Water-gas shift catalysis

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Objective is to develop water-gas shift catalysts for on-board fuel processing

- Meet the DOE technical targets of
  - ✓ gas-hourly space velocity (GHSV) ≥ 30,000 h^{-1}
  - ✓ CO conversion of ≥ 90%
  - ✓ selectivity of ≥ 99%
  - ✓ lifetime of > 5000 h
  - ✓ cost of <\$1/kW_e
- Address issues with commercial CuZn catalysts
  - ✓ Eliminate the need for well-controlled *in situ* preactivation
  - ✓ Improve tolerance to temperature excursions
  - ✓ Eliminate the need to sequester during shutdown

This work addresses technical barriers J, L, and N.

Approach

- Explore metal/support combinations that exhibit the bifunctional mechanism.

$* + CO \rightleftharpoons *\text{-}CO_{ad}$	* = metal surface site, adsorbs CO
$2MO_2 + *\text{-}CO_{ad} \rightarrow M_2O_3 + CO_2 + *$	oxidation of CO via oxygen transfer from support
$M_2O_3 + H_2O \rightarrow 2MO_2 + H_2$	reoxidation of support via dissociation of water

- Metals (Pt, Ru, Co, Cu) that have CO adsorption energies between 20-50 kcal/mol.
- Metal oxides that exhibit redox activity under WGS reaction conditions.

Industrial collaborations/interactions

- Work For Others (WFO) contract with Toyota Motor Corporation to develop WGS catalysts.

- Cu/oxide and Pt/mixed oxide samples are being evaluated by
  - ✓ Nissan Motor Corporation
  - ✓ Aspen Systems
  - ✓ H2Gen Innovations

Reviewers' comments from FY2002 Annual Review

- Activities too low to meet DOE target for GHSV.

  Increased the activity of our Pt catalyst with a bimetallic formulation.

- More emphasis on deactivation is needed.

  Investigated the effects of temperature, H_2S, and CO_2 on the rate of deactivation of our Pt catalyst resulting in decreased deactivation with a bimetallic formulation.

- Select additional mixed-oxide systems for study to improve activity and durability.

  Investigated the effect of dopants to increase the activity of Ce-based catalysts. Also investigated other oxide promoters.

- More emphasis on sulfur tolerance.

  Working on it with some interesting results.

Project timeline

Oct 1997: Initiated work on Pt shift catalyst

May 1999: Began work on non-precious metal catalysts

Aug 1999: Demonstrated Pt catalyst with 0.14 wt% loading

May 2000: Demonstrated Cu-mixed metal oxide catalyst

Oct 2000: Optimized Cu-mixed metal oxide formulation

May 2001: Demonstrated Co and Ru promoted catalyst

April 2002: Began long-term durability and H_2S poisoning studies

May 2002: Demonstrated 90% Conv., 0.15 L/kW_e, <0.1 kg/kW_e, \$0.9/kW_e with Cu-mixed oxide catalyst

Oct 2002: Began work on Pt bimetallic formulation

Mar 2003: Demonstrated Pt bimetallic with higher activity and better stability

June 2003: Begin testing of catalysts supported on monoliths

FY2003 accomplishments

- Pt catalysts
  - ✓ Improved the activity and stability of the Pt-Ce catalysts with a bimetallic formulation.
  - ✓ Identified Zr and Gd as dopants for ceria that can improve shift activity at temperatures >300°C compared to undoped Pt-Ce.
  - ✓ Demonstrated that 5 ppm H_2S does not contribute to deactivation of Pt-Ce catalyst at 300°C but does promote deactivation at 400°C.
- Non-Pt catalysts
  - ✓ Identified Cu sintering and oxide agglomeration as modes of deactivation for Cu/mixed oxide catalyst.
  - ✓ Investigated Re, Ni-Re, and Mn as promoters to enhance the activity of Cu catalysts.

Use of modeling helps define our goals

- The shift reaction is under kinetic control over the temperature range of 280-375°C.

- The activity of precious metal catalysts must be increased by a factor of 4 to achieve the GHSV target of 30,000 h^{-1}.

