

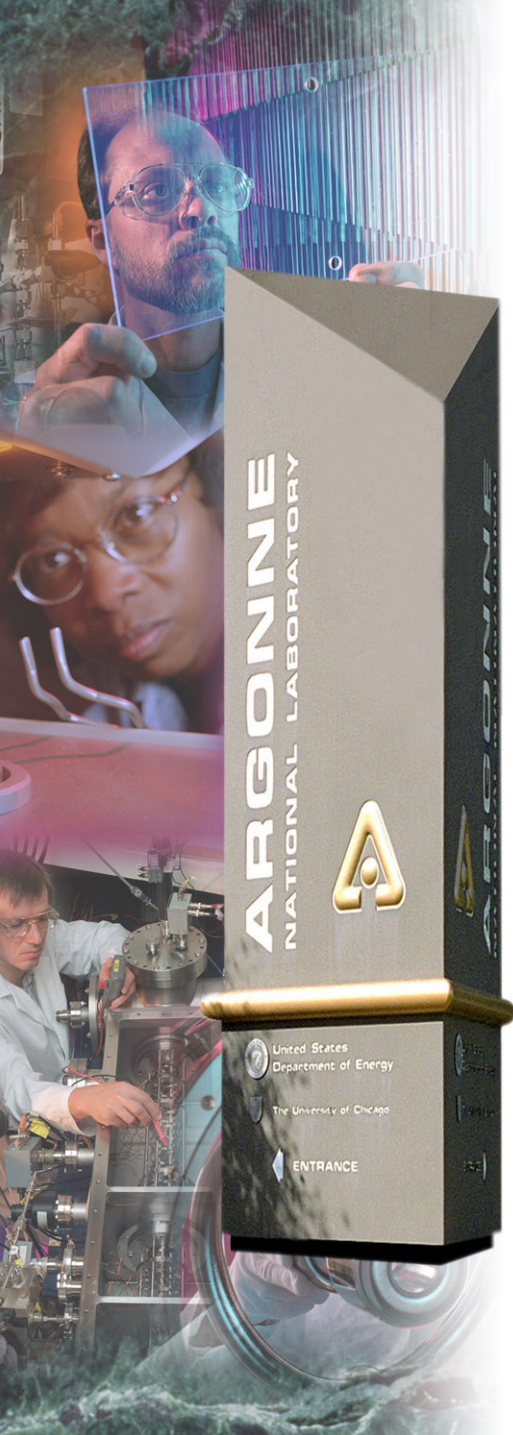
Catalysts for Autothermal Reforming

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Argonne National Laboratory
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Project ID # FC25

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Overview

- **Timeline**

- FY95 – Initiate catalyst development for on-board reforming of gasoline
- FY2005 – Switched focus to off-board reforming of natural gas and LPG
- FY2010 – Deliver sulfur-tolerant, non-precious metal (PM) reforming catalyst

- **Budget**

- FY04 - \$400K
- FY05 - \$400K

- **Barriers**

(Distributed generation fuel processing – Task 12)

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

- **Partners/Interactions**

- University of Alabama (Prof. Alan Lane, Prof. Ramana Reddy)
- University of Puerto Rico at Mayagüez (Prof. José Colucci)
- GE/University of Minnesota

Objectives

- **Project**

- Develop advanced fuel processing catalysts that meet performance requirements for distributed generation fuel processing.
- Define operating parameters (e.g., O₂:fuel and steam:fuel ratios, temperature, gas-hourly space velocity (GHSV),) to optimize catalyst performance and lifetime.
- Improve understanding of reforming reaction mechanisms, catalyst deactivation, and sulfur poisoning.

