Sulfur Removal from Reformate

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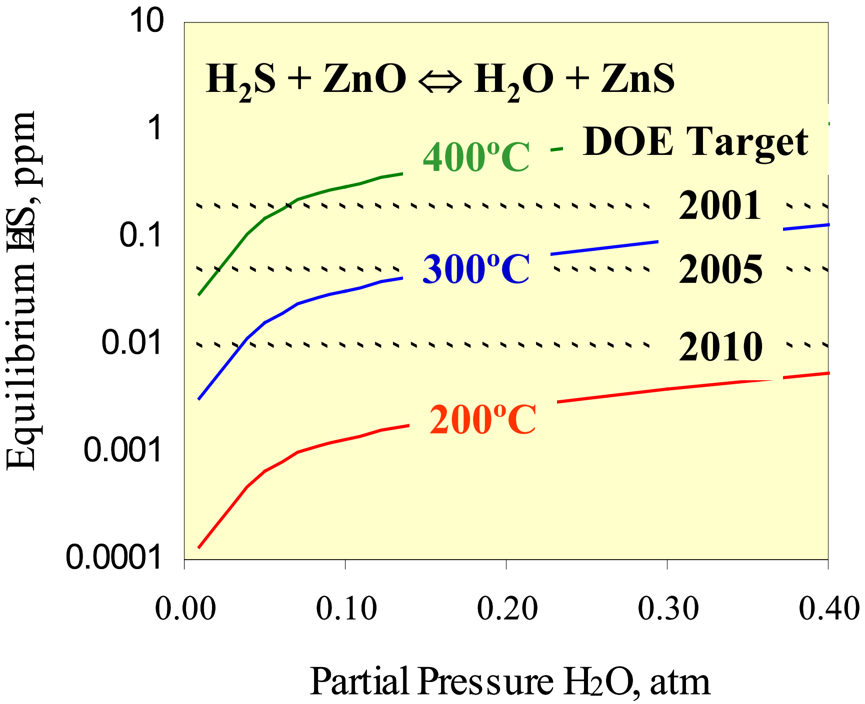
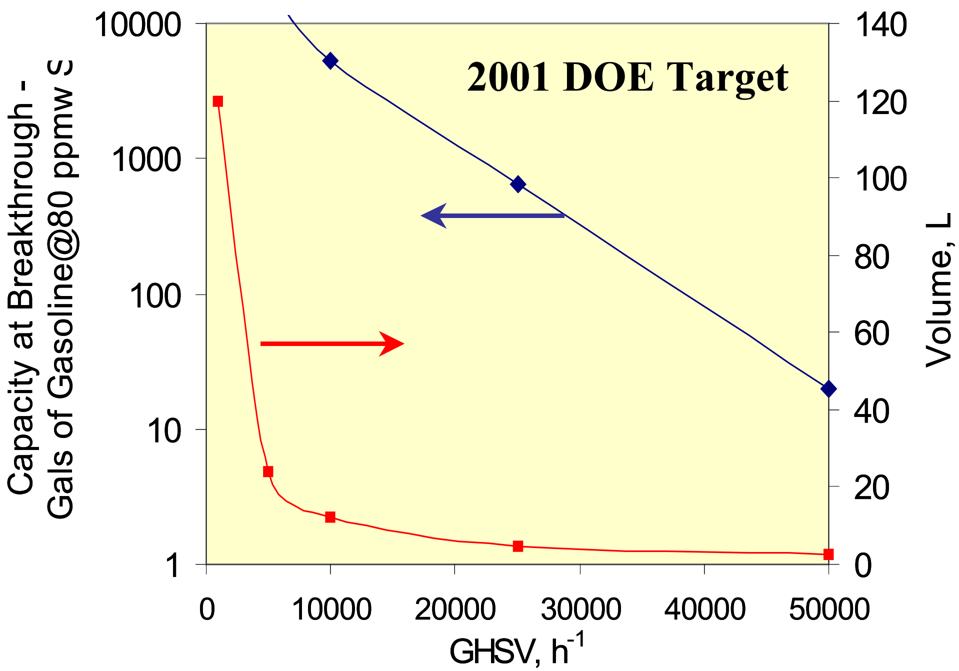
2002 National Laboratory R&D Meeting
DOE Fuel Cells for Transportation Program
Denver, CO
May 9-10,2002

Objective

- Develop new or improve existing technologies for removing sulfur to meet DOE targets:
  - H_2S concentration in reformate
    - <200 ppb (2001)
    - <50 ppb (2005)
    - <10 ppb (2010)
  - Reactor size and space velocity
    - <0.06 L/kWe (<0.06 kg/kWe)
    - GHSV of 50,000 h^{-1}
  - Cost <$1 kWe

