Fuel Processors for PEM Fuel Cells

D. Assanis, W. Dahm, E. Gulari, H. Im, J. Ni,

K. Powell, P. Savage, J. Schwank,

L. Thompson, M. Wooldridge, and R. Yang

University of Michigan
College of Engineering

May 24, 2005

Project ID# FCP14

MichiganEngineering

Overview

Timeline

- Start: November, 2001
- End: December, 2005
- Percent Complete: 75%

Budget

- Total: $4,135,547
  - DOE: $3,250,924 (78.6%)
  - UM: $884,623 (21.4%)
- FY 04 Funding: $546,300
- FY05 Funding: $54,291

Partners

- Süd Chemie
- Osram Sylvania

Barriers

I. Fuel Processor Startup/Transient Operation
J. Durability
K. Emissions and Environmental Issues
L. Hydrogen Purification/CO Cleanup
M. Fuel Processor System Integration and Efficiency
N. Cost

MichiganEngineering

Fuel Processor (Fuel Cell) Technical Targets

Characteristics	Units	Current Status (2003)	Target for Year: 2005	2010
Energy efficiency	%	78	78	80
Power density	W/L	700	700	800
Specific power	W/kg	600	700	800
Cost	$/kWe	65	25	10
Cold startup time to max power @ -20 °C ambient temperature @ +20 °C ambient temperature	 min min	 TBD <10	 2.0 <1	 1.0 <0.5
Transient response (10% to 90% power)	sec	15	5	1
Emissions		<Tier 2 Bin 5	<Tier 2 Bin 5	<Tier 2 Bin 5
Durability	hours	2000	4000	5000
Survivability	°C	TBD	-30	-40
CO content in product stream Steady state Transient	 ppm ppm	 10 100	 10 100	 10 100
H_2S content in product stream	ppb	<200	<50	<10
NH_3 content in product stream	ppm	<10	<0.5	<0.1

MichiganEngineering

Objectives

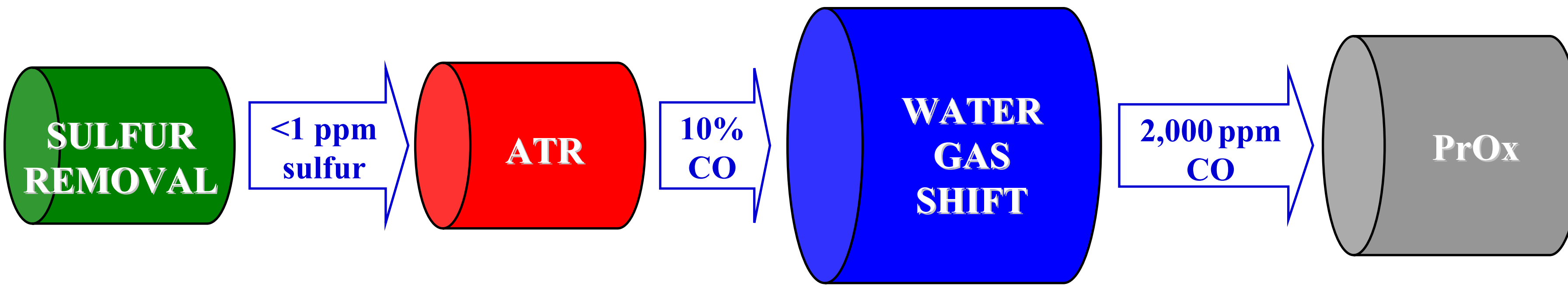
To demonstrate materials and reactors that enable low cost, high efficiency fuel processors.

- Develop high performance, low-cost materials
  - High capacity sulfur adsorbents for liquid fuels
  - High activity and durable catalysts
- Design and demonstrate microreactors employing high performance catalysts
- Design and demonstrate microvaporizer/combustor
- Design and demonstrate thermally integrated microsystem-based fuel processors
- Evaluate system cost

MichiganEngineering

Approach

Using a ***microsystems*** approach this project will produce highly ***integrated***, gasoline fuel processors that incorporate low-cost, ***high performance materials***.

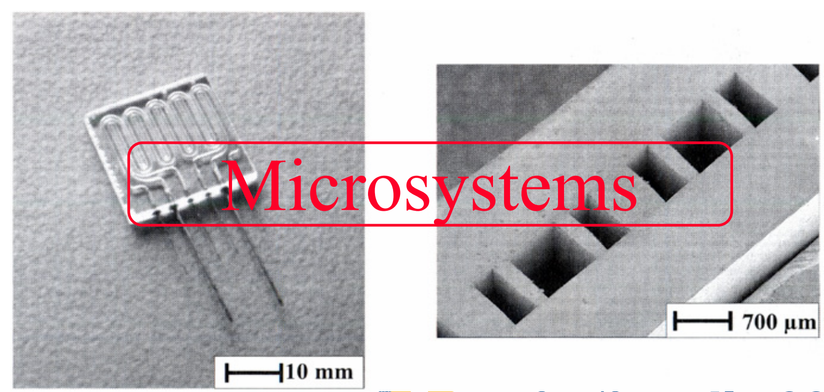


High Performance Materials

\+

High Degree of Integration

\+



If We Are Successful: 10 kW Fuel Processor

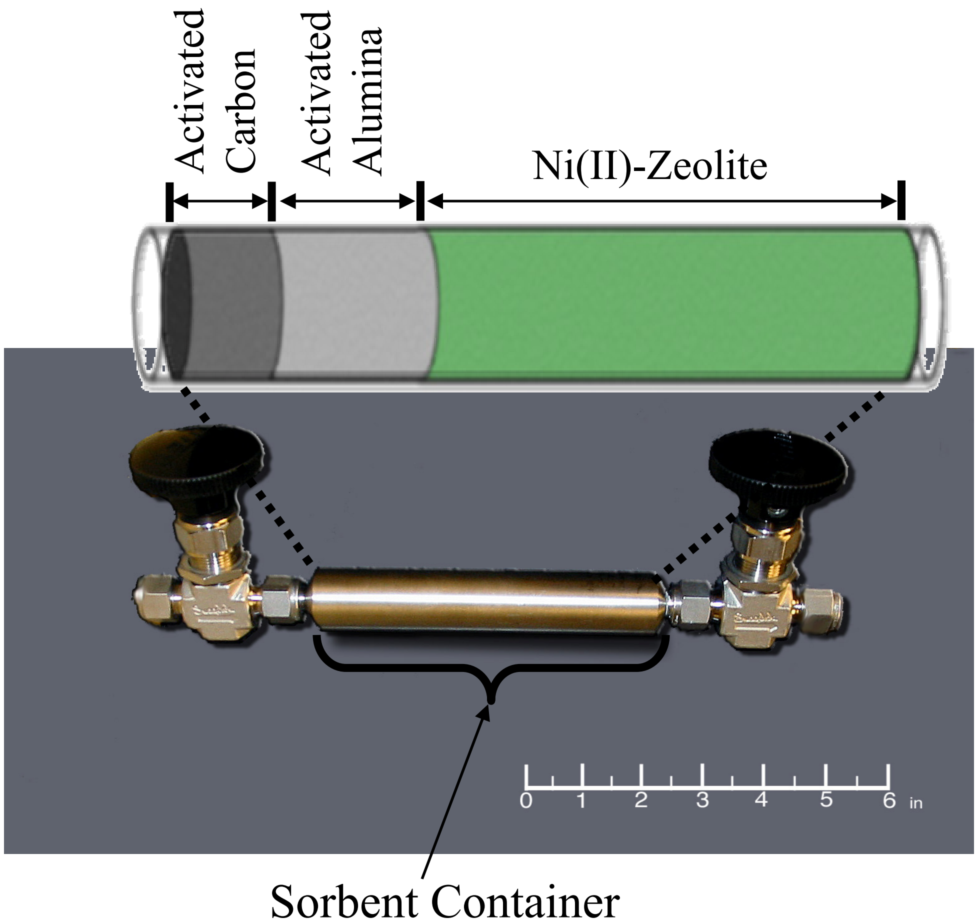
Component Weights (kg)	Current	Reduction Goal	Proposed Prototype	Comment
Fuel pump	0.45	50%	0.23	capillary action in microcombustor
Desulfurizer	2.42	35%	1.57	higher capacity liquid sorbents
Water tank	3.63	50%	1.81	better integration
Water pump	0.91	50%	0.45	capillary action in microcombustor
Fuel/water preheater	2.56	90%	0.26	microcombustor/microvaporizer
Reformer heat	4.40	90%	0.44	better thermal integration
Reformer	2.90	67%	0.96	better catalysts/microreactors
Shift reactors	11.88	67%	3.96	better catalysts/microreactors
Intercooler	2.27	90%	0.23	better thermal integration
Air compressor	0.60	0%	0.60	
Preferential oxidizer	3.30	67%	1.10	better catalysts/microreactors
Fuel cell air cooler	2.27	90%	0.23	better thermal integration
Fuel cell exhaust drier	0.23	50%	0.11	
Burner	3.40	50%	1.70	microcombustor/microvaporizer
Thermal insulation	0.91	50%	0.45	better thermal integration
Valves	0.28	0%	0.28	
Starter Battery	0.22	0%	0.22	
Instrumentation/controls	2.27	50%	1.13	novel strategies/sensors
Sub-total	44.9		15.74	
Component integration		10%	-1.57	
Total	44.9		14.17	Specific energy of 704 W/kg

