Nanoscale Water Gas Shift Catalysts

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DOE Fuel Cells Review Meeting
Golden, Colorado
May 10, 2002

DOE Contract Number: DE-FC02-98EE50529

Program Timeline

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Demonstration of Monolith in 10-kW WGS Reactor ★

Demonstration of Pellets in MTI's 50-kW Fuel Processor ★

Size/Weight/Cost Model (Generation II) ★

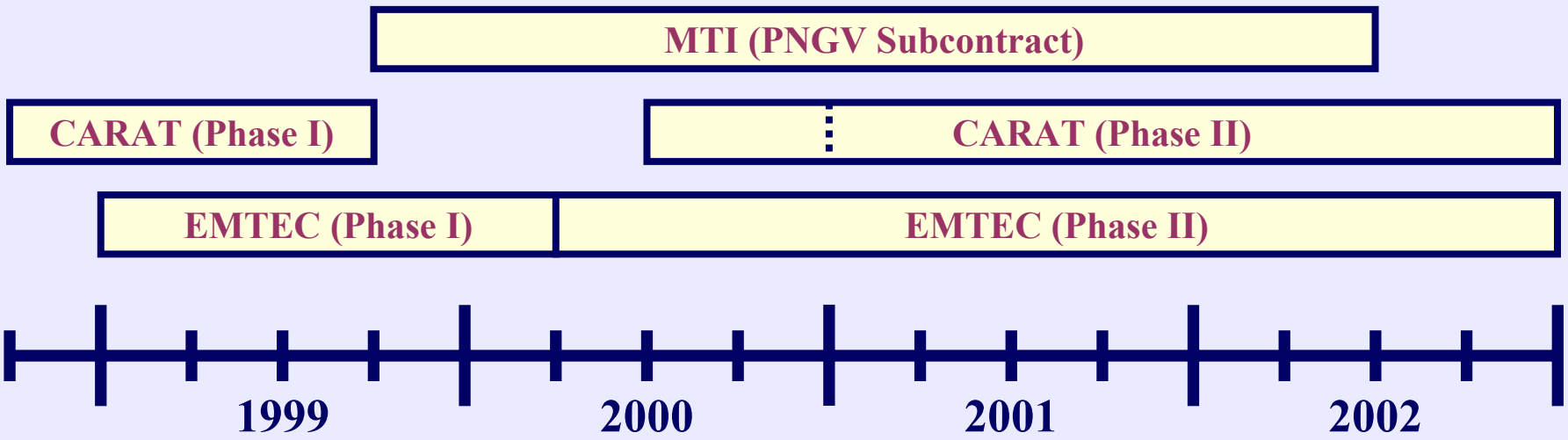
Demonstration of High Performance Monoliths ★

Development of Washcoating Process ★

★ Established Catalyst Synthesis Methods

★ Size/Weight/Cost Model (Generation I)

★ Demonstration of High Performance Catalysts



Pt/Ceria Catalysts

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Potential Advantages

- Temperature Stability
- No Activation is Needed
- Non-Pyrophoric
- Washcoating is Possible

Questions being Addressed

Can we afford precious metal catalysts for the application?

- How low can we push exit CO contents (without excessive size and cost)?
- What are the de-activation mechanisms, and how can we suppress de-activation?
- Can high performance be achieved in monolith-supported catalysts?

Technical Approach

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Synthesis of Nanoscale Ceria

↓

Incorporation of Platinum

↓

Washcoating of Monoliths

Development Issues

- **Nanoscale Ceria Material**
  - oxygen storage capability
  - surface area stability
  - dispersion of nanoscale oxides
- **Platinization**
  - compatibility with ceria material
  - maximize platinum dispersion
  - minimize carbon and chlorine
- **Washcoating**
  - optimize suspension chemistry
  - maximize platinum utilization
  - maintain high performance

