Water-Gas Shift Catalysis

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Objective of this effort

- Develop water-gas shift catalysts that
  - meet the DOE goals of 90% CO conversion, 99% selectivity, 30,000 hr^{-1} GHSV, <$1/kWe
  - eliminate the need to sequester reactor during shutdown
    - Cu/ZnO and FeCr oxide must be protected from air and condensate
  - eliminate the need for careful ***in situ*** catalyst activation
    - Cu/ZnO requires *in situ* activation with dilute hydrogen
  - are tolerant to temperature excursions
    - FeCr oxide active at >350°C; Cu/ZnO must be kept <260°C
  - have lifetimes of >5000 hrs.

Approach: Metal/support combinations explored based on bifunctional mechanism

Overall Reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$

Bifunctional Mechanism:

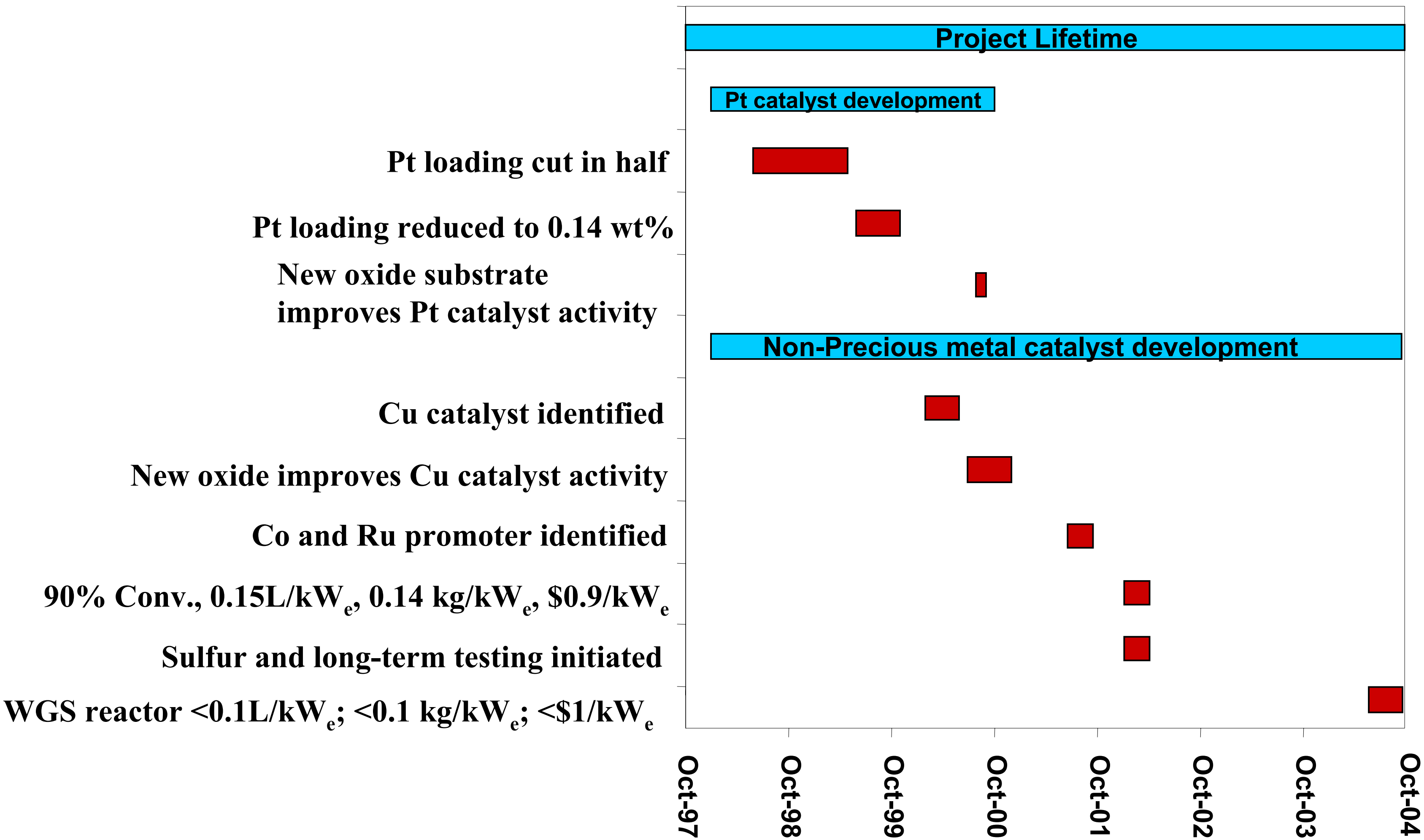
$* + CO \rightleftharpoons CO_{ad}$ * = metal surface site, adsorbs CO

$2MO_2 + CO_{ad} \rightleftharpoons M_2O_3 + CO_2$

$M_2O_3 + H_2O \rightleftharpoons 2MO_2 + H_2$ oxide support dissociates water

- Metals - CO adsorption energies between 20-50 kcal/mol
  - **Pt**, **Ru**, Pd, PtRu, PtCu
  - **Co**, **Cu**, Ag, Fe, Mo, Au
- Oxide Supports – Redox activity or oxygen vacancies under reformate conditions

