Catalytic Autothermal Reforming

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Objectives

- To reduce the cost and improve the catalytic activity of our ATR catalysts in order to reduce the size and cost of the fuel processor and improve start-up time

- To develop a better understanding of reaction mechanisms in order to optimize the catalyst performance (activity, durability, sulfur-tolerance)

Approach

- Synthesize materials that meet ANL selection criteria and DOE cost goals.
- Determine the H_2, CO, CO_2, CH_4 and C_nH_m yields for various fuels versus temperature and space velocity.
- Work with catalyst manufacturers to optimize the performance of structured forms of the catalysts.
- Conduct fundamental studies to gain insight into the reaction mechanisms.

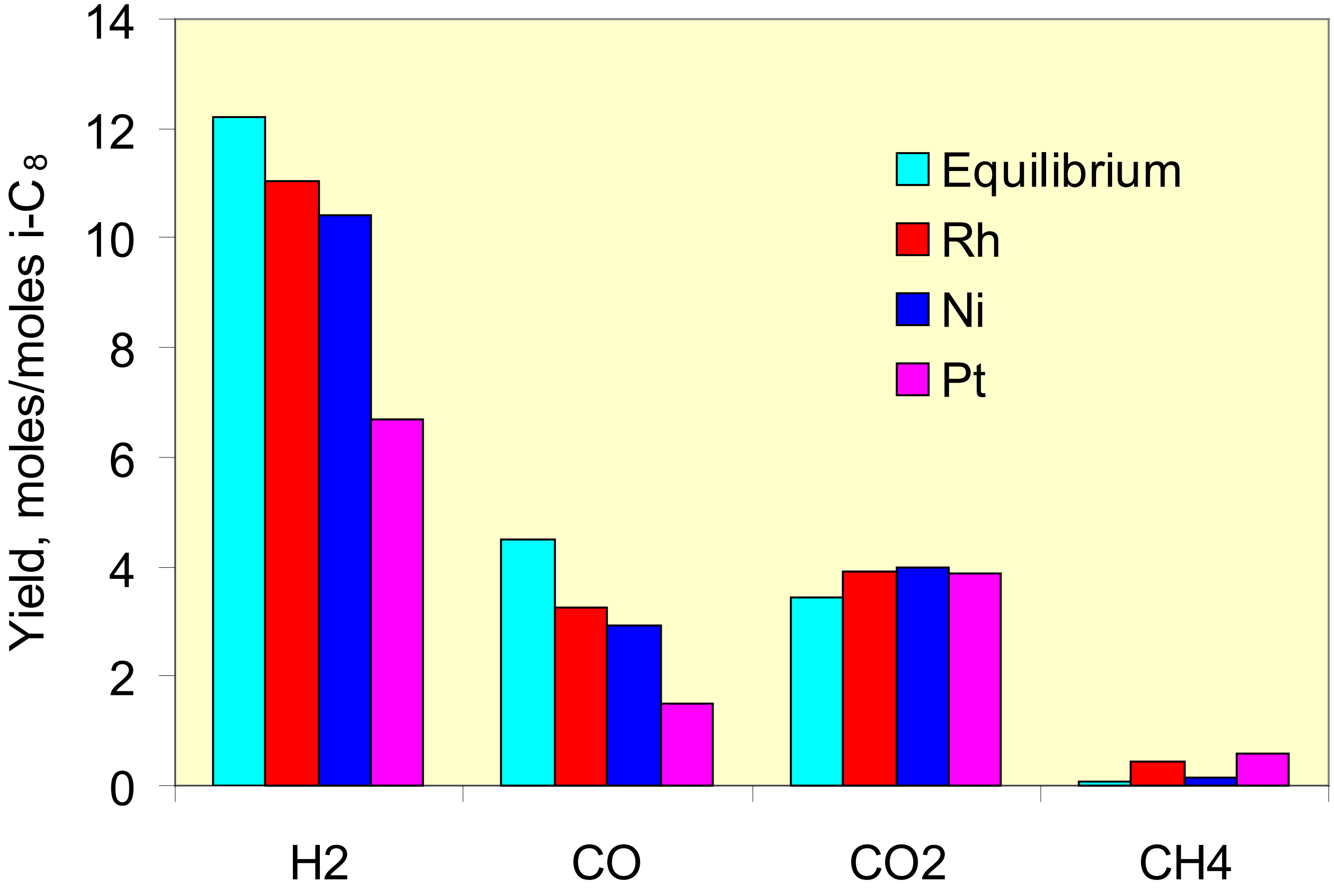
Reviewers' Comments from FY2001 Annual Review