MichiganEngineering

Technical Accomplishments

- Optimized high capacity, sulfur sorbents and developed regeneration protocols
- Enhanced activity and deactivation resistance of ATR catalysts
- Enhanced activity of WGS catalysts by an order of magnitude
- Enhanced selectivity and activity of PrOx catalyst
- Demonstrated high efficiency micro-combustor/vaporizer subsystem
- Demonstrated breadboard fuel processor system incorporating foam-supported catalysts

Sulfur Adsorber Prototype

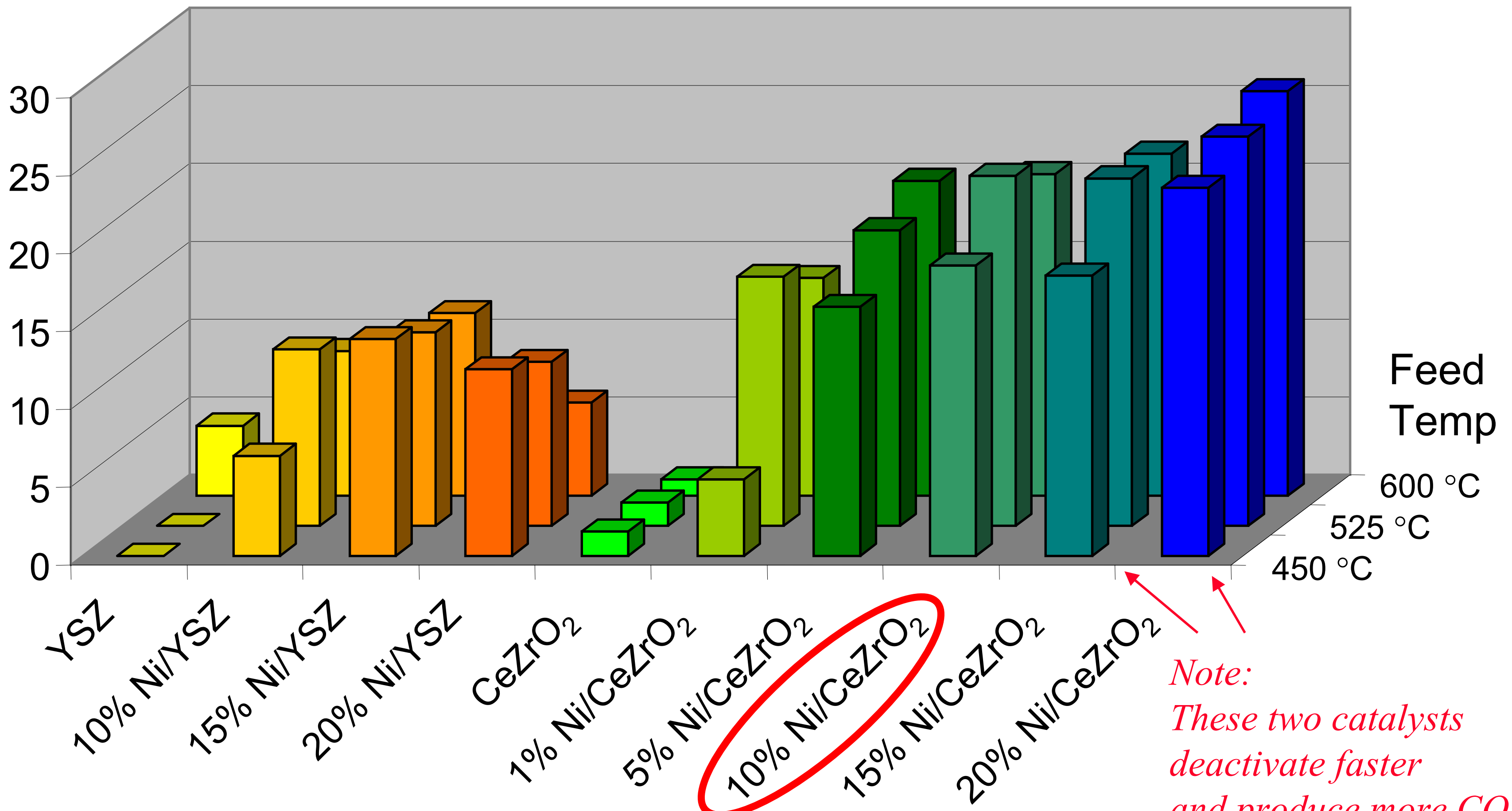


- Three Sorbent Layers
  - Activated Carbon (12.4 wt%)
  - Activated Alumina (23 wt%)
  - Ni(II)-Y (64.6 wt%)
- Gasoline Rate: 50 mL/hr
- Equivalent H_2 Output: 2.8 moles/hr (100 W_e)
- Effluent Concentration: ~ 0.3 ppmw sulfur
- Operation Cycle: 9-10 hrs

Yang et al., U.S. and foreign patents applied.