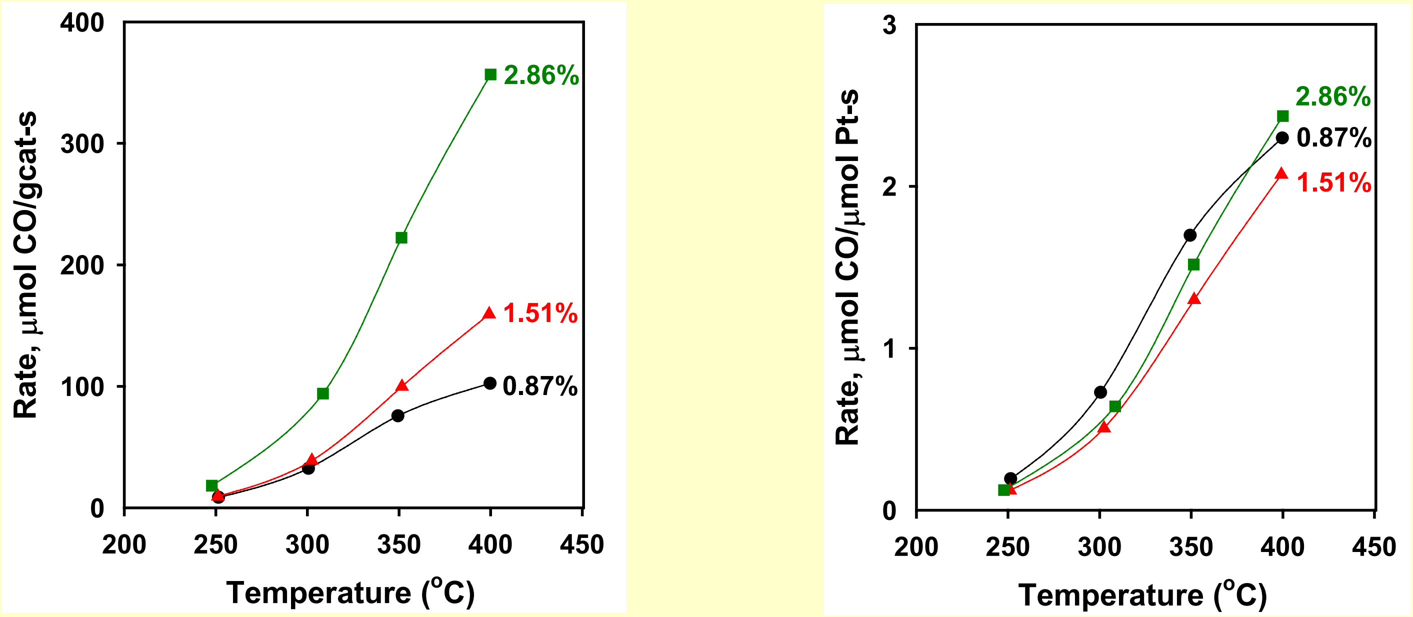
- The merit of increasing the water content to improve the kinetics and to raise the temperature of the low temperature shift reactor is being evaluated.

For Pt-CeO_2, our effort is directed to improve H_2O dissociation and oxygen transfer rates

- Kinetic studies* show that the rate is zeroth order in CO and half-order in H_2O (rate α P_{CO}^{0} $P_{H_2O}^{0.5}$)
  - ✓ Metal surface is saturated with CO
  - ✓ Reaction may be controlled by
    - rate of reoxidation of ceria by water
    - rate of oxygen transfer from ceria to metal interface
    - metal dispersion and surface area
- Improve ceria redox/oxygen transfer rates by cation doping
- Improve water dissociation on Pt surface by addition of a second metal
- Stabilize Pt against sintering

* Bunluesin et al., *Appl. Catal. B* **15** (1998) 107-114; Hilaire et al., *Appl. Catal. A* **215** (2001), 271-278; Wang et al., *J. Catal.* **212** (2002) 213-230.

