Gas-phase microreactor technology – some experiences

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Microreactors

- Microstructured reactor:
  - At least one inner dimension in the micrometre range

- Benefits of microreactors:
  - High heat transfer rates
  - Short diffusion distances
  - Small inner volume: Safety
  - Efficient kinetic investigation and catalyst screening
Microreactor - advantages

• Faster transfer of research results into on-site production
• High safety – small amounts of components
• Easy *number-up* to production capacity
• Smaller plants for production at distributed sites
• Smaller consumption of chemicals
• High surface-to-volume ratio
• Narrow residence time distribution (RTD)
Microreaction technology: total reaction control at all length scales

- Reactor plates: $10^{-3}$ m
- Microchannels: $10^{-4}$ m
- Coatings: $10^{-5}$ m
- Clusters: $10^{-6}$ m
- Micropores: $10^{-7}$ m
- Chemical engineering
- Materials science
- Mechanical engineering
- Organic chemistry
- Catalysis
Gas-phase microreactor
During the past 25 years processes have been developed for the fabrication of three-dimensional microdevices from a wide variety of materials based on electronic technologies.

Microstructures = 100 – 500 μm
1 μm = 10⁻⁶ m
Objectives

• To design and build the equipment

• To develop a catalyst (preparation, screening, characterization)

• To study the SCR of NOx and preparation of chemicals in microreactors

• To develop kinetic and reactor models
Plates manufacture

- **Level 1:** Micro-channel formation (EDM)
  - Stainless Steel plate
  - Aluminum plate with micro-channels
- **Level 2:** Washcoating deposition (Anodic oxidation)
  - SS plate with alumina layer
  - 'Monolith' micro-reactor
- **Level 3:** Catalyst deposition (impregnation)
  - Post-treatments
  - Aluminum plate with coated micro-channels

Stacking & Bonding
Plates impregnation (ÅA)
Characterization

SEM pictures of the plates

SEM pictures of raw platelet – 50X

SEM pictures of raw platelet – 200X
Modelling of microchannels

• Modelling of microreactors still immature.
• Nevertheless, reliable results due to dimensions
• Laminar flow (almost no turbulent flow observed)
• Big differences in Lab-on-a-chip and micro total analysis (μTAS) with not-so-micro channels
Geometry for microchannel analysis

 Geometry for the analysis
H = 460 µm
L = 12500 µm

SEM picture of a microplate - 50X
Differences between a macro- and microflow

• Flow in microchannels is usually laminar but turbulent in macrochannels
• Diffusion paths in microchannels for heat and mass transfer are short
• High surface-to-volume ratio
• Solid wall material are important. Surface heat transfer effects
# Dimensions and fluid properties

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>125000 µm</td>
</tr>
<tr>
<td>Width</td>
<td>460 µm</td>
</tr>
<tr>
<td>Height</td>
<td>75 µm</td>
</tr>
<tr>
<td>Pressure</td>
<td>101 kPa</td>
</tr>
<tr>
<td>Temperature</td>
<td>373 K</td>
</tr>
<tr>
<td>Temperature at the wall</td>
<td>373 K</td>
</tr>
<tr>
<td>Viscosity</td>
<td>2e-5 Pa*s</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>28 kg/kmol</td>
</tr>
</tbody>
</table>

Kn all the time in non-slip domain, usual continuum description and all the components of the velocity are zero close to the walls.
Flow in microchannels

- What are the boundaries?
- What is microscale?
- Are the classical equations valid?

Gas-phase microreactor system with spare parts
What is Knudsen number?

- Continuum flow with no-slip boundary conditions ($Kn < 10^{-2}$, $10^{-3}$)
- Continuum flow with slip boundary conditions ($10^{-2} < Kn < 10^{-1}$)
- Transition flow ($10^{-1} < Kn < 10$)
- Free molecular flow ($Kn > 10$)

\[
K_n = \frac{\lambda}{L}
\]

\[
\lambda = \frac{k_B T}{\sqrt{2}pd^2}
\]
Macroflows relationships are valid!

\[ \rho \left( \frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} \right) = -\frac{\partial p}{\partial x_i} + \rho g_i + \frac{\partial}{\partial x_k} \left[ \mu \left( \frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} - \frac{2}{3} \delta_{ik} \frac{\partial u_j}{\partial x_j} \right) \right] \]

- Convection
- Gravity
- Pressure difference
- Viscous dissipation
The total area of the channels was approximated to that of an ellipse

\[ A = \frac{\pi \cdot a \cdot b}{2} \]

**Parameters:**

Navier-Stokes (2D)

**Boundary settings:**
- 2 & 19 → No slip
- Inflow Velocity

According to figure

**Flow properties:**

\[ \rho = f(T, p) \sim 1.251 \text{ Kg/m}^3 \]

\[ \eta = f(T) \sim 2e^{-5} \text{ Pa.s} \]

**Mesh**
CFD modelling

Volumetric Flow = 20 mL/min

Volumetric Flow = 100 mL/min
Reactor modelling

Models

1. Axial dispersion
2. Laminar flow and radial diffusion
Diffusion effects in modelling

- Nevertheless of the thickness of the catalytic layer and depending on the reaction conditions, diffusion limitation inside the microchannels might play a role in the system.