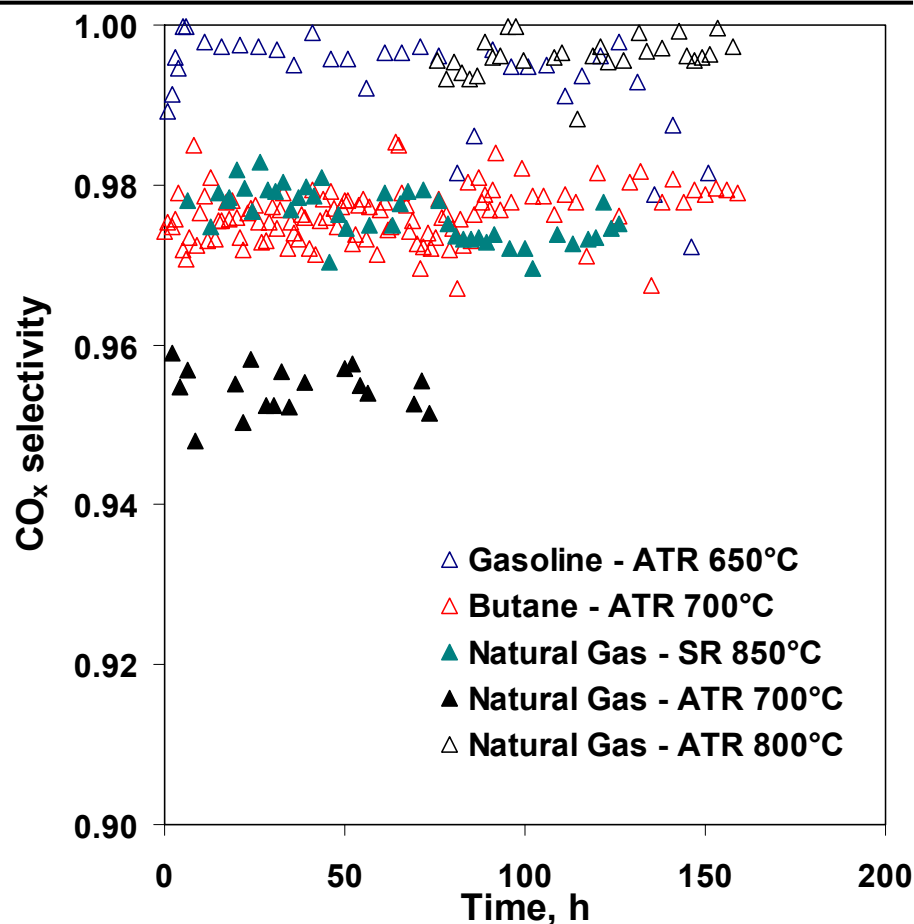
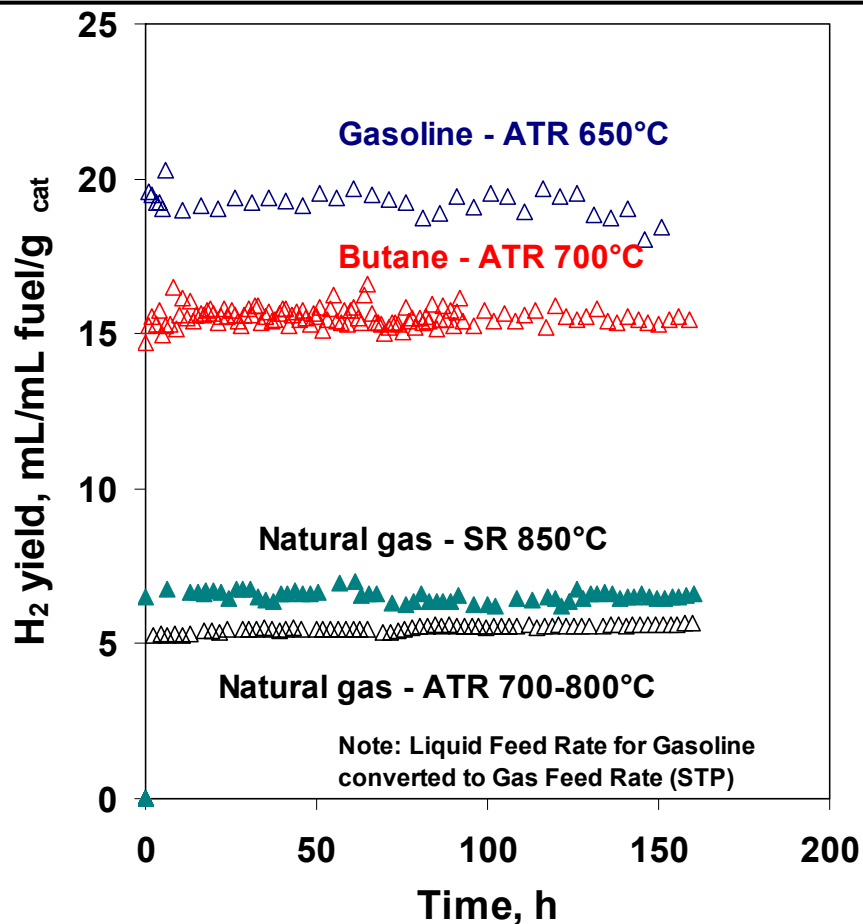
- **FY05**

- Redirect focus from on-board reforming of gasoline to off-board reforming of natural gas and liquefied petroleum gas (LPG).
- Evaluate performance of Rh catalyst, developed for autothermal reforming (ATR) of gasoline, for ATR and steam reforming of natural gas and LPG .
- Reduce/eliminate the precious metal (PM) loading.
- Improve understanding of reaction mechanisms and catalyst deactivation.

Approach

- **Building on past ANL experience and the technical literature, investigate transition metals supported on refractory or reducible oxide substrates.**
- **Conduct reactor studies to evaluate catalyst performance (H_2 yield, CO_x selectivity, hydrocarbon breakthrough, fuel conversion, and durability) as a function of:**
 - **catalyst composition,**
 - **fuel composition and sulfur content, and**
 - **operating parameters: $O_2:C$ and $H_2O:C$ ratios, temperature, GHSV.**
- **Conduct catalyst characterization and mechanistic studies to identify**
 - **factors influencing activity and selectivity,**
 - **causes of deactivation, and**
 - **how sulfur affects catalyst performance.**

