New Directions in Reactor Design Through Miniaturization

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Miniaturization Progress
Microelectronics to MEMS

MOORE'S LAW

transistors

100,000,000
10,000,000
1,000,000
100,000
10,000
1000


8008
8086
4004

Pentium® Processor
486™ DX Processor
386™ Processor
286

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Microchemical Systems

Miniature reaction and other unit operations, possessing *specific advantages* over conventional chemical systems.
Outline

● Microreactors—What?
● Benefits of Miniaturization—Why?
● Examples of Microreactors: Fabrication, Characterization, and Reaction—How?
● Conclusions
Microreactors—What Are They?

- Not your mother’s microreactor
- At least 10X smaller than benchtop “microreactor” of the past

(Forschungszentrum Karlsruhe GmbH)
Microreactors—What Are They?

(Ehrfeld, et.al., IMM)

(Besser, et.al., IfM)

(Jensen, et.al., MIT)
Integration-Industrial Processes

Input flows must be divided and reduced
Output flows must be combined

(Merck production plant using micromixers)
Benefits of Miniaturization—Why?

- Surface to Volume Ratio
- Low Inventory ("Hold Up")
- Residence Time Distribution
- Low Transport Resistances
- Robust Materials
- Cost
Benefits: Surface to Volume

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

Schematic of As⁺ Ion Implanter

Phosgene Reactor, Geismar, LA

- Safety
- Environment
Benefits: Residence Time Distribution

Precise Control Over Geometry
Tuning of residence time
Improved selectivity

\[ \text{Reaction equations:} \]
\[ C_2H_4 + H_2O \rightarrow C_2H_5OH \]
\[ 2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \]
Benefits: Low Transport Resistances

Overall Heat Transfer Coefficient

\[ q_x = -k \frac{dT}{dx} \]  
(conduction)

\[ U = 25,000 \text{ W/m}^2\text{K} \]
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
Microreactor Example—How?

- Reactor Fabrication
- Reactor Characterization
- Reaction Results
Microreactor Device

- Inlet Via
- Outlet Via
- Inlet Channel
- Manifold
- Microchannels (5 µm)
- Catalyst
- Pyrex Cover
- Silicon Chip
- 3.1 cm
Fabrication: Photolithography

(a) Coat with photoresist

Ultraviolet radiation

Glass mask

(b) Expose photoresist (positive, bonds broken)

(c) Remove exposed resist

(Shackelford)
Fabrication: Silicon Etching

Structured Catalyst Support in Reaction Zone

Alcatel Deep Reactive Ion Etch System
Pyrex-to-Silicon Bonding

Anodic Bonding

(750 VDC, 450°C)

(Kovacs)
Characterization Experiment

Setup

- Mass Spec
- Microreactor
- P Transducer 1
- MFC1
- Vent
- P Transducer 3
- MFC3
- Bubbler
Examples: Reactions

- Hydrocarbon hydrogenation/dehydrogenation
  - Cyclohexene hydrogenation/dehydrogenation
  - Benzene hydrogenation
- Hydrogen + oxygen in explosive regime
- Syngas conversion
- Catalytic combustion
Cyclohexene Hydrogenation/Dehydrogenation

\[
\text{Cyclohexene} \xrightarrow{Pt} \text{Cyclohexane} + 2\text{H}_2
\]

\[
\text{Cyclohexene} + \text{H}_2 \xrightarrow{Pt} \text{Cyclohexane}
\]

Models for hydrotreating and reforming reactions
Effect of Temperature on Selectivity

- Room temperature activity for both products
- Hydrogenation favored at $T_{room}$ to 150°C
- Dehydrogenation favored above 150°C
- Time and temperature dependent deactivation
- 5 µm reactor more tolerant of T and t
Implementation of Microchemical Systems

Technology
- Arrays for parallel characterization (R&D)
- On-site, on-demand production
- Special environments
- New factory paradigm

Application
- Catalyst discovery; process development
- Toxics
- Fuel processing (fuel cells)
- Space; offshore platforms
- Highly selective synthesis (pharma, fine chemicals)
- DOE Vision 2020-30% reduction in waste, pollution
Conclusions

- Microreactors possess special properties due to their **small dimensions** (< 500 µm).

- Various choices of **robust materials** are available suitable for a variety of applications (metal, ceramic, silicon, polymer).

- **Silicon** microreactor example illustrates reactor fabrication, operation, and characterization.

- **Model hydrocarbon catalytic hydrogenation and dehydrogenation** reactions illustrate ability to take relevant reaction engineering data safely and with low consumption.

- Microreaction technology will find a number of **niches** in analytical and process chemistry in the new millenium.
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