- Mass transfer limitation from the bulk phase to the surface of the coating could appear, mainly via molecular diffusion.
Catalyst layer and microchannels

Catalyst layer

\[ \varepsilon_p \frac{dc_i'}{dt} = r_i \rho_p + \frac{D_e}{\delta^2} \left( \frac{d^2 c_i'}{dx^2} + \frac{s}{x} \frac{dc_i'}{dx} \right) \quad s \in [0,2] \]
\[ x \in [0,1] \]

Mass balance in the microchannels:

\[ \frac{dc_i}{dt} = D_i \left( \frac{d^2 c_i}{dr^2} + \frac{1}{r} \frac{dc_i}{dr} \right) + \frac{d(c_i w)}{dl} \]
\[ w = \left( 1 - \left( \frac{r}{R} \right)^2 \right) \cdot w_0 \]

Boundary conditions:

\[ \frac{dc_i}{dr} = 0, r = 0 \]
\[ \frac{D_e}{\delta} \left( \frac{dc_i'}{dx} \right)_{x=0} = D_i \left( \frac{dc_i}{dr} \right)_{r=R} \]
\[ \left( \frac{dc_i'}{dx} \right)_{x=1} = 0 \]
Layer thickness

A distribution function $\omega(\delta)$ as a function of the thickness $\delta$:

$$\frac{D_e}{\delta} \left( \frac{dc_i'}{dx} \right)_{x=0} = D_e \int_{\delta_{\min}}^{\delta_{\max}} \omega(\delta) \left( \frac{dc_i'}{dx_\delta} \right)_{x_\delta=0} d\delta$$

Equation to be solved:

$$\frac{dc_i}{dt} = D_i \left( \frac{d^2 c_i}{dr^2} + \frac{1}{r} \frac{dc_i}{dr} \right) + \frac{d(c_i w)}{dl}$$

$$w = \left( 1 - \left( \frac{r}{R} \right)^2 \right) \cdot w_0$$
Preparation of ethylene oxide in a microreactor

Possibility for on-site production
Ethylene oxide

• Important organic intermediate
  – global production ca. 19 million metric tons
  – used in e.g. cellulose derivates

• Produced in gas-phase by partial oxidation of ethylene over silver.
  – exothermic reaction and toxic components
  – safety issues
Reaction scheme

- Two parallel competing oxidation reactions
  - partial and complete oxidation
- Total oxidation of ethylene oxide considered to be negligible
Experimental work

• Utilizing microreactor technology in partial oxidation of ethylene.
• Preparation of silver catalysts for microreactor
• Obtaining kinetic data and determining a kinetic model for partial oxidation of ethylene
Reactor system - scheme
Reactor system - picture
Microreactor
Catalysts

- Silver catalysts
- Preparation
  - incipient wetness
  - washcoating
- Characterization
  - BET and SEM-EDS
Catalysts - summary

- Four catalysts
  - Three silver-alumina catalysts
    - Silver content from 14 wt-% to 18 wt-%
  - One commercial pure silver catalyst
Catalysts – SEM images
Experiments

• A series of experiments to determine the effect of e.g. reaction temperature

• Range of reaction conditions
  – pressure 1 atm
  – temperature range 220 - 300°C
  – total flow range 6 - 10.5 ml/min
  – ethylene and oxygen concentration varied from 5 vol-% to 25 vol-%
The effect of pretreatment
The effect of temperature

Conversion of ethylene
Yield of ethylene oxide
Selectivity to ethylene oxide
The effect of total flow

![Graph showing the effect of total flow on conversion, yield, and selectivity of ethylene and ethylene oxide. The x-axis represents total flow in ml/min, and the y-axis represents conversion, yield, and selectivity in %. The graph includes lines for conversion of ethylene, yield of ethylene oxide, and selectivity to ethylene oxide.]
The effect of oxygen concentration

![Graph showing the formation of ethylene oxide as a function of oxygen concentration in the feed.](image_url)
The effect of ethylene concentration

![Graph showing the effect of ethylene concentration on the formation of ethylene oxide.

The x-axis represents the concentration of ethylene in feed [%], ranging from 0 to 30.

The y-axis represents the formation of ethylene oxide [mol/s], ranging from 0 to 1.2E-07.

Different lines represent the formation of ethylene oxide at different oxygen concentrations in the feed, such as oxygen 5%, 10%, 15%, 20%, and 25%.