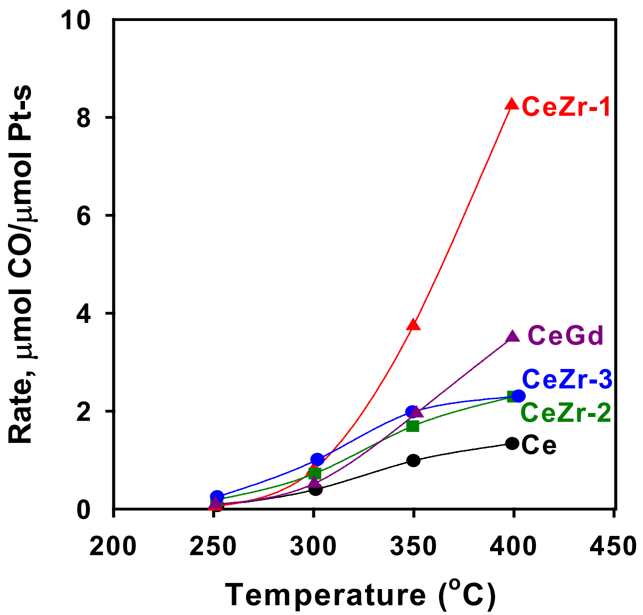
CO conversion per mole of Pt was independent of Pt loading from 0.87-2.86 wt%



Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 600,000-1,800,000 h^{-1}, 0.05-0.1 ml catalyst diluted with α-Al_2O_3

- By increasing the Pt loading, the CO conversion per unit volume of reactor can be increased.
- Increasing the Pt loading will make it difficult to achieve the cost target of \$1/kW_e.

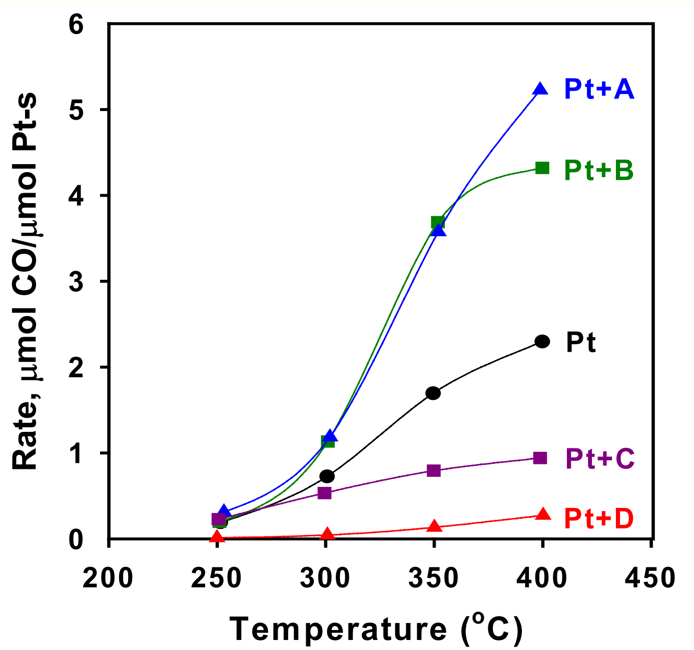
Doping CeO_2 with Gd or Zr increased activity at temperatures above 300°C



Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 600,000 h^{-1}, 0.1 ml catalyst diluted with 0.4 ml α-Al_2O_3

- Doping CeO_2 is known to lower the temperature at which Ce^{4+} reduction occurs and to increase oxygen release rates.
- Our results suggest that doping Ce will not significantly improve its activity below 300°C.