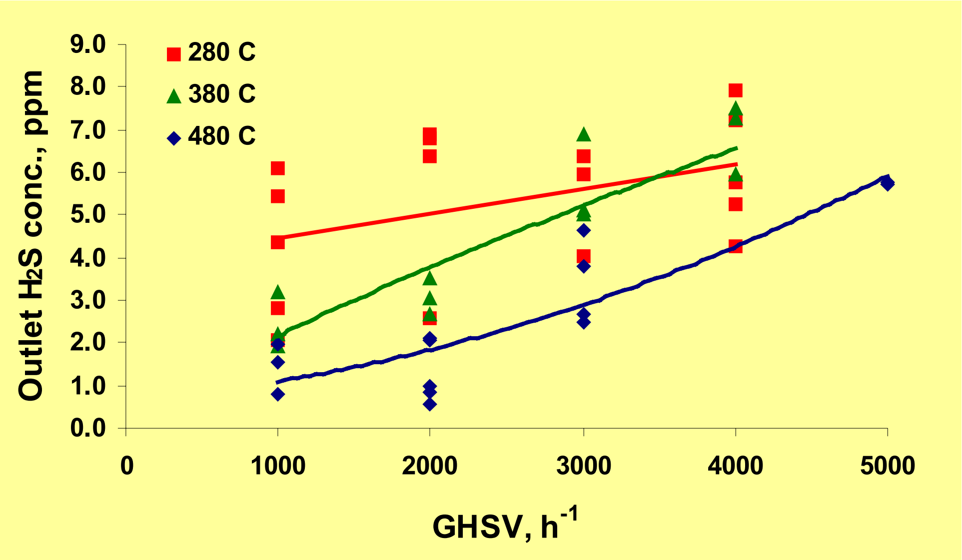
ZnO is the Benchmark Technology For H_2S Removal via Gas-Solid Adsorption





For ZnO, High Temperature and Low GHSV Are Required to Achieve ~1 ppm H_2S

- Although equilibrium favors lower temperatures, slow kinetics favor higher temperatures



19 ppm H_2S, 32% H_2, 6.4% CO, 6.4% CO_2, 18% H_2O, bal. N_2

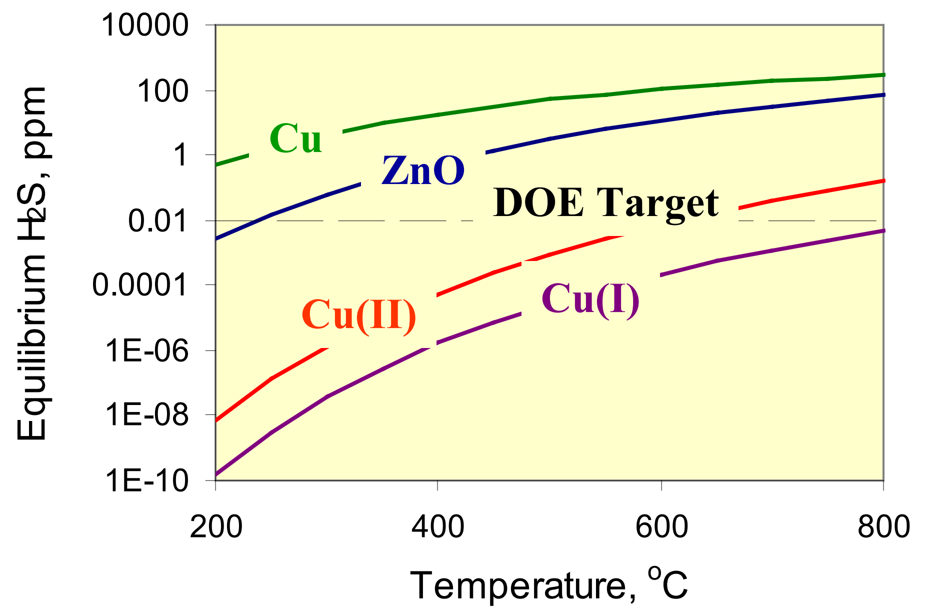
- Balancing the reaction rate with equilibrium suggests that ~ 1 ppm H_2S may be the minimum attainable

Selected Reviewers' Comments from FY2001 Annual Review

- Focus on evaluating new materials and approaches, followed by targeted effort to develop detailed understanding of promising candidates
- Consider impact of catalytic adsorption approach
- Investigate liquid phase sulfur removal

Based on Thermodynamics, Cu Oxides Could Reduce the H_2S Concentration to < 1 ppb

- Benefits
  - Among the lowest H_2S equilibrium concentration of all metal oxides.
  - Lower vapor pressure than ZnO allows for higher operating temperatures.
- Challenges
  - Cu oxides reduces to metallic Cu under fuel processing conditions.
  - Metallic Cu has less favorable H_2S equilibrium than ZnO.