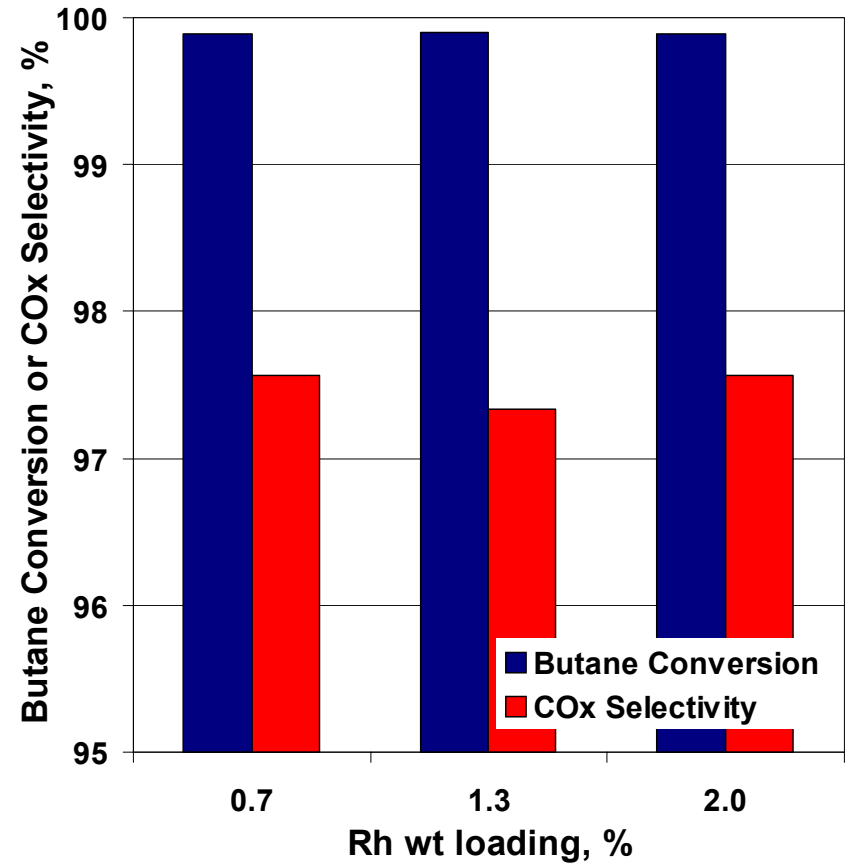
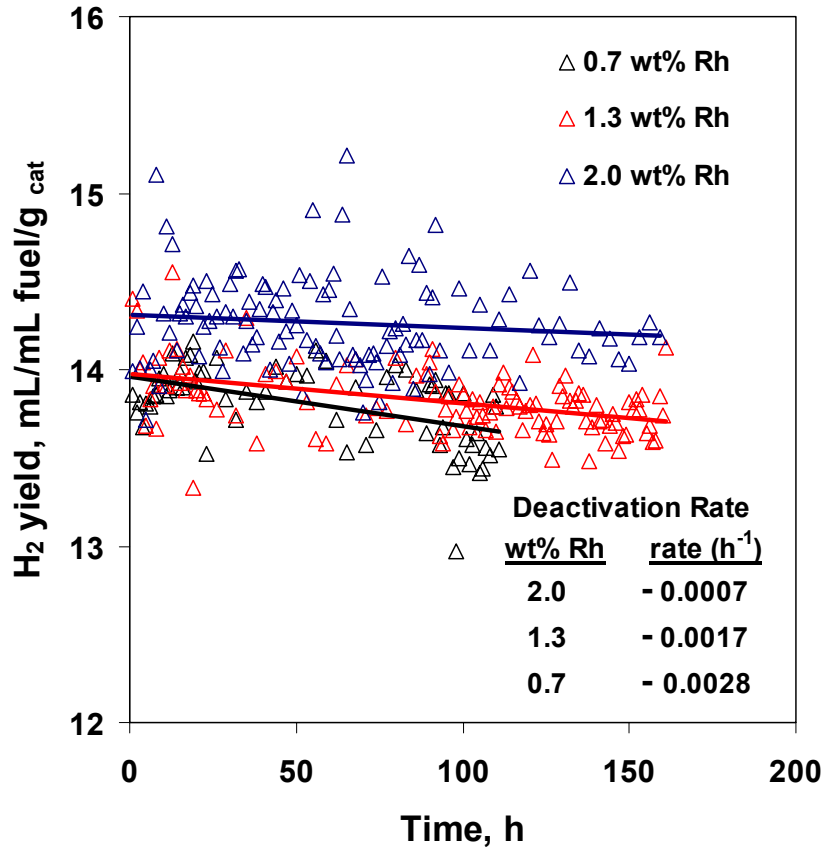
High H₂ yields and CO_x selectivities for ATR of natural gas and butane with Rh catalyst developed for ATR of gasoline



Feed rates: Gasoline – 15 mL/g_{cat}/h (liquid)
 Natural Gas (ATR) – 14 L/g_{cat}/h
 ATR: O₂/C = 0.5 H₂O/C = 2

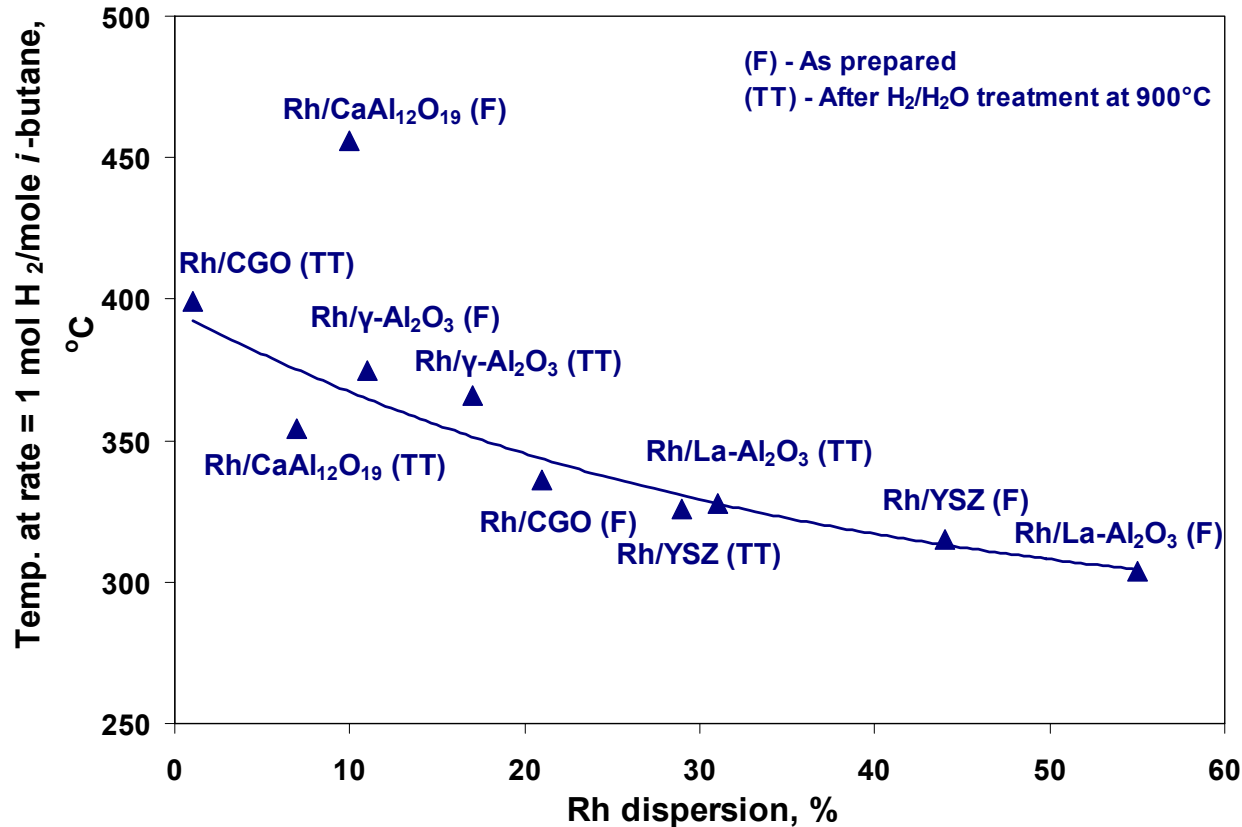
Butane – 3.8 L/g_{cat}/h
 Natural Gas (SR) – 7 L/g_{cat}/h
 SR: H₂O/C = 3

