Microchemical Systems: New Solutions to Chemical Engineering Problems Through Miniaturization

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Outline

• Introduction to NJCMCS
• Definition of MCS
• Advantages of MCS
• Major application areas
  – Miniaturization and Intensification
• Examples
  – Extended: Fuel processing for portable power (CPM)
  – Brief: Catalytic hydrogenation for pharaceuticals (CPI)
Stevens Institute of Technology

- Private University founded in 1871
- The Stevens family: First Urban Ferry Business in New York Harbor
- 1700 undergraduates, 2800 graduates
- Engineering, Science, Technology Management
- Incoming Freshman GPA: 3.8 and SAT 25%-75%: 1200-1400
New Jersey Center for MicroChemical Systems (NJCMCS)

- Official start in September 2002
  - $7.5M commitments to date
  - $10.0M pending for state-wide infrastructure
  - $34M financial goal from 2005 to 2009

- Vision
  - Leadership for rational microchemical device/system design methodology and tools development

- Systems-level concept demo with our key partners
  - Army-Picatinny, Bristol-Myers Squibb, FMC, and Lucent-Bell Labs
  - Portable power, pharmaceutical, and chemical applications
NJCMCS People

• Besser Group

• Lawal Group
  – Dr. R. Halder, Dr. D. Qian, J. Adeosun, S. Tadepalli, Y. Voloshin

• Lee Group

• Affiliated Faculty

• Consultants
  – Dr. A. Kaufman, Dr. J. Manganaro, F. Shinneman, M. Urken

• Center Administration
  – Prof. Lee (Director) and Prof. Besser and Prof. Lawal (Co-directors)
  – Aqsa Quresh and Pat Downes

Main contributors to the contents of this seminar.
Microchemical Systems

Miniature reaction and other unit operations, possessing *specific advantages* over conventional chemical systems
Microreactors—What Are They?

- “Microreactor” traditionally means lab bench reactor
- Dimensions 1/10 bench reactors

(Forschungszentrum Karlsruhe GmbH)

(Ehrfeld, et.al., IMM)

(Besser, et.al., IfM)

(Jensen, et.al., MIT)
Benefits of Miniaturization—Why?

• Surface to Volume Ratio
• Low Inventory ("Hold Up")
• Low Transport Resistances
• Robust Materials
• Cost
Benefits: Surface to Volume

- Surface Area (SA) Increasing → Volume (V) Constant

Heat Management
Surface Reaction
Explosion-Safe
Benefits: Low-Inventory (Hold-Up)

Schematic of As$^+$ Ion Implanter

Phosgene Reactor, Geismar, LA

- Safety
- Environment
Benefits: Low Transport Resistances

Overall Heat Transfer Coefficient

<table>
<thead>
<tr>
<th>Hx Type</th>
<th>U (W/m²K)</th>
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<tbody>
<tr>
<td>Tubular</td>
<td>150-1200</td>
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<tr>
<td>Spiral</td>
<td>700-2500</td>
</tr>
<tr>
<td>Plate</td>
<td>1000-4000</td>
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</table>

Microchannel: 3800-6800 W/(m²K)
Benefits: Robust Materials

• High strength, high melting point materials:
  – Metals
  – Ceramics
  – Silicon

• Array of fabrication processes (MEMS technology)

• Non-traditional reactor materials
  – Polymers
Benefits: Cost

- Reactor Fabrication
  - High volume batch
    - Si integrated circuit fabrication model
    - Metal/ceramic micromachining techniques
    - Interface of reactor to plant (?)

- Scale-Up Process
  - Linear process
  - Characterize unit module; scale up throughput by addition of modules
Major Application Directions

**Chemical Process Miniaturization**
- Same functionality per volume as macro
- Miniature size is distinguishing factor
- Portability may be important

**Chemical Process Intensification**
- Higher functionality density than macro
- Size reduction is not paramount
- May involve access to new chemistry routes
- Generally leverages transport advantage
Fuel Cells: Applications & Power Ranges

Power (Watts)

Ship Service Fuel Cell

Taken from Robert Nowak, DARPA
Can We Use Microchemical Systems for Portable Power?