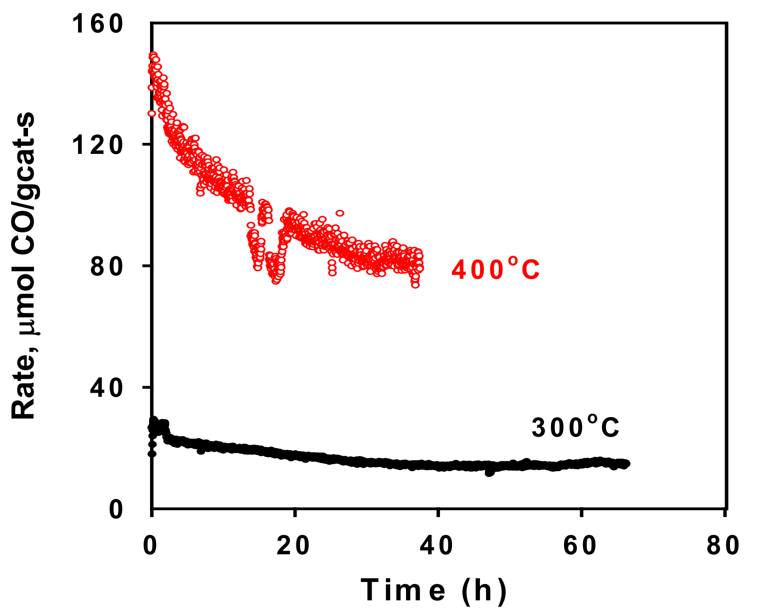
Increased the activity by a factor ~2 with certain Pt bimetallic formulations

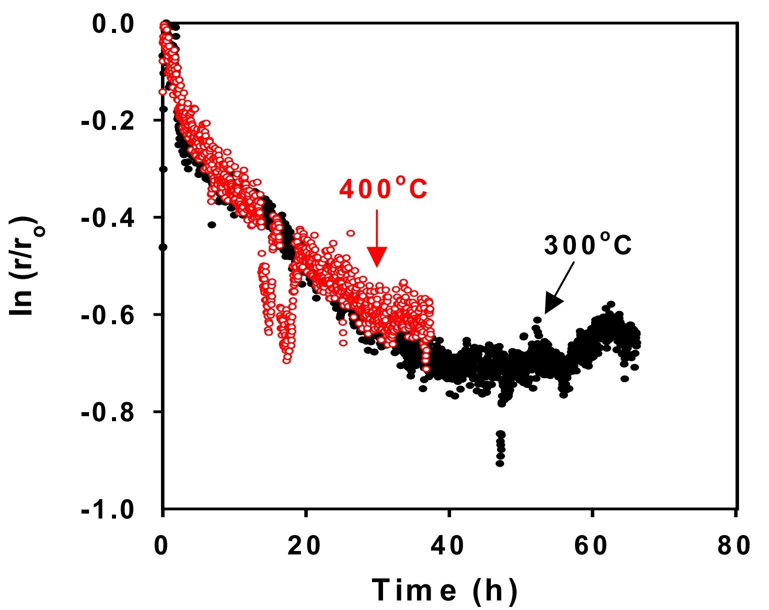


Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 200,000-1,500,000 h^{-1}, 0.05-0.4 ml catalyst diluted with α-Al_2O_3

- Selection of bimetallic formulation based on theoretical studies of the energetics of H_2O dissociation and reaction between CO_{ads} + OH_{ads} on Pt-mixed metal clusters (Ishikawa et al., *Surface Science* **513** (2002) 98-110).