Although H₂ yields remain high, rate of deactivation increases as Rh loading decreases for ATR of butane



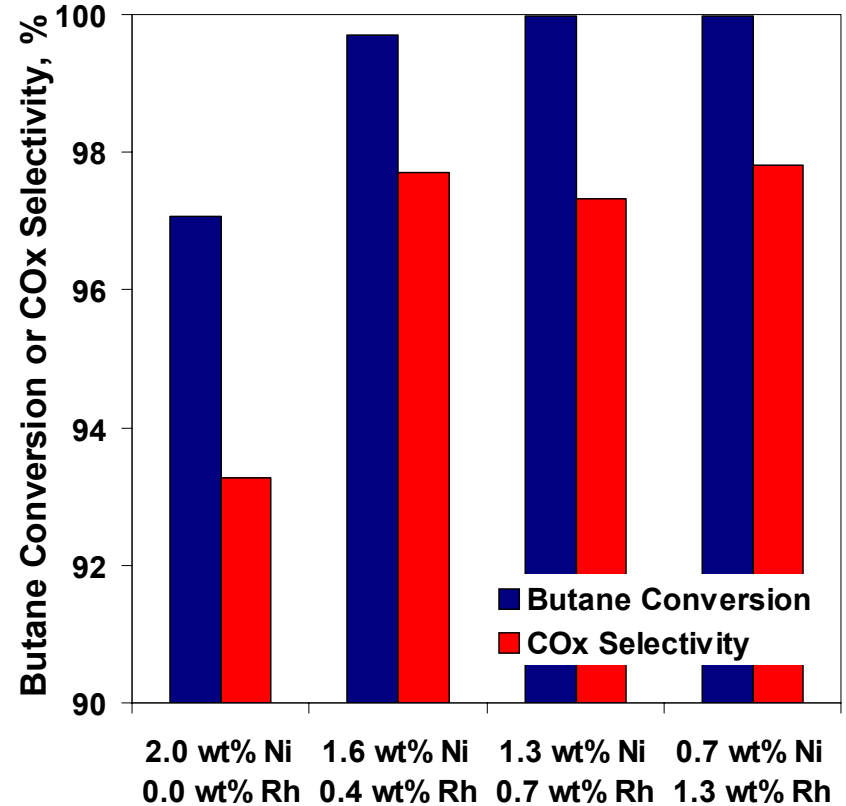
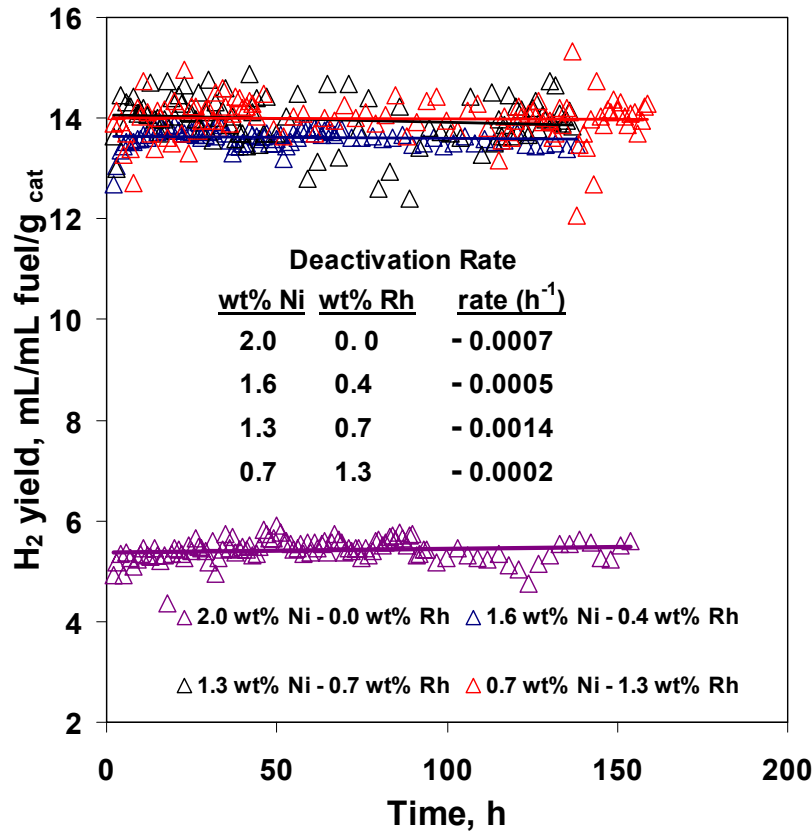
Conditions: Natural Gas (ATR) – 14 L/g_{cat}/h, O₂/C = 0.5, H₂O/C = 2

Activity of Rh catalyst depends on dispersion, no evidence oxide support influences activity