MichiganEngineering

High Performance ATR Catalysts

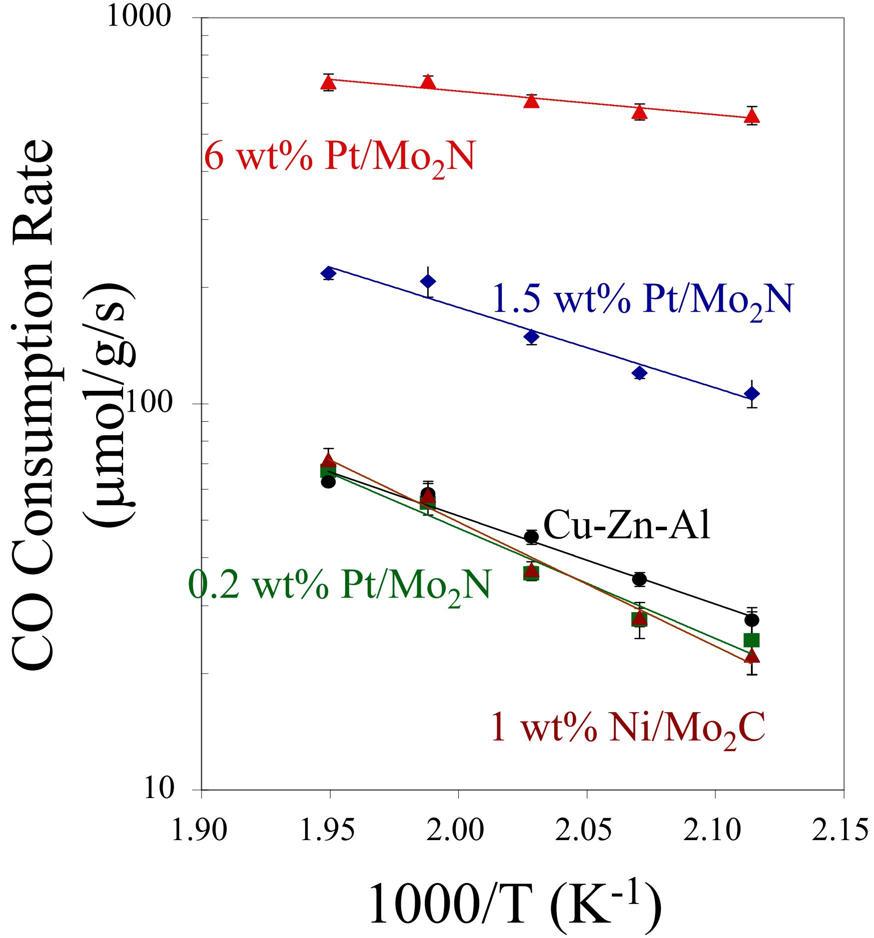


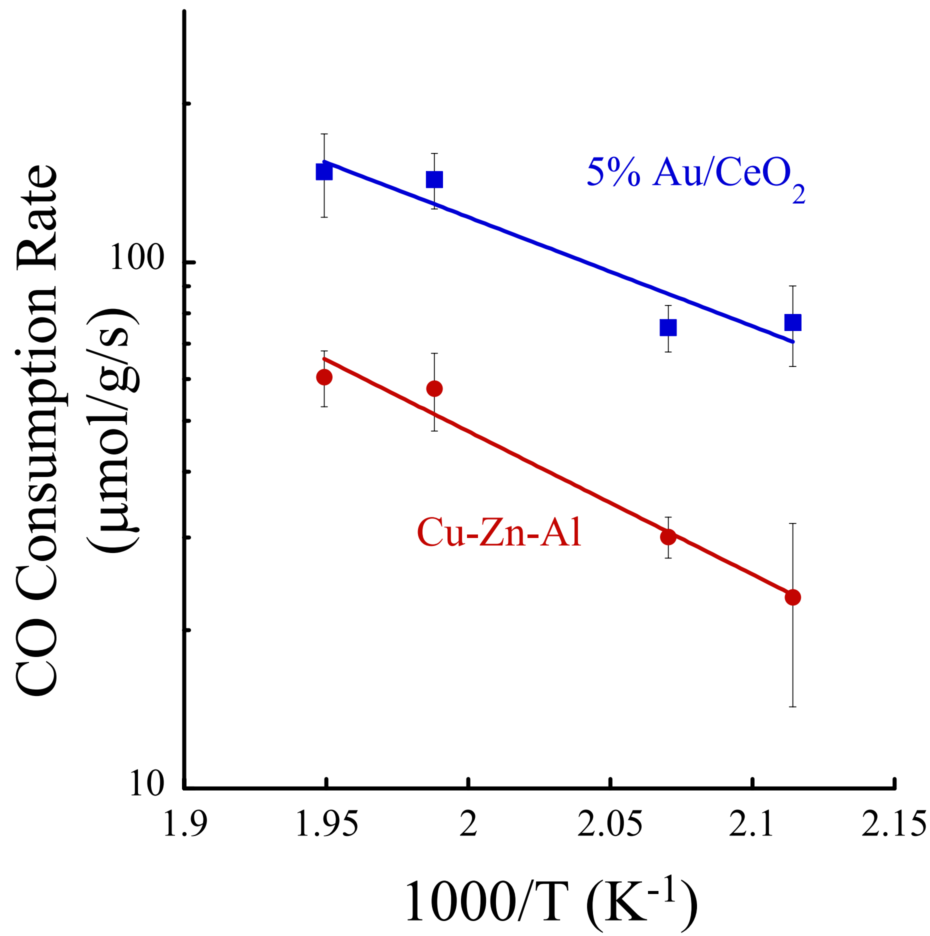
Experimental Conditions:

Packed Bed, $H_2O/C = 2$, $O/C = 1$, GHSV =250,000 hr^{-1}

"This presentation does not contain any proprietary or confidential information."

High Performance WGS Catalysts



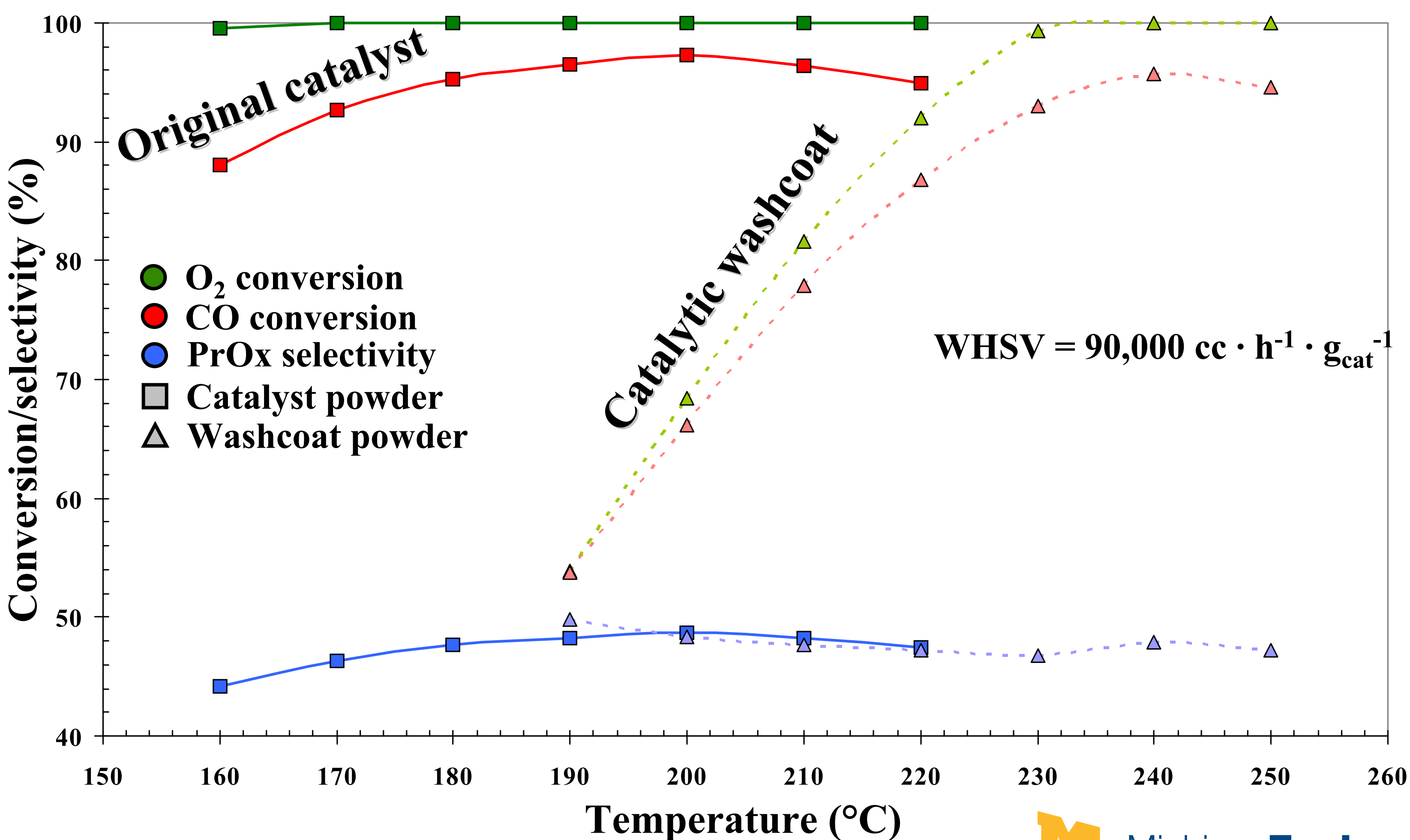


GHSV ~750,000 h^{-1}; CO-9%, H_2O-30%, CO_2-6%, H_2-39%, N_2-16%

"This presentation does not contain any proprietary or confidential information."

