Alternative Water-Gas Shift Catalysts

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Issues/problems with conventional water-gas shift catalysts

- Conventional process carried out in two distinct temperature regimes for stationary systems
- High-temperature catalyst - Fe/Cr
  - requires activation by pre-reduction in situ
  - activity drops off sharply at <300°C
  - loses activity upon exposure to air
- Low-temperature catalyst - Cu/Zn oxide
  - requires activation by careful pre-reduction in situ
  - pyrophoric; loses activity upon exposure to air
  - operating temperature <250°C

Objective of this effort

- Develop alternative water-gas shift catalyst to
  - eliminate the need to sequester catalyst during shutdown
  - eliminate the need to activate catalyst *in situ*
  - increase tolerance to temperature excursions
  - reduce size/weight of shift reactor(s)
  - extend lifetime of catalyst

Approach: Metal/Support Combinations Explored Based on Bifunctional Mechanism

Bifunctional Mechanism:

$* + CO \;^{\circ}\; CO_{ad}$ * = metal surface site, adsorbs CO

$M_2O_3 + H_2O \;^{\circ}\; 2MO_2 + H_2$ oxide support dissociates water

$2MO_2 + CO_{ad} \;^{\circ}\; M_2O_3 + CO_2$

- Metals - CO adsorption energies between 20-50 kcal/mol
  - **Pt**, Ru, Pd, PtRu, PtCu
  - Co, Ag, Fe, Cu, Mo
- Oxide Supports - Redox activity under reformate conditions
  - Lanthanide oxides
  - Manganese oxide
  - Vanadium oxide

Catalyst activity tests were conducted in a microreactor with simulated reformate

- Reviewer's Comment: Evaluate catalysts at S/C ratios more typical for these reactors: 6.5 is too high.

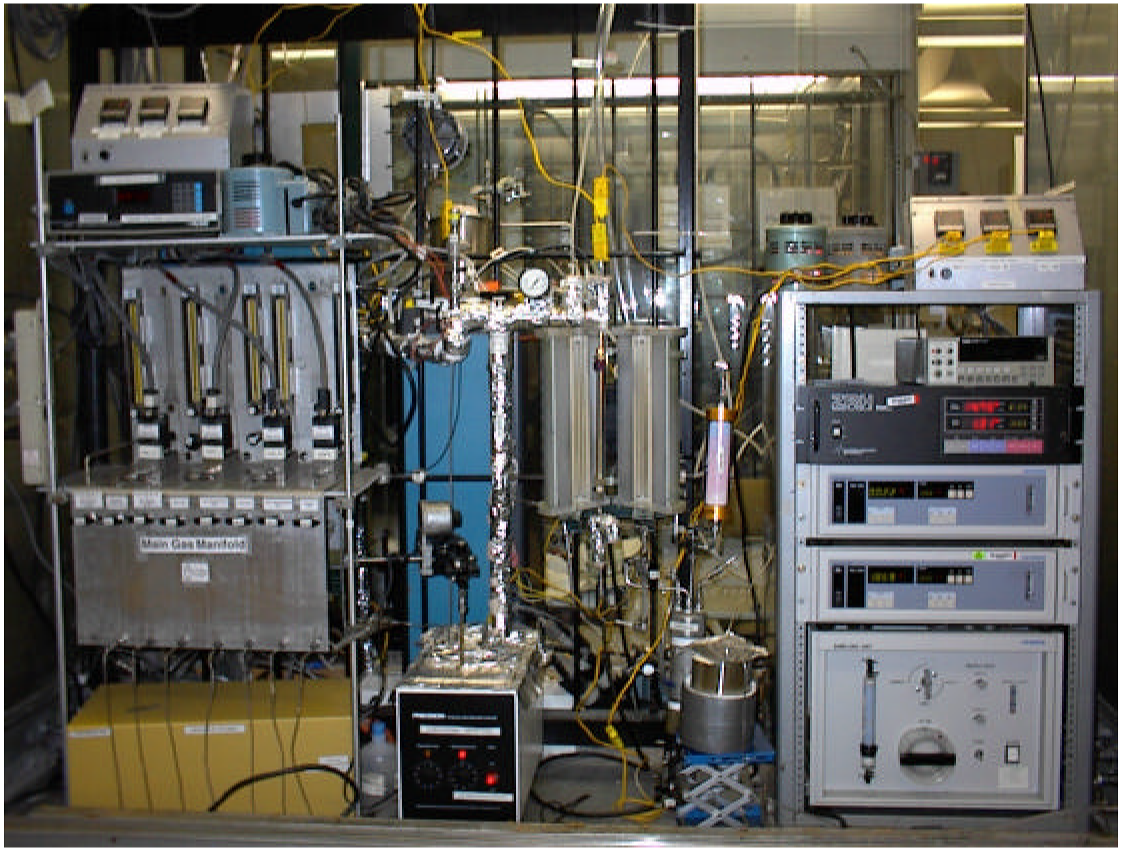
<u>Test Conditions</u>

Catalyst Activity Screening:

