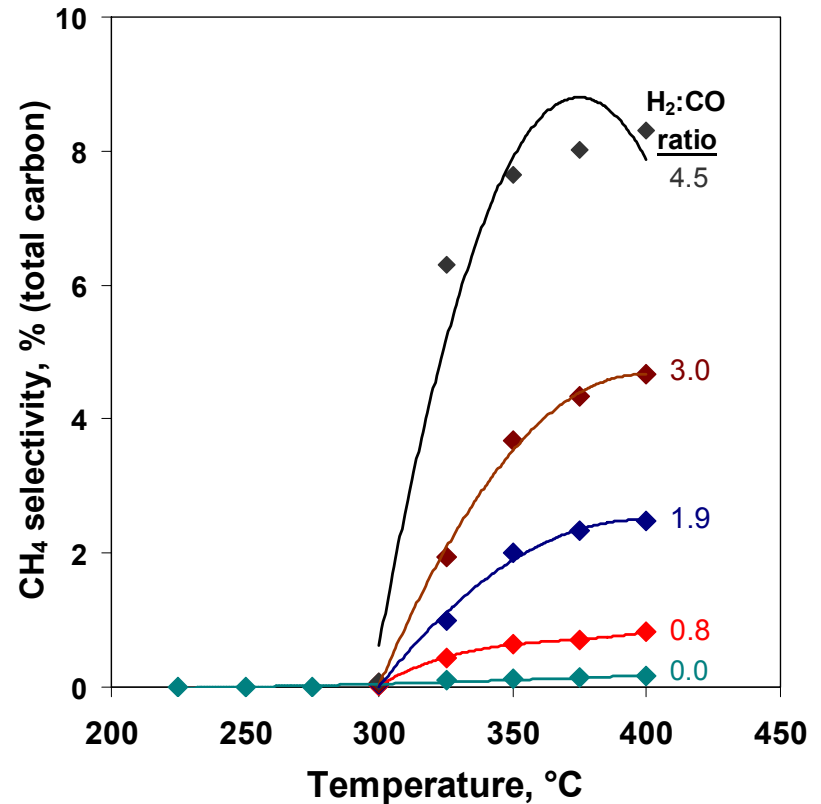
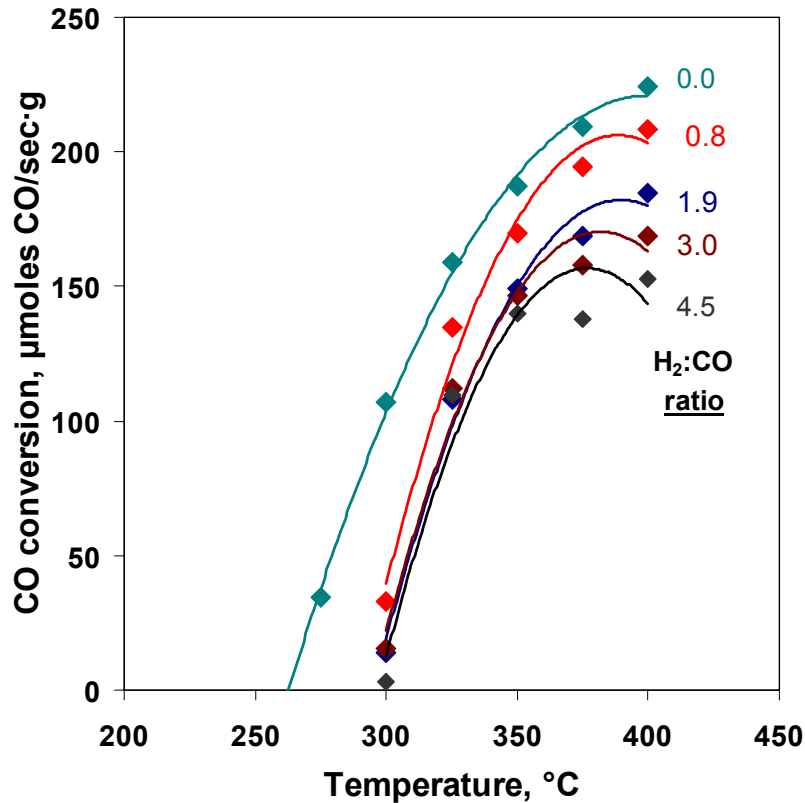
- Co catalysts exhibited higher selectivity to CO₂ (less selectivity to CH₄) than Ru catalysts.
- Addition of Re to Co increased CO conversion rate, but also increased carbon selectivity to CH₄ compared to Co alone.