Catalyst Development

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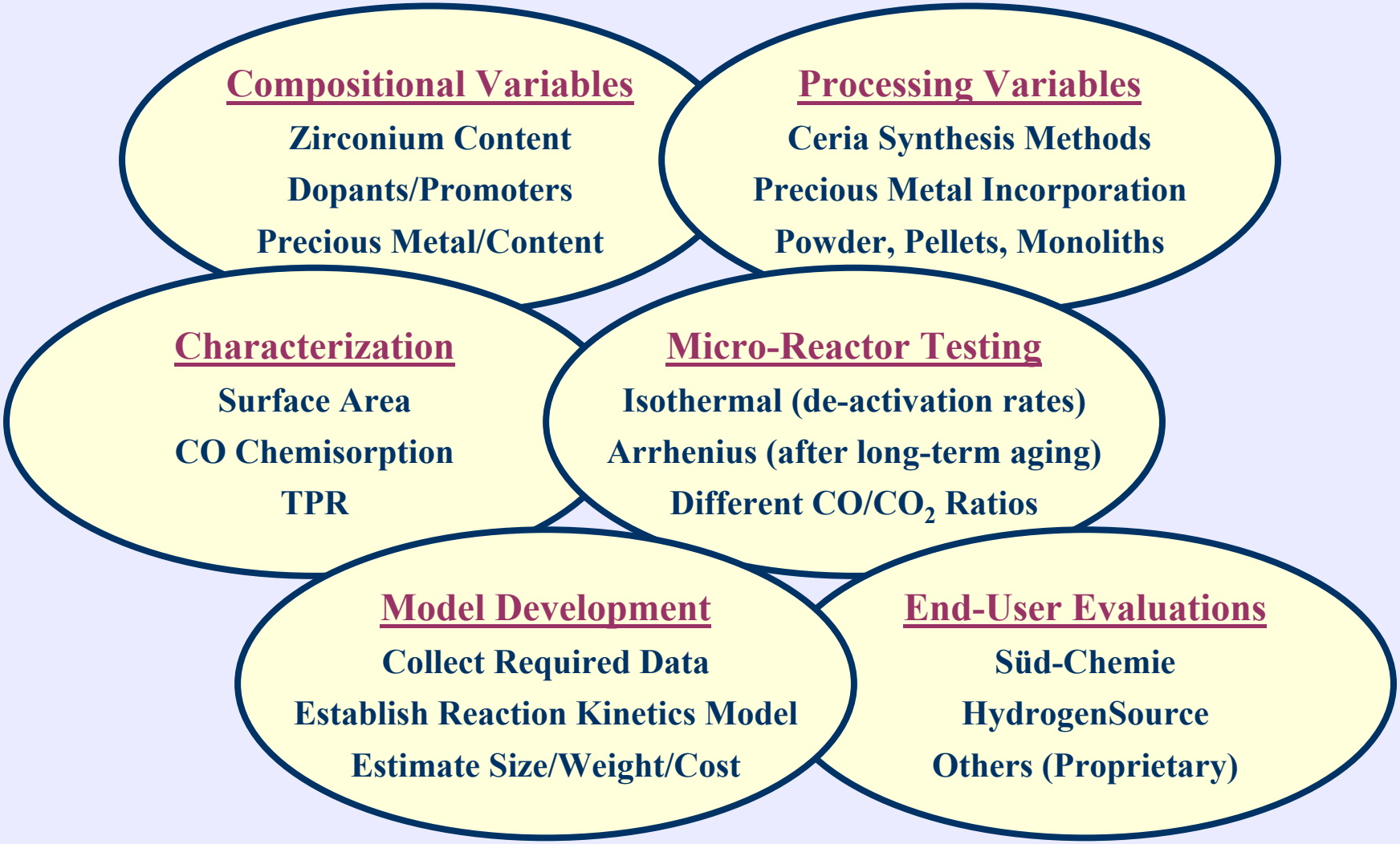

Technical Status

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- Active WGS formulations demonstrated.
- Formulations and processes modified to minimize de-activation rates.
- High performance demonstrated in washcoated monoliths.
- Established fundamental understanding of WGS kinetics for Pt/ceria catalyst system.
- Performance model confirmed that size, weight and cost targets are achievable.
- Catalyst samples (powder, pellets and monoliths) provided to numerous developers and end-users.

Micro-Reactor Testing

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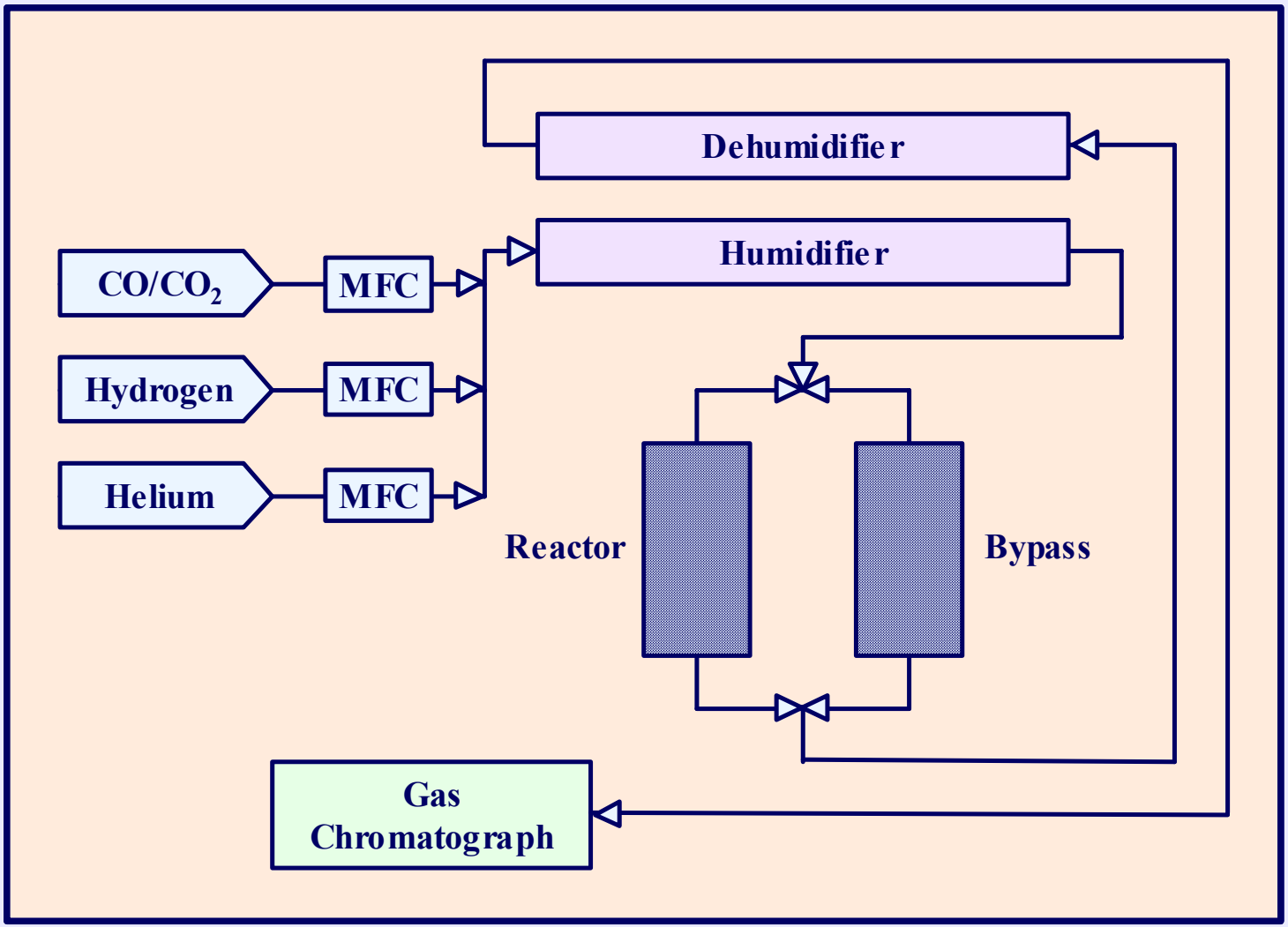