As the concentration of ethylene in the feed increases, the formation of ethylene oxide also increases, indicating a direct relationship between the two.](image-url)
Kinetic model

- Two models for the formation of the ethylene oxide were developed
  - Langmuir-Hinshelwood mechanism
  - rate-limiting step: surface reaction
  - competitive adsorption of ethylene and oxygen on the silver surface
  - the effects of products and internal diffusion assumed to be negligible
Kinetic model

- Model 1 assumed a competitive adsorption of ethylene and dissociatively adsorbed oxygen on the surface.
- Model 2 assumed a competitive adsorption of ethylene and molecular oxygen on the surface.
Kinetic model

- Best fit to the experimental data was achieved with model 2 and following rate equation was proposed for the formation of ethylene oxide:

\[ r_1 = \frac{kK_E K_O c_E c_O}{(1 + K_E c_E + K_O c_O)^2} \]
Kinetic model – parity plot

![Parity plot showing comparison between experimental and estimated formation of ethylene oxide (mol/s).](image-url)
Kinetic model – fit to experimental data

- Formation of ethylene oxide (ethylene 5% in feed)
- Formation of ethylene oxide (ethylene 10% in feed)
- Formation of ethylene oxide (ethylene 15% in feed)
- Formation of ethylene oxide (ethylene 25% in feed)
Ethylene oxide - conclusions

• Ethylene oxide was successfully synthesized in a microreactor over silver-alumina and silver catalysts.

• The microreactor technology was suitable for studying fast gas-phase heterogeneous catalytic reaction and many advantages could be employed e.g. inherent safety.
Microreactors in selective catalytic reduction of NOx from biofuels

Catalyst development and modelling of kinetics and flow pattern
Set-up

Agilent 3000 Micro GC

1. Helium
2. NO/He Gas Mixture
3. Oxygen
4. Calibration Gas (GC)
5. Calibration Gas (NOx Analyzer)
6. Mass Flow Controller (Gas)
7. Mass Flow Controller (Water)
8. Evaporator
9. Microdialysis Pump (Water, Hexadecane)
10. Pre-Heater
11. Microreactor
12. Condenser (-5°C)
13. Condenser (-20°C)
14. Gas Chromatograph
15. NOx Analyzer
16. Computer
Gas-phase microreactor

- Inlet I
- Inlet II
- Outlet
- Heating/Cooling
- Heating Cartridges
- Lower part
Production of bio-diesel

Renewable source

Natural fats & oils

Catalyst

Biodiesel

Bio-Catalyst

Bio oils

Esterification

FAME

Hydrotreatment

NExBTL

Renewable Diesel

Biomass

Gasification

Fischer-Tropsch

BTL

Renewable Diesel

\[ C_nH_{2n+2} \]
HC-SCR of NO\textsubscript{x}

Biofuels-assisted SCR of NO$_x$ in microchannels

First generation biodiesel-FAME

Second generation biodiesel-Decarboxylation of vegetable oils, e.g., (NExBTL)

*Hernández Carucci et al. European congress on catalysis VIII, Turku, Finland (2007)*
Experimental conditions

- Total flow rate 50 ml/min
- $150 < T < 550 \, ^\circ C$
- Carrier gas: He
- 500-2000 ppm NO
- 187-1500 ppm Hexadecane
- 3-15% $O_2$
- 12% $H_2O$

hexadecane, $C_{16}H_{34}$

Model paraffin diesel compound (cetane number 100)
Variation of NO concentration

NO to N$_2$ conversion (%)  

C$_{16}$H$_{34}$ to CO$_2$ + CO conversion (%)

SCR of NOx with hexadecane, O$_2$=6%, 187.5 ppm C$_{16}$H$_{34}$, H$_2$O=12%

*Hernández Carucci et al. XVIII International Conference on Chemical Reactors, Malta (2008)  
*Hernández Carucci et al. submitted to JCE (2008)
Hexadecane concentration

NO to N$_2$ conversion (%)  

C$_{16}$H$_{34}$ to CO$_2$ + CO conversion (%)

SCR of NOX with hexadecane, O$_2$=6%, NO=500ppm, H$_2$O=12%

*Hernández Carucci et al. XVIII International Conference on Chemical Reactors, Malta (2008)
*Hernández Carucci et al. submitted to JCE (2008)
Oxygen concentration

NO to $N_2$ conversion (%)

$C_{16}H_{34}$ to $CO_2 + CO$ conversion (%)

SCR of $NO_x$ with hexadecane, NO=500ppm, C1/NO=6, $H_2O=12\%$

*Hernández Carucci et al. XVIII International Conference on Chemical Reactors, Malta (2008)
*Hernández Carucci et al. submitted to JCE (2008)
Proposed mechanism

Adsorption:

\[ \text{C}_{16}\text{H}_{34} + \text{O}^* + \text{*} \rightarrow \text{C}_{16}\text{H}_{33}^* + \text{OH}^* \]

\[ \text{O}_2 + 2\text{*} \rightarrow 2\text{O}^* \]

\[ \text{NO} + \text{*} \rightarrow \text{NO}^* \]