Re improves the stability of Co and Ru with Ru-Re catalyst showing promising long-term stability



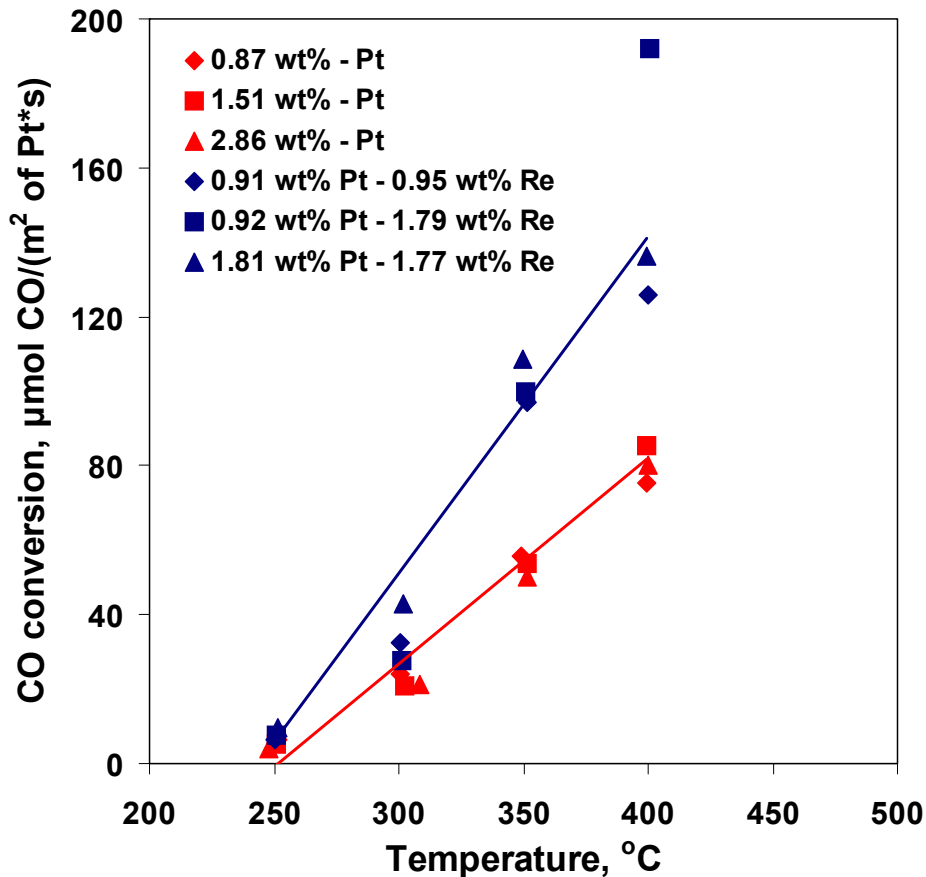
- Addition of Re stabilized both Ru and Co catalysts although the effect was greater with Ru than Co.
- Initial decrease in methane selectivity coincides with decrease in the rate of CO conversion.

Development of membrane-shift reactors should benefit base metal catalysts



- CO conversion independent of H₂:CO ratio above 300 °C (when equilibrium is taken into account).
- Temperature control will be critical to minimizing methanation.