- Put more emphasis on explaining kinetics – relative roles of partial oxidation and steam reforming not explained.
- Get additional people (lab/universities) working in this area examining the fundamentals.
- Test best catalyst formulations with real world gasoline that contains sulfur.

Industrial/Academic Collaboration

- Industrial
  - Süd-Chemie, Inc.
    - Catalyst manufactured under non-exclusive licensing agreement
    - CRADA to optimize POX catalysts
  - H2Fuel
    - CRADA for the commercialization of the reformer
- Academic
  - University of Alabama, Tuscaloosa
    - Characterization studies (SEM, TEM, XPS) of POX catalyst
    - Mechanistic and kinetic studies of POX catalyst
  - University of Puerto Rico, Mayagüez
    - Determine reaction condition boundaries for carbon formation

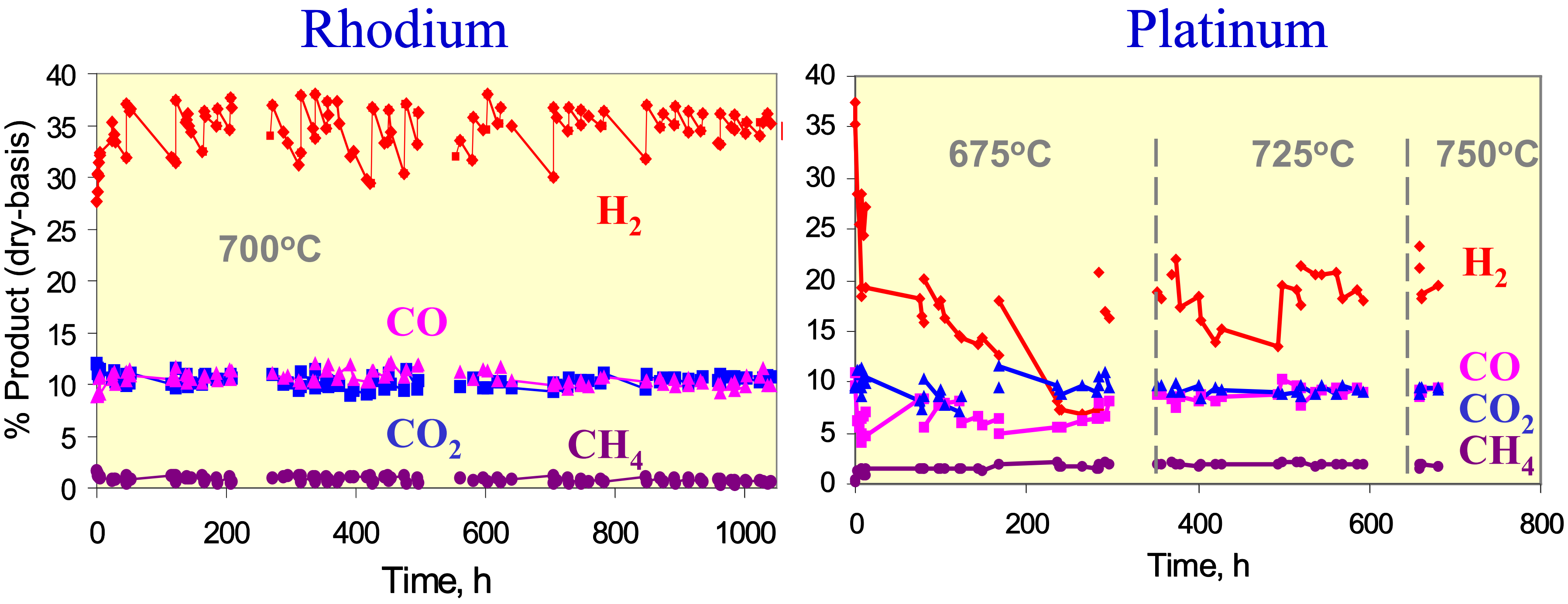
For Monoliths, Rh and Ni are More Active than Pt For Isooctane Reforming at 700°C