Project timeline

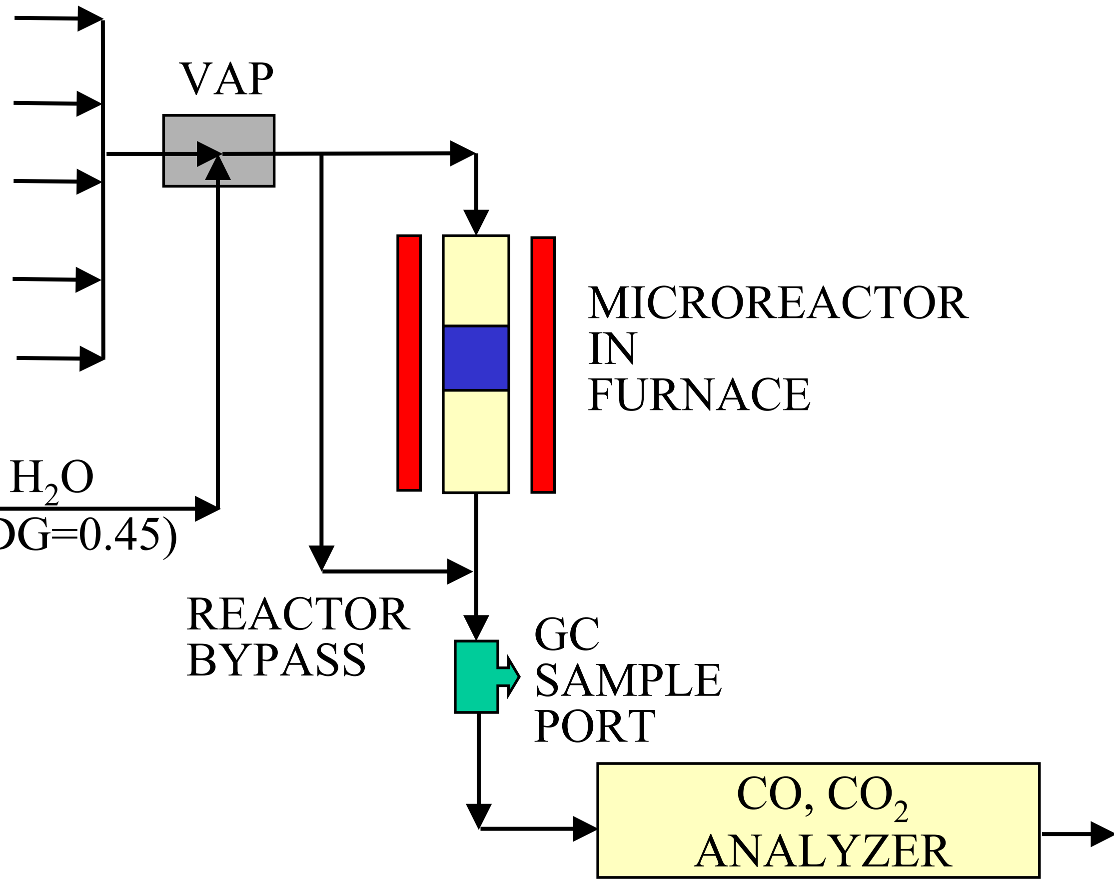


Reviewers comments from 2001 Annual Review

- Compare kinetic equations of the different classes of catalysts
- Stability of copper catalysts under rigorous conditions not shown
- Maintain a critical outlook towards whether new copper-based catalysts will provide a real overall advantage
- Testing should evaluate effects of startup, shutdown on catalysts' performance
- Enhance transfer/collaboration as project develops "real" catalysts
- Need faster transition to supported catalysts
- Durability and sulfur tests should be done early in the program

Catalyst activity tests were conducted with simulated reformate

HTS	LTS	w/Sulfur	
10.2	5.0	11.4	CO
15.4	15.4	7.5	CO_2
43.3	44.5	45.7	H_2
0	0	6.2 ppm	H_2S
31.1	35.1	35.1	N_2



WGS rate equation on various catalysts

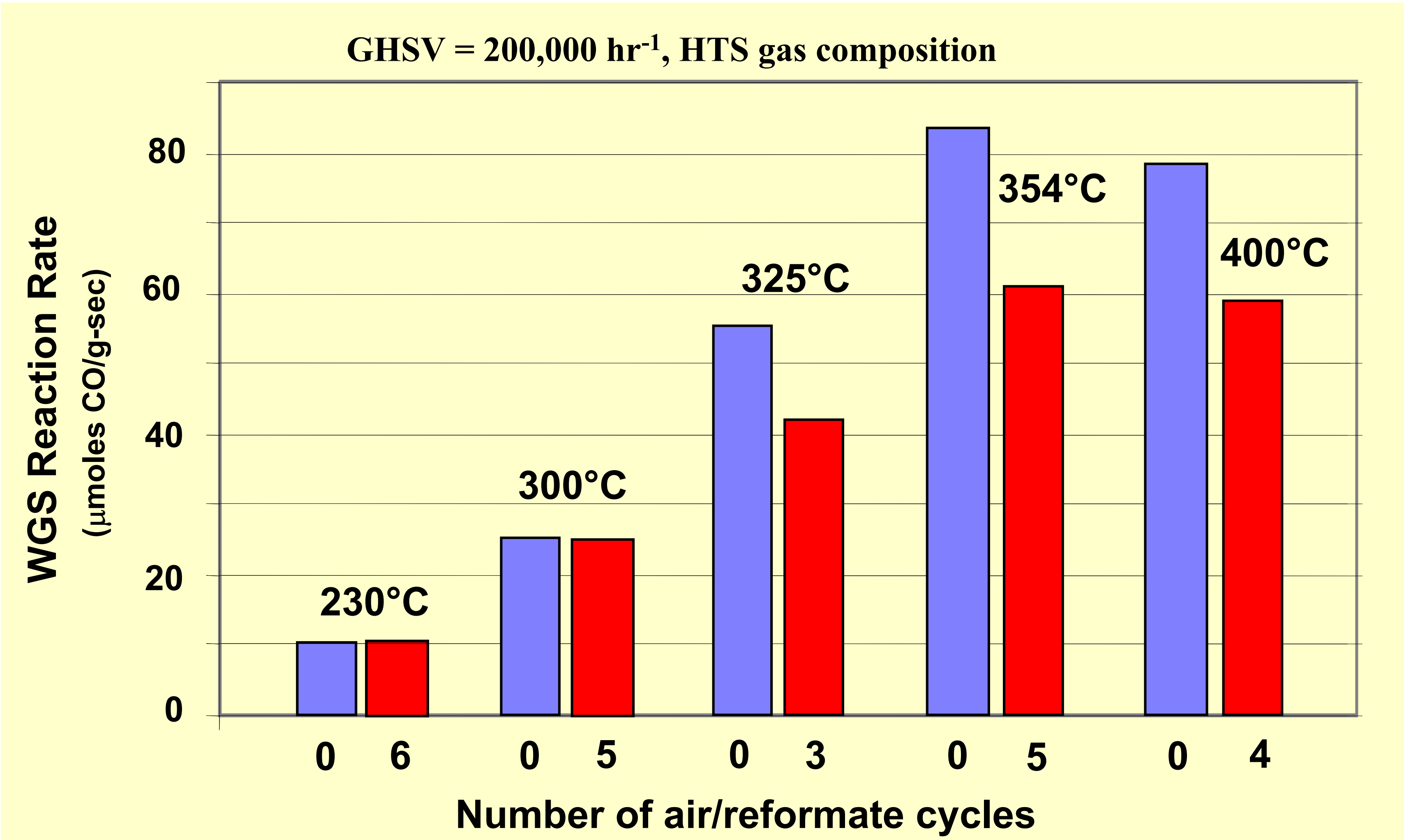
- $\text{Rate} = k\,(CO)^l\,(H2O)^m\,(CO2)^n\,(H2)^q \times (1-\beta)$