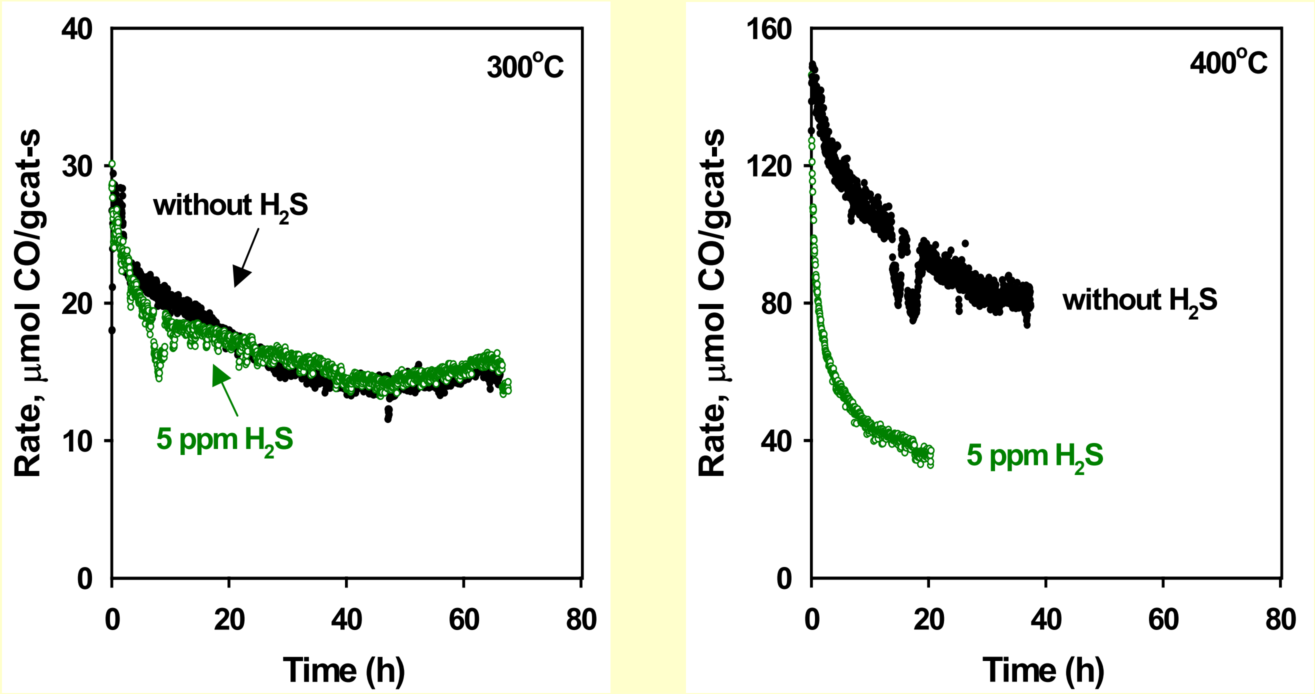
~50% loss of activity was observed over 40 h at both 300 and 400°C with Pt catalyst





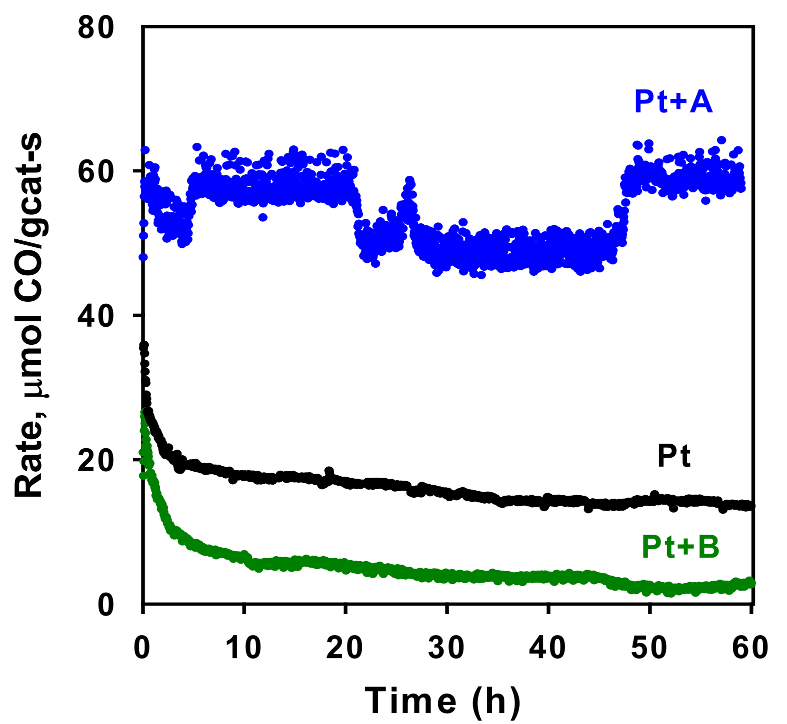
Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 300,000-1,200,000 h^{-1}, 0.03-0.1 ml catalyst diluted with α-Al_2O_3

5 ppm H_2S increased the rate of deactivation at 400°C, but not at 300°C with Pt catalyst