Micro-Reactor Testing

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- **Samples:**
  - Formulation (A): 2 wt% Pt
  - Formulation (B): 2 wt% Pt
  - Formulation (C): 1 wt% Pt
  - Commercial: C18-7 (Süd-Chemie)
- **Simulated Reformate:**
  - Gas Composition (1): $CO/CO_2 = 40/60$
  - Gas Composition (2): $CO/CO_2 = 20/80$

- **Gas Flows:**
  - He: 75 cc/min
  - H_2: 78 cc/min
  - $CO+CO_2$: 48 cc/min
  - H_2O: 65 cc/min
- **Test Conditions:**
  - Sample: 0.10 grams catalyst, diluted with Al_2O_3
  - Sample particle size: 35-80 mesh
  - Temperature: 240 to 360°C
  - Pressure: ~1 psig

Testing Results

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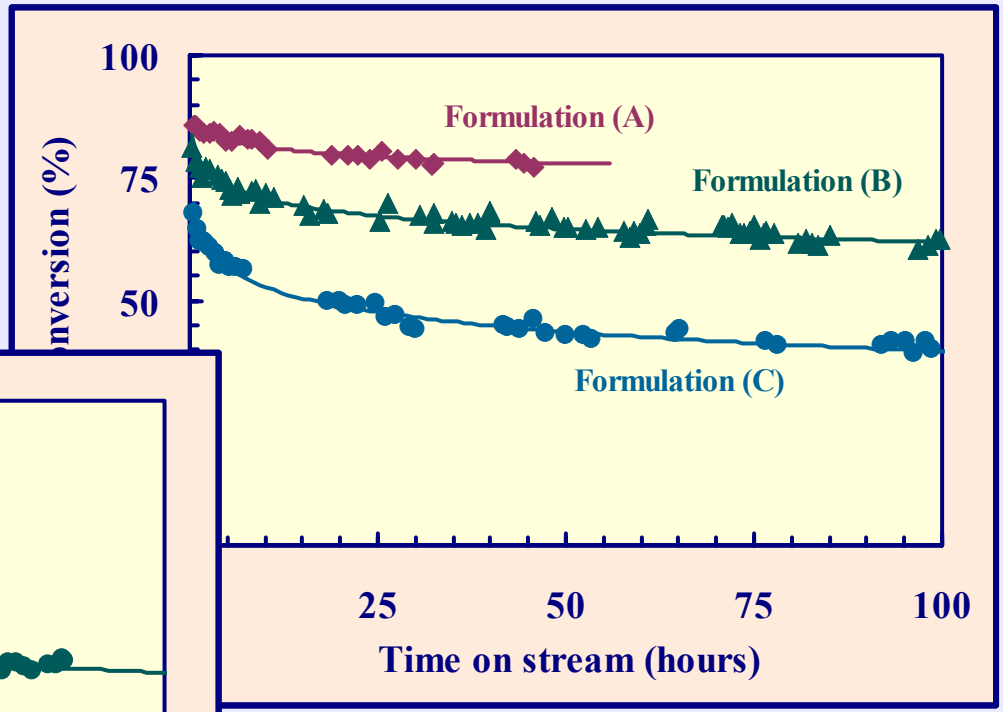
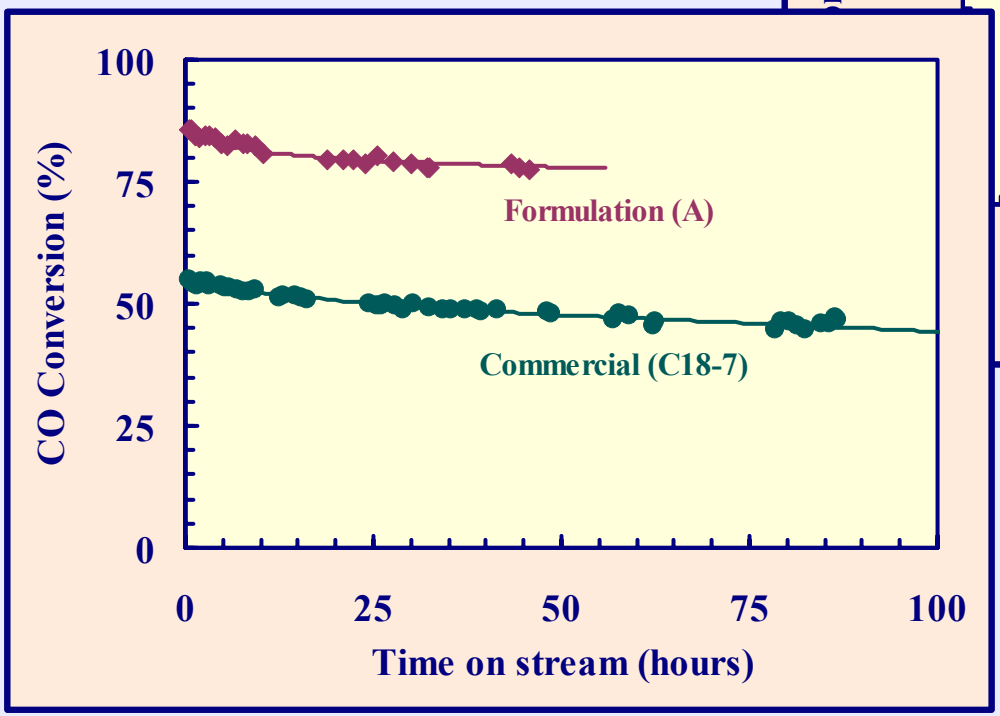
Test Conditions