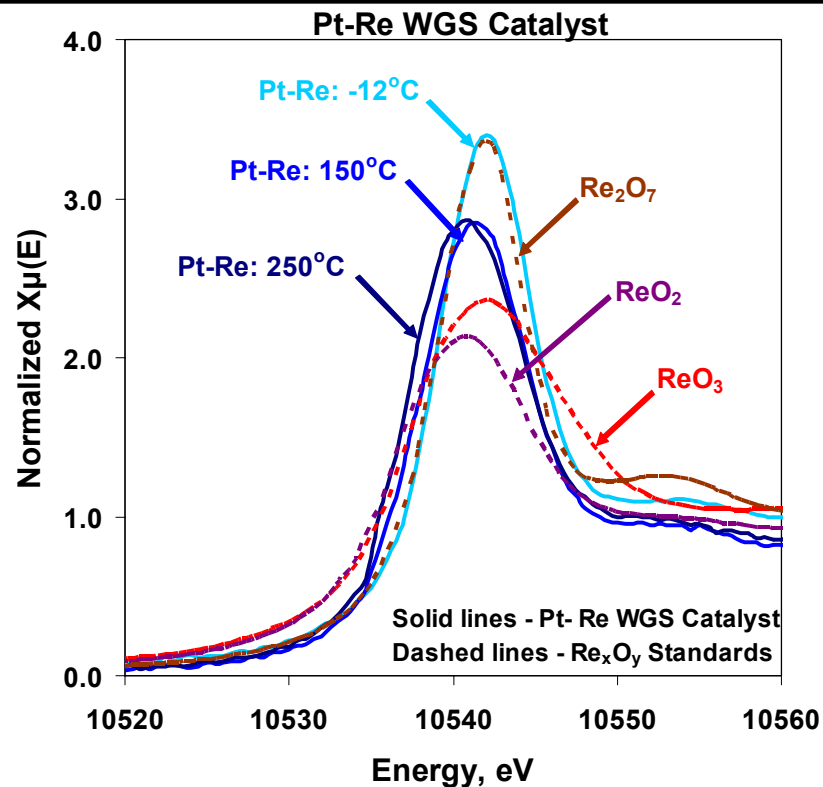
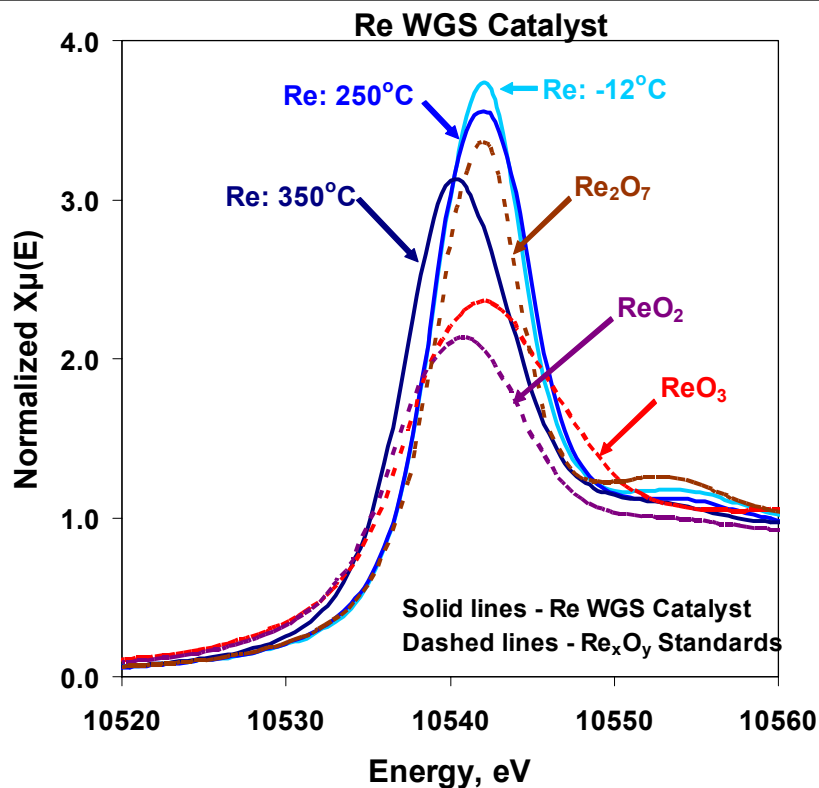
For Pt-Re catalyst, the enhancement due to Re addition is more complicated than increasing Pt dispersion



| <u>Sample</u> | <u>Dispersion (%)</u> | <u>Pt surface area (m²/g_{cat})*</u> |
|-------------------------|-----------------------|---|
| 0.87 wt% Pt | 60 | 1.4 |
| 1.51 wt% Pt | 48 | 1.9 |
| 2.86 wt% Pt | 60 | 4.5 |
| 0.91 wt% Pt-0.95 wt% Re | 83 | 2.0 |
| 0.92 wt% Pt-1.9 wt% Re | 69 | 1.7 |
| 1.81 wt% Pt-1.9 wt% Re | 86 | 4.1 |

- CO chemisorption shows that the Pt dispersion is greater on Pt-Re catalyst than on Pt catalyst at similar Pt wt loading.
- Higher rate of CO conversion per m² of exposed Pt suggest the role of Re in enhancing the rate is more than simply increasing the Pt dispersion.