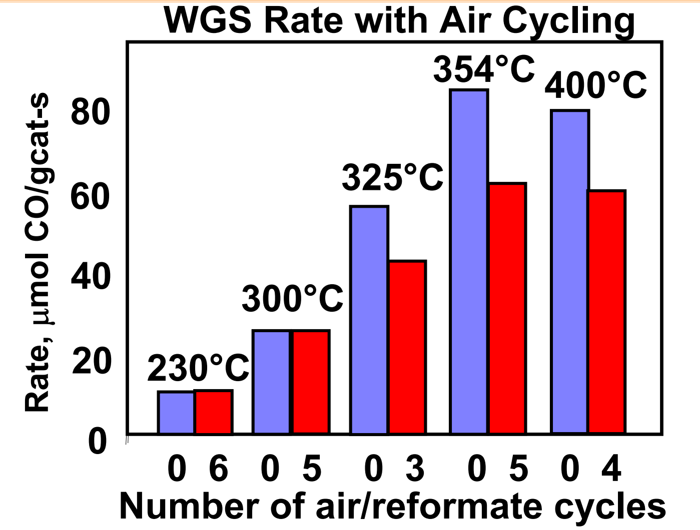
Conditions: 5 ppm H_2S, 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 300,000-1,200,000 h^{-1}, 0.03-0.1 ml catalyst diluted with α-Al_2O_3

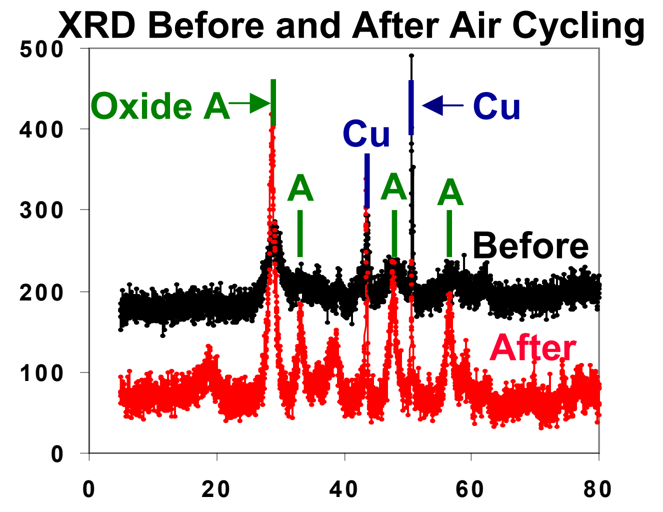
Pt+A bimetallic was more stable than Pt at 300°C



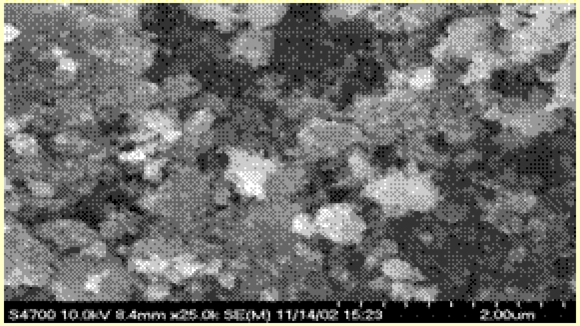
Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 300,000-400,000 h^{-1}, 0.10-0.12 ml catalyst diluted with α-Al_2O_3

Deactivation of Cu/mixed oxide at >300°C likely caused by sintering of Cu and agglomeration of oxide