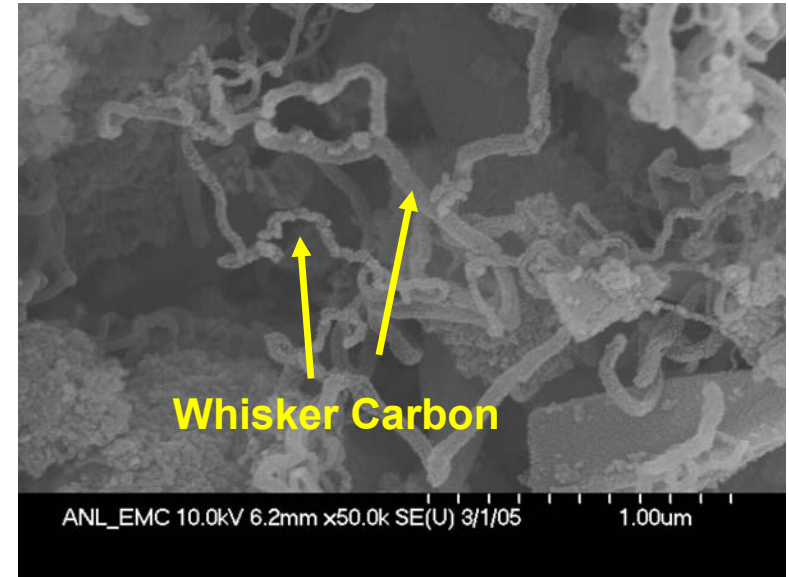
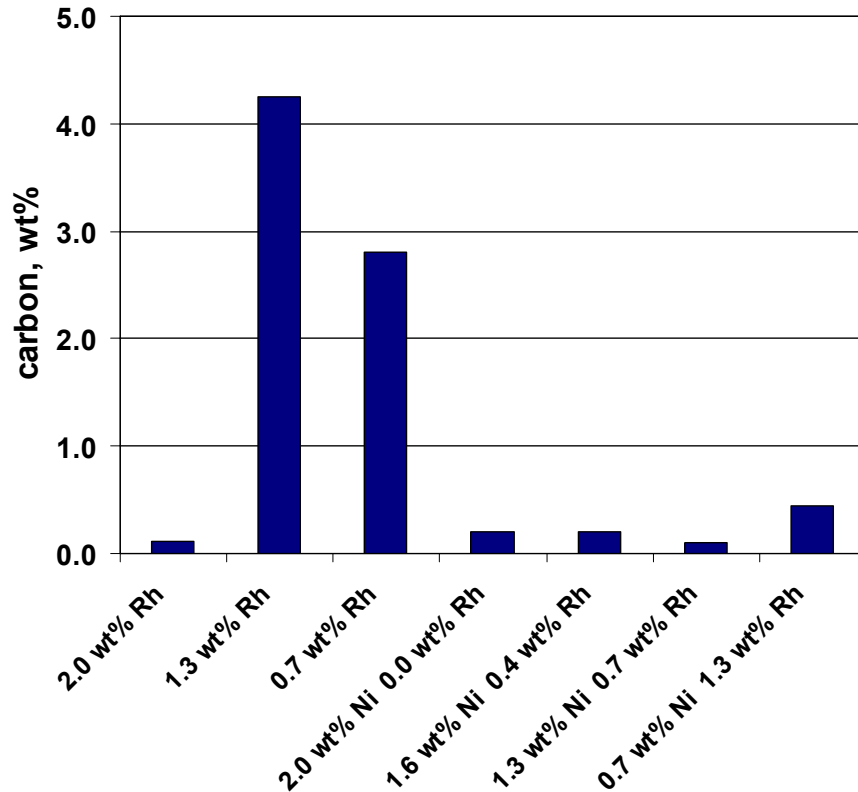
- Activity appears to be proportional to Rh surface area. Results are consistent with J. Wei and E. Iglesia (J. Catal. 225 (2004) 116).
- Role of support is to stabilize Rh dispersion. No evidence for Rh-support interaction that influences activity.

High H₂ yields and low deactivation rates for ATR of butane with bimetallic Ni-Rh catalysts



- Lower deactivation rate observed with Ni-Rh than Rh catalysts for similar Rh loading.
- For 2 wt% Ni catalyst, low H₂ yield and high catalyst temperatures (not shown) during ATR suggests little steam reforming is occurring.

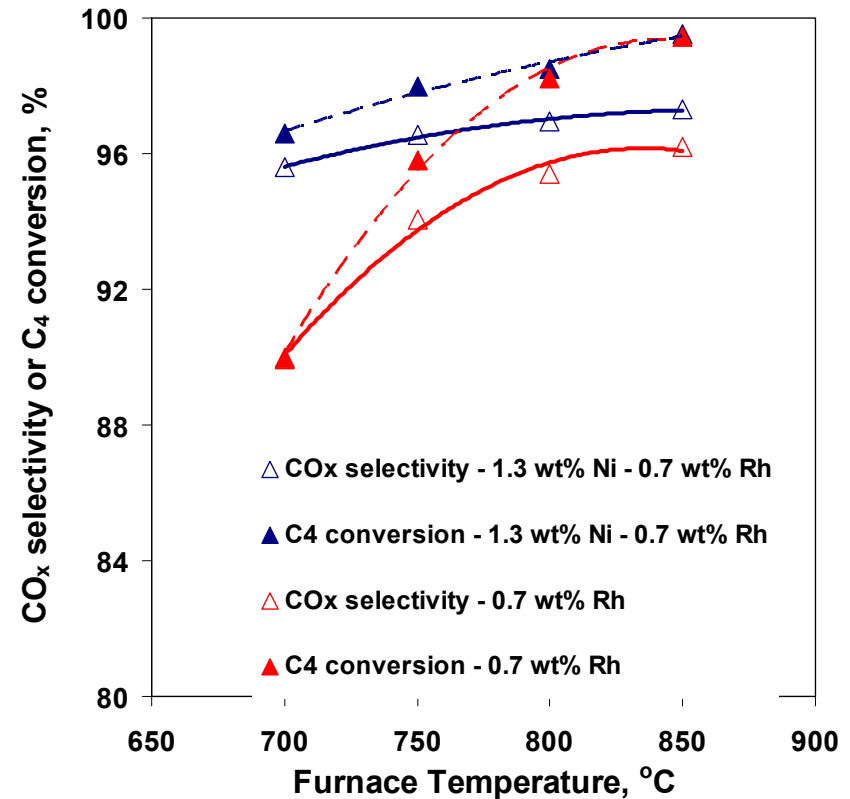
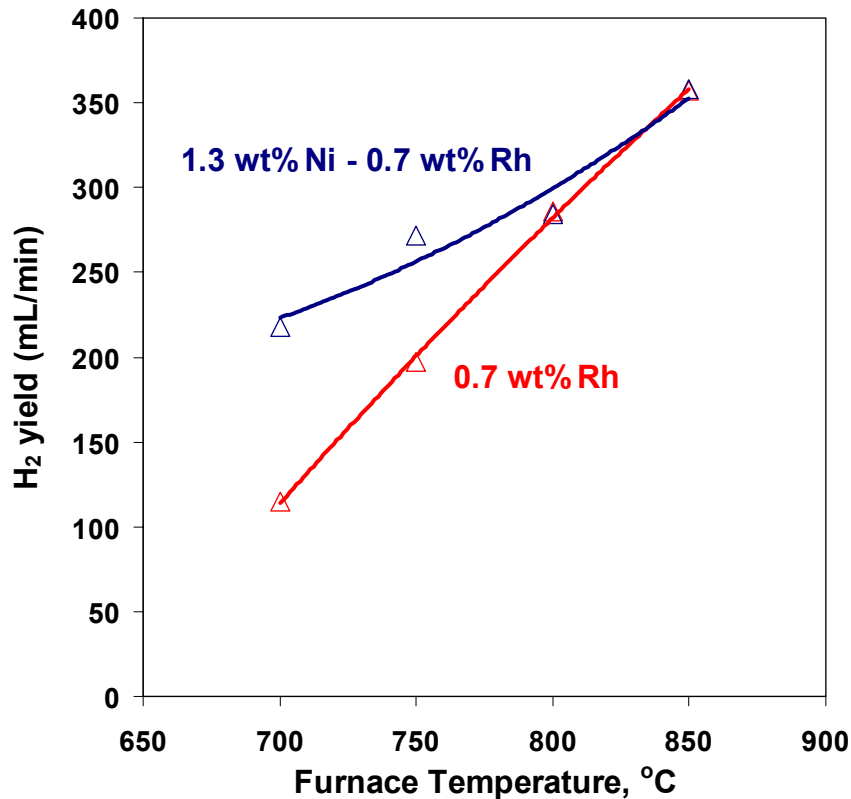
Lower coke formation on bimetallic Rh-Ni catalysts during ATR of butane