230-250°C,
0.45% CO, 11.3% CO_2,
22.3% H_2, 55% H_2O, bal. N_2
GHSV: 59,000-151,000 hr^{-1}

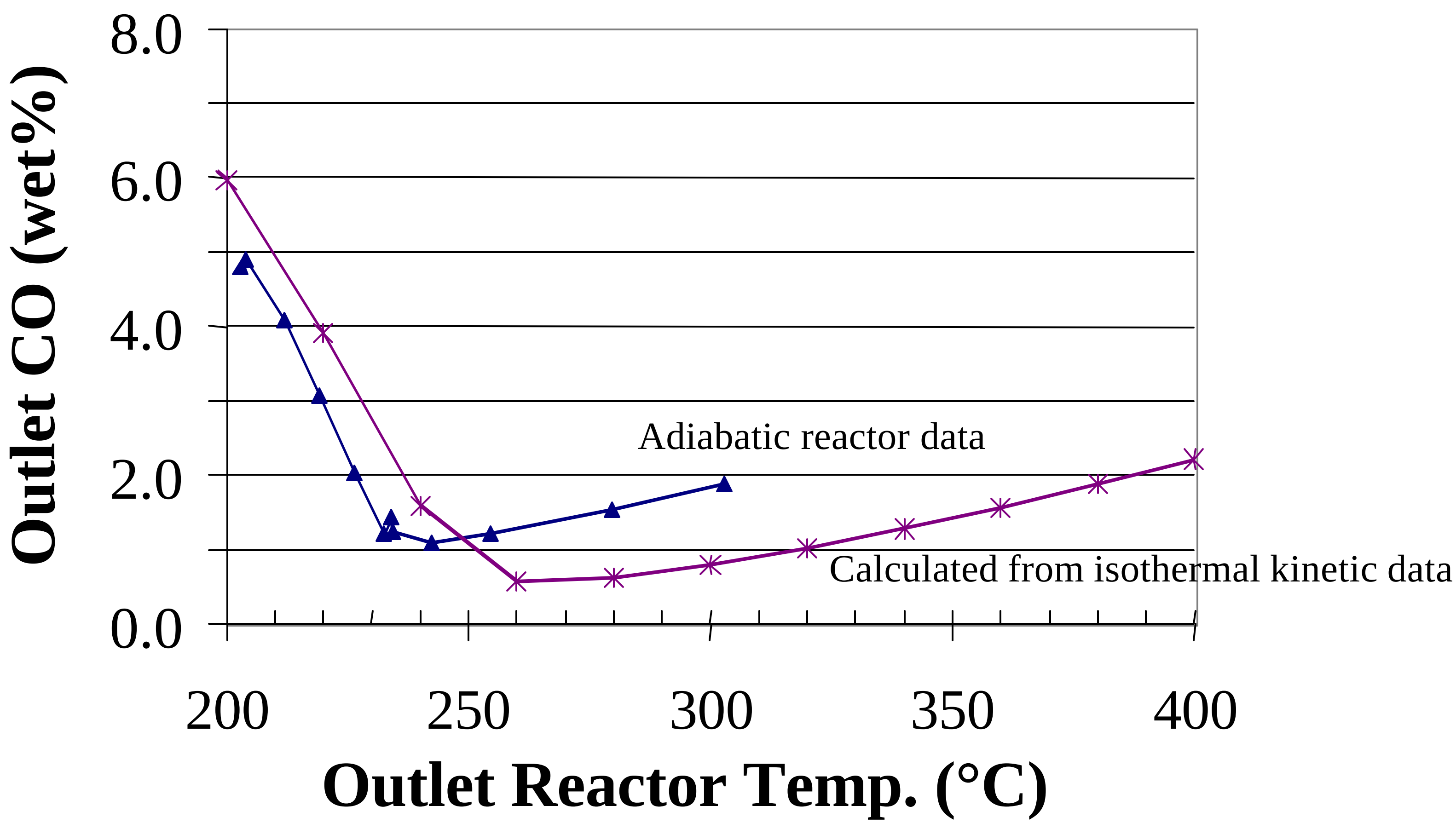
Catalyst Kinetic Studies:

180-400°C,
8.6% CO, 15.0% CO_2,
29.7% H_2, 30.9% H_2O, bal. N_2
GHSV: 120,000-199,000 hr^{-1}



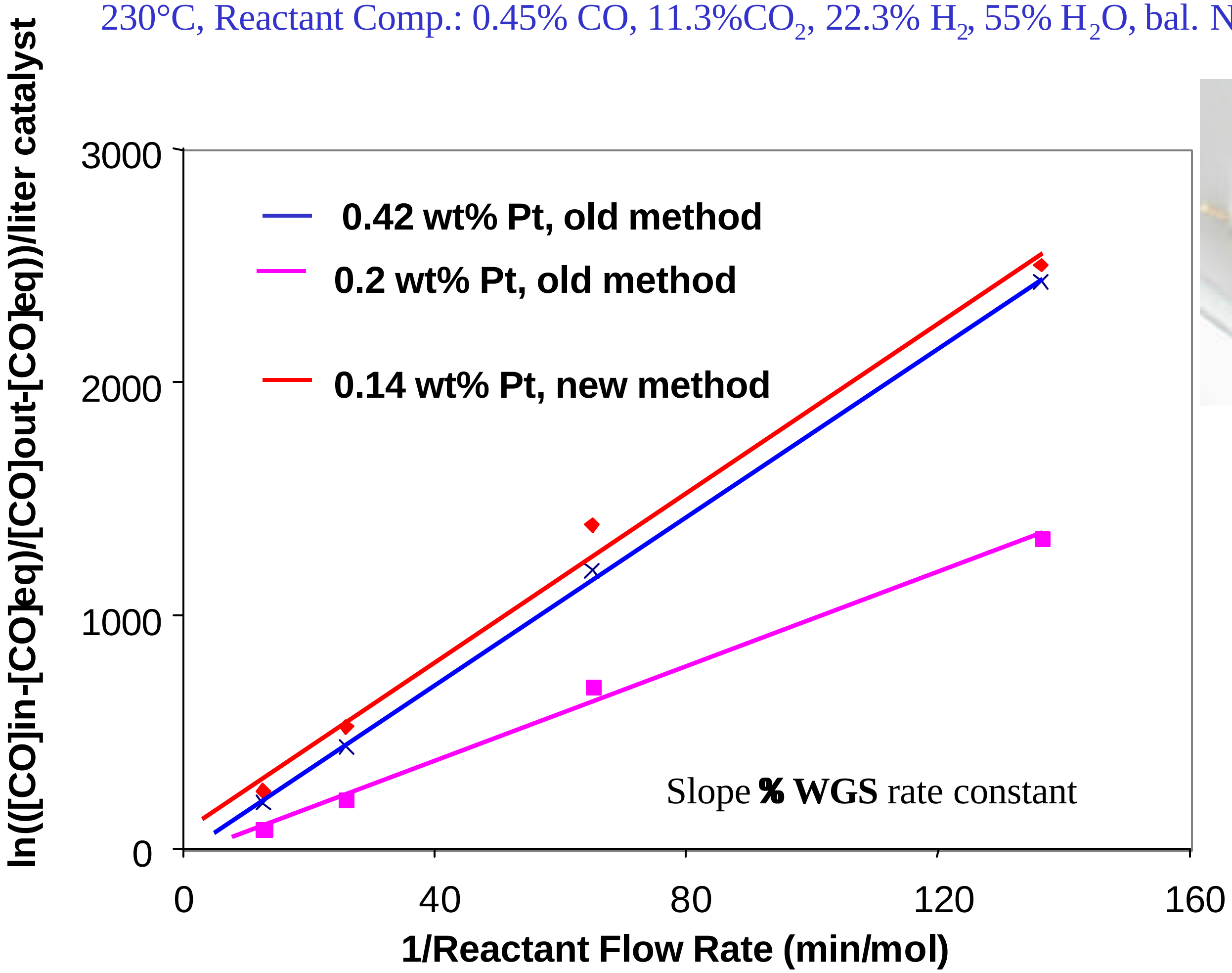
Pt/mixed oxide/alumina catalyst demonstrated to reduce CO to 1.1%

Inlet Gas Composition: 7.7% CO, 9.5% CO_2, 31.8% H_2,1.39% CH_4, 26.9% H_2O, bal. N_2