- T = 300°C
- CO/CO_2 = 40/60
- SV ~ 160,000 cc/g-hr





Monolith Development

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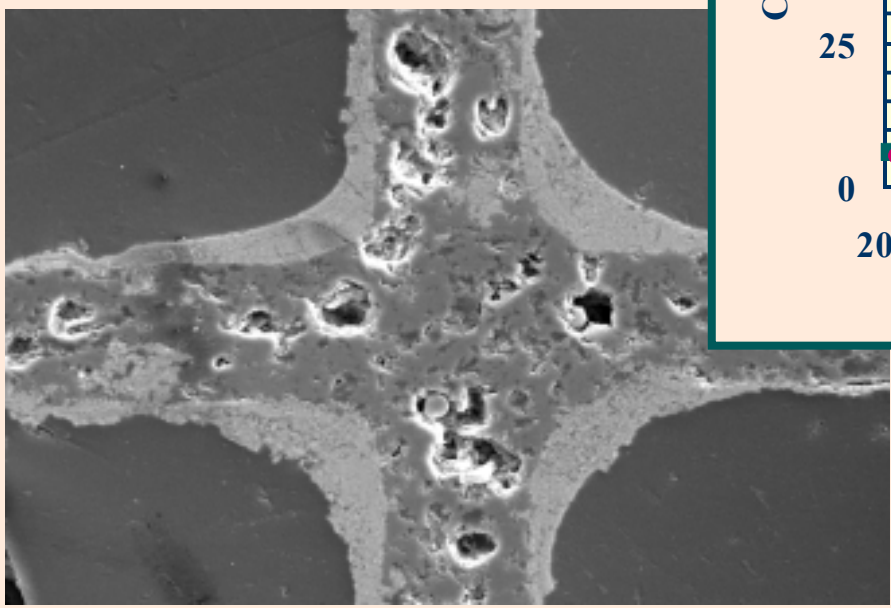
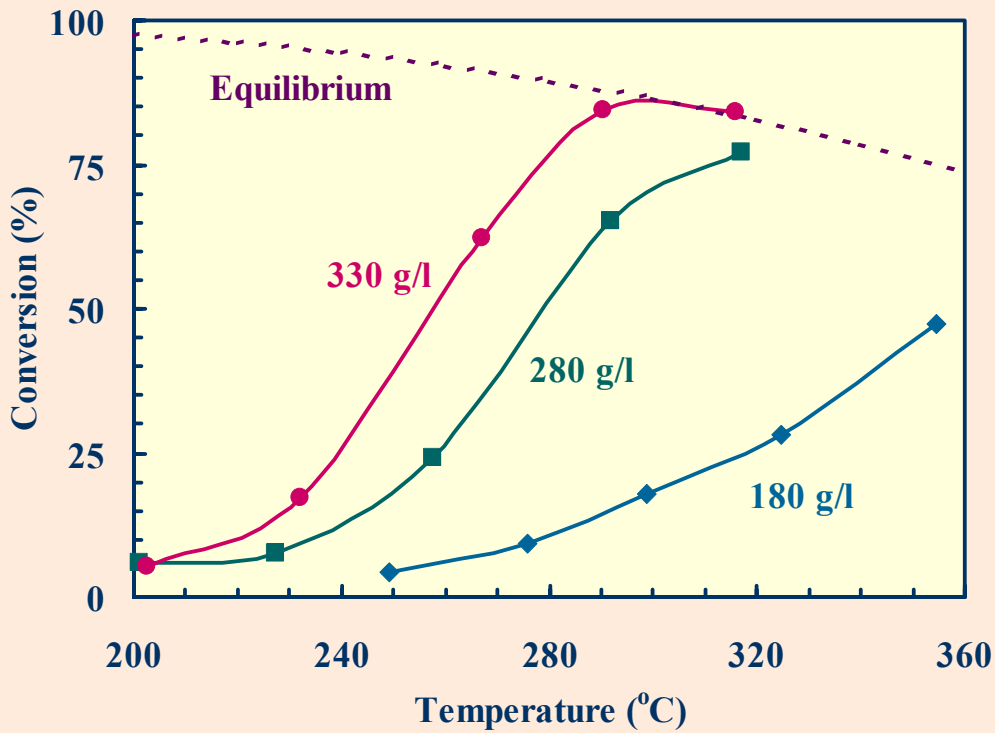
SCI Test Conditions