• MCS: Superior heat and mass transfer
  – Thermal management, excellent mixing

• MCS: Compactness
  – Energy density:
    • Advanced Li-MnO₂ battery: 169 W-h/kg
    • MeOH: 6000 W-h/kg
Model Study: Preferential Oxidation ("PrOx")

CO poisons PEM fuel cell catalysts
CO must be reduced below 10 ppm for viability
CO Poisons FC Catalyst

Goals of the Project

• Construct strong support infrastructure for MCS understanding and design

• Apply this infrastructure to understanding PrOx for portable fuel cells

• Demonstrate a PrOx reactor for a 1-$W_e$ fuel processing system
PrOx Design Challenges

**Design Criteria**
- 150-200° C and ~1 atm
- Minimum volume, \( \Delta P \)
- Conversion, selectivity, stability.

**Air** @ 2 \( \mu \text{mole/s} \)

**Reformate** @ 20 \( \mu \text{mole/s} \)
- CO: 1.7%
- \( \text{H}_2 \): 68.5%
- \( \text{H}_2\text{O} \): 8.1%
- CO\(_2\): 21.7%
- CH\(_3\)OH: 27 ppm

**Treatment** Reformate
- CO: 9 ppm
- Low \( \text{H}_2 \) conversion

\[ CO + \frac{1}{2} O_2 \rightarrow CO_2 \]
Approach

Experiment

- Thin-Film Catalyst Synthesis w/ Nanoscale Control (Chen)
- Microreactor Design/Fab. for Microkinetic Studies (Shin)
- Microarray Instrumentation for Parallel Evaluation (Ouyang)

Synthesis

- Kinetic Model w/ CHEMKIN (Ho)
- Mechanism Development (Bednarova)
- Transport Model w/ Fluent (Qian)

Comprehensive Reactor Design

Simulation

STEVENS Institute of Technology
Microreactor Fabrication

- Photo-patterning process
- High-rate silicon dry etching (DRIE)
- Anodic bonded Pyrex cover
- Batch processing
- 8-in. Si wafers, Bell Labs
Thin-Film Wall Catalyst: Why?

- Low pressure drop compared to packed bed
- Less clogging
- Better mass transport than packed bed or washcoat
Catalyst Infiltration

Open Channel

Closed Channel

Pyrex®

Closed Channel Infiltrated
Microreactors Fabricated for PrOx Research Project

8-in. Si wafer, Bell Labs

Long-channel reactor

Short-channel reactor

Short-channel reactor under test
Relevant Reaction Characterization: How?

Silicon Microkinetic Array Approaches

- No independent reaction control
- Individual channels
- Highly integrated array
- No detailed reaction info
- Micropipette array
- Complex fabrication
- Single substrate
- Cross contamination

Jensen, et al., MIT, 2001
Symyx®, 1999
Ryu, et al., UIUC, 2001

Ouyang, et al., 2000

Individual microreactors
Independent reaction control
Fast sample loading and unloading
No cross-contamination
Process relevant reaction info

Inert Carrier Gas
8-Port 2-Position Valve
10 GCMS
To Exhaust
14-Port Manifold
16-Port 16-Position Multiposition Valve
Mass Flow Controllers for Reactants
Cooling Water Channels
Pressure Controllers
Pressure Gauges
Micoreactor on Interface Block
Reactants
Micro-Kinetic Test Bed

Microkinetic array
Four reactors in parallel
Independent reaction parameters
Shared analytical

Test reactor found to mitigate CO in 0.25 $W_e$ flow with $\approx 1$mg catalyst
CHEMKIN Simulation: Surface Reactions