SEM of Rh-Ni catalyst after ATR of butane

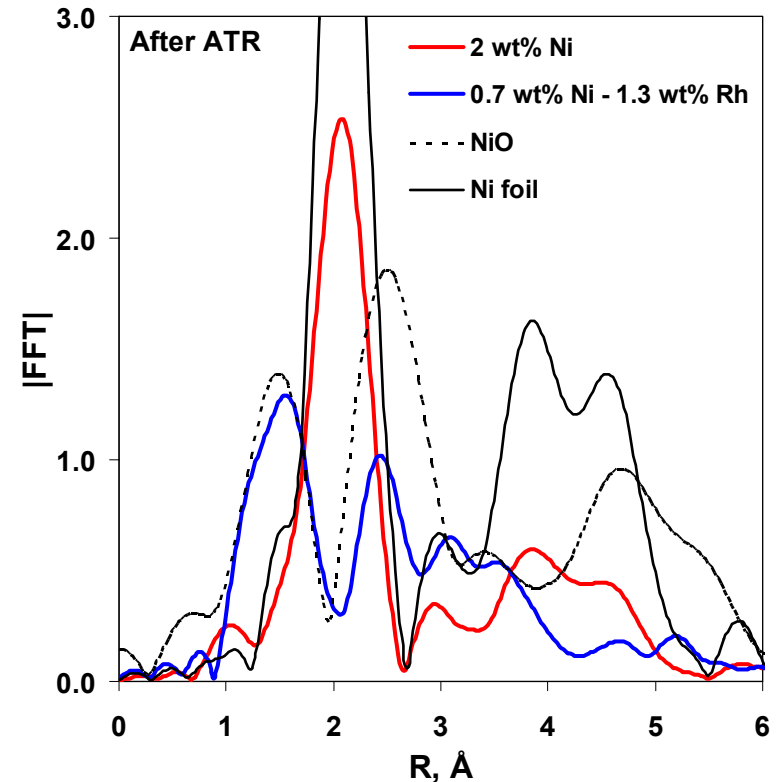
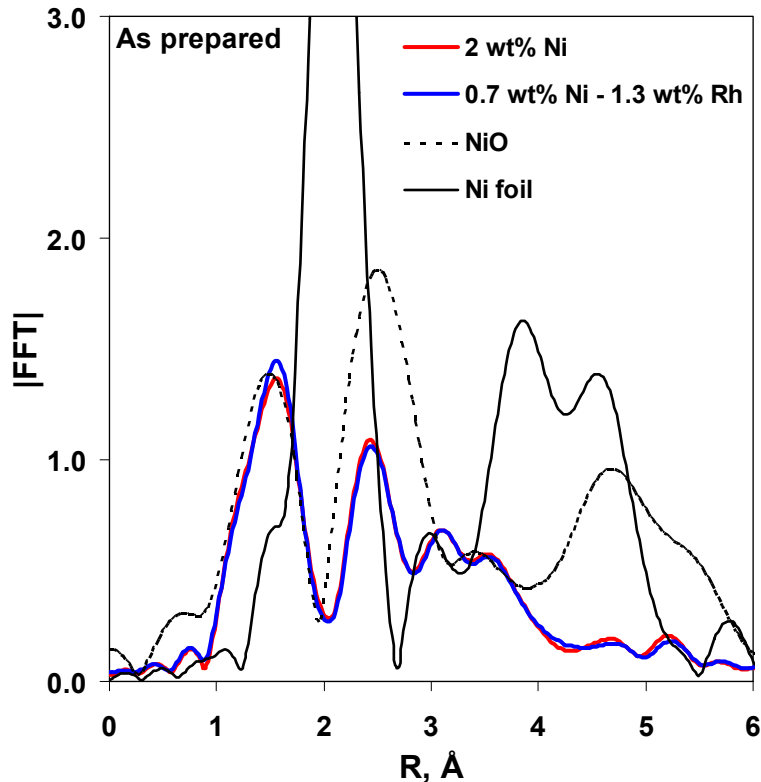
- Whisker carbon is indicative of carbon formation on Ni particles.
- Amorphous carbon (not shown) may result from non-catalytic process.
- Choice of oxide support may be critical to minimize whisker formation.