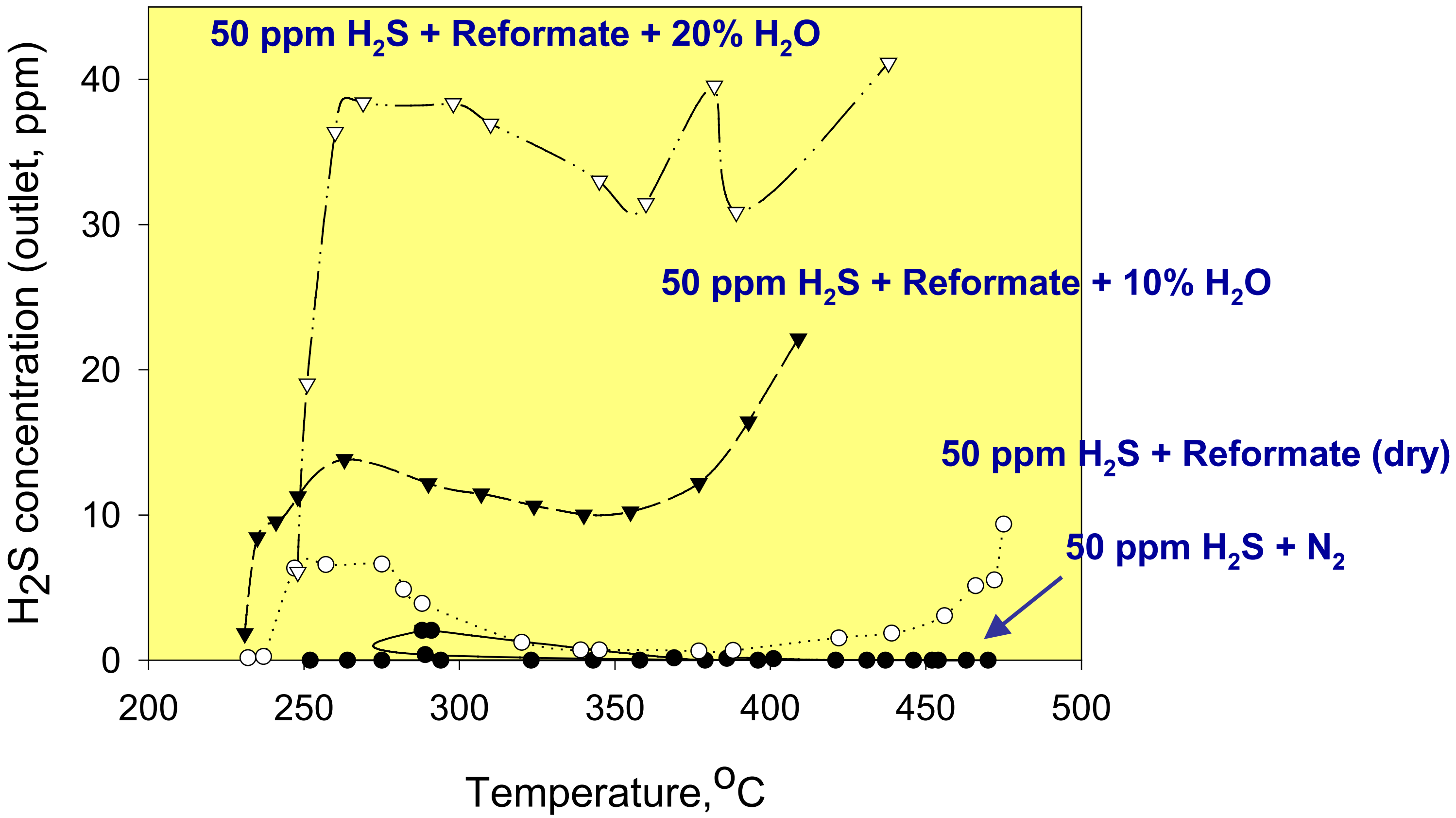
The Challenges of H_2S Adsorption Under Fuel Processing Conditions