1. $\text{H}_2 + \text{Pt}(s) + \text{Pt}(s) \rightarrow \text{H}(s) + \text{H}(s)$
2. $\text{O}_2 + \text{Pt}(s) + \text{Pt}(s) \rightarrow \text{O}(s) + \text{O}(s)$
3. $\text{H}_2\text{O} + \text{Pt}(s) \rightarrow \text{H}_2\text{O}(s)$
4. $\text{CO}_2 + \text{Pt}(s) \rightarrow \text{CO}_2(s)$
5. $\text{CO} + \text{Pt}(s) \rightarrow \text{CO}(s)$
6. $\text{CO}(s) \rightarrow \text{CO} + \text{Pt}(s)$
7. $\text{CO}_2(s) \rightarrow \text{CO}_2 + \text{Pt}(s)$
8. $\text{C}(s) + \text{O}(s) \rightarrow \text{CO}(s) + \text{Pt}(s)$
9. $\text{CO}(s) + \text{Pt}(s) \rightarrow \text{C}(s) + \text{O}(s)$
10. $\text{CO}(s) + \text{O}(s) \rightarrow \text{CO}_2(s) + \text{Pt}(s)$
11. $\text{CO}_2(s) + \text{Pt}(s) \rightarrow \text{CO}(s) + \text{O}(s)$
12. $\text{CO}(s) + \text{OH}(s) \rightarrow \text{CO}_2(s) + \text{H}(s)$
13. $\text{CO}_2(s) + \text{H}(s) \rightarrow \text{CO}(s) + \text{OH}(s)$
14. $\text{H}(s) + \text{O}(s) \rightarrow \text{OH}(s) + \text{Pt}(s)$
15. $\text{OH}(s) + \text{Pt}(s) \rightarrow \text{H}(s) + \text{O}(s)$
16. $\text{H}_2\text{O}(s) + \text{Pt}(s) \rightarrow \text{H}(s) + \text{OH}(s)$
17. $\text{OH}(s) + \text{OH}(s) \rightarrow \text{H}_2\text{O}(s) + \text{O}(s)$
18. $\text{H}_2\text{O}(s) + \text{O}(s) \rightarrow \text{OH}(s) + \text{OH}(s)$
19. $\text{H} + \text{Pt}(s) \rightarrow \text{H}(s)$
20. $\text{H}(s) \rightarrow \text{H} + \text{Pt}(s)$
21. $\text{O} + \text{Pt}(s) \rightarrow \text{O}(s)$
22. $\text{O}(s) \rightarrow \text{O} + \text{Pt}(s)$
23. $\text{OH} + \text{Pt}(s) \rightarrow \text{OH}(s)$
24. $\text{OH}(s) \rightarrow \text{OH} + \text{Pt}(s)$
25. $\text{H}(s) + \text{H}(s) \rightarrow \text{Pt}(s) + \text{Pt}(s) + \text{H}_2$
26. $\text{O}(s) + \text{O}(s) \rightarrow \text{Pt}(s) + \text{Pt}(s) + \text{O}_2$
27. $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O} + \text{Pt}(s)$
28. $\text{H}(s) + \text{OH}(s) \rightarrow \text{H}_2\text{O}(s) + \text{Pt}(s)$
Chemkin Simulation Output

- Concentration of 8 gas and surface species along channel
- Virtual experiments
- Robust design possible
- New experiment directions generated
How Does the Reactor Perform?

- What is the conversion behavior?
- What is the selectivity?
- How productive is the reactor?
- What are the transport limitations?
- What is the activation/deactivation behavior?
- What is the catalyst stability?
Conversion Behavior

Reformate: 5 sccm
Air: 0.5 sccm
Comparison: Experiment vs. Simulation

Conversion of 
- CO
- O2
- H2 

Reformate: 5 sccm 
Air: 0.5 sccm
Catalyst Activity Comparison

<table>
<thead>
<tr>
<th>References</th>
<th>Catalyst System</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>P CO (Torr)</th>
<th>P O₂ (Torr)</th>
<th>λ</th>
<th>TOF (s⁻¹)</th>
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<td>Fe₃O₄-Al₂O₃ (T=19%)</td>
<td>100°C</td>
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<td>Nibbelke, et al</td>
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<td>Zafiri, et al</td>
<td>Fe₃O₄-Al₂O₃(0011))</td>
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<td>10.00</td>
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</table>

TOF’s of thin-film catalyst:

≈same activity as others at lower temperature (<150°C)

better activity at higher temperature (>200°C)
Mass Transport Limitation

\[ C_{WP} = \eta \phi_1^2 = \frac{-r''_{O_2}(obs) \rho_c L_c^2}{D_e C_{O_2(s)}} \]

\[ C_{WP} << 1 \]

\[ C_{CO(s)} / C_{CO(b)} > 0.95 \]

\[ C_{O_2(s)} / C_{O_2(b)} > 0.95 \]
Conversion Comparison

**CO Conversion**

- **Oh, et al.**
  - Packed-Bed Tube Reactor
  - WHSV = 11.9 hr⁻¹

- **Kahlich, et al.**
  - Packed-bed Tube Reactor
  - WHSV = 1254.1 hr⁻¹

- **Choi, et al.**
  - Packed-bed Tube Reactor
  - WHSV = 109 hr⁻¹

- **Our work**
  - Thin-Film Catalyst
  - WHSV = 1480.5 hr⁻¹
2-D Finite Difference Model

\[ CO + \frac{1}{2} O_2 \xrightarrow{\Delta H = -67 \text{ kcal/mol}} CO_2 \]

\[ H_2 + \frac{1}{2} O_2 \xrightarrow{\Delta H = -58 \text{ kcal/mol}} H_2O \]

\[ CO_2 + H_2 \xrightarrow{\Delta H = 9.8 \text{ kcal/mol}} CO + H_2O \]