MichiganEngineering

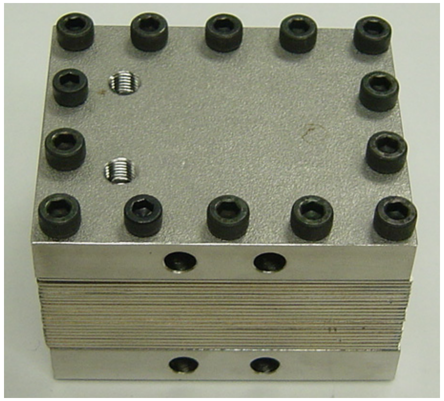
High Performance PrOx Catalysts



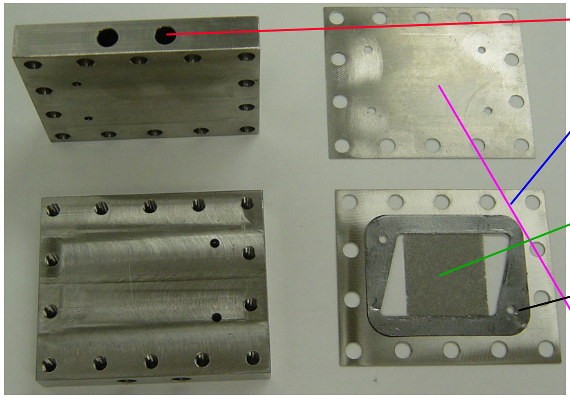
MichiganEngineering

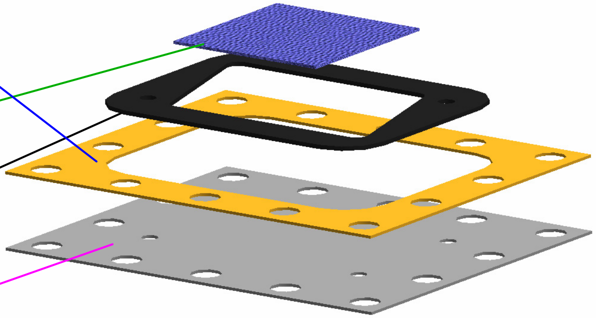
GEN2 Prototype Design

- ***Modular*** design enabled rapid integration of components
- Enhanced manufacturability achieved through ***layer-based*** design
- ***Flexible*** design for component and integrated system analysis



Assembled Module (25 stacks)
(77 X 64 X 54 mm)





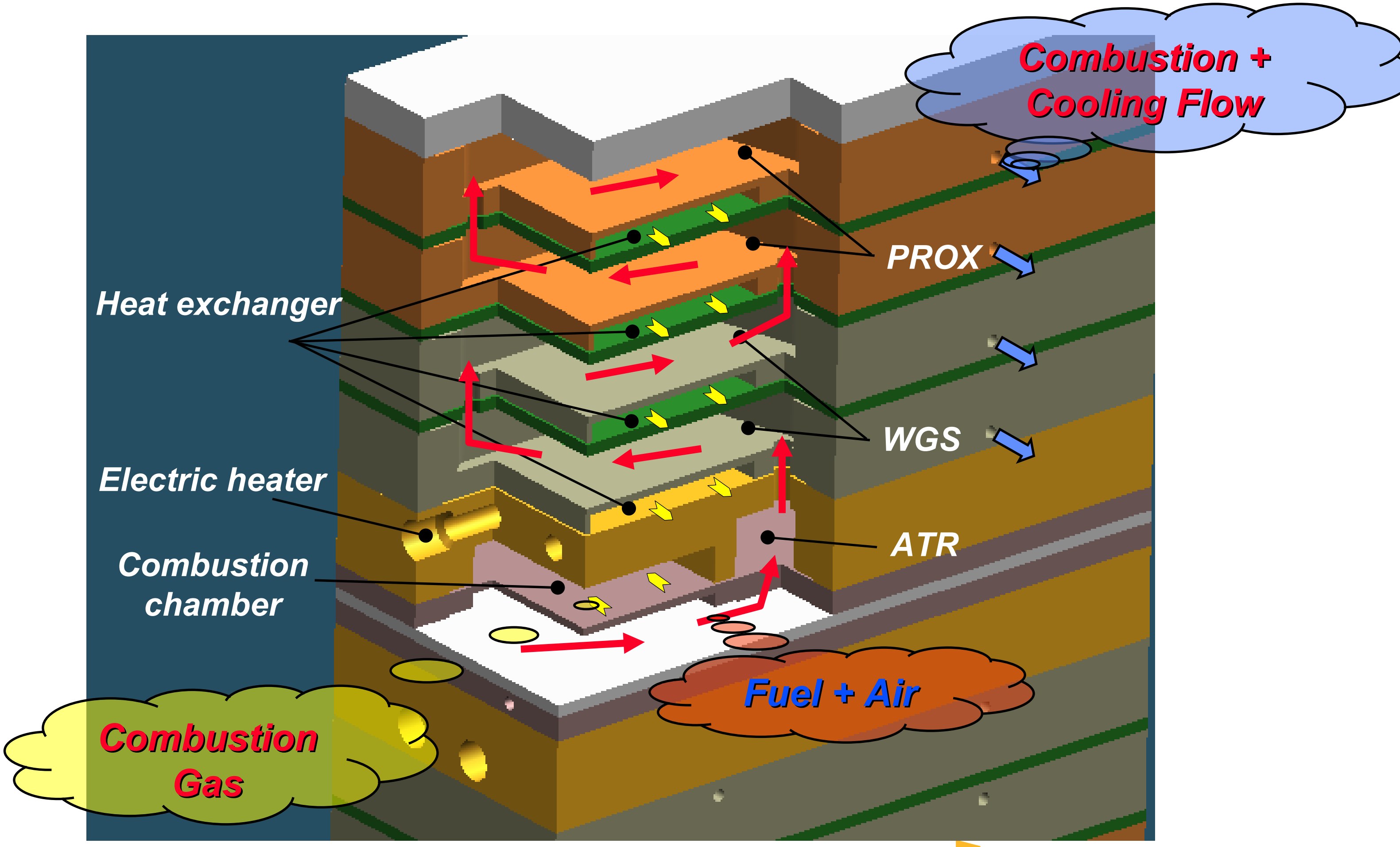
Fabricated Parts

Core Layers

MichiganEngineering

"This presentation does not contain any proprietary or confidential information."