Conditions: Isooctane fuel, 700ºC, $O_2/C = 0.5$, $H_2O/C = 1.2$

Argonne Electrochemical Technology Program

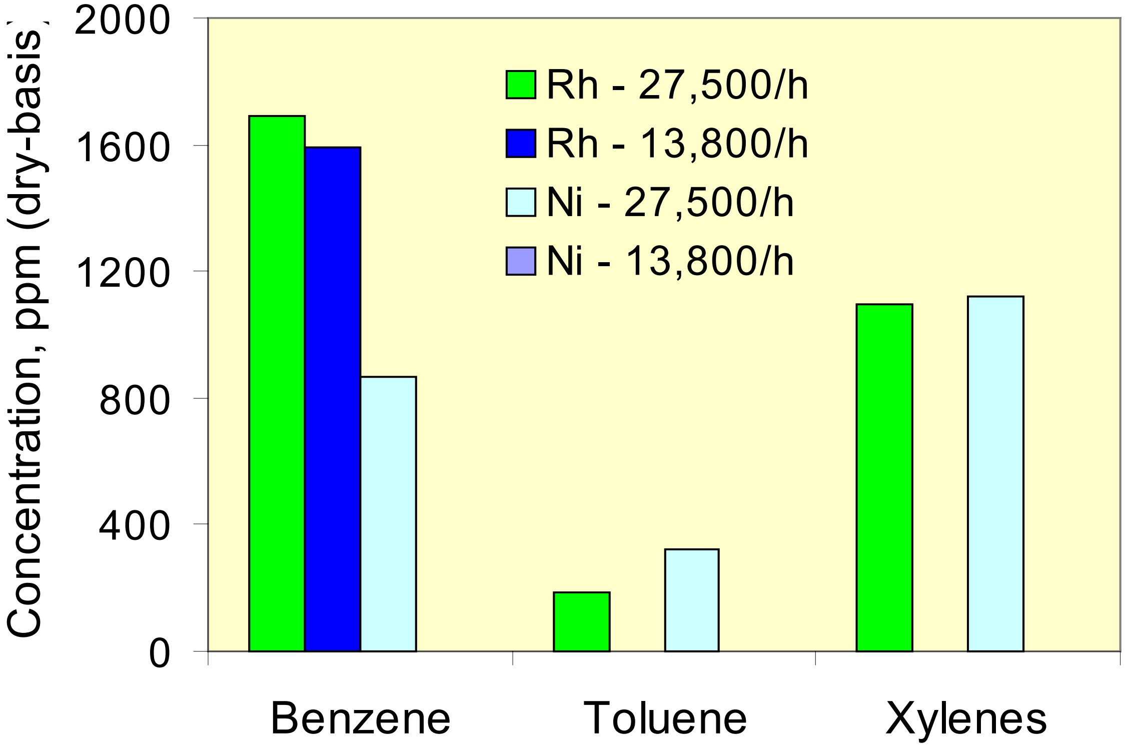
Rh Monolith Has Better Long-Term Performance For Reforming Benchmark Fuel



Conditions: Benchmark Fuel, $O_2/C = 0.44$, $H_2O/C = 1.6$, GHSV = 9000 hr^{-1}

- Benzene and toluene were present in the reformate produced by Rh and Pt. For Rh, benzene concentration was ~200-300 ppm and toluene concentration was <~100 ppm (both on a dry-basis).