Desorption:

\[ \text{NO}_3^* \rightarrow \text{NO}_3^* \rightarrow \text{NO}_3^* \rightarrow \text{NO}_3^* \rightarrow \text{NO}_3^* \rightarrow \text{NO}_3^* \rightarrow \text{NO}_3^* \]

\[ \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} \]

\[ \text{CO}_2 + \text{H}_2\text{O} \]

Ag/Al\text{O}_3 \text{ surface}
Kinetic analysis

- Adsorption, surface reaction and desorption steps, were included in the model.
- Plug flow model used for the microchannel
- Mass balances for every reactant/intermediate/product
- Based on the data of the components in the gas phase
HC-SCR Model

\[ P = R + Q - J \]

\( P \): # of basic routes (9)
\( Q \): # balance equations (1)
\( J \): # intermediates (13)
\( R \): # of steps (21)

1. \[ 2C_{16}H_{34} + 49O_2 \rightarrow 32CO_2 + 34H_2O \]
2. \[ 2C_{16}H_{34} + 33O_2 \rightarrow 32CO + 34H_2O \]
3. \[ C_{16}H_{34} + NO + 24O_2 \rightarrow 16CO_2 + 17H_2O + 0.5N_2 \]
4. \[ C_{16}H_{34} + NO + 16O_2 \rightarrow 16CO + 17H_2O + 0.5N_2 \]
5. \[ C_{16}H_{34} + NO + NO_2 + 23O_2 \rightarrow 16CO_2 + 17H_2O + N_2 \]
6. \[ C_{16}H_{34} + NO + NO_2 + 15O_2 \rightarrow 16CO + 17H_2O + N_2 \]
7. \[ CO + 0.5O_2 \rightarrow CO_2 \]
8. \[ NO + 0.5O_2 \rightarrow NO_2 \]
9. \[ 2NO + 2CO \rightarrow N_2 + 2CO_2 \]

*Hernández Carucci et al. XVIII International Conference on Chemical Reactors, Malta (2008)
*Hernández Carucci et al. submitted to JCE (2008)
### Proposed model

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Rate Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( NO + * \Leftrightarrow NO^* )</td>
<td>( r_{+1} = k_{+1}c_{NO} \theta_v \theta_{NO} )</td>
</tr>
<tr>
<td>2</td>
<td>( NO^* + * \rightarrow N^* + O^* )</td>
<td>( r_2 = k_2 \theta_{NO} \theta_v )</td>
</tr>
<tr>
<td>3</td>
<td>( O_2 + 2* \Leftrightarrow 2O^* )</td>
<td>( r_{+3} = k_{+3}c_{O_2} \theta_v^2 )</td>
</tr>
<tr>
<td>4</td>
<td>( 2N^* \rightarrow N_2 + 2* )</td>
<td>( r_3 = k_3 \theta_O^2 )</td>
</tr>
<tr>
<td>5</td>
<td>( NO^* + O^* \rightarrow NO_2 + 2* )</td>
<td>( r_4 = k_4 \theta_N^2 )</td>
</tr>
<tr>
<td>6</td>
<td>( CO + * \Leftrightarrow CO^* )</td>
<td>( r_5 = k_5 \theta_{NO} \theta_O )</td>
</tr>
<tr>
<td>7</td>
<td>( CO^* + O^* \rightarrow CO_2 + 2* )</td>
<td>( r_6 = k_{+6}c_{CO} \theta_v \theta_{CO} )</td>
</tr>
<tr>
<td>8</td>
<td>( C_{16}H_{34} + O^* + * \rightarrow C_{16}H_{33} * + OH^* )</td>
<td>( r_7 = k_7 \theta_{CO} \theta_O )</td>
</tr>
<tr>
<td>9</td>
<td>( C_{16}H_{33} * + NO^* \rightarrow C_{16}H_{33}NO^* + * )</td>
<td>( r_8 = k_{+8}c_{hex} \theta_O \theta_v )</td>
</tr>
<tr>
<td>10</td>
<td>( 2C_{16}H_{33}NO^* \rightarrow N_2 + 2C_{16}H_{33}O^* )</td>
<td>( r_9 = k_9 \theta_{hex} \theta_{NO} )</td>
</tr>
<tr>
<td>11</td>
<td>( C_{16}H_{33} * + O^* \rightarrow C_{16}H_{33}O^* + * )</td>
<td>( r_{10} = k_{10}^2 \theta_{hex-NO}^2 )</td>
</tr>
<tr>
<td>12</td>
<td>( 2OH^* \rightarrow H_2O + O^* )</td>
<td>( r_{11} = k_{11} \theta_{hex} \theta_O )</td>
</tr>
<tr>
<td>13</td>
<td>( C_{16}H_{33}NO^* + NO^* \rightarrow N_2 + C_{16}H_{33}O^* + O^* )</td>
<td>( r_{12} = k_{12} \theta_{hex} \theta_O )</td>
</tr>
<tr>
<td>14</td>
<td>( NO_2 + * \Leftrightarrow NO_2^* )</td>
<td>( r_{13} = k_{13} \theta_{OH}^2 )</td>
</tr>
<tr>
<td>15</td>
<td>( C_{16}H_{33}^* + NO_2^* \rightarrow C_{16}H_{33}NO^* + O^* )</td>
<td>( r_{14} = k_{14} \theta_{hex-NO} \theta_{NO} )</td>
</tr>
<tr>
<td>16</td>
<td>( N^* + CO^* \rightarrow NCO^* )</td>
<td>( r_{15} = k_{+15}c_{NO_2} \theta_v \theta_{NO_2} )</td>
</tr>
<tr>
<td>17</td>
<td>( N^* + NO^* \rightarrow N_2O^* + * )</td>
<td>( r_{16} = k_{16} \theta_{hex} \theta_{NO_2} )</td>
</tr>
<tr>
<td>18</td>
<td>( N_2O^* + * \Leftrightarrow N_2 + O^* )</td>
<td>( r_{17} = k_{17} \theta_N \theta_{CO} )</td>
</tr>
<tr>
<td>19</td>
<td>( N_2O^* + * \Leftrightarrow N_2 + O^* )</td>
<td>( r_{20} = k_{20} \theta_N \theta_{NO} )</td>
</tr>
<tr>
<td>20</td>
<td>( N_2O^* + * \Leftrightarrow N_2 + O^* )</td>
<td>( r_{21} = k_{21} \theta_{N_2O} \theta_v )</td>
</tr>
</tbody>
</table>
Model equations