- CO: 7 mol%
- CO_2: 10 mol%
- H_2: 51 mol%
- H_2O: 30 mol%
- SV ~ 20,000 hr^{-1}





Performance Model

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Objectives of Modeling Effort

- Allow comparisons with different test conditions
- Allow realistic comparisons with other catalyst systems
- Predict size, weight and cost of monolith reactors

Modeling Approach

- Micro-reactor testing with application-specific gas feeds
- Establish kinetic model with accurate rate expression
- Obtain Arrhenius data, calculate reaction rate constants
- Calculate size/weight/cost for full-scale monoliths

Primary Assumptions

- Plug-flow reactor model
- Reaction rate orders based on best fit to data
- Single-stage shift reactor (isothermal)

Reaction Rate Expressions

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	Cu/ZnO	Pt/Ceria (*)
CO:	first order	zero order
H_2O:	first order	½ order
H_2:	inverse first order	inverse first order
CO_2:	inverse first order	inverse ½ order

(*) Gorte, et al, Applied Catalysis B215, 271-278 (2001)

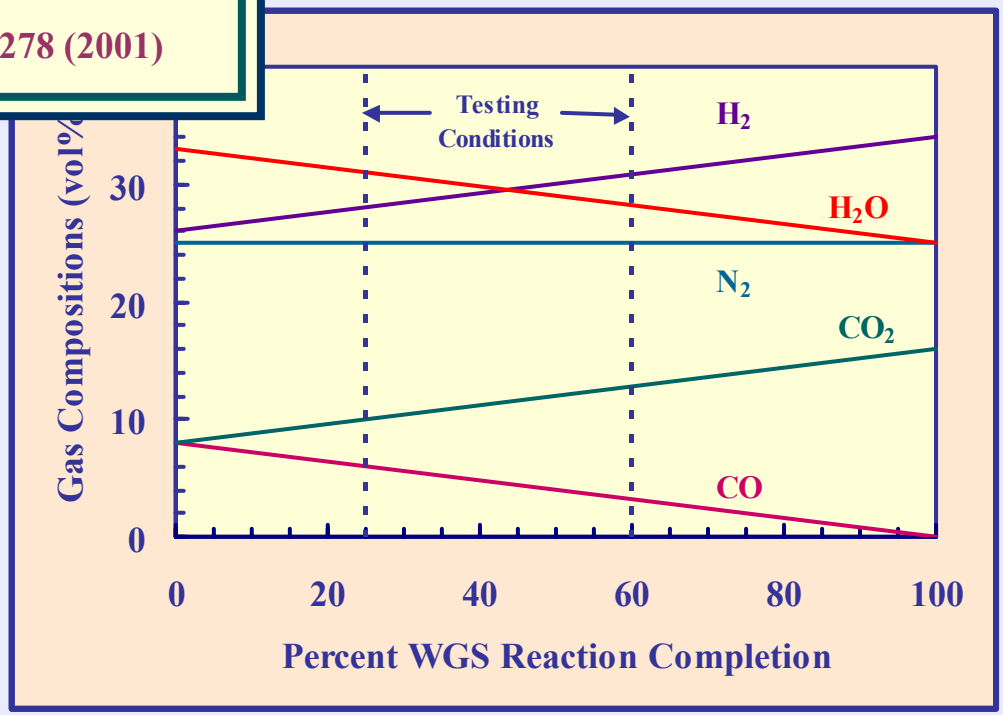
$$r_C = k \frac{(p_{CO})^a (p_{H2O})^b}{(p_{CO2})^c (p_{H2})^d}$$

Implications

Pt/ceria catalysts perform better with lower CO contents.

Testing should be conducted within range of expected gas compositions.

Reactor sizing models should be based on true rate expression.