New synthesis method cut platinum loading by 1/3 while retaining activity

230°C, Reactant Comp.: 0.45% CO, 11.3%CO_2, 22.3% H_2, 55% H_2O, bal. N_2

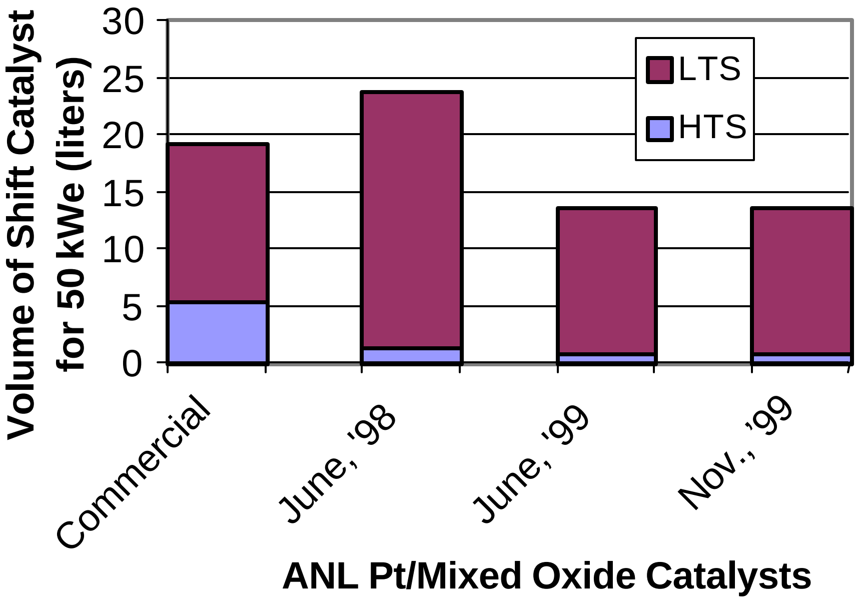


Catalyst Properties:

- Does not have to be reduced *in situ*
- Tolerant to exposure to air at room temp. to 400°C
- Active 180-400°C, <0.1% methane at 400°C

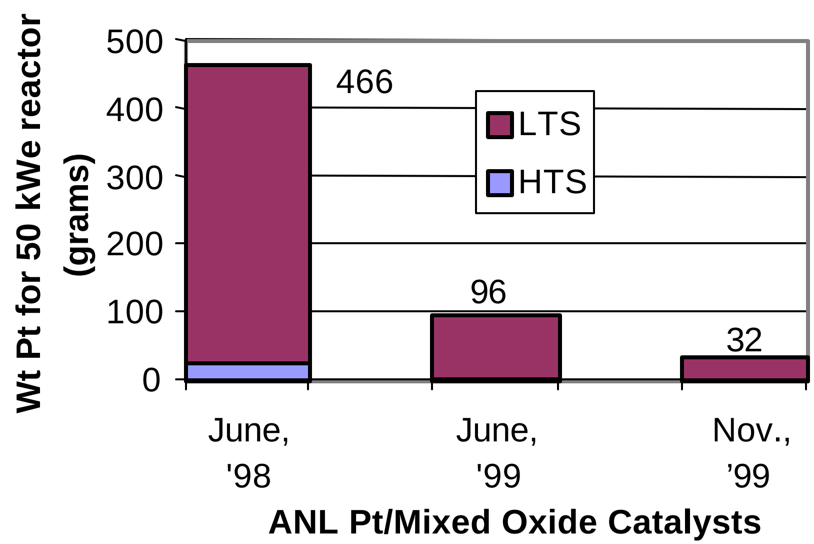
Projected size and cost of ANL shift reactors have been reduced

- Reviewer's Comment: Disturbing Lack of cost data. Provide cost estimate data...



Based on intrinsic reaction rates and activation energies, adiabatic high-temperature and low-temperature shift stages

CO reduced to 1% (dry) from entering reformate (wet): 10% CO, 10% CO_2, 34% H_2, 13% H_2O, 33% N_2. Additional water added to reach HTS and LTS temps.