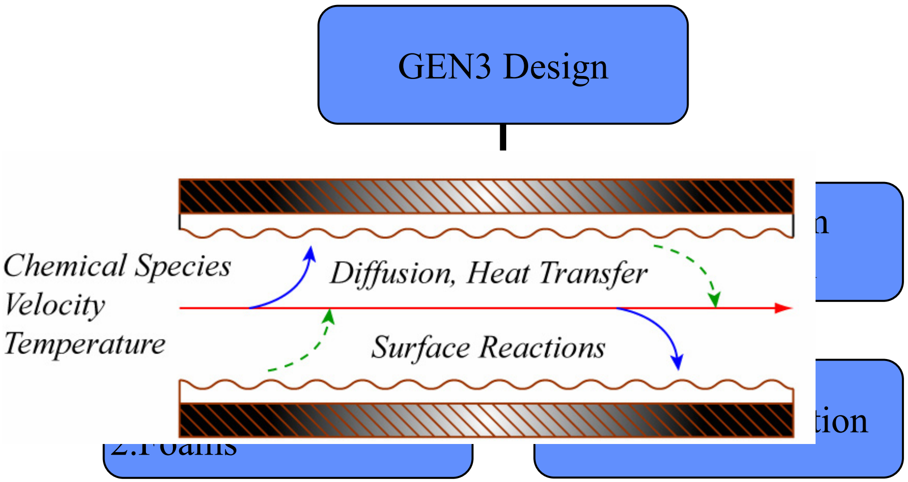
GEN3 Prototype Design

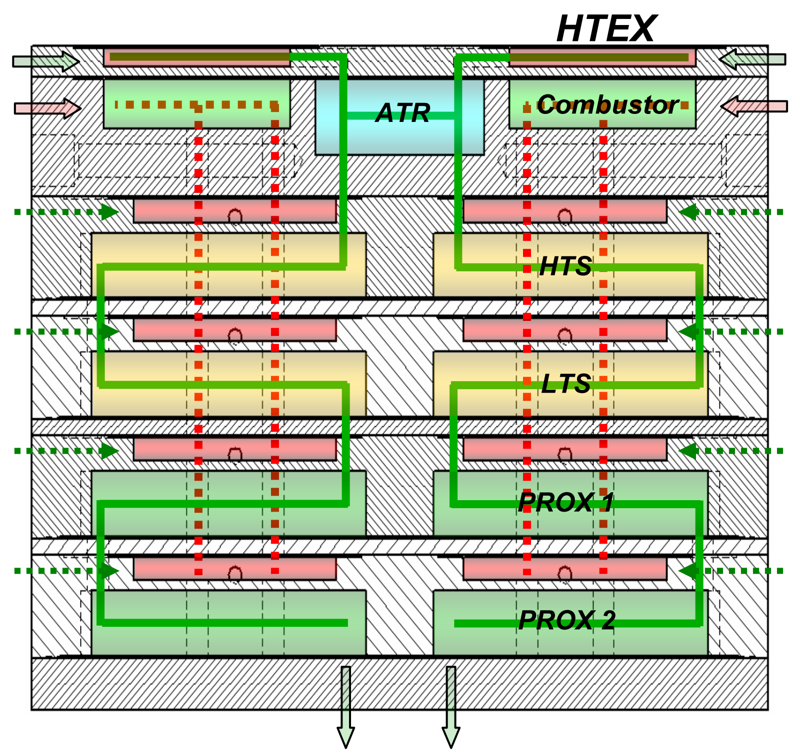


MichiganEngineering

"This presentation does not contain any proprietary or confidential information."

GEN3 Prototype Reactor Modeling

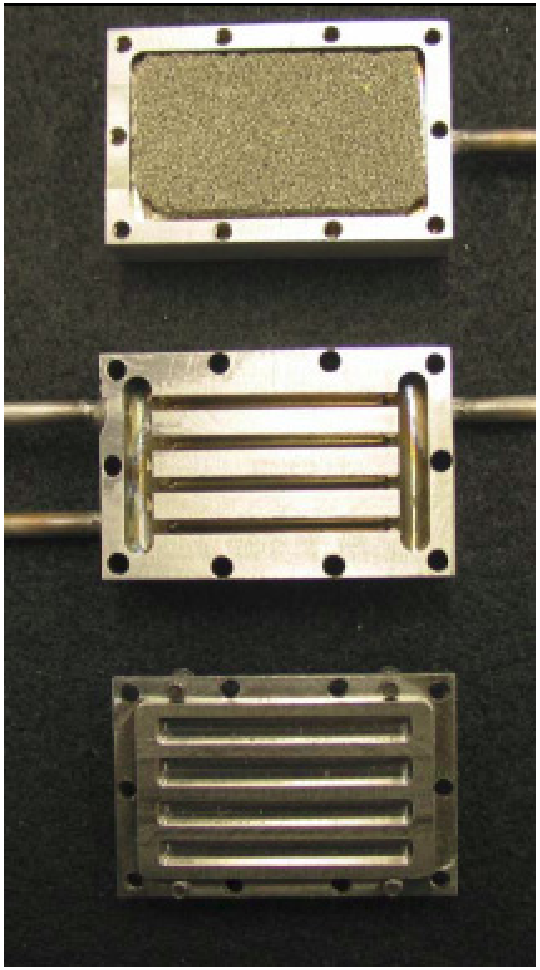




- High fidelity reactor model
- Incorporates heat and mass transfer effects
- Incorporates reaction rate expressions to predict temperature and concentration profiles

MichiganEngineering

Combustor/Vaporizer Prototype



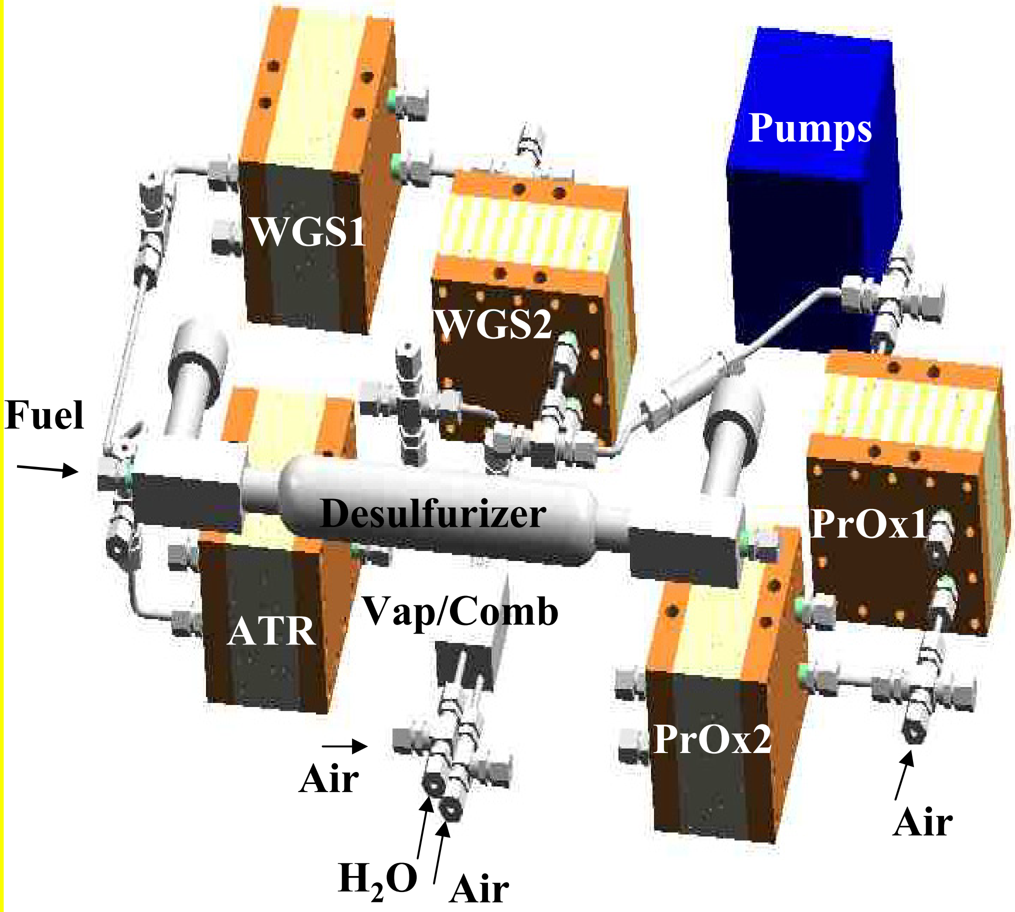
Combustor:

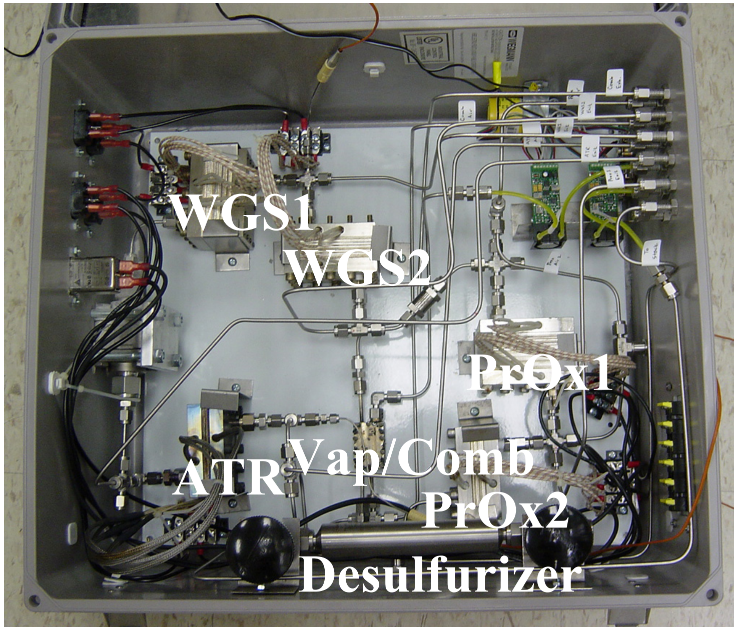
- Recuperative combustor
- Catalytic combustor

Vaporizer:

- Microchannel heat exchanger
- Microchannel flash vaporizer

System Development Approach Assembled Components

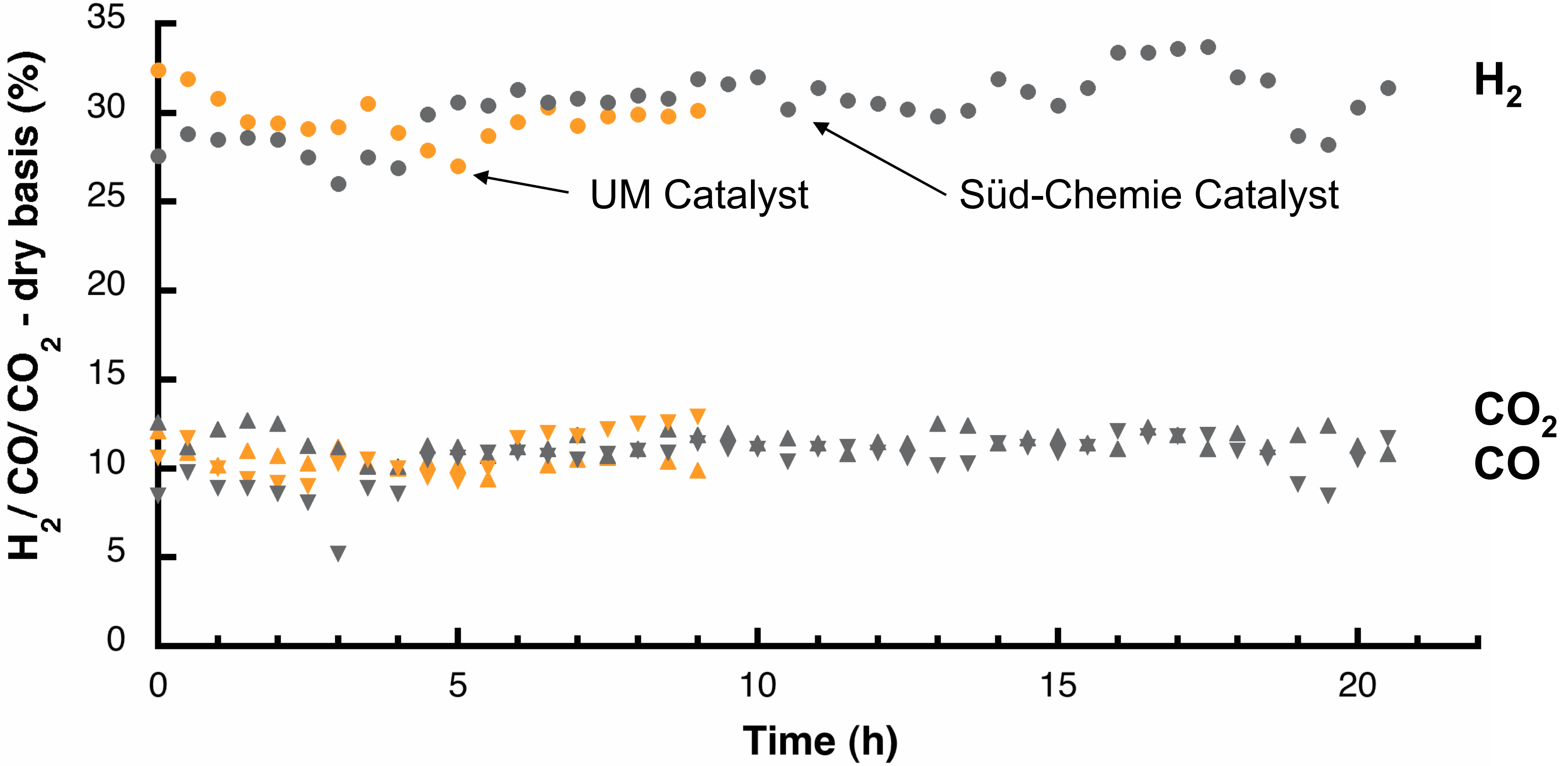




MichiganEngineering

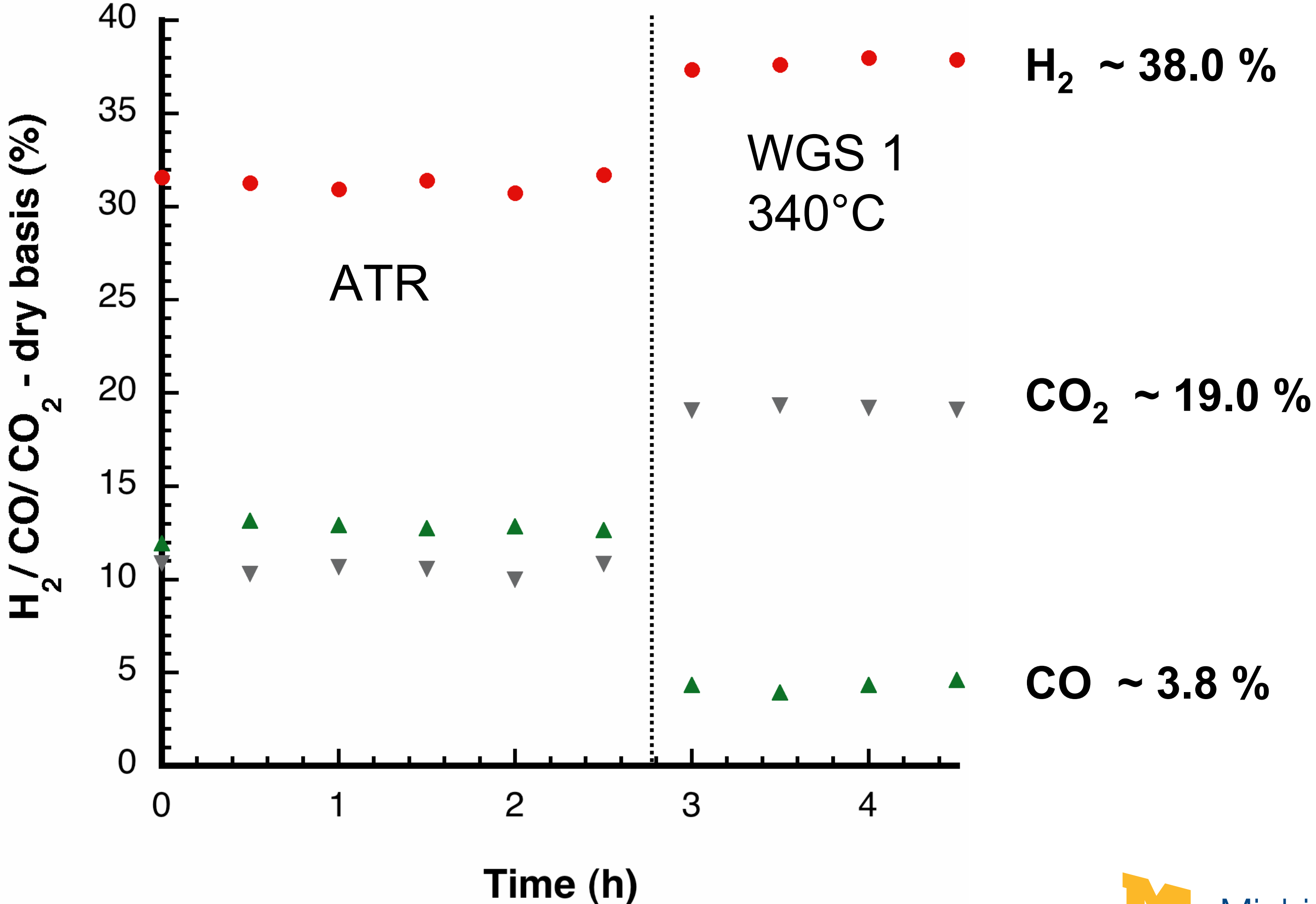
Assembled Components: ATR

Total Flowrate: ~ 2.0 *l/min* (dry basis)