TPR shows that Pt promotes the reduction of Re oxide in Pt-Re catalyst

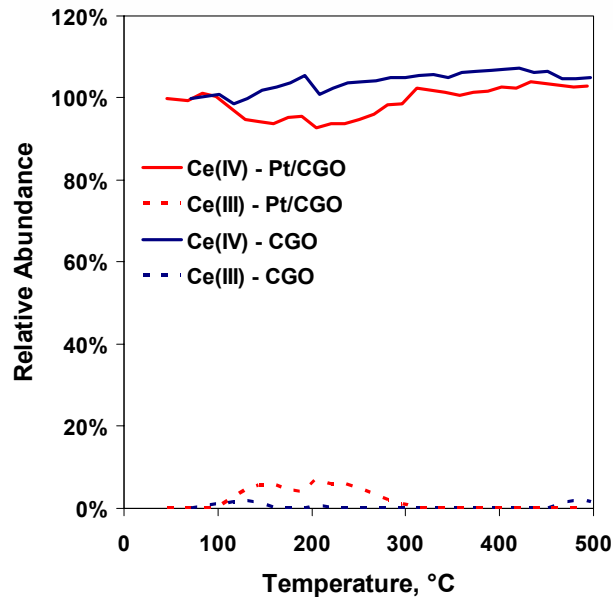
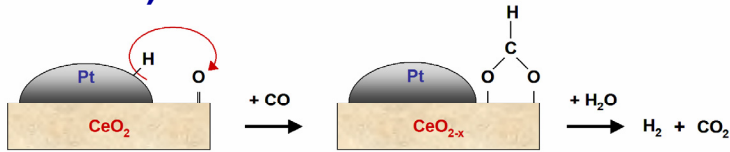


- Reduction of $Pt^{+2/+4}$ to Pt^0 (data not shown) was observed at 100-150°C whether or not Re was present.
- Reduction of Re probably occurs by “hydrogen spillover” from Pt.
- Re oxide may activate water by a mechanism similar to ceria.

H₂ TPR shows that the dopant may influence reaction mechanism for Pt-ceria catalysts

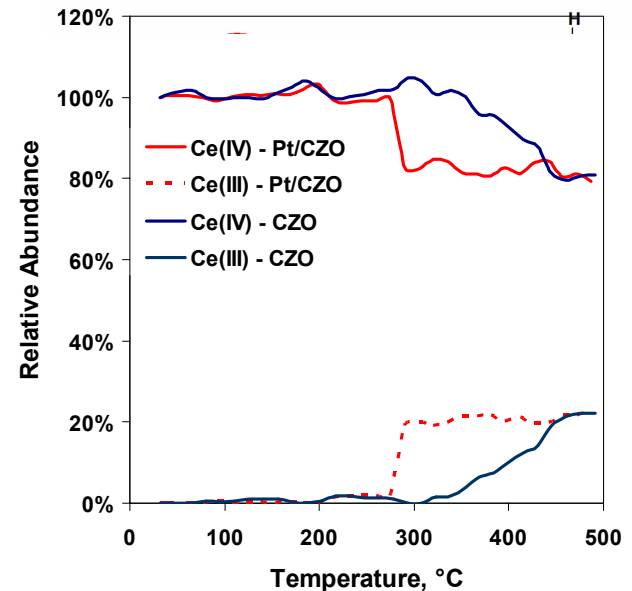
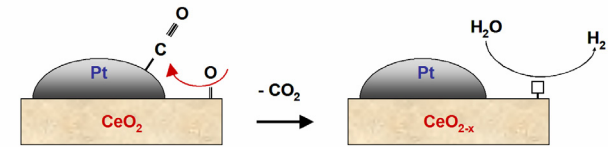
CeO₂-Gd₂O₃

- Reduction of Ce(IV) to Ce(III) not observed, suggesting that transfer of oxygen from Ce to Pt during WGS does not occur (Formate mechanism).