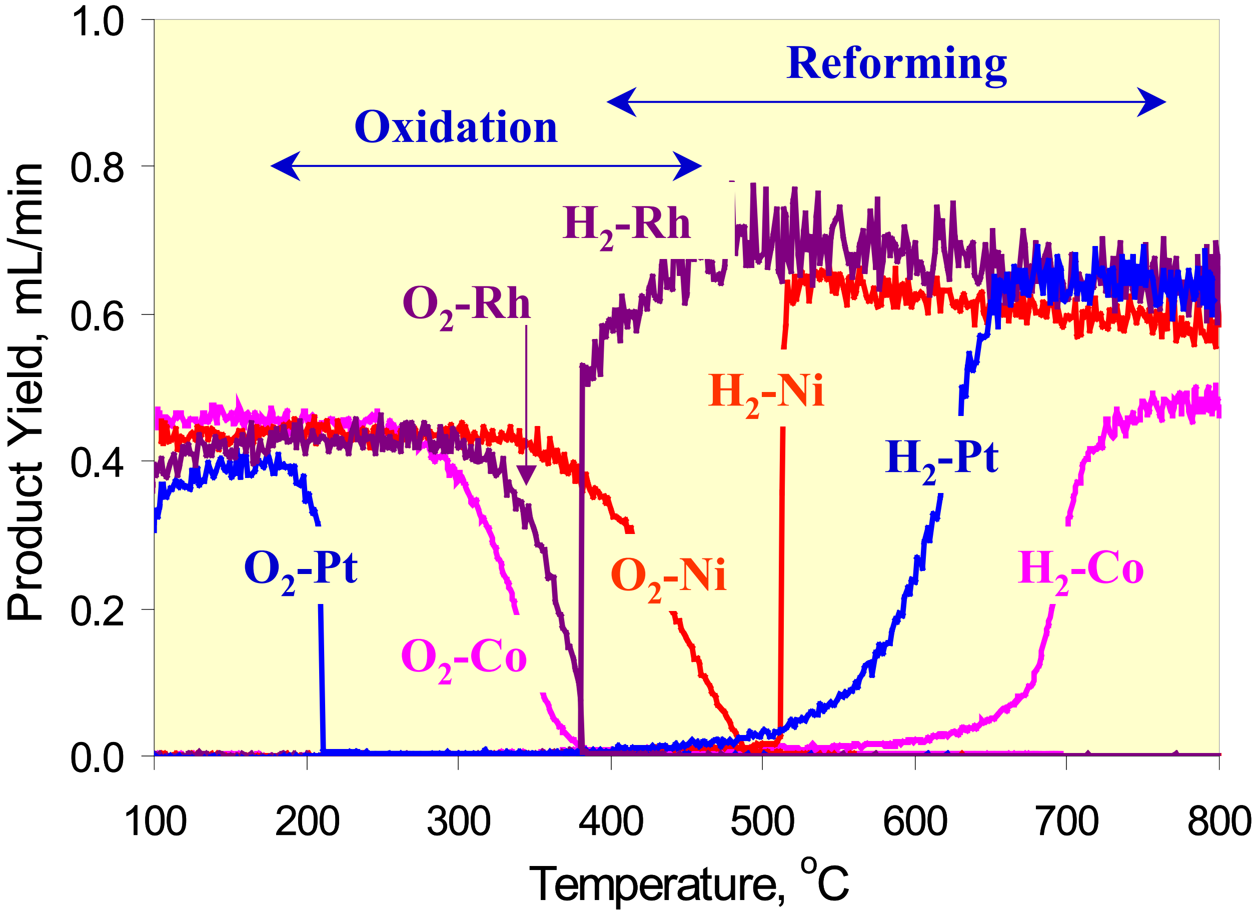
Short-Term Tests Suggest that Ni May Reduce Aromatic Breakthrough



- Rh – No toluene or xylenes detected at 13,800/h
- Ni – No benzene, toluene, or xylenes detected at 13,800/h