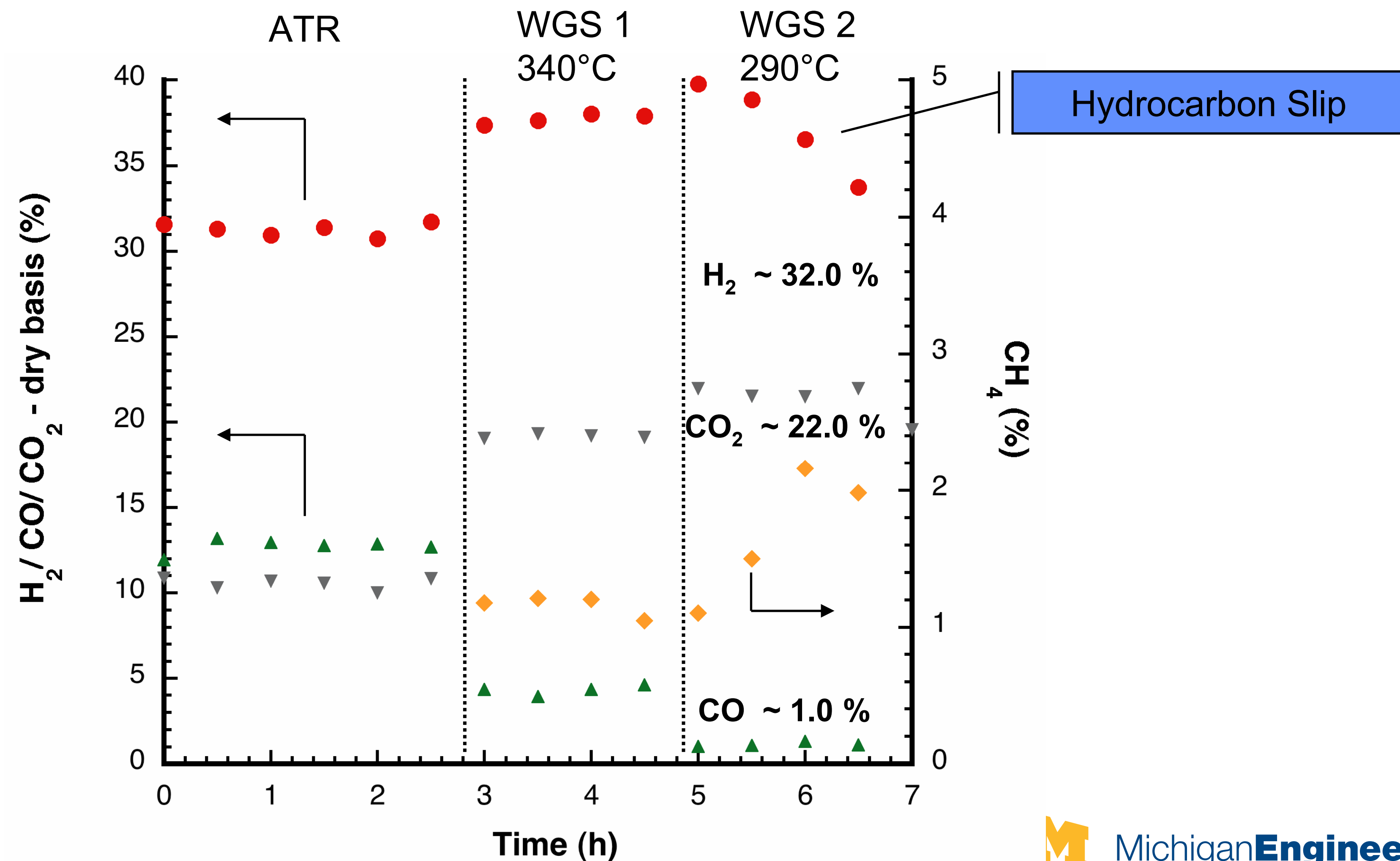
MichiganEngineering

Assembled Components: ATR - HTS



MichiganEngineering

Assembled Components: ATR - HTS - LTS

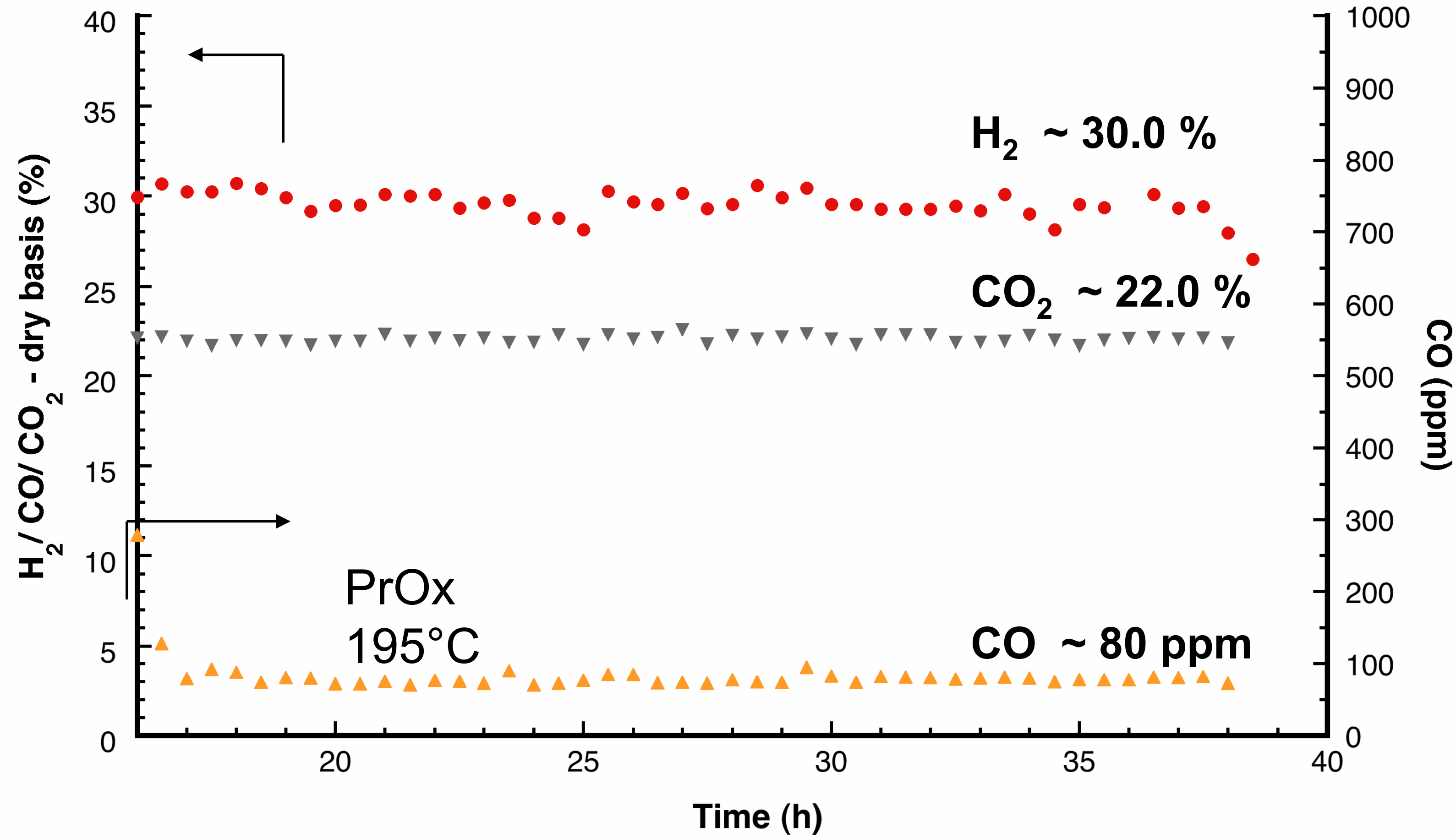


"This presentation does not contain any proprietary or confidential information."