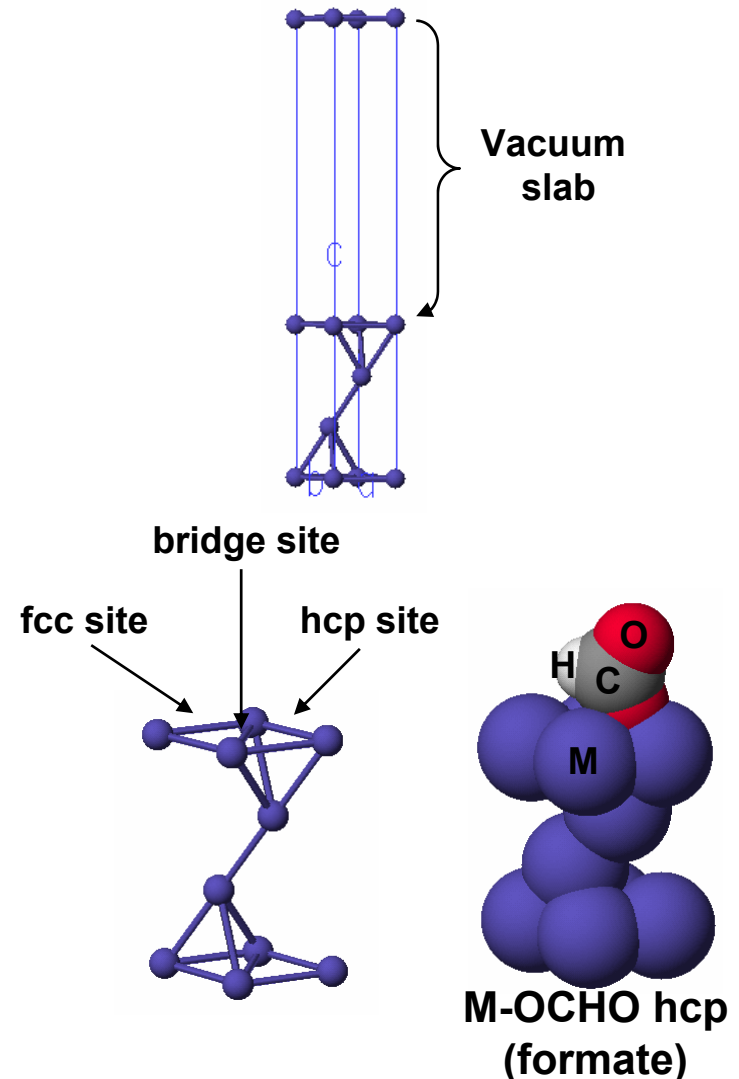
CeO₂-ZrO₂

- Reduction of Ce(VI) to Ce(III) observed suggesting that transfer of oxygen from Ce to Pt during WGS may occur (Redox mechanism).



Incorporating modeling to understand reaction pathways and the role of support and additive interactions

- Most model studies for the WGS reaction assume the reaction occurs only on a metal surface (neglect bimetallic and support interactions).
- We are using the Vienna *ab initio* Program (VASP) to model both WGS and methanation reactions.
- Currently, we are baselining our models for WGS and methanation reactions against models reported in the literature.
- Goal is to better understand how the choice of metal and metal-support and metal-additive interactions influence CO conversion to CO_2 or CH_4 .



Response to Previous Year Reviewers' Comments

- **“Catalyst cost and durability”**
 - Our primary focus in FY05 has been to develop the non-precious metal catalysts.
 - We have increased our effort to address the catalyst durability issue by conducting more long-term (50 h or more) reactor studies.
- **“Progress made in understanding challenges to developing base metal catalysts, but still a long way to go”**
 - Many base metals and non-PMs exhibit higher turnover rates than Pt for the shift reaction but promote methanation. Inhibiting methanation without compromising shift activity will be challenging, but we believe that we are making significant strides towards achieving this goal.