Better performance for steam reforming of butane with bimetallic Ni-Rh catalyst



Conditions: Butane – 4.6 L/g_{cat}/h, H₂O/C = 3

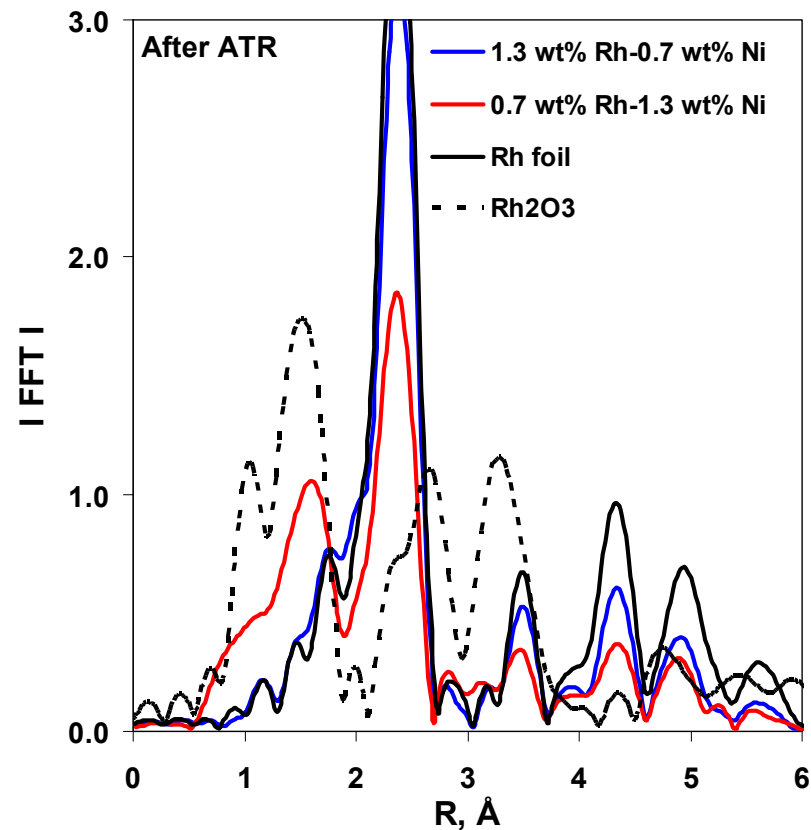
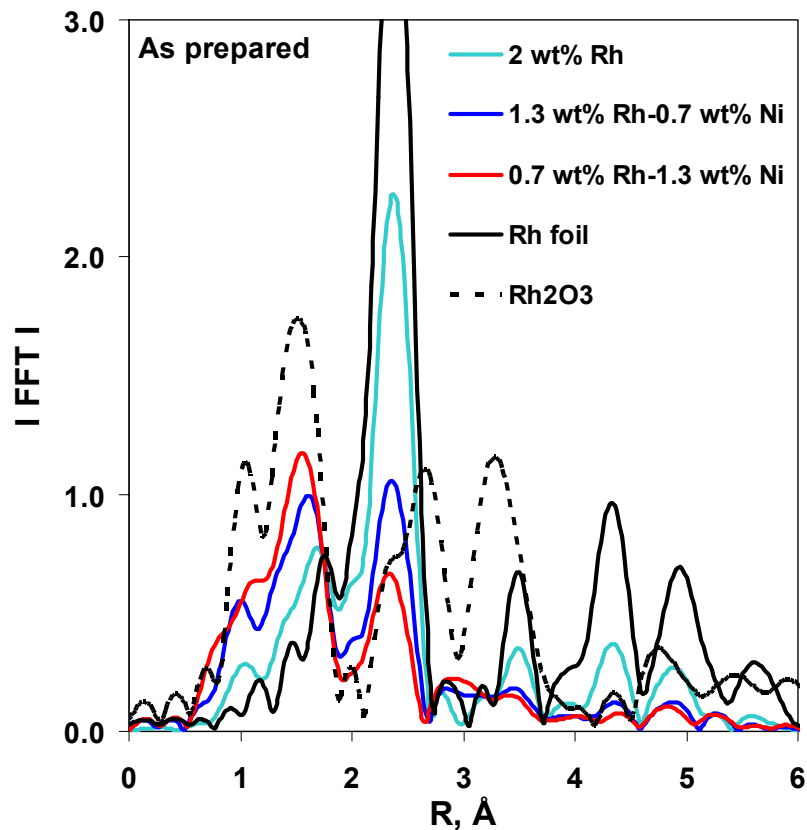
Rh does not appear to promote the reduction of Ni in bimetallic Ni-Rh catalyst during ATR



- Ni structure is similar on Ni and bimetallic Ni-Rh catalyst.
- Ni is highly oxidized. Evidence suggests Ni is diffusing into oxide support.

- Ni is highly reduced on Ni catalyst.
- Ni structure is unchanged on bimetallic Ni-Rh catalysts.

Ni appears to stabilize oxidized Rh in bimetallic Ni-Rh catalyst during butane ATR

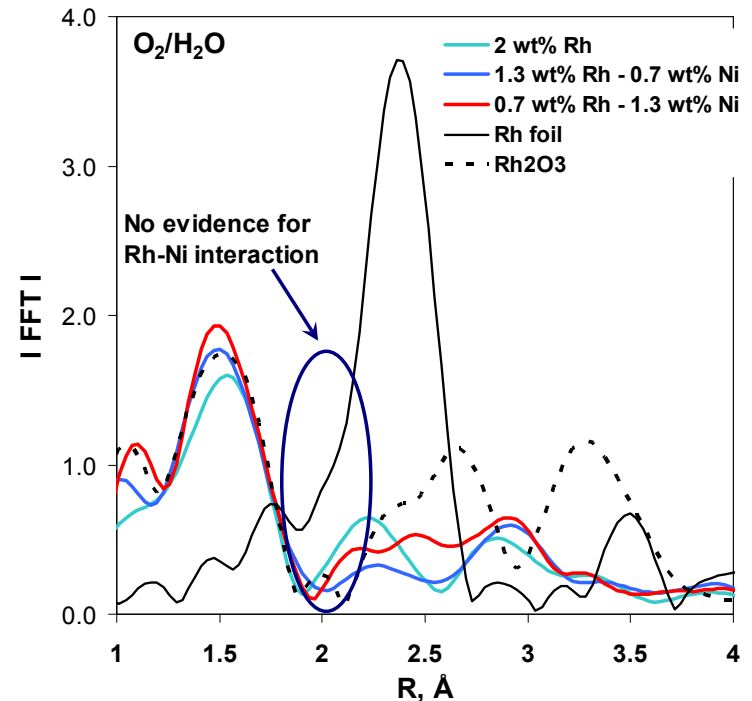
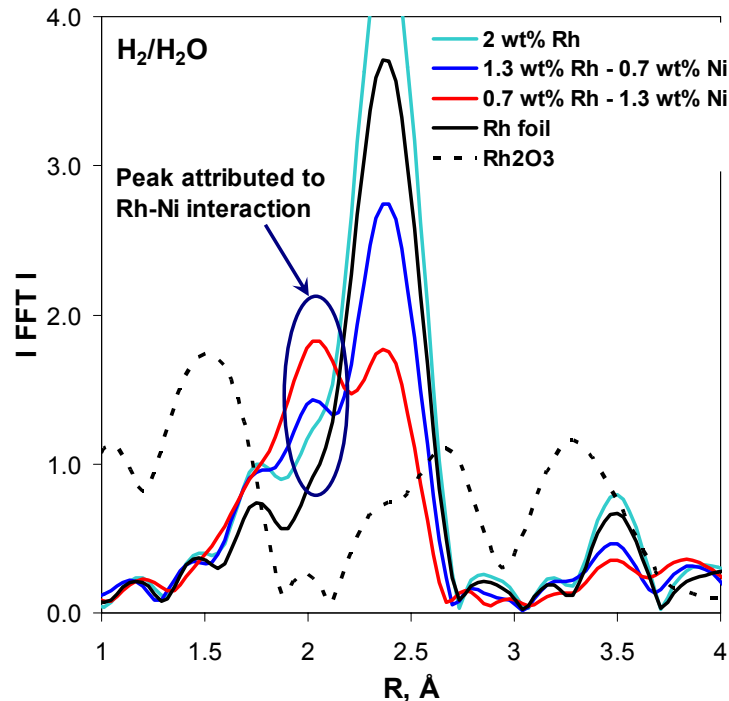