**Adsorption steps**

\[ \theta_{NO} = K_1 p_{NO} \theta_v \]
\[ \theta_O = \sqrt{K_3 p_O} \theta_v \]
\[ \theta_{CO} = K_6 p_{CO} \theta_v \]
\[ \theta_{NO_2} = K_{15} p_{NO_2} \theta_v \]

**Coverage of hexadecane:**

\[ \theta_{hex} = \frac{k_6 p_{hex} \sqrt{K_3 p_O} \theta_v}{k_9 K_1 p_{NO} + k_{12} \sqrt{K_3 p_{O_2} + k_{16} k_{15} p_{NO_2}}} \]

**Coverage of hex-NO:**

\[ \theta_{hex-NO} = \left( \frac{-k_{14} K_1 p_{NO} + \sqrt{k_{14}^2 K_1^2 p_{NO}^2 + 8k_{10} k_8 p_{hex} \sqrt{K_3 p_{O_2}}}}{4k_{10}} \right) \theta_v \]

**Coverage of N:**

\[ \theta_N = \left( \frac{-k_{17} k_6 p_{CO} - k_{20} k_1 p_{NO} + \sqrt{(k_{17} k_6 p_{CO} + k_{20} k_1 p_{NO})^2 + 8k_4 k_2 k_1 p_{NO}}}{4k_4} \right) \theta_v \]

**Coverage of OH:**

\[ \theta_{OH} = \left( \frac{k_8 p_{hex} \sqrt{K_3 p_{O_2}}}{2k_{13}} \right) \theta_v \]

**Coverage of vacant sites:**

\[ \theta_v = \frac{1}{1 + \theta_{NO} + \theta_O + \theta_{CO} + \theta_{NO_2} + \theta_{hex} + \theta_{hex-NO} + \theta_{OH} + \theta_N} \]

*Hernández Carucci et al. XVIII International Conference on Chemical Reactors, Malta (2008)*

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Mathematical tools (MODEST)

- ODE-solver suitable for stiff differential equations. Temperature dependence expressed as:

\[ k = k_{ave} \exp \left( -\frac{Ea}{R} \left( \frac{1}{T} - \frac{1}{T_{ave}} \right) \right) \]

\[ k_{ave} = Ae \left( \frac{Ea}{RT_{ave}} \right) \]

\[ \theta = \sum (y_i - \hat{y}_i)^2 \]
Modeling results

[Graphs showing the concentration of NO, CO₂, Hexadecane, and N₂ against length.

Response simulation (Dump file) for each graph.]
A total of 30 parameters estimated!