Conditions: Benchmark Fuel, 700ºC, $O_2/C = 0.44$, $H_2O/C = 1.6$

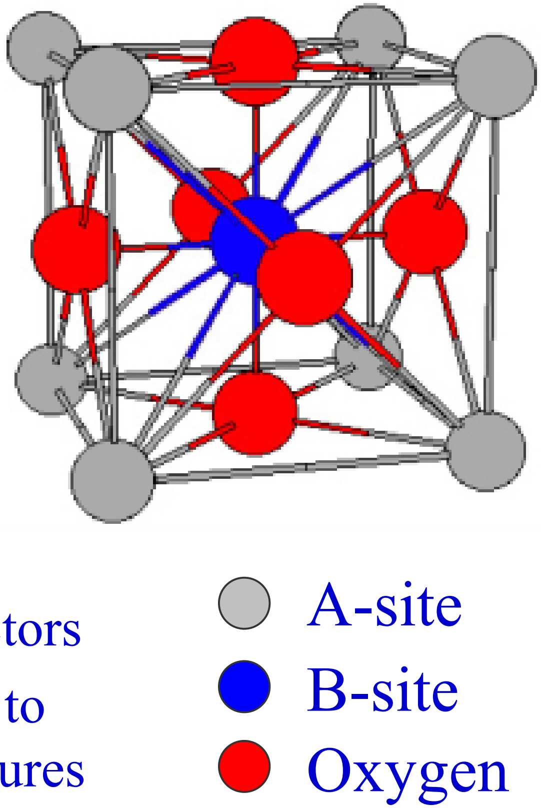
Metals Exhibit Different Oxidation and Reforming Activity



Conditions: Isobutane fuel, $O_2/C = 0.5$, $H_2O/C = 1.0$, Total Flow = 50 mL/min (Balance He), GHSV = ~$50,000\ h^{-1}$

Part II: Perovskite ATR Catalysts

- *Potential Benefit is lower cost*—no noble metals
- What is a Perovskite?
  - General formula: ABO_3
    - B cation smaller than A cation
    - Example: $LaCoO_3$
- Why Perovskites as ATR Catalysts?
  - Many perovskite oxides are good oxygen ion conductor and/or good mixed electronic conductors
  - $La_{1-x}Sr_x(Mn,Fe,Co)O_3$ shown to be comparable to Pt/Al_2O_3 for methane oxidation at low temperatures (<600°C)