$\beta=(CO_2)(H_2)/K_{eq}(CO)(H_2O)$

	Ea (kJ/mol)	l (CO)	m (H_2O)	n (CO_2)	q (H_2)
FeCr Oxide	110 GS	0.9 DN	0.25 DN	-0.6 DN	0 DN
Cu/Zn Oxide	53 GS, ANL	0.8 DN	0.5 DN	-0.15 DN	0 DN
Pt/Ceria	46 RG 72 ANL	0 RG, ANL	0.5 RG	-0.5 RG	-1 RG
ANL Cu/Oxide	64	0.9	1.1	TBD	TBD

GS=Somorjai, 1980 RG=Gorte, 1998&2001 DN=Newsome, 1980

Cu/Oxide maintains activity with air exposure up to 300°C

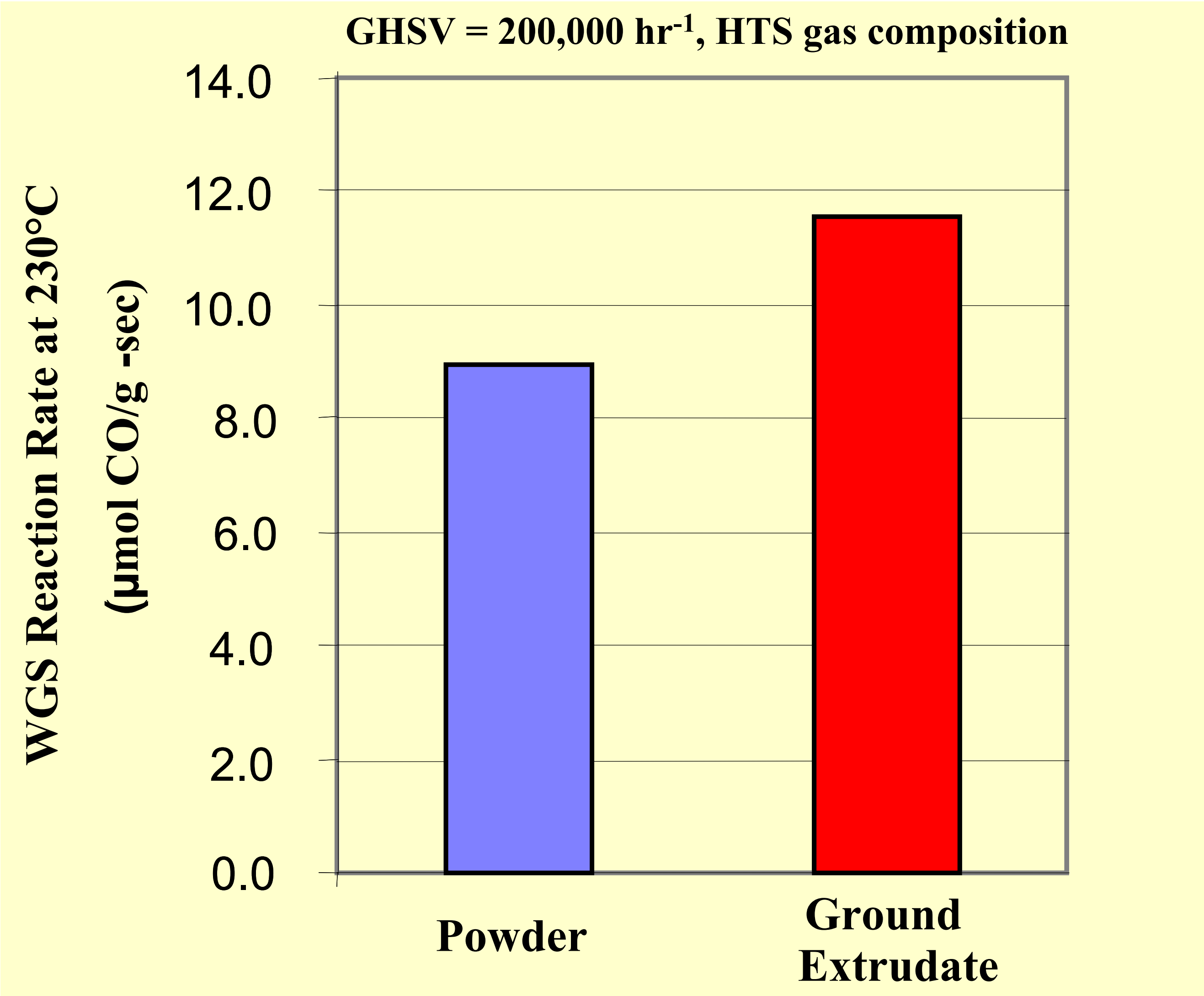


Pyrophoricity of ANL's Cu/Oxide vs. Cu/ZnO

25 cc of tablet/extrudate catalysts sieved to –10/+12, 1" insulated reactor tube, 4 longitudinal thermocouples