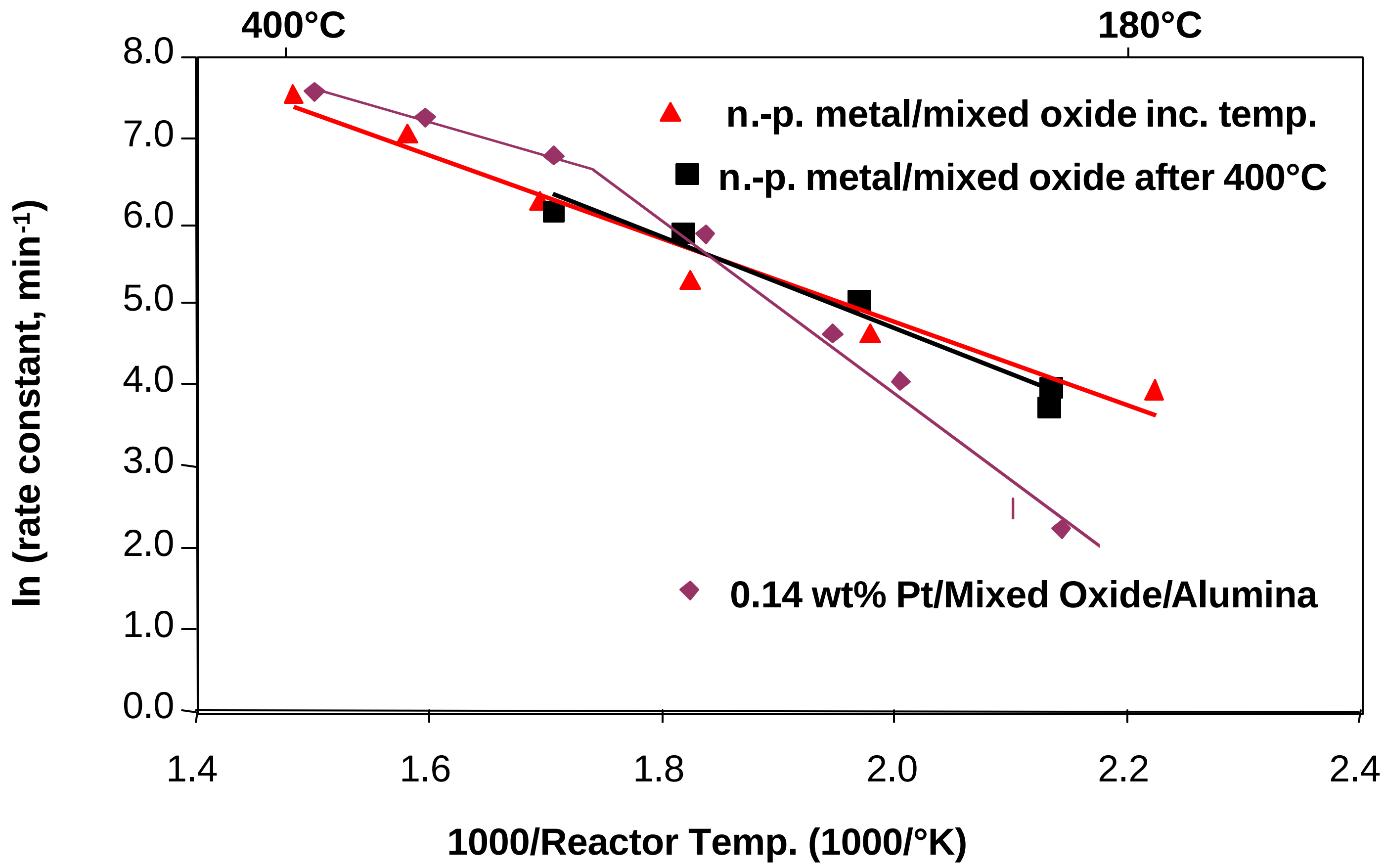


Commercial: LTS is Cu/ZnO at 200°C,
HTS is Fe/Cr at 400°C

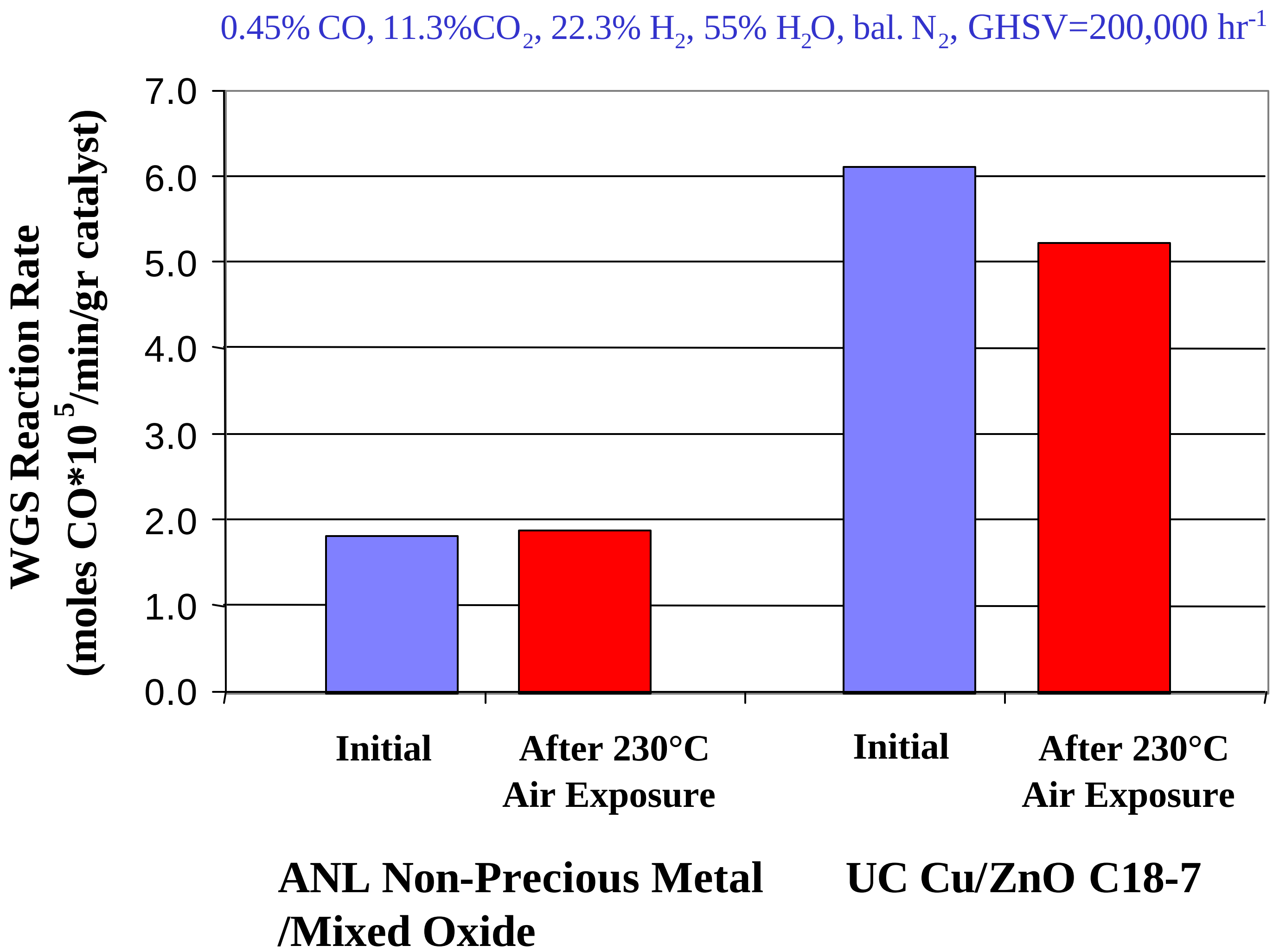
ANL: LTS at 300°C, HTS at 400°C

Non-Precious metal/mixed oxide is a potential alternative to Pt/mixed oxide

- Reviewer's Comment: Increase overall activity
- Reactant Comp.: 8.6% CO, 15.0% CO_2, 29.7% H_2, 30.9% H_2O, bal. N_2



Non-Precious metal/mixed oxide catalyst retains activity when exposed to air at 230°C



Alternative Approach to Developing non-Precious Metal WGS Catalysts

- Use bimetallic or polymetallic oxide mixtures to perform the regenerative water-gas shift mechanism

$$M^{a}_{red}O/M^{b}_{ox}O + CO \rightarrow M^{a}_{red}O/M^{b}_{ox} + CO_2$$

$$M^{a}_{red}O/M^{b}_{ox} \xrightarrow{\text{electron transfer}} M^{a'}_{red}O/M^{b'}_{ox}O$$

$$M^{a'}_{red}O/M^{b'}_{ox}O + H_2O \rightarrow M^{a}_{red}O/M^{b'}_{ox}O + H_2$$

$$M^{a}_{red}O/M^{b'}_{ox}O + CO \rightarrow M^{a}_{red}O/M^{b}_{ox}O + CO_2$$

- **Each metal oxide catalyzes one-half of the WGS reaction**
- **Metals need to be in intimate contact for efficient electron transfer**