Model Development

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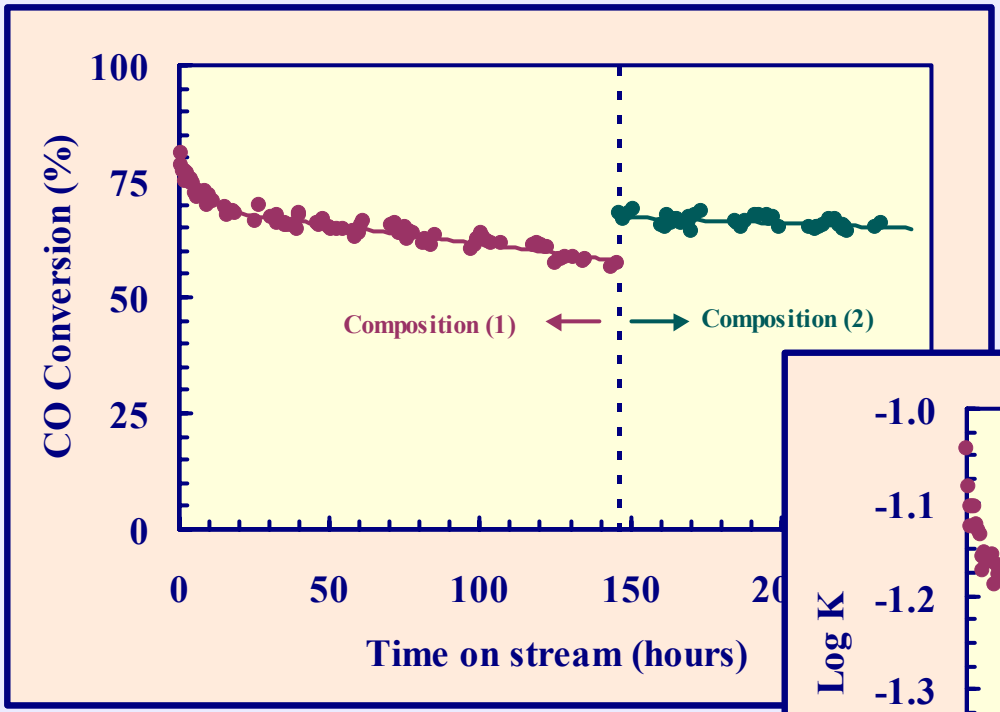
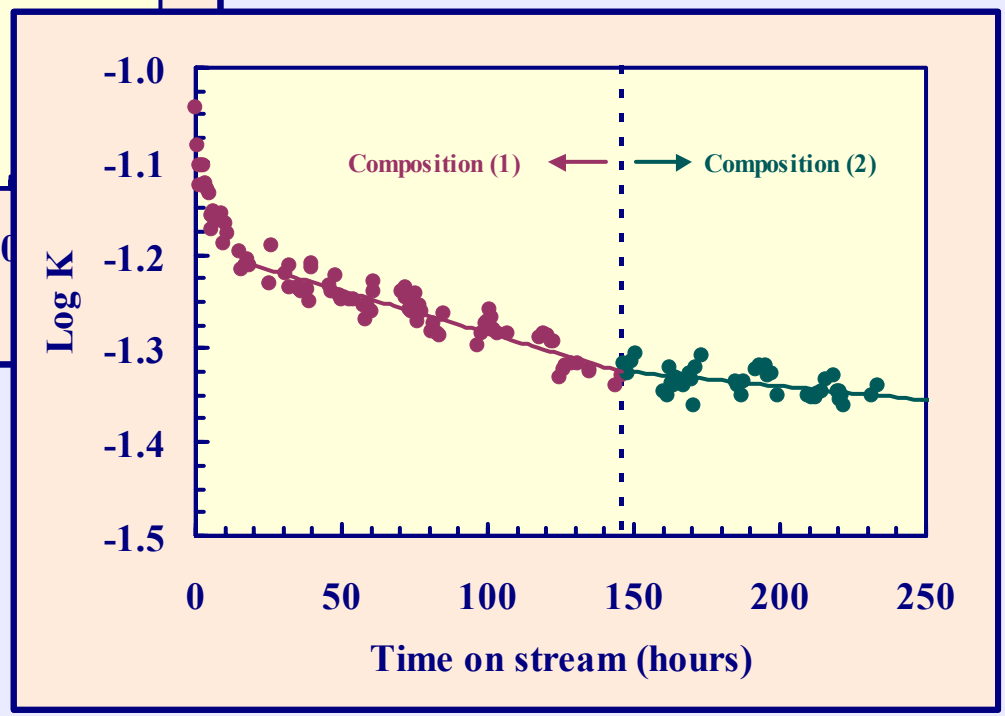