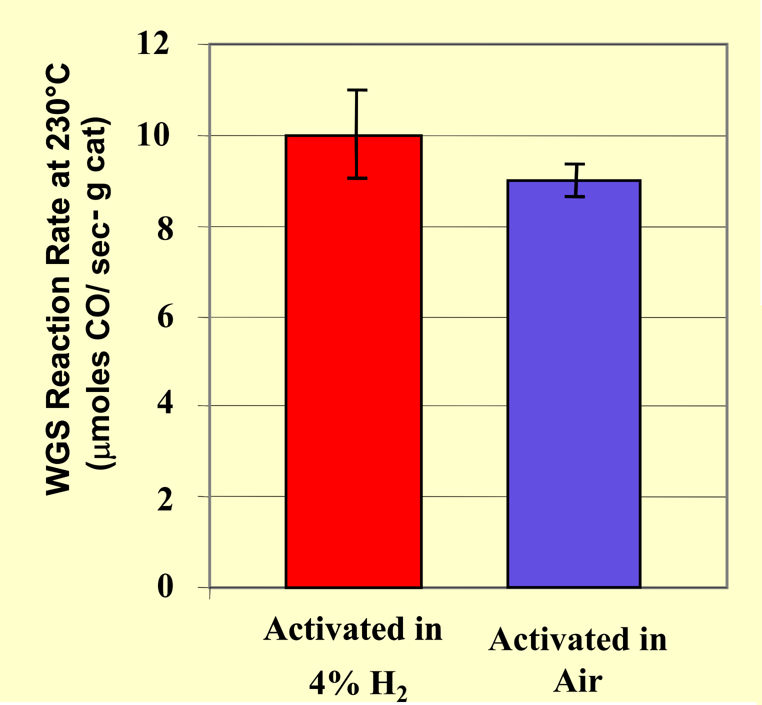
Catalyst	Exposure	Base T (°C)	ΔT (°C)
Cu/ZnO	1st Air	201	**202**
Cu/ZnO	2nd Air	198	212
Cu/ZnO	1st Air	25	**30**
Cu/Oxide	1st Air	233	**157**
Cu/Oxide	2nd Air	203	154
Cu/Oxide	1st Air	25	**0**