Fresh Sample



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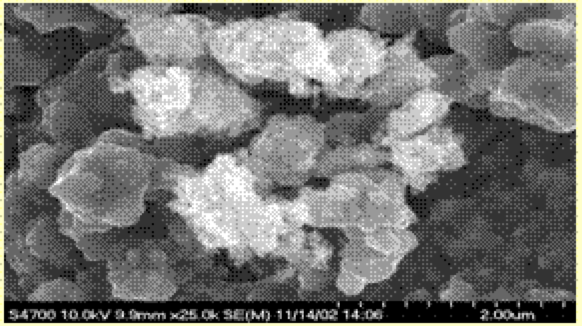
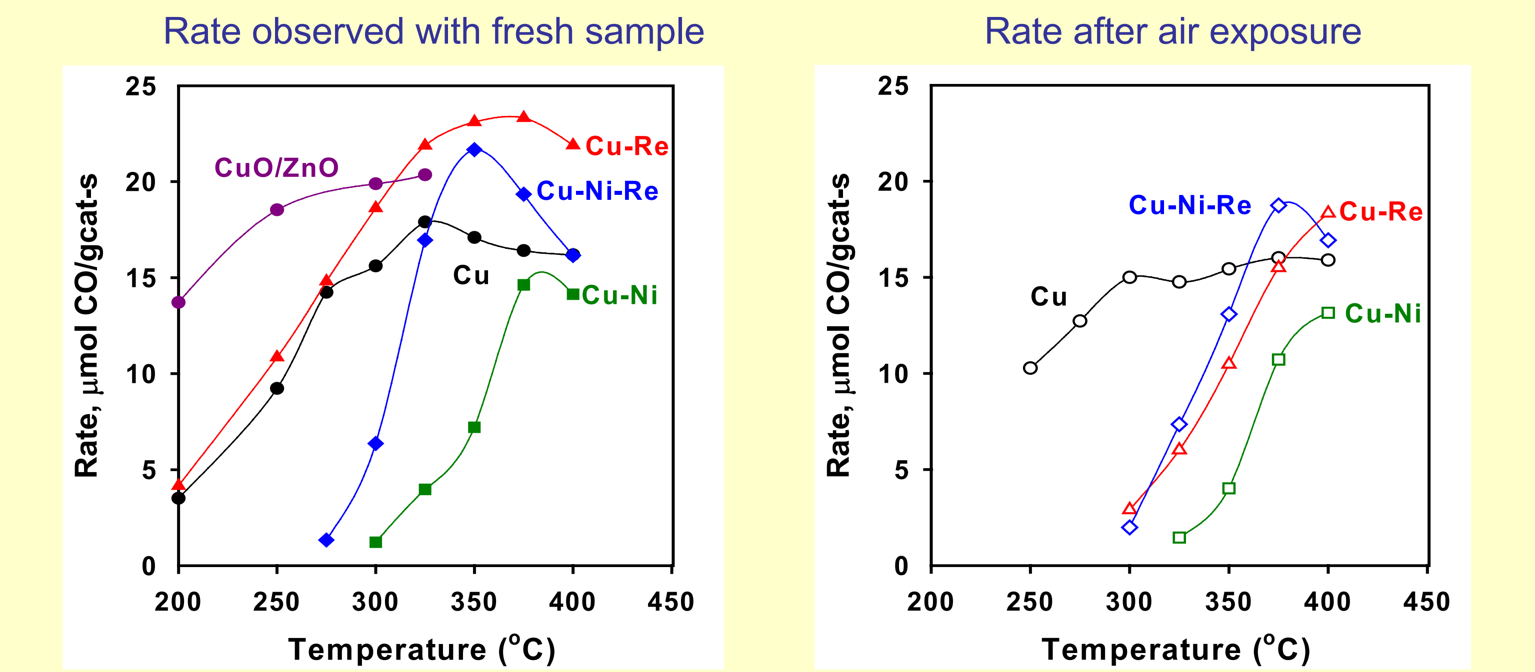