Possible oxide formulations for WGS catalyst based on thermodynamic calculations

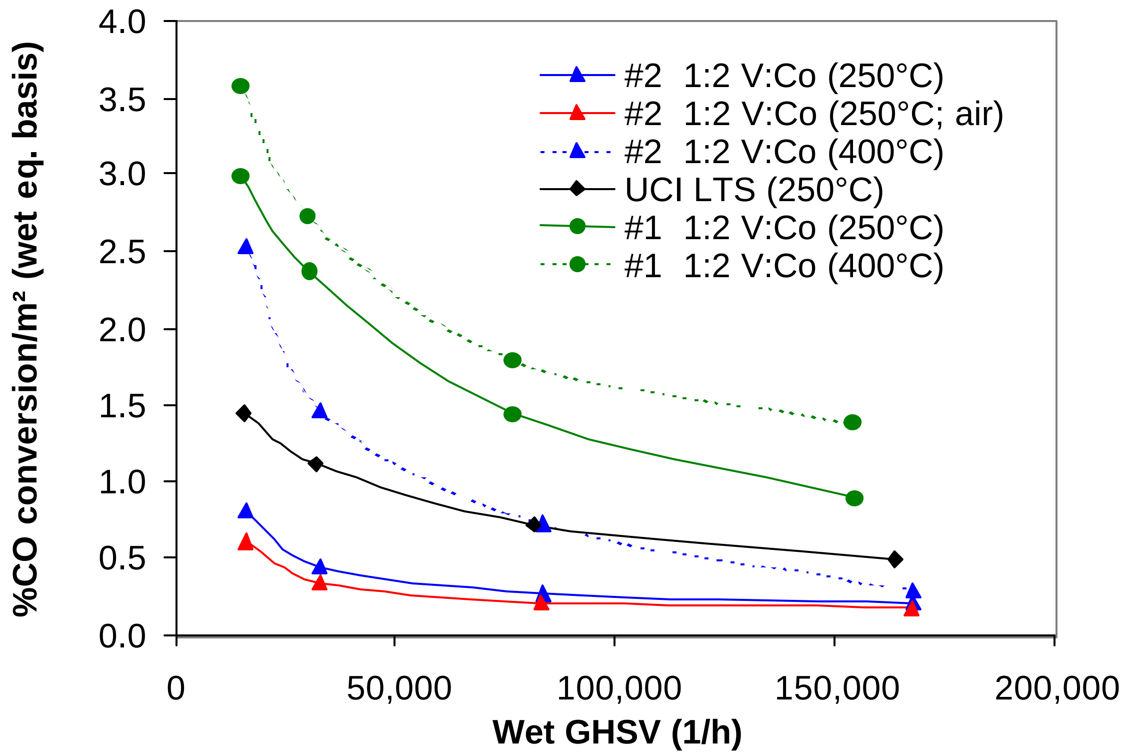
- ***V*** with ***Fe, Co, Cu,*** Mo, W, Mn, Ni, Ag, Sn, Se, Pb, Bi
- ***Sn*** with ***Mo, Mn, Fe, Co, Ni, Cu, Bi*** ,W, Cd, Ge, Pb
- ***Ce*** with ***Mo, Mn, Fe, Co, Sn,*** W, Ru, Ge

- Used phase diagrams to further refine the proposed formulations

- Look for materials with solid state structures

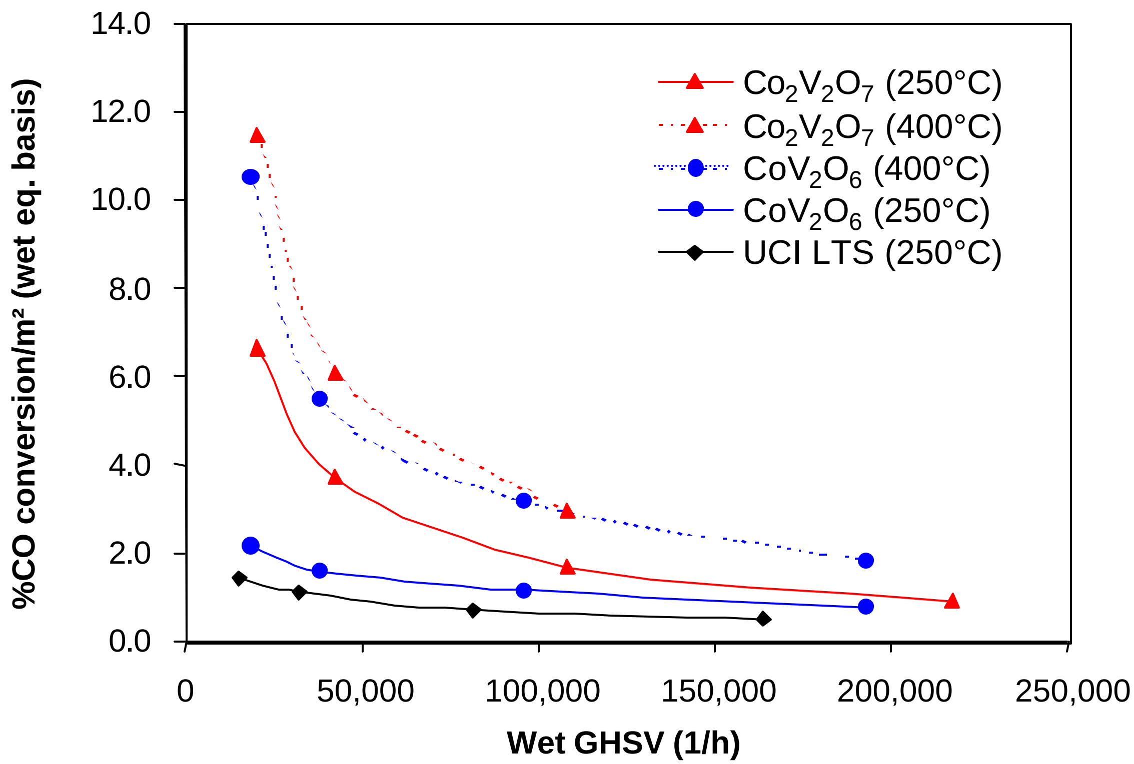
- Metal ratios in oxides may be important