MichiganEngineering

Assembled Components: ATR - WGS - PrOx

Total Flowrate: ~ 2.0 *l/min* (dry basis)



"This presentation does not contain any proprietary or confidential information."

Performance Summary

	ATR		WGS-1		WGS-2		PrOx	
	6 hr	40hr	6hr	40hr	6hr	40hr	6hr	40hr
H_2	30%	22%	38%	30%	40%	32%	38%	30%
CO	12%	12%	4%	4%	1%	1%	80 ppm	80 ppm
CO_2	11%	11%	19%	19%	22%	22%	22%	22%

- Total Flowrate: ~ 2.0 *l/min* ⟶ 0.76 *l/min* H_2 (0.6 *l/min*)
- 0.01 *l/sec* of $H_2 \approx$ 142W (107 W)
- H_2 Efficiency ($\eta_{thermal}$): 0.4 *ml/min* of C_8H_{18} = 209 W

  $\Delta H_{out}/\ \Delta H_{in}$ = 142 W/ 209 W = 0.68 (0.51)

MichiganEngineering

Responses to Previous Year Reviewers' Comments

- ✓ The objective of a low cost system is not yet met.
  - Cost projections are part of future work.
- Sound approach, but still need to address and demonstrate viable durability and weight, i.e. gravimetric power density.
  - Difficult to accomplish given funding modifications.
- ✓ Lacks systems integration. Could partner with a systems integrator.
  - Initiated integration; not able to engage integration partner due to cost.
- ✓ The lack of evidence that coking occurs in the ATR needs to verified under repeated start up and shut down cycles.
- ✓ If durability is not going to be directly addressed, then ensure projections are based on credible data, i.e. performance loss rate and material degradation measurements and mechanisms.

MichiganEngineering

Responses to Previous Year Reviewers' Comments

- ✓ The catalysts coating on the microchannels may negate the effects of rapid heat transfer.
  - Metal foam supports provide for high catalyst loading and heat transfer.
- ✓ Unclear how this system will design.
- Start up time and energy are not sufficiently addressed.
  - These are beyond the scope of the program.
- ✓ Focus on new materials and materials development.
- ✓ One reviewer suggests that you can't remove thiophenes with an absorbent,so, sulfur may still be there.
  - Detection limit for our analyzer is 0.02 ppmw S; have also published calibration and analysis.
- ✓ Needs better diagnostics and verification of data through models.
  - Additional diagnostics and modelling.

Future Work

- Remainder of FY05
  - Increase module power densities
    - Increase catalyst loading and utilization
    - Decrease parasitic weight (reactor and foam)
  - Evaluate performance of 200-500 W breadboard systems
  - Evaluate cost and final size
  - Estimate start-up time
  - Demonstrate integrated module
- FY 06
  - Assemble and evaluate 1 kW system

Publications and Presentations

Publications:

S. Srinivas, A. Dhingra, H. Im and Erdogan Gulari, "A Scalable Silicon Microreactor for Preferential CO Oxidation: Performance Comparison with a Tubular Packed-Bed Microreactor," Applied Catalysis A: General **116**, 150 (2004).

A, Luengnaruemitchai, S. Osuwan and E. Gulari. "Selective Catalytic Oxidation of CO in the Presence of H_2 Over Gold Catalyst," Int. J. Hydrogen Energy **29** (4), 429 (MAR 2004).

Y-W Lee and E. Gulari, "Selective NOx Reduction With H_2+CO Over a Pd/Alumina Catalyst," Catalysis Communications **5**, 499 (2004).

J.J. Christopher Brown and E. Gulari, "Hydrogen Production From Methanol Decomposition Over Pt/Al_2O_3 and Ceria Promoted Pt/Al_2O_3 Catalysts," Catalysis Communications **5**, 431 (2004).

A.J. Hernandez-Maldonado, F.H. Yang, G. Qi and R.T. Yang,"Desulfurization of Transportation Fuels by π-Complexation Sorbents: Cu(I)-,Ni(II)-, and Zn(II)- Zeolites," Appl. Catal. B. **56**, 111 (2005).

F.H. Yang, A.J. Hernandez-Maldonado and R.T. Yang, "Selective Adsorption of Organosulfur Compounds from Transportation Fuels by Π-Complexation," Separ. Sci. Tech. **39**, 1717 (2004).

A.J. Hernandez-Maldonado and R.T. Yang, "Desulfurization of Transportation Fuels by Adsorption," Catalysis Reviews – Sci. & Eng. **46**, 111 (2004).

C.H. Kim and L.T. Thompson, "Deactivation of Au/CeOx Water Gas Shift Catalysts," J. Catal. **230**, 66 (2005).

Publications and Presentations

Presentations:

E. Gulari, Y-W Lee, J. Cavataio, "NOx reduction with fuel processor gas," American Institute of Chemical Engineers Annual Meeting, Austin, TX, November 2004.

E. Gulari, O. Srivannavit, S. Ocharoen, S. Srinivas, X. Zhou, "Silicon/Glass Microreactors for Biosynthesis and Heterogeneous Catalysis," American Institute of Chemical Engineers Annual Meeting, Austin, TX, November 2004.

C.H. Kim and L.T. Thompson, "Surface Chemistry of Ceria-Supported Gold Water Gas Shift Catalysts," 7th Natural Gas Conversion Symposium, June 6-10, 2004.

J. Patt, S. Bej and L. Thompson,"Carbide- and Nitride-Based Fuel Processing Catalysts," 7th Natural Gas Conversion Symposium, June 6-10, 2004.

L. Thompson, "Microfabricated Fuel Cells and Novel Materials and Reactors for Hydrogen Production, "Shanghai Jo Tong University, Shanghai, China, June 24, 2004.

A. Wong-Foy and L. Thompson,"Novel Supports: Preparation of Group VI Carbide and Nitride Supported Nickel Catalysts," American Institute of Chemical Engineers Annual Meeting, Austin, TX, November 2004.

T.E. King, S.K. Bej and L.T. Thompson, "Water Gas Shift Mechanism for Carbide Supported Catalysts," American Institute of Chemical Engineers Annual Meeting, Austin, TX, November 2004.

L. Thompson,"Nanomaterials for Hydrogen Production," Northwestern University, December 2, 2004.

L. Thompson,"Materials for Hydrogen Production," Georgia Institute of Technology (Materials Science and Engineering Department), January 28, 2005.

L. Thompson,"Carbide- and Nitride-Based Catalysts," ExxonMobil Corp., Baytown, TX, February 24, 2005.

L. Thompson,"Catalytic and Surface Properties of Carbides and Nitrides," Southwestern Catalysis Society Meeting, Houston, TX, February 25, 2005.

Hydrogen Safety

Most significant hydrogen hazard associated with this project is:

Ignition of hydrogen in the exhaust from fuel processors. Ignition could cause fire, injuries to personnel and destruction of facilities.

MichiganEngineering

Hydrogen Safety

Our approach to deal with this hazard:

- *All hydrogen gas cylinders are equipped with flame arresters.*
- *All exhaust is vented into fume hoods.*
- *All heating elements are located away from potential hydrogen sources.*
- *Doors on fume hoods are always secured during the experiments.*

MichiganEngineering