After
WGS
at 325°C
for 167 h

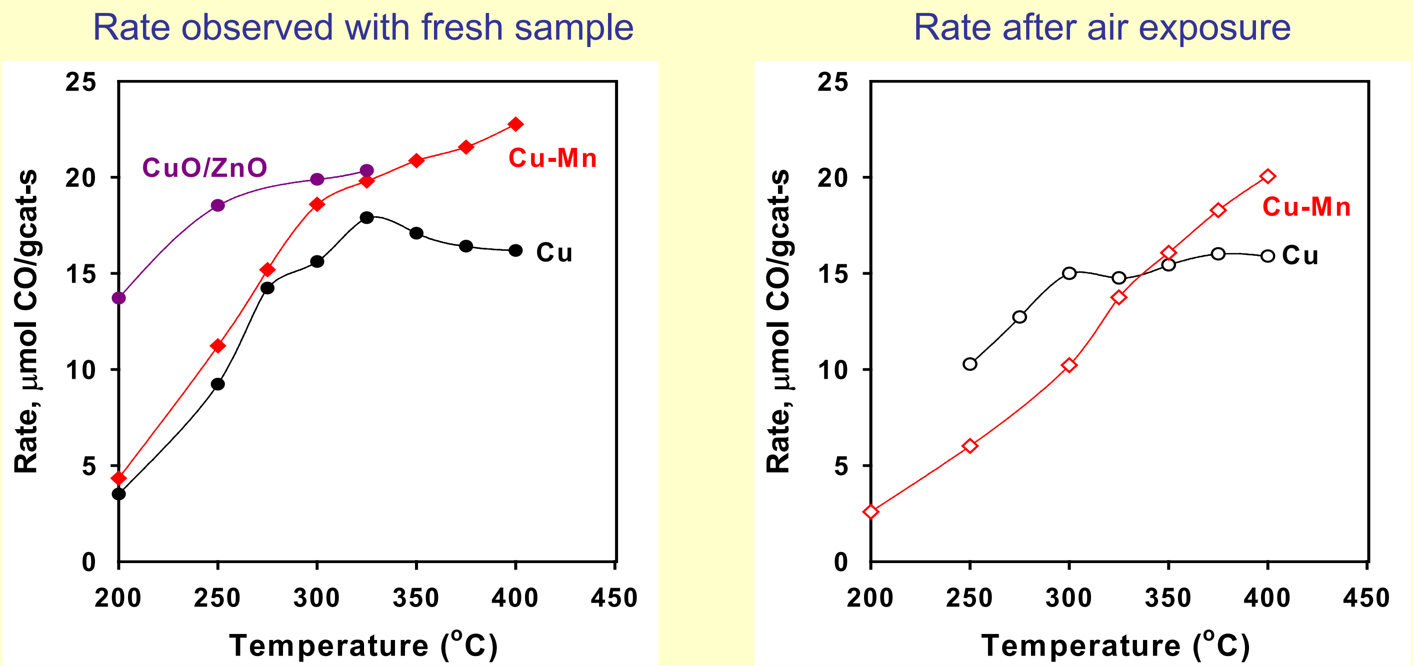
Investigated Ni and Re as promoters for improving activity and stability of Cu catalysts operating at 250-400°C



Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O, GHSV = ~40,000 h^{-1}

- Our previous work has shown that Re stabilizes Co-based catalysts.
- Ni and Cu form a solid solution that can accommodate ~10 atom% Re.

Investigated Mn as a promoter for improving activity and stability of Cu catalysts operating at 250-400°C


Rate observed with fresh sample

Rate after air exposure

Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O, GHSV = ~40,000 h^{-1}

- Mn enhances Cu activity as observed with Re and Ni-Re.
- Cu-Mn is more active than Cu after air exposure at >350°C.

FY2003 milestones

Milestone	Date
Improve low-temperature (<250°C) activity of catalyst to >9 μmoles CO g^{-1} s^{-1}.	02/03
We have developed a Cu that yields 10 μmoles CO g^{-1} s^{-1} at 250°C. Long-term stability is still an issue.	
Complete 1000 h test of catalyst using sulfur-free synthetic reformate.	02/03
We have completed a 250 h test of Pt-Ce that we have extrapolated to 1000 h.	
Improve sulfur tolerance of non-precious metal catalyst in reformate containing 3 ppm H_2S.	06/03
Work in progress – has proven to be challenging.	
Demonstrate $\leq$1% CO out using a structured form of the catalyst(s).	09/03
Coating of monoliths is in progress. Testing to begin 6/03.	

Future work

- Pt-Ce catalysts
  - ✓ Optimize bimetallic formulation to increase activity while decreasing Pt loading to achieve DOE cost target
  - ✓ Retard Pt sintering
  - ✓ Address H_2S poisoning at temperature of 400°C
  - ✓ Evaluate catalyst performance on monolith

- Cu catalysts
  - ✓ Increase low temperature (230-300°C) activity
  - ✓ Reduce Cu sintering through the addition of promoters to improve stability
  - ✓ Improve sulfur tolerance

- Conduct characterization studies (SEM/TEM and EXAFS/XANES) to improve activity and reduce deactivation.