- Water
  - Equilibrium ($ZnO + H_2S \Leftrightarrow ZnS + H_2O$)
  - Competitive adsorption between H_2S and H_2O
- CO_2
  - Surface carbonates
  - Formation of COS ($ZnS + CO_2 \Leftrightarrow ZnO + COS$)
- CO
  - Chemisorption of CO
  - Formation of COS ($ZnS + CO \Leftrightarrow Zn + COS$)
- H_2
  - Equilibrium ($M + H_2S \Leftrightarrow MS + H_2$, where M = metal)

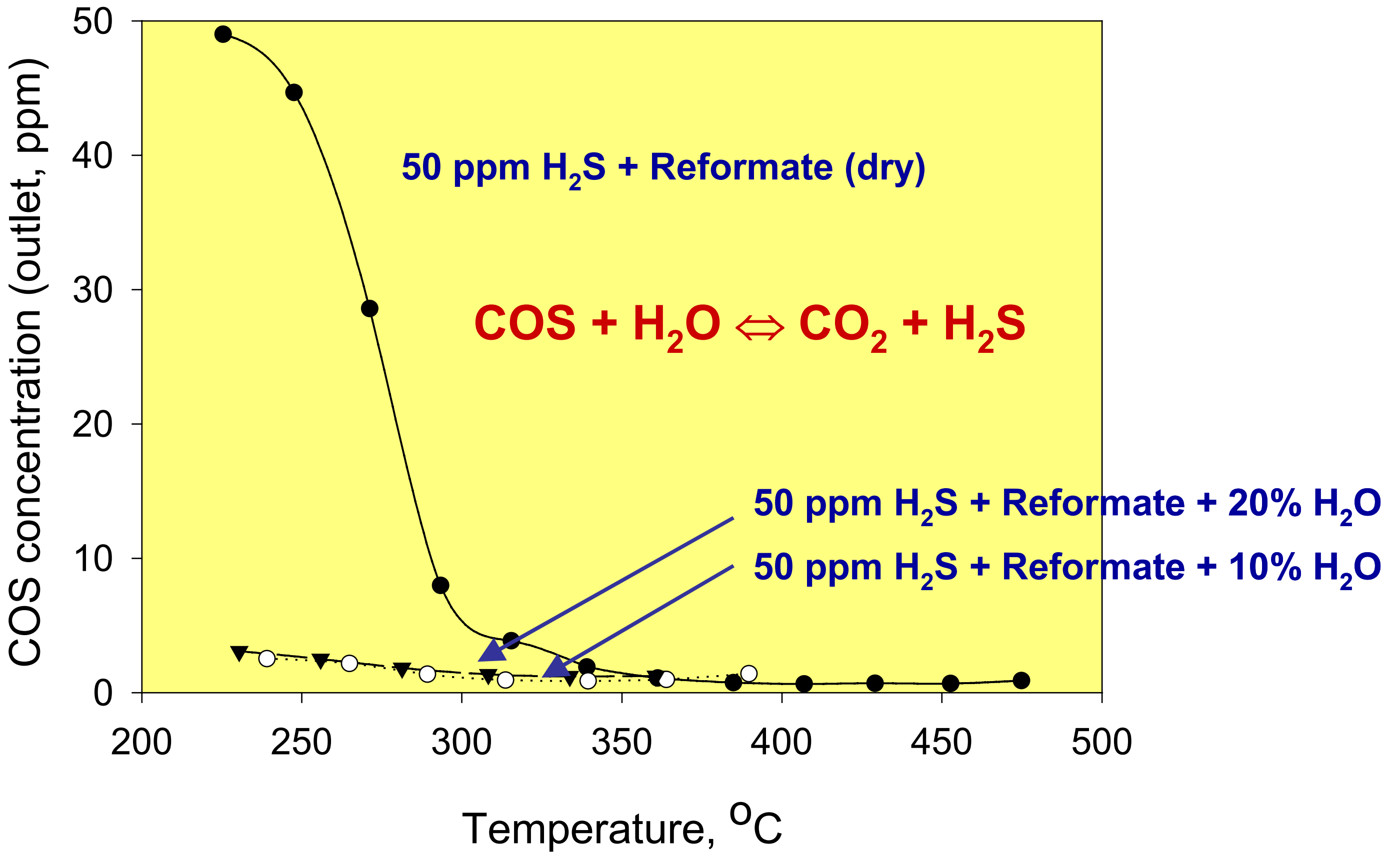
Approach

- Synthesize new mixed metal oxides containing Cu oxide for H_2S adsorption
- Improve the rate of H_2S uptake by ZnO through the use of metal/metal oxide doping
- Determine the H_2S and COS concentration as a function of temperature and gas composition (H_2O, CO, and CO_2)