Rate Orders

- CO: +0.40
- CO_2: +0.50
- H_2: -0.94
- H_2O: +1.00



Formulation (B)
T = 300°C

Model Results

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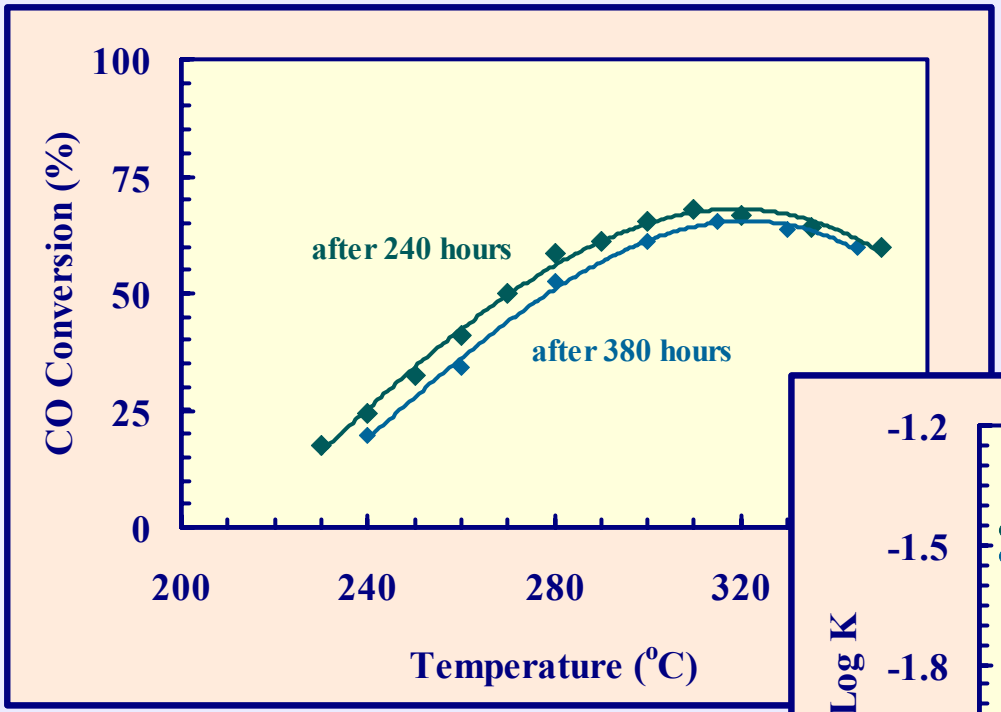

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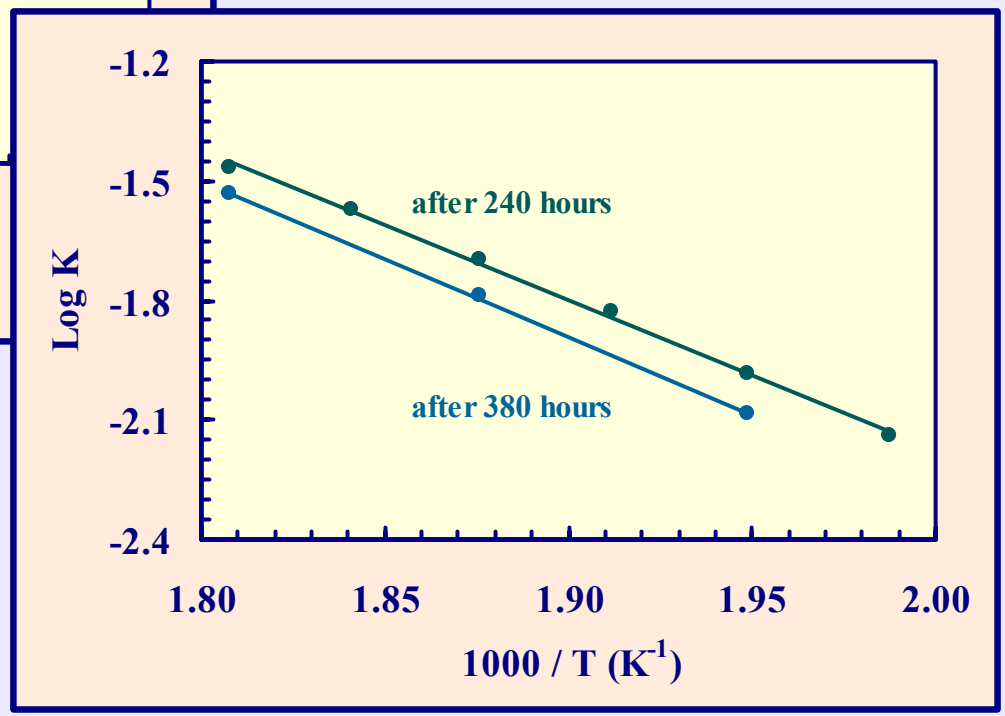