B-site Substitution Stabilizes $LaNiO_3$ and $LaCoO_3$ under ATR Conditions

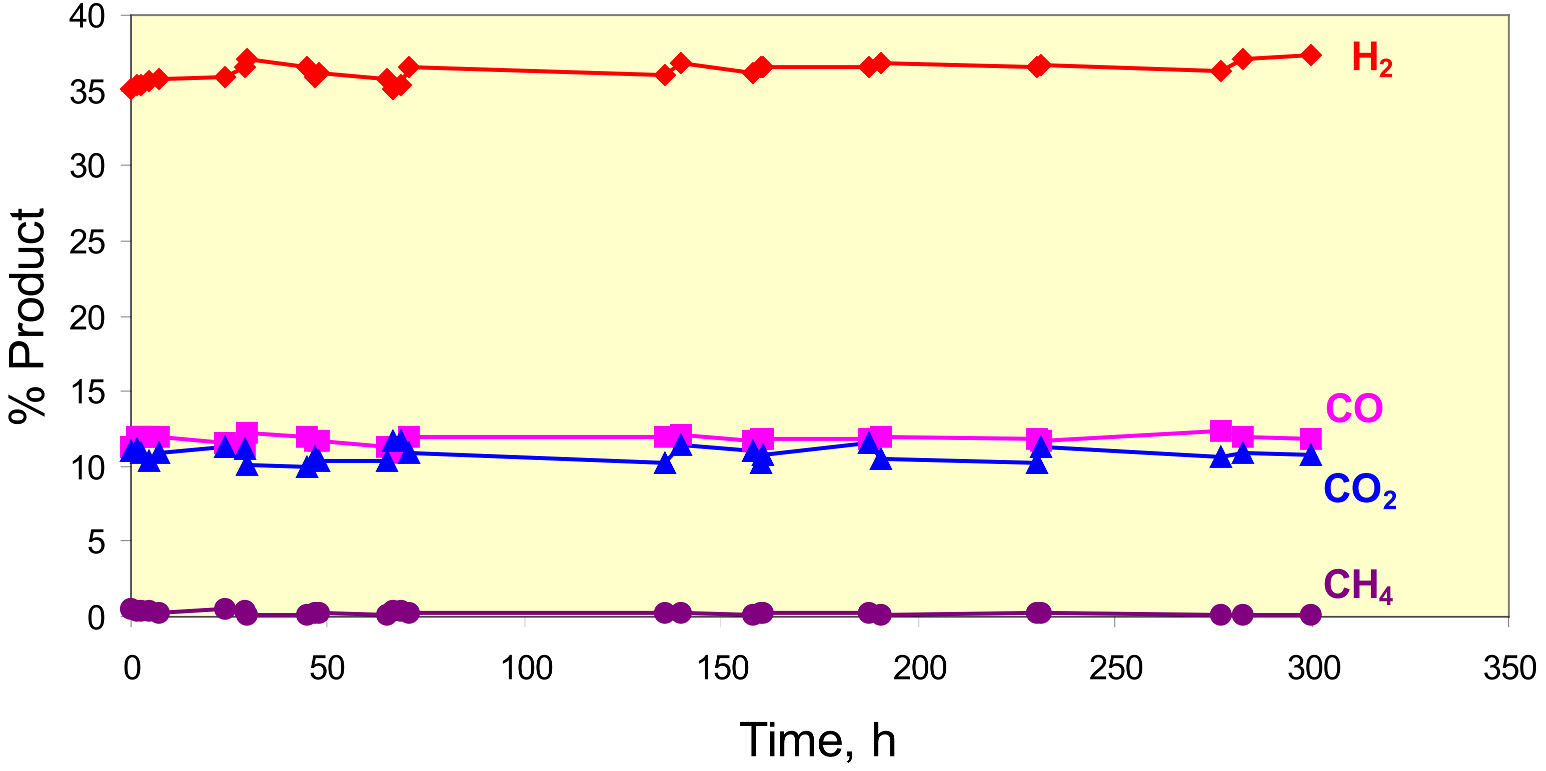
- Substituting at least 50% of the Ni or Co with selected transition metals stabilizes the perovskite structure under ATR conditions
- However, when the amount of Ni or Co is reduced, performance degrades

	Moles H_2/Mole C_8H_{18} Feed		
Catalyst	700°C	650°C	600°C
$LaNiO_3$	14.3	12.7	10.8
B-site modified $LaNiO_3$	12.6	11.7	10.0

A-site Substitution Improves H_2 Yield

Catalyst	Moles H_2/Mole C_8H_{18} Feed 700°C	600°C
$LaNiO_3$	14.3	10.8
B-site modified $LaNiO_3$	12.6	10.0
A,B-site modified $LaNiO_3$ (I)	13.1	13.5
A,B-site modified $LaNiO_3$ (II)	13.2	11.3

Stabilized Ni Perovskite Catalyst Maintains Activity Over 300 Hours



Conditions: A,B-site modified $LaNiO_3$ catalyst, Benchmark Fuel, 700ºC

Future Plans

- Continue work to improve the performance of catalyst supported on structured forms
- Continue work to improve the performance of stabilized perovskite catalysts
- Work to improve the sulfur tolerance of non-Pt catalysts
- Continue work with academic collaborators to gain better insight into reaction mechanisms

Timeline

May 1995: Started screening for hydrocarbon reforming catalysts

Apr 1997: Demonstrated conversion of gasoline

Nov 1997: Demonstrated catalyst performance in engineering scale reactor

May 1999: Initiated licensing discussions with Süd-Chemie, Inc.

May 2000: Demonstrated 1,000 hour life

Aug 2000: US Patent (6,110,861) awarded

Oct 2000: CRADA w/H2Fuel to commercialize reformer

Feb 2002: CRADA w/Süd-Chemie to optimize catalyst performance.