Cu/Oxide catalyst has been fabricated in a structured form

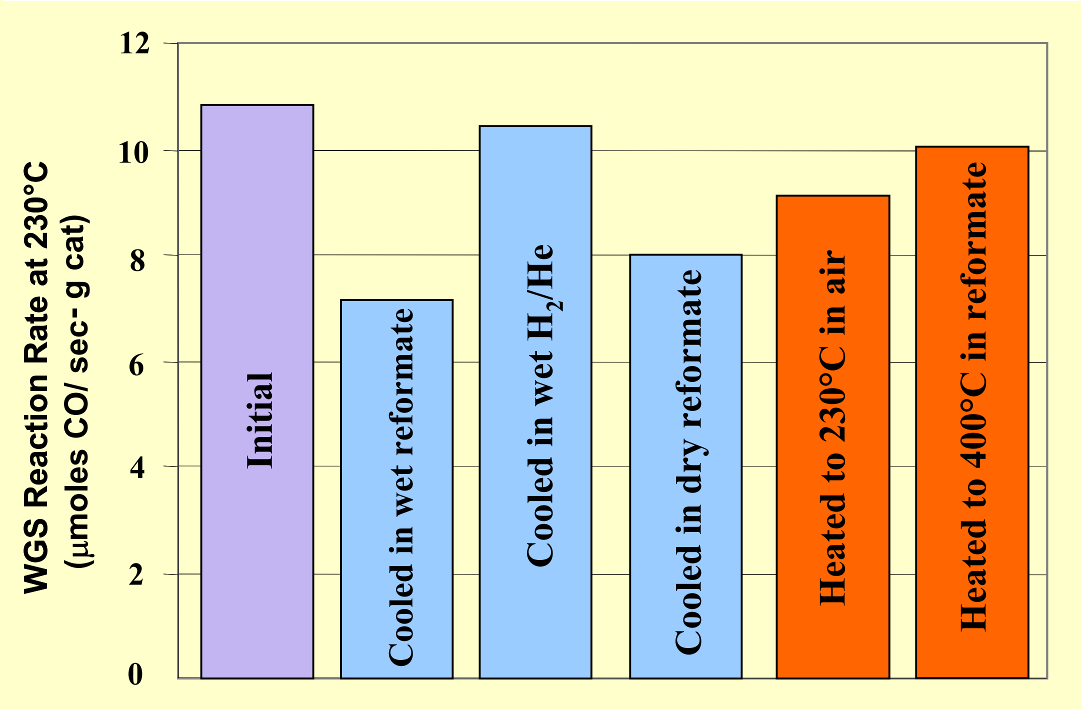


Activation procedure and exposure to condensate

GHSV = 200,000 hr^{-1}, HTS gas composition

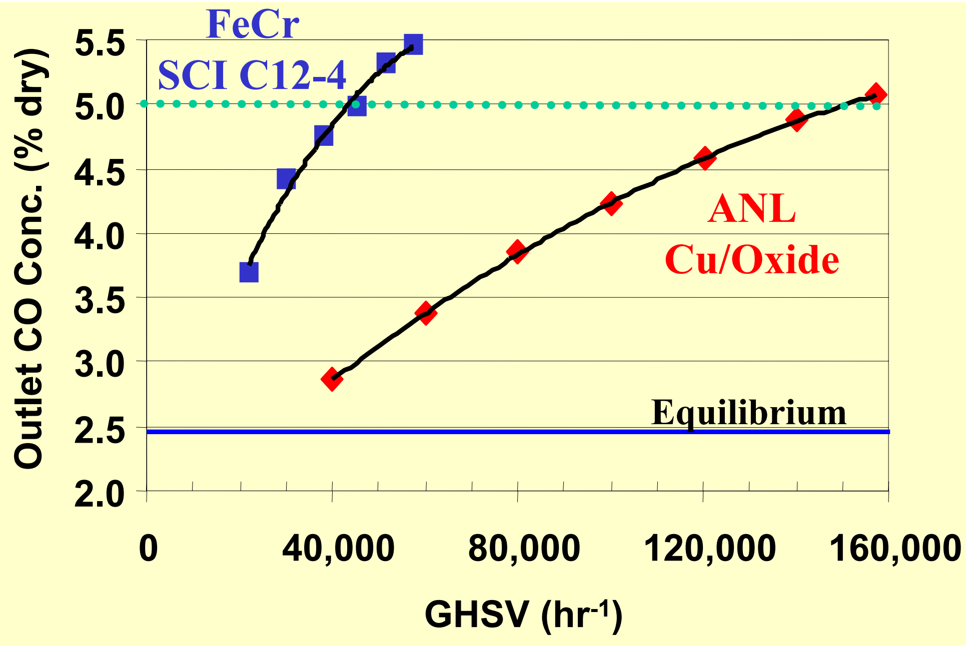


- Catalyst does not lose activity when exposed to condensate