Formulation (B)
Composition (2)
after 240 hours

Model Results

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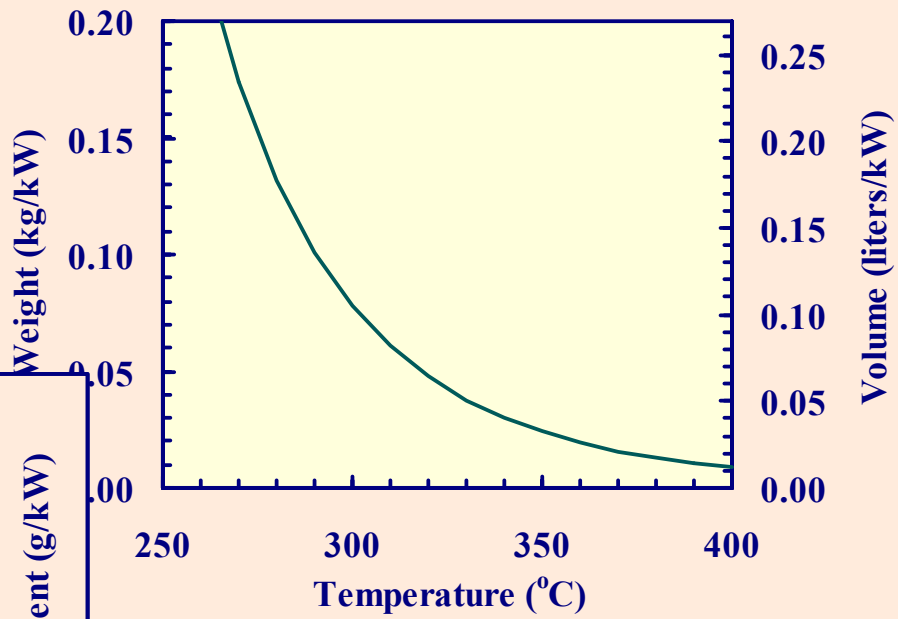
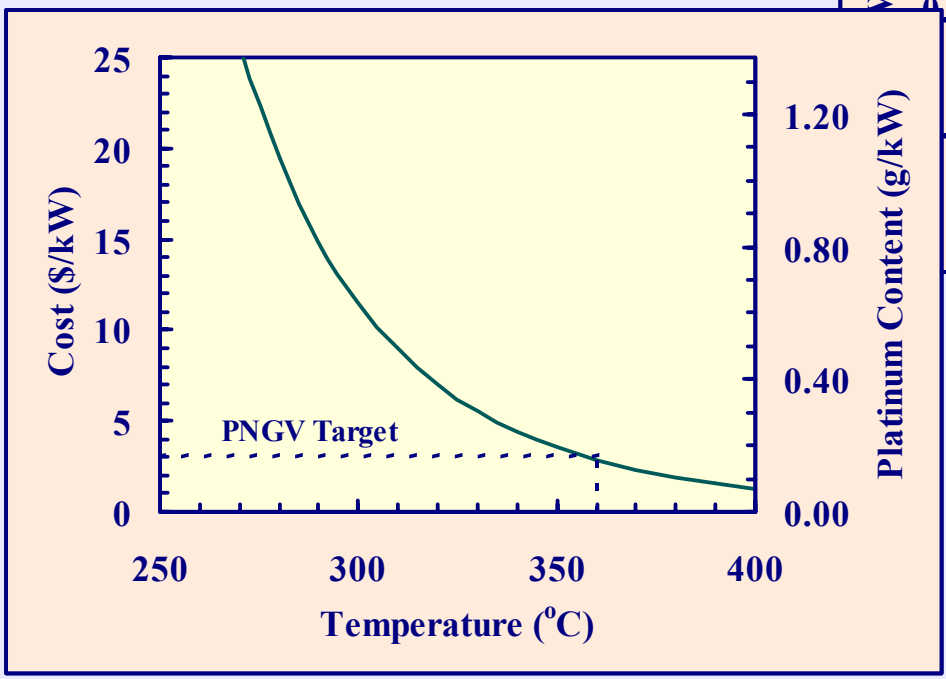
Simulated ATR Feed

- CO: 8 mol%
- CO_2: 8 mol%
- H_2: 26 mol%
- H_2O: 33 mol%
- N_2: 25 mol%





Formulation (B)
Composition (2)
after 240 hours

Note: Exit CO content at 360°C = 0.9%

Remarks from 2001 Review

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- Activity too low for application?
  - Our recent data suggests otherwise.
- Deactivation and long-term stability
  - Primary focus of work in past year.
  - Significant progress achieved (but not done yet).
- Need to address size, weight and cost
  - Developed kinetic model based on rate expressions.
  - Model suggests targets can be met.
- Monolith test results needed
  - Exciting results obtained.
  - Monolith samples being evaluated by end-users.
- Correlation between properties and performance?
  - We have to hold something back!

Future Work

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- **Formulation development**
  - Continued focus on addressing deactivation
  - Accelerated testing methodology
- **Size/weight/cost modeling**
  - Micro-reactor testing to refine rate order assumptions
  - Refine model (eliminate questionable assumptions)
  - Correlate micro-reactor data with monolith test results
- **Washcoating and testing of monoliths**
  - Continued process refinements, testing at Süd-Chemie
  - Scale up of washcoating process to larger monoliths
  - Evaluation in 10-kW reactor at HydrogenSource
- **Continued sampling to developers and end-users**

Acknowledgments

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Collaborators

University of Pennsylvania
Catalyte, LLC
Süd-Chemie, Inc.
HydrogenSource, LLC
McDermott Technology, Inc.

NexTech Co-Workers

Bill Dawson
Matt Seabaugh
Buddy McCormick
A-M Azad
Kevin Dalley

Funding

U.S. Department of Energy
EMTEC