Ethyl and methy chloride synthesis in microreactors

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Methyl and ethyl chloride

$\mathrm{CH}_3\mathrm{Cl}\quad\mathrm{C}_2\mathrm{H}_5\mathrm{Cl}$

$10^6$ tons/year to important everyday products

$\sim100,000$ tons/year direct use and ethyl cellulose
Production

- Hydrochlorination of ethanol and methanol

\[ \text{R-OH} + \text{HCl} \rightarrow \text{R-Cl} + \text{R-O-R} \]

- In case of ethanol also ethylene, acetaldehyde
- \( T \sim 300 \, ^\circ\text{C} \), catalyst: Alumina, Zinc chloride / Alumina
- Very rapid reactions
Microreactors

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

- Benefits of microreactors:
  - High heat transfer rates
  - Short diffusion distances
  - Small inner volume: Safety
    - Perspective in on-site production of chemical intermediates
    - Useful to study fast reactions; low in- and output of chemicals
Why microreactor: 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
- ”Keep the tiger in the cage!”
Why microreactor: Diffusion

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

- Catalyst studies
- Catalyst coating technique for the microreactor
- Kinetic and thermodynamic investigations
- Mathematical modeling
- Product separation
The experimental setup
The microreactor

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

- He/HCl
- He
- MeOH
- Neutralization bottle
- Sampling section, septum
- Microreactor / Tubular reactor
- Washing bottle
- PC
- GC
- MeOH
- MeCl
- DME
Catalysts
The catalyst

- Industrially pure Alumina and ZnCl$_2$/Alumina
- Active sites: Lewis acid sites (Al$^{3+}$ centers)

\[
\begin{align*}
\text{Al} & \quad \text{O} \\
\text{HCl} & \quad \rightarrow \\
\text{Cl} & \quad \text{H} \\
\text{Al} & \quad \text{O}
\end{align*}
\]

- Activity and selectivity can be improved by addition of zinc chloride
  - Formation of highly active and selective molecular zinc sites on the support from BAS (zeolites) and surface hydroxyl groups (alumina)
  - Formation of bulk species starting at 5-10 wt% zinc
Catalysts for methanol hydrochlorination

- Tested catalysts:
  - Neat alumina
  - Zinc chloride modified alumina
  - Zinc chloride modified zeolites
Effects of zinc modification

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

- Support: 5 wt% Zn on alumina and zeolites
Catalyst of choice

• Neat alumina is least active and selective, but cheap and robust catalyst
  • Catalyst of choice

• Zinc modified alumina is stable in the tubular reactor but selectivity decreases in the microreactor

• Zeolites are the most active but least stable catalysts
Catalyst coating

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

- Confocal microscopy: Morphology, thickness and surface roughness

- Coating thickness: 15 μm, channel depth: 90 μm
Kinetic studies and mathematical modeling
Methyl chloride synthesis

- Hydrochlorination of methanol at 300 °C
  \[ CH_3OH + HCl \leftrightarrow CH_3Cl + H_2O \]  
  \( K_{eq} = 398 \)  

- Lightly exothermic, main reaction: -30 kJ/mol

- The reactions are not completely irreversible!
Performance of one and two microreactors

- A very high conversion and selectivity can be reached with two microreactors
Reaction modeling inside the catalyst layer

- **Kinetic model**: Langmuir-Hinshelwood

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

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

- **Diffusion model**: Mean transport pore model

\[
D_{ei} = \left(\frac{\varepsilon_p}{\tau_p}\right)D_i
\]

\[
\frac{dc_i}{dt} = \varepsilon_p^{-1} \left( \rho_p \sum \nu_{ij} R_j a_j + D_{ei} \left( \frac{d^2 c_i}{dr^2} + \frac{s}{r} \frac{dc_i}{dr} \right) \right)
\]
Reactant concentration profile inside the catalyst layer

- Kinetic study in the microreactor revealed diffusion limitations in conventional reactors

- Wrong activation energies reported in literature

Microreactor
Effectiveness factor: 0.93

Conventional fixed bed
Effectiveness factor: 0.1-0.06
Ethanol hydrochlorination

\[
\text{EtOH} + \text{HCl} \rightarrow \text{EtCl + H}_2\text{O}
\]

\[
\text{EtCl + H}_2\text{O} \rightarrow \text{EtOEt + HCl}
\]

Reversible reactions:

\[
\text{EtOEt + H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + \text{EtOH}
\]

\[
\text{C}_2\text{H}_4 + \text{HCl} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2
\]

At high T:

\[
\text{EtOH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}
\]
Selectivity to side products

- **DEE**: decrease with time and temperature
- **C$_2$H$_4$**: increase with temperature and time (at t≥300°C)

DEE + HCl → EtCl + EtOH
DEE → C$_2$H$_4$ + EtOH
ETCl → C$_2$H$_4$ + HCl (at 340°C)

- **Acetaldehyde**: very low
Kinetic model

- Kinetic model:
  1) EtOH + HCl → EtCl + H₂O
  2) 2 EtOH → DEE + H₂O
  3) EtOH → C₂H₄ + H₂O
  4) EtOH → CH₃CHO + H₂
  5) DEE + HCl → EtCl+ EtOH

- Langmuir-Hinshelwood:

\[
r_1 = k_1 \frac{c_{EtOH} c_{HCl} - \frac{c_{EtCl} c_{H₂O}}{K_I}}{D^2}
\]

\[
D = (1 + K_{EtOH} c_{EtOH} + K_{HCl} c_{HCl})
\]
Product distribution at varying reactant concentrations

- **EtCl**
- **DEE**
- Ethylene

Graphs showing the concentration of EtCl, DEE, and Ethylene over time, with annotations indicating overestimated and underestimated values.
Influence of HCl on ether and ethylene formation

- Solution: C$_2$H$_4$ and DEE are catalyzed by HCl on the alumina surface due to increased acidity

- Expression:

$$r_2 = k_2 \frac{c_{EtOH}^2 - \frac{c_{DEE}c_{H2O}}{K_{II}}}{D^2}$$

$\alpha$: Parameter: impact of HCl catalysis

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

- Improved description
- Precise description

- Dependence of product distribution on reactant concentration is improved but not precise
- Exact dependence of kinetics on catalyst surface is complex
Product Separation
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 -10 °C

Cooling surface: 210 cm²
Efficiency of separation: gas phase

- Composition of the gas phase at maximum conversion (97.6%)
- Composition comparable for all condensers at -10 °C
- MeCl and DME are efficiently separated from the liquid

<table>
<thead>
<tr>
<th></th>
<th>Prior to condenser</th>
<th>After condenser</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>2,5</td>
<td>0,12</td>
</tr>
<tr>
<td>DME</td>
<td>1,6</td>
<td>0,74</td>
</tr>
<tr>
<td>MeCl</td>
<td>95,9</td>
<td>99,14</td>
</tr>
</tbody>
</table>

/wt%
Efficiency of separation: liquid phase

- Collected at 83.3% conversion

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

- 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 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)
Thank you for your attention!

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