- Catalyst can be activated in air

<1% CO out achieved at 20,000 hr^{-1} with ANL Cu/Oxide



HTS Stage at 400°C

<u>10.2% to 5.0% CO</u>

FeCr: 45,000 hr^{-1}

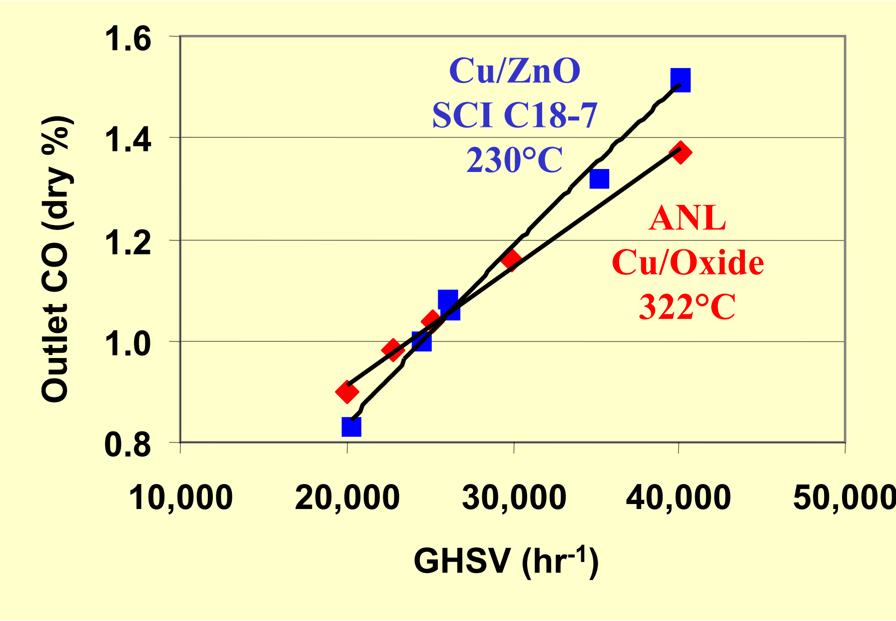
Cu Oxide: 157,500 hr^{-1}

LTS Stage at 230, 322°C

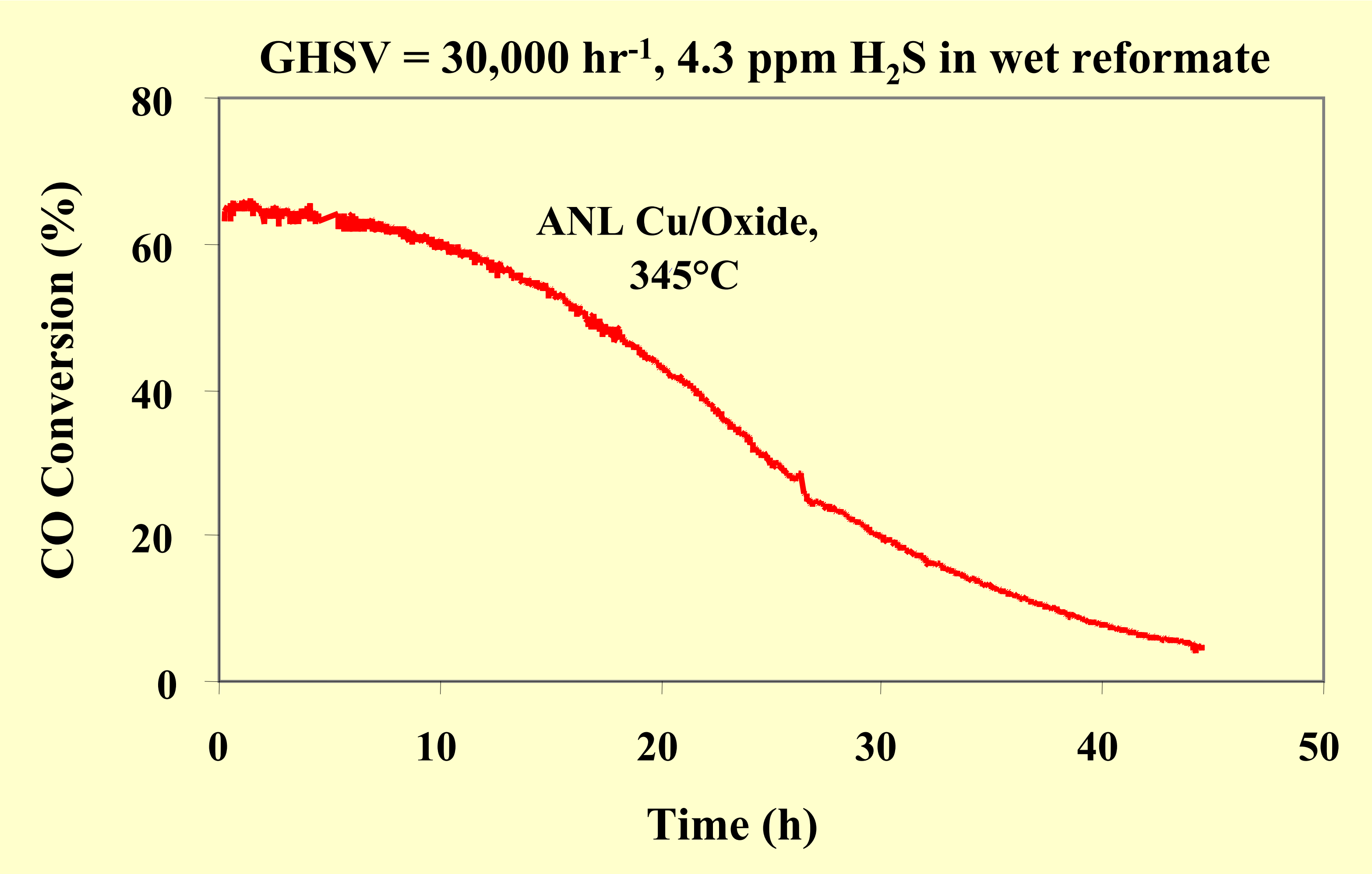