<table>
<thead>
<tr>
<th>Pre-exponential factor/Equilibrium Constant</th>
<th>Estimated values</th>
<th>Activation Energy [J/mol]</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 [m$^3$/mol]</td>
<td>2.98 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2 [mol/m$^3$s]</td>
<td>5.13 ± 0.08</td>
<td>Ea$_2$</td>
<td>(1.02 ± 0.052)E+05</td>
</tr>
<tr>
<td>A3 [m$^3$/mol]</td>
<td>13.0 ± 0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A4 [mol/m$^3$s]</td>
<td>0.527 ± 0.004</td>
<td>Ea$_4$</td>
<td>(0.785 ± 0.493)E+05</td>
</tr>
<tr>
<td>A5 [mol/m$^3$s]</td>
<td>0.0225 ± 0.0143</td>
<td>Ea$_5$</td>
<td>(1.299 ± 0.129)E+05</td>
</tr>
<tr>
<td>A6 [m$^3$/mol]</td>
<td>0.962 ± 2.260</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A7 [mol/m$^3$s]</td>
<td>2.12 ± 8.73</td>
<td>Ea$_7$</td>
<td>(0.252 ± 0.384)E+05</td>
</tr>
<tr>
<td>A8 [mol/m$^3$s]</td>
<td>0.519 ± 0.070</td>
<td>Ea$_8$</td>
<td>(0.386 ± 0.134)E+05</td>
</tr>
<tr>
<td>A9 [mol/m$^3$s]</td>
<td>9.74 ± 9.94</td>
<td>Ea$_9$</td>
<td>(0.581 ± 0.404)E+05</td>
</tr>
<tr>
<td>A10 [mol/m$^3$s]</td>
<td>25.5 ± 42.5</td>
<td>Ea$_{10}$</td>
<td>(0.613 ± 0.677)E+05</td>
</tr>
<tr>
<td>A12 [mol/m$^3$s]</td>
<td>3.35 ± 15.9</td>
<td>Ea$_{12}$</td>
<td>(0.291 ± 0.919)E+05</td>
</tr>
<tr>
<td>A13 [mol/m$^3$s]</td>
<td>5.14 ± 4.81</td>
<td>Ea$_{13}$</td>
<td>(0.498 ± 0.304)E+05</td>
</tr>
<tr>
<td>A14 [mol/m$^3$s]</td>
<td>11.4 ± 22.9</td>
<td>Ea$_{14}$</td>
<td>(1.241 ± 0.381)E+05</td>
</tr>
<tr>
<td>A15 [m$^3$/mol]</td>
<td>25.4 ± 13.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A16 [mol/m$^3$s]</td>
<td>3.60 ± 3.94</td>
<td>Ea$_{16}$</td>
<td>(0.692 ± 0.439)E+05</td>
</tr>
<tr>
<td>A17 [mol/m$^3$s]</td>
<td>14.2 ± 44.8</td>
<td>Ea$_{17}$</td>
<td>(0.887 ± 0.270)E+05</td>
</tr>
<tr>
<td>A20 [mol/m$^3$s]</td>
<td>14.3 ± 1.51</td>
<td>Ea$_{20}$</td>
<td>(0.699 ± 0.250)E+05</td>
</tr>
</tbody>
</table>
Laminar flow with radial diffusion

Mass balance in the catalytic layer:

\[ \varepsilon_p \frac{dc_i'}{dt} = r_i \rho_p + D_e \frac{\delta^2}{\delta^2} \left( \frac{d^2 c_i'}{dx^2} + s \frac{dc_i'}{x \ dx} \right), \quad s \in [0,2] \text{ and } x \in [0,1] \]

Mass balance in the microchannel:

\[ \frac{dc_i(r,l)}{dt} = D_{M,l} \left( \frac{d^2 c_i(r,l)}{dr^2} + r \frac{dc_i(r,l)}{r \ dr} \right) - \frac{d(c_i(r,l)w(r))}{dl} \]

with the axial flow velocity as: \( w(r) = \left( 1 - \left( \frac{r}{R} \right)^2 \right) \cdot 2 \cdot w_0 \)

Boundary conditions:

Symmetry: \( \frac{dc_i}{dr} = 0, r = 0 \) for all \( l \)

No gradients when \( l=1 \): \( \left( \frac{dc_i'}{dx} \right)_{x=1} = 0 \)

Diffusion: \( \frac{D_e}{\delta} \left( \frac{dc_i'}{dx} \right)_{x=0} = D_{M,l} \left( \frac{dc_i'}{dr} \right)_{r=R} \)

Nomenclature:

- \( c_i \) = concentration of species in the bulk phase
- \( c'_i \) = concentration of species in the catalyst layer
- \( D_e \) = Effective diffusion coefficient
- \( D_{M,l} \) = Molecular diffusion coefficient
- \( L \) = axial coordinate
- \( R \) = radial coordinate
- \( r_i \) = reaction rates
- \( s \) = form factor
- \( w(r) \) = flow velocity in the l direction
- \( \delta \) = thickness of the catalytic layer
- \( \varepsilon_p \) = porosity of the coating
- \( \rho_p \) = density of the catalyst particle

Profiles in microchannel

*N. Hernández Carucci et al., International Symposium on Chemical Reaction Engineering, Japan (2008)*
Flow patterns inside the microchannels have been modelled. At higher flows the pressure drop augments.

A model for the RTD has been developed.

Kinetic phenomena have been discovered.