\( T_{\text{wall}} = \text{Constant} \)
Temperature Non-Uniformity: Hot Spots

2-mm radius
WHSV: 1500 hr\(^{-1}\)
Predicted Conversion Characteristics

![Graph showing CO conversion vs temperature for different reactors. The graph indicates that the microreactor and m-PBR with 0.2 cm radius have higher conversion percentages compared to the m-PBR with 0.4 cm radius at lower temperatures. The curves peak at different temperatures, with the microreactor reaching full conversion at a higher temperature than the other two.](image-url)
Flow Distribution Optimization

2-D Design for equal flow distribution in channels
Design: $1W_e$ PrOx Reactor

Assumes 38% FC efficiency

29 Parallel Channels

1. Standalone design
2. Can be thermally integrated to other components (e.g., vaporizer) for heat recovery; poor shape for heat retention.
3. Design based on isothermal condition

Interfaces to MKA for characterization

Mixer

Manifolds engineered for equal flow distribution

3.1 cm x 2.5 cm
Fabricated 1W PrOx Reactor

Actual Chip; 29 x (450 x 400 $\mu$m$^2$) Channels

4 Reactors on 4-in. Wafer
Next Step: Component Integration from a System Perspective

Example: Energy management with ASPEN simulations
An Integration Example for SR, PrOx, and Heat Exchangers

Vaporizer (260°C)  SR (260°C)  PrOx (160°C)

Q = 10.1 W  Q = 6.0 W

Air

Exhaust

Methanol

Water

To fuel cell

Fuel for combustor
Bringing New Drugs Faster and More Safely to the Marketplace

Adapted from S. Kiang, Bristol-Myers Squibb, 2003
Intensification for Pharma: Catalytic Hydrogenation

20% of all pharma manufacturing processes

- Currently: batch reactors, 100s of liters in size
- \( \text{H}_2 \) at high pressure (safety)
- Highly exothermic-low duty cycle, high heat removal (cost, energy efficiency)
- Residence time several hours

Continuous flow microreactors

- Low \( \text{H}_2 \) hold-up
- Superb heat extraction, high-duty cycle, low peak cooling
- Residence time minutes

\[ \begin{align*}
\text{o-nitroanisole} & \quad \text{OCH}_3 \quad \text{NO}_2 & \quad + & \quad 3\text{H}_2 & \quad \xrightarrow{\text{CATALYST}} & \quad \text{o-nitroanisidine} \\
& \quad \text{OCH}_3 \quad \text{NH}_2 & \quad + & \quad 2\text{H}_2\text{O} & 
\end{align*} \]
Intensification for Pharma: Catalytic Hydrogenation

Challenges:
- Transport Effects in Multiphase flow
- Effective Reactants Mixing
- Minimization of Pressure Drop
- Minimization of Heat and Mass Transfer Resistances
- Catalyst Selection/Preparation/Deposition for High Yield and Selectivity
- Intrinsic Kinetics Analysis for Microreactor Design
- Microreactor Design & Optimization
Core Competence
Being Built at NJCMCS (2002-2004)

• Thin-film Synthesis and Characterization Labs
  – Multifunctional surface design and control for micro-kinetic and micro-fluidic functions
  – Processing/microstructure/property/performance relationships
  – Integration with microfabrication practices

• Microkinetic Lab
  – Rate mechanisms: the key to rational micro-reactor design
  – Rapid parallel kinetics studies and performance evaluation
  – New microkinetic measurement tools development and integration

• Modeling and Simulations Lab
  – Quantification of complex surface effects
  – Flow distribution designs that will enable “numbering up” concepts
  – Novel mass transfer enhancement approaches via surface patterning
  – Integration with kinetic modeling, CFD simulations, ASPEN process analysis
Collaborators and Sponsors

- Dr. E. Dada, FMC
- Dr. P. Ho, Reaction Design
- Dr. D. Ivanov, NJ Institute of Technology
- Mr. D. Kientzler, Bristol-Myers Squibb
- Dr. S. Pau, Lucent-Bell Labs
- Mr. W. Mansfield, Lucent-Bell Labs