Milestones

| Task | Date |
|--|--------------|
| <p>Demonstrate improved activity of ANL shift catalysts at temperatures of 275–325°C</p> <p><i>Status: Increasing the weight loading of Ru improved its activity in the temperature range of 275-325°C. Increasing the reducibility of Ru below 300°C needs to be addressed.</i></p> | 01/05 |
| <p>Demonstrate reduced methanation of base metal shift catalysts (<5% selectivity to CH₄)</p> <p><i>Status: Cobalt catalysts show low methane selectivity; however, stability is an issue. The addition of Re to Ru was shown to reduce the methane selectivity from ~25% to <10% without sacrificing performance.</i></p> | 05/05 |
| <p>Determine the effect of sulfur, olefins and aromatics on the activity of precious metal and base metal catalysts</p> <p><i>Status: Task not yet started.</i></p> | 09/05 |

Future Work

- **Continue development of Ru-Re and Co-Re catalysts**
 - optimize catalyst formulation and synthesis procedure
 - reduce methanation
 - address long-term durability
 - develop kinetic models
- **Characterization studies of Ru-Re and Co-Re catalysts**
 - metal particle morphology (particle size, composition)
 - mechanistic studies (role of additive and support) Can we find an alternative to Re to further reduce cost?
- **Effect of impurities, such as olefins and sulfur, on catalyst performance**
- **Modeling studies focusing on metal-additive and metal-support interactions**

Publications and Presentations

- Publications

- **“Pt-Re bimetallic supported on CeO₂-ZrO₂ mixed oxides as water–gas shift catalysts,” Sara Yu Choung, Magali Ferrandon and Theodore Krause, *Catal. Today*, 99 (2005) 257-262.**

- Presentations

- **“Catalyst Development and Engineering Considerations for Reducing the Size of the Shift Reactor in Fuel Processors,” T. R. Krause, S. Y. Choung, D. D. Papadimas, and R. Souleimanova, Presented at the 2004 Fuel Cell Seminar, San Antonio, Texas, November 1-5, 2004.**
- **“Effect of doping CeO₂ with Gd₂O₃ or ZrO₂ on the reducibility of Pt and Ce in Pt-CeO₂ water–gas shift catalysts,” M.J. Castagnola, M. Ferrandon, A. J. Kropf, and T.R. Krause, Presented at the 2005 Users Meeting for the Advanced Photon Source and the Center for Nanoscale Materials, Argonne, Illinois, May 2-6, 2005.**

Hydrogen Safety

- **The most significant hydrogen hazard associated with this project is:**
 - Experimentalists being unfamiliar with the hazards associated with using hydrogen in experimental work leading to a potentially explosive or flammable gas mixture.

Hydrogen Safety

- **Our approach to dealing with this hazard is:**
 - **All experimental activities performed in this program are conducted under the guidance of safety review documents, as required by Argonne National Laboratory.**
 - **The safety review document provides the user with the following information:**
 - **a description of experimental plan that will utilize the equipment,**
 - **a description of the equipment and how it works,**
 - **defines the operating procedures including the allowable range of operating parameters,**
 - **provides procedures for safe shutdown of the equipment if an operating parameter, such as pressure or temperature, is outside of its allowable range,**
 - **identifies any potential hazardous situations that may arise, such as the potential for fire or explosion, as well as the proper response,**
 - **identifies safety issues, such as the use of toxic or hazardous chemicals, and provides procedures for handling these chemicals, and**
 - **describes the procedures for accumulating and disposing of chemical wastes.**

19

Hydrogen Safety (cont.)

- **The safety review document is written by the scientist, referred to as the Principle Investigator, responsible for maintaining and overseeing the experimental work and the operation of the equipment described in the document.**
 - **The document is reviewed by a committee of scientific, Divisional safety officers, and ANL ES&H personnel.**
 - **The supervisor of the Principle Investigator is responsible for approving the safety review document.**
 - **The safety review document is reviewed and the approval is renewed annually.**

- **Every employee participating in the experimental plan described in the safety review must be trained prior to beginning any work.**
 - **The training is conducted by the Principle Investigator.**
 - **After an individual is trained, their name is added to a document that contains a list of qualified personnel permitted to execute the experimental plan described in the safety review.**