Laminar flow with radial diffusion is a good model for gas-phase microreactors.
Synthesis of chemical intermediates in microreactors

Sabrina A. Schmidt, Tapio Salmi, Dmitry Murzin, José Hernández Carucci, Narendra Kumar, Kari Eränen

Teknisk kemi & reaktionsteknik
Åbo Akademi
Methyl and ethyl chloride

\[
\begin{align*}
\text{CH}_3\text{Cl} & \quad \text{Cl} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \quad \text{H} \\
\end{align*}
\]

~10^6 tons/year to important everyday products

~100,000 tons/year direct use and ethyl cellulose production

Production

• Hydrochlorination of ethanol and methanol

• $\text{R-OH} + \text{HCl} \rightarrow \text{R-Cl} + \text{H}_2\text{O}$

  – Ether as side-product formed
  – In case of ethanol also ethylene, acetaldehyde

  – $T \sim 300 \, ^\circ\text{C}$, catalyst: Alumina, Zinc chloride / Alumina

Very rapid gas phase reactions
Why microreactor: safety

- Highly flammable and toxic gases

- Transportation and storage = ☹ / a risk and a cost
- Failure (e.g. runaway) of a big unit is dangerous

- Idea: produce alkyl chloride on-site in a microreactor in the amounts needed
- ”Keep the tiger in the cage!”
Why microreactor: diffusion

- Efficiency: EtCl / MeCl formation are very fast!
  - Low diffusion distances
  - Increased catalyst and space efficiency
  - Ideal tool for kinetic studies
Research strategy

• Catalyst studies

• Catalyst coating technique for microchannels

• Kinetic and thermodynamic investigations

• Mathematical modelling
The microreactor

- IMM GPMR-mix: Gas phase microreactor with mixing and catalyst zone
- Material: stainless steel
Microreactor and tubular reactor

He/MeOH

He/MeCl

He/Tubular reactor

Heated elements

MeOH

Neutralization bottle

Sampling section, septum

Washing bottle

PC

GC

MeOH
MeCl
DME
Two microreactors
Catalysts

- Neat Alumina
- Active sites: Lewis acid sites (LAS, e.g. Al\textsuperscript{3+} centres)

![Chemical structures]

- Alternatively: ZnCl\textsubscript{2}/Alumina
  - Introduction of zinc based LAS
- ZnCl\textsubscript{2}/ Zeolites
  - Tunable acidity
Effects of zinc support

• Support: 5 wt% Zn on alumina and zeolites

Effects of zinc support

- Support: 5 wt% Zn on alumina and zeolites

Effects of zinc loading

- Loading: 0-21 wt% Zn on alumina
Effects of zinc loading

- Loading: 0-21 wt% Zn on alumina

Catalyst of choice

- Activity and selectivity can be improved by addition of zinc chloride
- Zeolites are the most active but least stable and selective catalysts
- Zinc modified alumina is stable in the tubular reactor but selectivity decreases in the microreactor
- Neat alumina is least active but selective, stable and inexpensive catalyst
  - **Catalyst of choice**
Catalyst coating

• Binder-free slurry coating method
• Adhesion through:
  – Thermal surface treatment
  – Ball milled catalyst (<32 µm)
• Amount of catalyst in one microreactor: 3.4 mg
Characterisation of coating

- Confocal microscopy: Morphology, thickness and surface roughness

- Coating thickness: 15 μm, channel depth: 90 μm
Kinetic and thermodynamic investigations
- Mathematical modelling
Methanol hydrochlorination

- Hydrochlorination of methanol at 300 °C

\[
\begin{align*}
CH_3OH + HCl & \leftrightarrow CH_3Cl + H_2O & (I) \quad & K_{eq} = 398 \\
2CH_3OH & \leftrightarrow CH_3OCH_3 + H_2O & (II) \quad & 12 \\
CH_3OCH_3 + HCl & \leftrightarrow CH_3OH + CH_3Cl & (III) \quad & 36
\end{align*}
\]

- Lightly exothermic, main reaction: -30 kJ/mol
- The reactions are not completely irreversible!

• A very high conversion and selectivity can be reached with two microreactors

Reaction modeling - catalyst layer

- Kinetic model: Langmuir-Hinshelwood
- Plug flow model for the reactor

\[
\begin{align*}
    r_1 &= k_1 \frac{(c_{CH3OH}c_{HCl} - \frac{c_{CH3Cl}c_{H2O}}{K_1})}{D^2} \\
    r_2 &= k_2 \frac{(c_{MeOH}^2 - \frac{c_{DME}c_{H2O}}{K_2})}{D^2} \\
    r_3 &= k_3 \frac{(c_{DME}c_{HCl} - \frac{c_{MeOH}c_{MeCl}}{K_3})}{D^2}
\end{align*}
\]

\[D = K_{HCl}c_{HCl} + 1\]
Kinetic model

- Detailed description of MeCl formation
- DME formation shows deviation
  - Significantly lower concentration, rough description of reaction 3