Vanadium-cobalt oxides prepared by combustion technique have activities (per m²) comparable to Cu/ZnO



• XRD data: for new $Co_3O_4 + V_2O_3$; for spent $Co_3V_2O_8$

Co-V oxides prepared by solid state techniques appear to have higher WGS activity (per m²) than Cu/ZnO



- $Co_2V_2O_7$ XRD data: for new $Co_2V_2O_7$ + V_2O_5 ; for spent Co-V-O
- CoV_2O_6 XRD data is inconclusive for both new and spent samples

Industrial Interactions/Interest

- Reviewer's Comments: Form collaborations with other labs…preferably industry. Increase outreach to industry.

- DaimlerChrysler and Hydrogen Burner Technology are evaluating ANL's extrudate catalyst

- New catalyst composition will be transferred to industrial catalyst manufacturer for scale-up

Project Timeline

12/97
Construction of micro-reactor completed

6/98-5/99
Pt loading cut in half and WGS activity quadrupled

11/99
Pt loading reduced to 0.14 wt%, no loss in activity ($512 for 50 kW_e)

10/97
Began

1/98
Identified active WGS catalyst Pt/mixed oxide powder

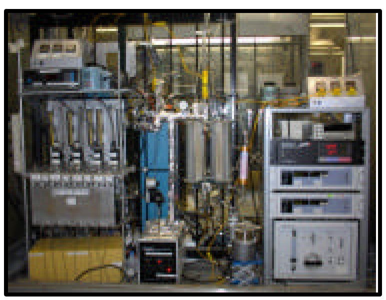
6/99
Catalyst made as extrudates, 0.42 wt% Pt, 124 m^2/g

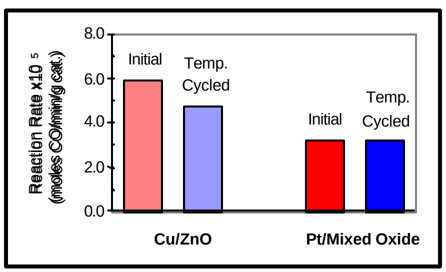
2/00
Promising non-precious metal WGS catalyst identified

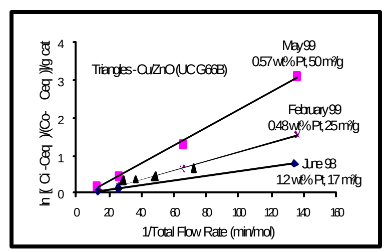
$

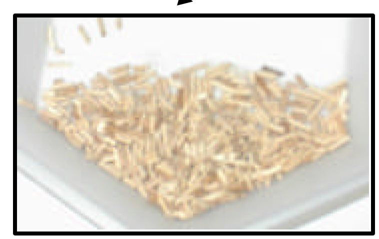
FY 98 | FY 99 | FY 00

Goals for 50 kW_e WGS Catalyst:
30,000 hr^{-1} GHSV, <5 L, <5 kg, <$50, Conversion: 10% to 1% CO









Accomplishments/Progress

- Demonstrated <1% CO at 230-300°C from diesel and 1.1% CO from simulated reformate (11/99 Milestone)
- ANL Pt/mixed oxide shift catalyst reduces WGS catalyst volume to 68% of Fe/Cr - Cu/ZnO combination and does not lose activity with exposure to air (not pyrophoric)
- A non-precious metal/mixed oxide catalyst was identified that reduces cost of catalyst to <1% of Pt/mixed oxide
- Binary oxides show promise as inexpensive, air and thermally stable WGS catalysts

Future work

- Increase low temperature activity of non-precious metal catalysts
- Explore other metal/oxide and oxide/oxide combinations
- Determine durability and stability of metal/mixed oxide catalysts under reformate conditions, including tolerance to sulfur
- Set up catalyst fabrication equipment to supply industry with evaluation scale quantities