<u>5.0% to <1% CO</u>

Cu/ZnO: 25,000 hr^{-1}

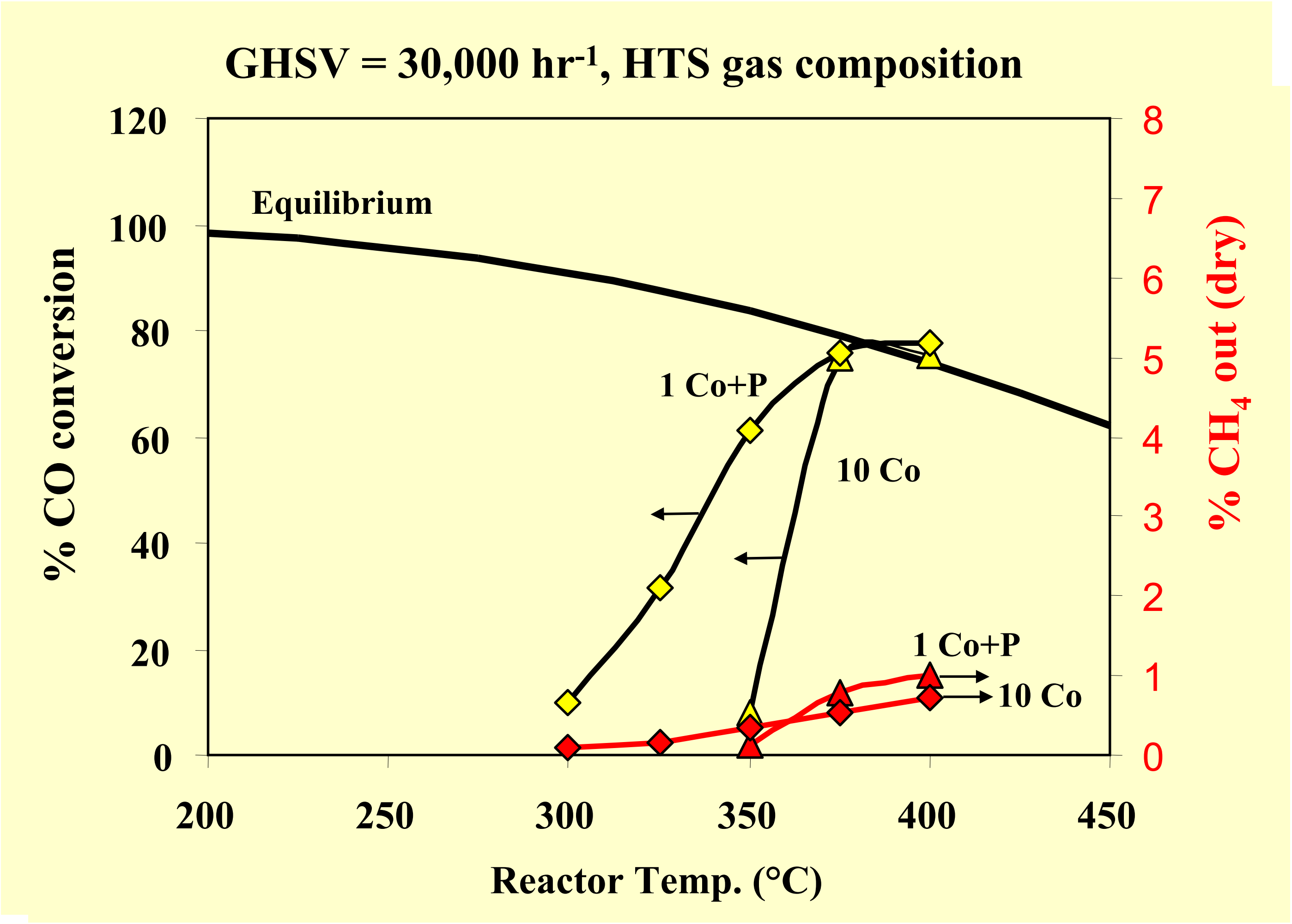
ANL Cu Oxide: 23,000 hr^{-1}



Sulfur tolerance of copper catalyst

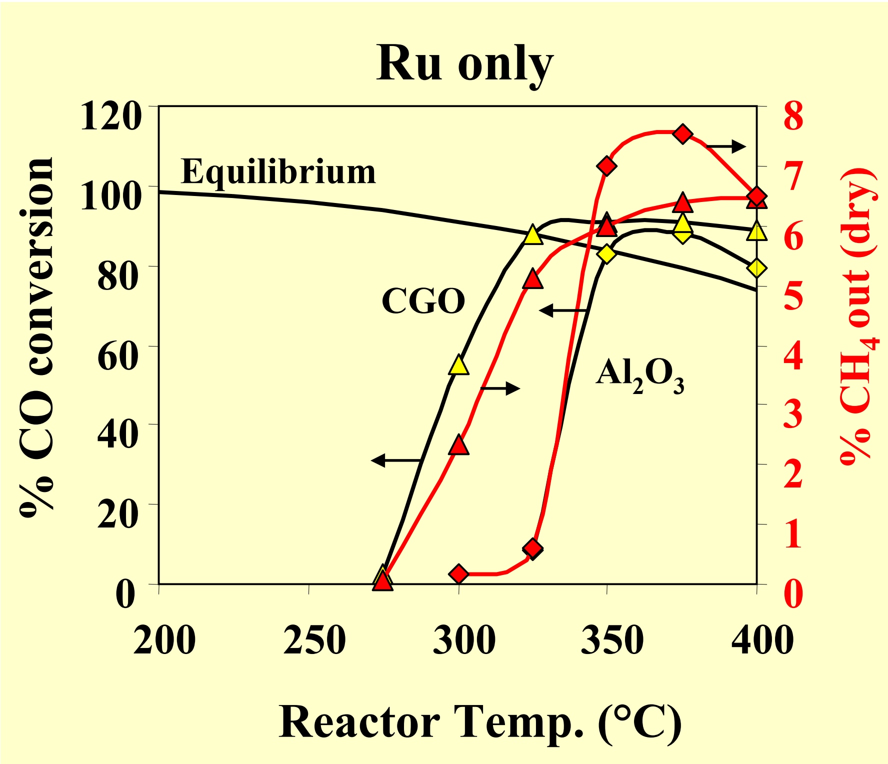


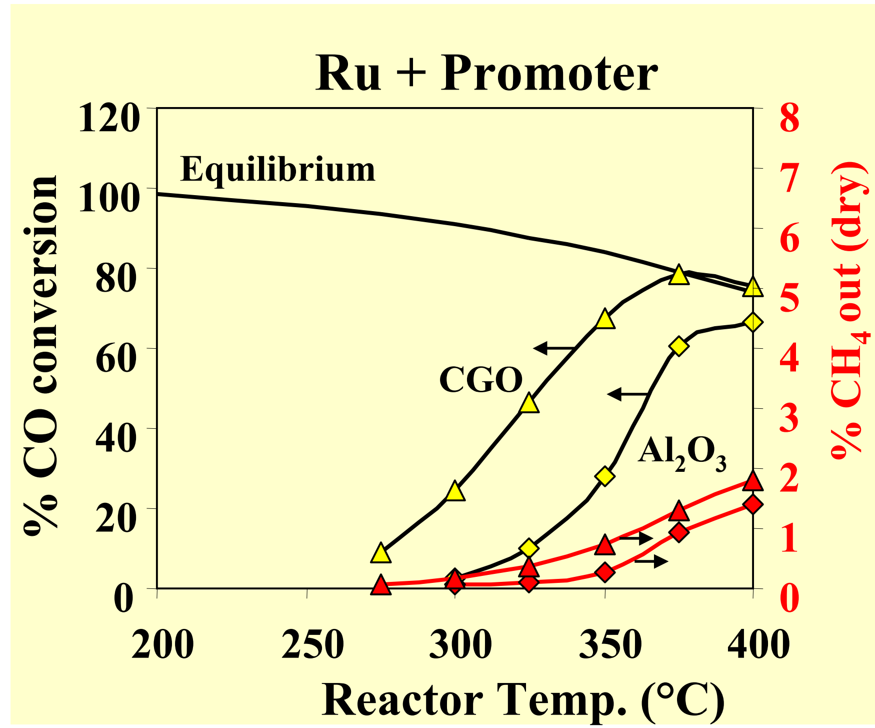
Promoter improves activity of Co/Al_2O_3 catalyst



