Methyl chloride synthesis in a microreactor

Sabrina Schmidt
Åbo Akademi

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Outline

- Introduction
  - Microreactor technology
  - Methyl chloride

- The work
  - Key points
  - Kinetics of MeCl synthesis in the microreactor

- Summary
Microreactors

- Microstructured reactor:
  - A device with a three dimensional inner structure with at least one dimension smaller than 1 mm
Microreactors

- Variable functions, shapes, material and sizes
Benefits of microreactors

- High surface/volume ratio:
  - High heat transfer rates
  - Increased safety

- Short diffusion distances

- Fast mixing

- Perspective in production of poisonous intermediates

- Useful to study fast reactions; low in- and output of chemicals
Methyl chloride

- Solvent in synthesis of butylrubber
- Reactant in:
  - Methyl cellulose (food thickener / glue) production
  - Silikone production

$10^6$ tons/year to everyday products
Methyl chloride and Safety

- Highly flammable and toxic gas
- Transportation and Storage = 😞 / a risk and a cost
- Failure (e.g. runaway) of a big unit is dangerous
- Idea: produce methyl chloride on-site in a microreactor in the amounts needed
Reactions in methyl chloride synthesis

\[ CH_3OH + HCl \leftrightarrow CH_3Cl + H_2O \]

\[ 2CH_3OH \leftrightarrow CH_3OCH_3 \]

\[ CH_3OCH_3 + HCl \leftrightarrow CH_3OH + CH_3Cl \]

- Industrial Catalyst: Alumina (pure or modified with ZnCl\textsubscript{2})
- Fast reaction, full conversion in ≤1s (200-300 °C)
- Feasible for a microreactor
Keypoints

- Catalyst Coating
- Determination of reaction kinetics
- Catalyst development
- ”Numbering up” and product separation
Microreactor

- IMM stainless steel gas-phase microreactor

Catalyst: μ-alumina
Conversion and Selectivity

- Conversions up to 83 %
- Selectivities up to 91 %
- Selectivity increases with conversion and is rather independent of temperature
Proposed model

- Langmuir-Hinshelwood Mechanism

\[ r_1 = k_1 \frac{(c_{CH_3OH}c_{HCL} - \frac{c_{CH_3Cl}c_{H_2O}}{K_1})}{D^2} \]

\[ r_2 = k_2 \frac{(c_{MeOH}^2 - \frac{c_{DME}c_{H_2O}}{K_2})}{D^2} \]

\[ r_3 = k_3 \frac{(c_{DME}c_{HCL} - \frac{c_{MeOH}c_{MeCl}}{K_3})}{D^2} \]

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

- Detailed description of MeCl formation
- DME formation shows deviation
- Significantly lower concentration
Mass transfer limitations

! Obtained activation energy of reaction 1 is about the double of the previously reported

Possible mass transfer limitations → modeling of diffusion in catalyst layer

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<th>Value</th>
<th>Error (%)</th>
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<td>Becerra et al. (1992)</td>
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<td>Thyagarajan et al. (1966)</td>
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Modeling of internal diffusion

- Methanol concentration profile inside the catalyst layer

- Diffusion limitations are prominent already at coating thicknesses of 50 μm
- Explains deviation from previously published activation energies
"Numbering up"

- Two microreactors are installed in series
- $T = 340 \, ^\circ\text{C}$
- Residence time: 0.17 s
- Conversion 97.3 % and Selectivity of 98.8 %
  - Close to the thermodynamic equilibrium
- This setup corresponds to a production of ca 4 kg/year
Summary

- Motivation: On site production of MeCl to minimize risks due to transportation and storage and increase process safety.

- Reasonable MeOH conversion and selectivity are reached in one microreactor

- Kinetic model for reaction system was developed with data collected in the microreactor

  - Mathematical modeling showed that significant diffusion limitations occur starting from catalyst layer thicknesses of 50 µm

- Thermodynamic equilibrium conversion can be reached using two microreactors
Thank you for your attention!