Reaction modeling - catalyst layer

- Obtained activation energy for MeCl formation is double of previously published
  
  - Suggests internal diffusion limitations

- Diffusion modelling in the catalyst layer
  
  - Mean transport pore model, Catalyst shape: slab

\[ D_{ei} = \left( \frac{\varepsilon_p}{\tau_p} \right) D_i \]
\[ \frac{d c_i}{d t} = \frac{1}{\varepsilon_p} \left( D_{ei} \frac{d^2 c_i}{d r^2} + r_i \rho_p \right) \]

Reactant concentration profiles inside the catalyst layer

- Microreactor
  - Effectiveness factor: 0.93 (high)

- Conventional fixed bed
  - Effectiveness factor: 0.1-0.06 (low)

- Wrong activation energies reported in literature
Ethanol hydrochlorination

EtOH (+HCl) → EtCl → EtOEt → C₂H₄ → CH₃CHO + H₂

Reversible reactions

(At high T)

EtOH conversion

Selectivity to side products

- **DEE**: decrease with time and increases with temperature
- **C₂H₄**: increase with temperature and time (at T≥300°C)
- **Acetaldehyde**: very low

Kinetic model

- Reactions in kinetic model:
  1) $\text{EtOH} + \text{HCl} \leftrightarrow \text{EtCl} + \text{H}_2\text{O}$
  2) $2 \text{EtOH} \leftrightarrow \text{DEE} + \text{H}_2\text{O}$
  3) $\text{EtOH} \leftrightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$
  4) $\text{EtOH} \leftrightarrow \text{CH}_3\text{CHO} + \text{H}_2$
  5) $\text{DEE} + \text{HCl} \leftrightarrow \text{EtCl} + \text{EtOH}$

- Langmuir-Hinshelwood:

\[
\begin{align*}
    r_1 &= \frac{c_{\text{EtOH}} c_{\text{HCl}} - c_{\text{EtCl}} c_{\text{H}_2\text{O}}}{K_I} \\
    D &= \frac{k_1}{D^2} \\
    D &= (1 + K_{\text{EtOH}} c_{\text{EtOH}} + K_{\text{HCl}} c_{\text{HCl}})
\end{align*}
\]

Model fit

• Variation of concentration profiles with temperature was well described

• Variation of ethanol/HCl concentration:
  – Standard Langmuir-Hinshelwood model does not describe well the product distribution
HCl & ether and ethene formation

- Solution: $C_2H_4$ and DEE formation are catalyzed by HCl on the alumina surface due to increased acidity

- Expression:

$$r_2 = k_2 \frac{c_{EtOH}^2 - \frac{c_{DEE}c_{H_2O}}{K_{II}}}{D^2}$$

$\alpha$: Parameter: impact of HCl catalysis

For $c_{HCl}$ or $\alpha \to 0$ the term approaches 1
Improved kinetic model

- Dependence of product distribution on reactant concentration is improved but not precise
- Exact dependence of kinetics on catalyst surface is complex
Product separation

- **Aim:** At the outlet of the reactor: only traces of MeOH, HCl and DME due to maximum conversion
- Methanol and water separation by condensation
- Glass made condenser, coolant: glycerin/water -10 °C
- Ongoing work with metal condenser

Cooling surface: 210 cm²
Efficiency: gas phase

- Composition of the gas phase at maximum conversion (97.6%)

Prior to condenser

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>2.5</td>
</tr>
<tr>
<td>DME</td>
<td>1.6</td>
</tr>
<tr>
<td>MeCl</td>
<td>95.9</td>
</tr>
</tbody>
</table>

After condenser

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>0.12</td>
</tr>
<tr>
<td>DME</td>
<td>0.74</td>
</tr>
<tr>
<td>MeCl</td>
<td>99.14</td>
</tr>
</tbody>
</table>

- MeCl and DME are efficiently separated from the liquid.

Efficiency: liquid phase

Composition of the liquid phase phase (at 83.3 % conversion)

- Methanol cannot be completely separated
- Largest part of HCl is contained in the condensate
- Water is well separated
- Only trace amounts of MeCl and DME in the condensate

Conclusions

- Neat alumina is the most stable catalyst
- Binder free slurry coating method for stable and uniform catalyst coating
- Microreactor suppresses severe diffusion limitations in methanol and ethanol hydrochlorination
- Detailed kinetic models were developed for methanol and ethanol hydrochlorination
- Separation of MeCl and DME from water, methanol and HCl is efficient at high conversion (97.6 % conversion; > 99 wt% MeCl)
Summary

✓ Microprocess technology is a great challenge
✓ Microprocess technology is strongly multidisciplinary: manufacturing, characterization of materials, screening, kinetics, mass and heat transfer, flow measurement, modelling
✓ Take the challenge, search for new applications!
Thank you!

Internship students: Arne Reinsdorf, Zuzana Vajglova and Quentin Balme

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