Promoter diminishes CO methanation on Ru catalysts

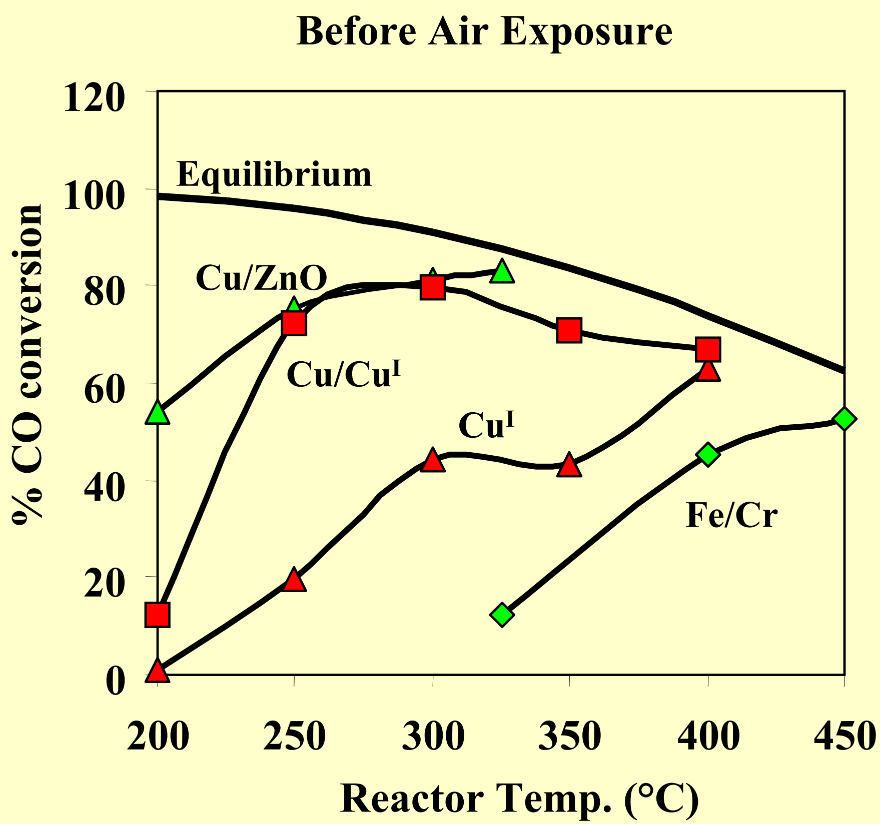
GHSV = 30,000 hr^{-1}, HTS gas composition

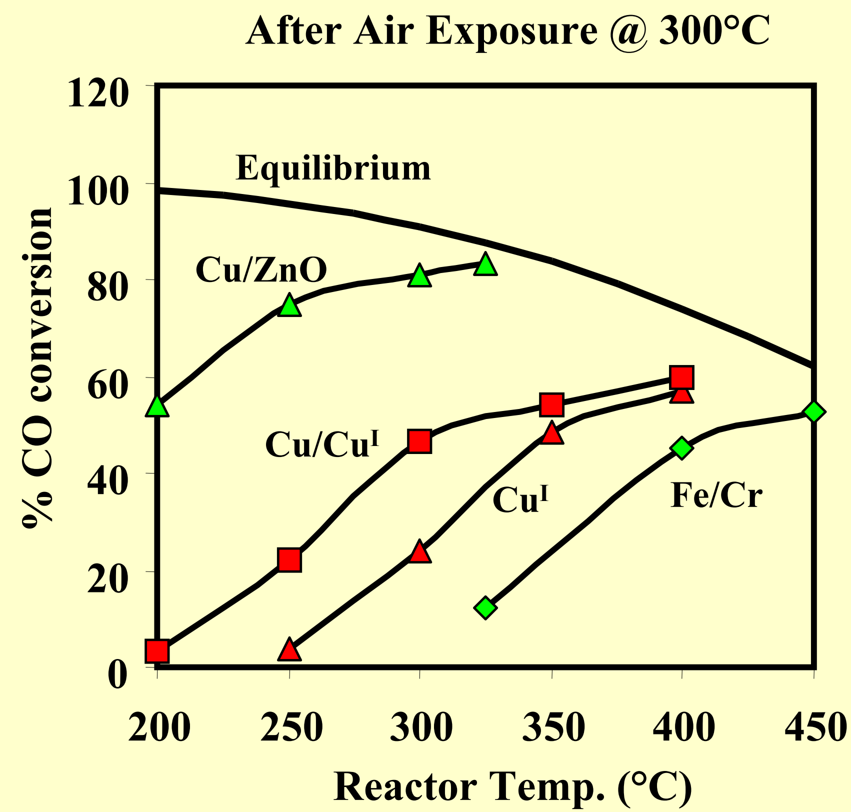




Cu on Cu^{1+} oxide has activity similar to Cu/ZnO, but loses activity with air exposure

GHSV = 30,000 hr^{-1}, HTS gas composition





Industrial interaction

- Cu/oxide and Pt/mixed oxide samples are being evaluated by:
  - HydrogenSource
  - H_2Gen Innovations
  - Süd-Chemie, Inc.
  - H-Power Enterprises

- Non-disclosure agreement with General Motors is in place

- Pt/mixed oxide catalyst has been used in the prototype of a commercial 5 kw_e natural gas fuel processor

Accomplishments

- Copper/mixed oxide catalyst has been fabricated as extrudates that have the same activity as the powder
- Demonstrated <1% CO at 20,000 hr^{-1} with Cu/Oxide vs. 16,000 hr^{-1} for FeCr oxide-Cu/ZnO
  (2/02 Milestone: <1% CO out at 30,000 hr^{-1})
- Determined sulfur tolerance of Cu/Oxide catalyst
  Catalyst loses all WGS activity after 45 hrs on 4.5 ppm H_2S
  (9/01 Milestone: 1000+ h test of metal/mixed oxide catalyst under reformate conditions, including tolerance to sulfur)
- Improved activity of Ru and Co catalysts while suppressing methanation by using a promoter

Future work

- Demonstrate $\leq$1% CO out at 30,000 hr^{-1} using a structured non-precious metal catalyst
(6/02 milestone)
- Determine lifetime and durability of catalysts under actual reformate conditions
(apparatus for long-term tests was completed 4/02)
- Improve low temperature activity (<300°C) of catalysts to >50 µmoles CO/sec-g catalyst (currently at 11 at 230°C)
(8/02 milestone)
- Develop a catalyst that is tolerant to 3-4 ppm H_2S in reformate