For Cu-Co, Good H_2S Uptake in Dry Reformate; However, H_2O is Problematic



For Cu-Co, Less COS Observed In Wet Reformate



Attempting to Improving ZnO Performance through Metal/Metal Oxide-doping

- Reaction Pathway for ZnO

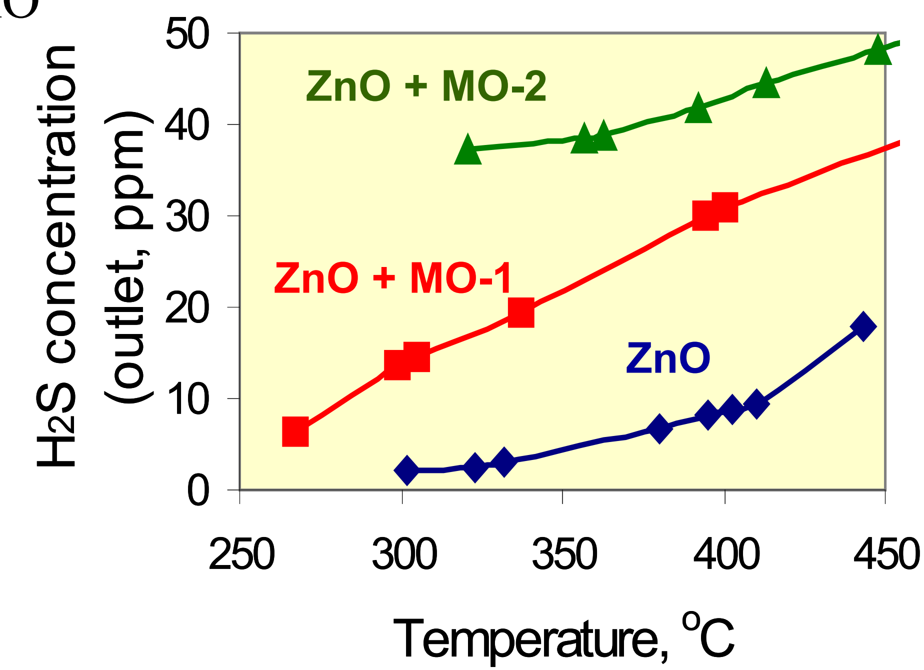
$$H_2S_{(g)} + ZnO \Rightarrow H^+\text{-}ZnO + HS^-\text{-}ZnO$$

$$HS^-\text{-}ZnO \Rightarrow HO^-\text{-}ZnS$$

- Approach is to promote "Spillover" from Metal/Metal Oxide to ZnO

$$H_2S_{(g)} + M \Rightarrow H^+\text{-}M + HS^-\text{-}M$$

$$HS^-\text{-}M \Rightarrow HS^-\text{-}ZnO$$



Conditions: 50 ppm H_2S + Reformate + 10% H_2O, GHSV = 5,000 h^{-1}

Milestones

- Demonstrate that a combination of ZnO and a mixed-metal oxide are capable of reducing the H_2S concentration to 100 ppb in a synthetic reformate containing 10 ppm H_2S. (February 2002 – *In Progress*)

- Demonstrate that a combination of ZnO and a mixed-metal oxide are capable of reducing the H_2S concentration to 100 ppb using reformate produced by autothermal reforming of a benchmark fuel containing a maximum of 80 ppm sulfur. (June 2002)

Future Plans

- Continue work on mixed metal oxide and metal-doped ZnO adsorbents.
- Evaluate most promising adsorbents under fuel processing conditions.
- Evaluate the impact of using liquid-phase sulfur absorption on the H_2S removal requirements in the fuel processor.
- Better define the sulfur removal requirements for the fuel processor based on results for sulfur tolerance studies of ATR and WGS catalysts.

Collaboration

- Worked with Süd-Chemie on evaluating ZnO monoliths.
- Current progress on new adsorbent materials is too immature for technology transfer at this time.
- Continued discussions with industry and academia on current state of sulfur removal technologies.

Timeline

FY98	**5/98 - Initiated project**
FY99	**2/99 - Established operating conditions for ZnO pellet bed**
FY00	**4/00 - Produced structured forms of ZnO**
FY01	**5/01 - Complete evaluation of commercial ZnO-coated monolith** **9/01 – Initiate work on Cu-mixed metal oxides/modified-ZnO**
FY02	**5/02 – Begin evaluating adsorbents using actual reformate**

GOAL

Develop a sulfur removal process to permit the use of gasoline with 30-80 ppm sulfur