- Rh appears more oxidized in Ni-Rh catalyst than in Rh catalyst.

- Amount of metallic Rh increased in both Ni-Rh catalysts.
- Higher concentration of oxidized Rh in Ni rich bimetallic Ni-Rh catalyst.

Evidence for Rh-Ni interaction

- Rh, Ni, and Rh-Ni catalysts were treated under $\text{H}_2/\text{H}_2\text{O}$ or $\text{O}_2/\text{H}_2\text{O}$ at 900°C for 48-100 h to simulate aging under SR or ATR conditions.



- Under $\text{H}_2/\text{H}_2\text{O}$, peak observed at $\sim 2\text{Å}$ attributed to Rh-Ni interaction (Nagaoka et al., J. Catal., 229 (2005) 185).

- Under $\text{O}_2/\text{H}_2\text{O}$, Rh remains oxidized in bimetallic Ni-Rh catalyst with no evidence for Rh-Ni interaction.

Response to Previous Year Reviewers' Comments

- **“Key is to eliminate or reduce precious metal without sacrificing activity.”**
 - Our primary focus this year is to eliminate/reduce the precious metal loading.
- **“Because sulfur can be removed from the gasoline (fuel), why continue to emphasize sulfur-tolerant catalysts”**
 - Until non-sulfur-containing odorants can be developed, sulfur will be an issue.
 - Gas-phase desulfurization of natural gas and LPG should be easier to accomplish than on-board liquid-phase desulfurization of gasoline. However, many of our discussions with industry during the past year have focused on the challenges with dealing with sulfur in natural gas.
- **“Understanding fundamental catalyst mechanisms and sharing this information openly”**
 - Two articles have been submitted to peer-reviewed journals for publication and more articles will be forthcoming.

Milestones

Task	Date
<p>Complete comparative performance evaluation of ANL reforming catalyst for autothermal and steam reforming of natural gas, LPG, and gasoline</p> <p><i>Status: ATR tests with methane, butane, and gasoline completed. Steam reforming tests with natural gas and butane completed.</i></p>	01/05
<p>Determine minimum precious metal loading in bimetallic catalysts for reforming natural gas, LPG, and gasoline</p> <p><i>Status: Good performance observed with Rh loading of 0.4 wt% for Ni-Rh catalyst. Kinetic studies in progress to measure the reaction rate as a function of Ni:Rh ratio.</i></p>	05/05
<p>Define reforming conditions for sulfur-containing fuels, natural gas and LPG</p> <p><i>Status: Studies with Rh, Pt, and Rh-Pt show a decrease in performance with as little as 3 ppm H₂S. Increasing temperature does not seem to be improve sulfur tolerance during methane reforming as was observed during gasoline reforming.</i></p>	09/05

Future work

- **Bimetallic Ni catalysts**
 - Kinetic steam reforming studies on natural gas and LPG to optimize Ni-Rh ratio.
 - Long-term steam reforming studies to investigate catalyst durability of Ni-Rh.
 - Investigate effect of Pt or Pd on Ni performance (Pt and Pd are more easily reduced than Rh).
 - Investigate the effect of reducible supports to minimize carbon formation on Ni bimetallic catalysts.
- **Characterization studies**
 - Investigate effect of synthesis procedure on Ni alloy formation.
 - X-ray spectroscopy studies to identify nature of Ni alloys during steam reforming or ATR.
- **Address the sulfur issues**

Publications and Presentations

- **Publications**

- **“Support Effects of Rh Catalysts for the Autothermal Reforming of Isobutane,”** Magali Ferrandon and Theodore Krause (submitted to Journal of Catalysis).
- **“Kinetic Study of the Steam Reforming of Isobutane using a Pt-CeO₂-Gd₂O₃ Catalyst,”** Chethan K. Acharya and Alan M. Lane (University of Alabama) and Theodore Krause (submitted to Journal of Catalysis).

- **Presentations**

- **“Effect of Sulfur on the Performance of Reforming Catalysts for Hydrogen Generation,”** Magali Ferrandon, Jennifer Mawdsley, James Ralph, and Theodore Krause, Presented at the American Institute of Chemical Engineers 2004 Annual Meeting, Austin, Texas, November 7-12, 2004.
- **“Reforming Catalyst Development for Distributed Hydrogen Production,”** Theodore Krause, Magali Ferrandon, John Kopasz, Laura Miller, and Daniel Applegate, To be presented at the 19th Meeting of the North American Catalysis Society, Philadelphia, Pennsylvania, May 21-28, 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.**

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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.**