Process Chemistry Centre

GSCE

Ethyl and methy chloride synthesis in microreactors

POKE Summerschool on Saaremaa

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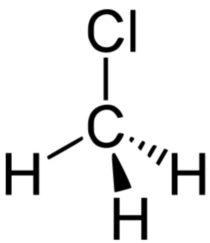
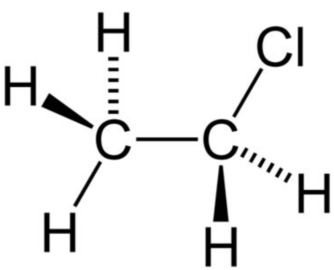
Methyl and ethyl chloride

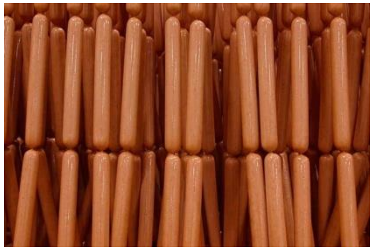
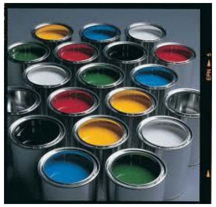


10^6 tons/year to important everyday products



~100.000 tons/year direct use and ethyl cellulose

ICIS Chemical Business Americas; 3/19/2007, Vol. 271 Issue 11, p50-50, 1p; Pictures: Wikipedia

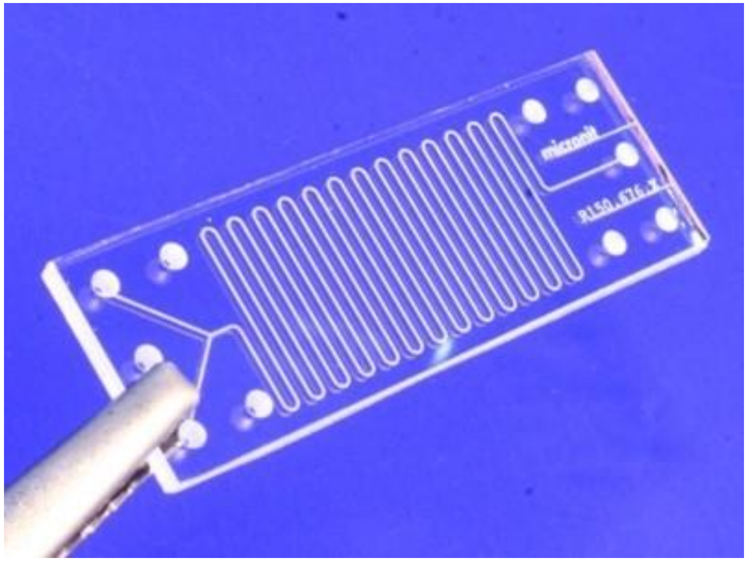
Production

- Hydrochlorination of ethanol and methanol
- **R-OH + HCl → R-Cl + R-O-R**

  - In case of ethanol also ethylene, acetaldehyde
  - T ~ 300 °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

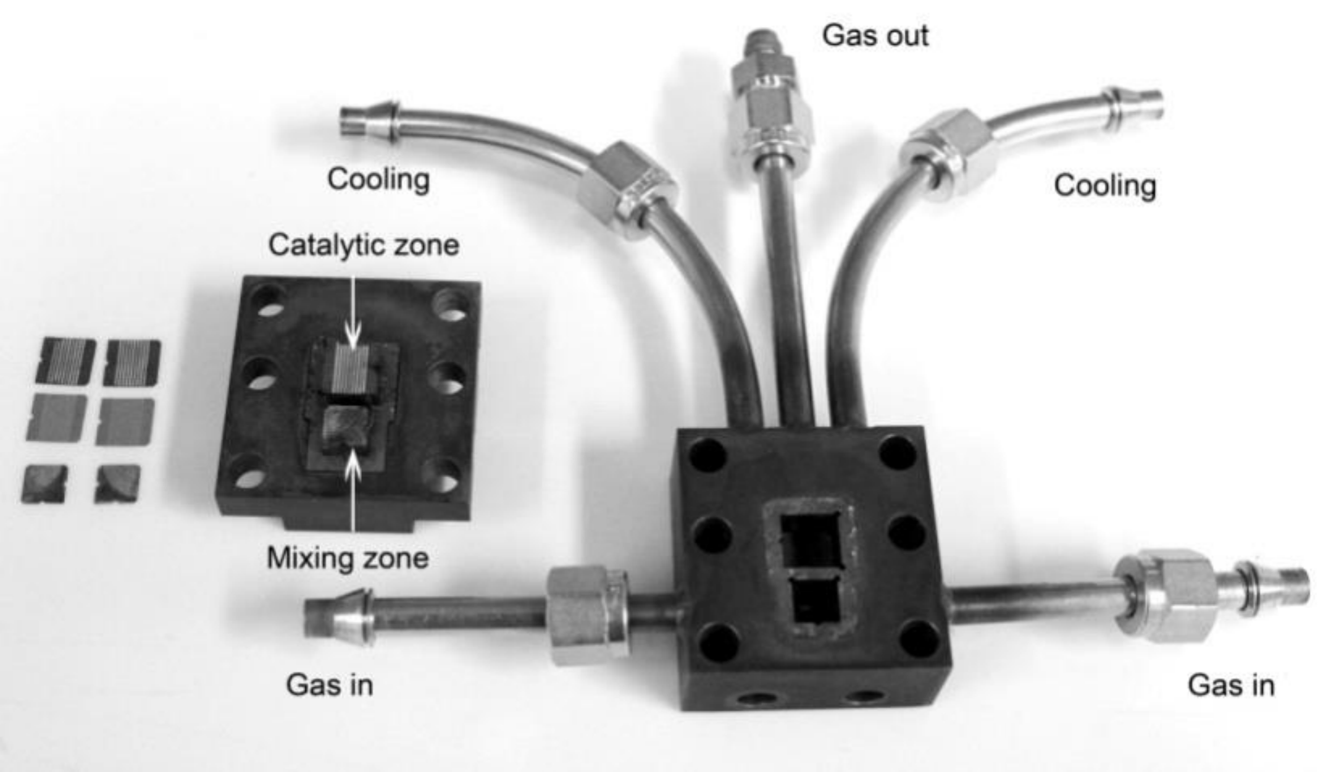
- Efficiency: EtCl / MeCl formation is very fast!
  - Low diffusion distances
  - Increased catalyst and space efficiency
  - Ideal tool for kinetic studies

Research strategy

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

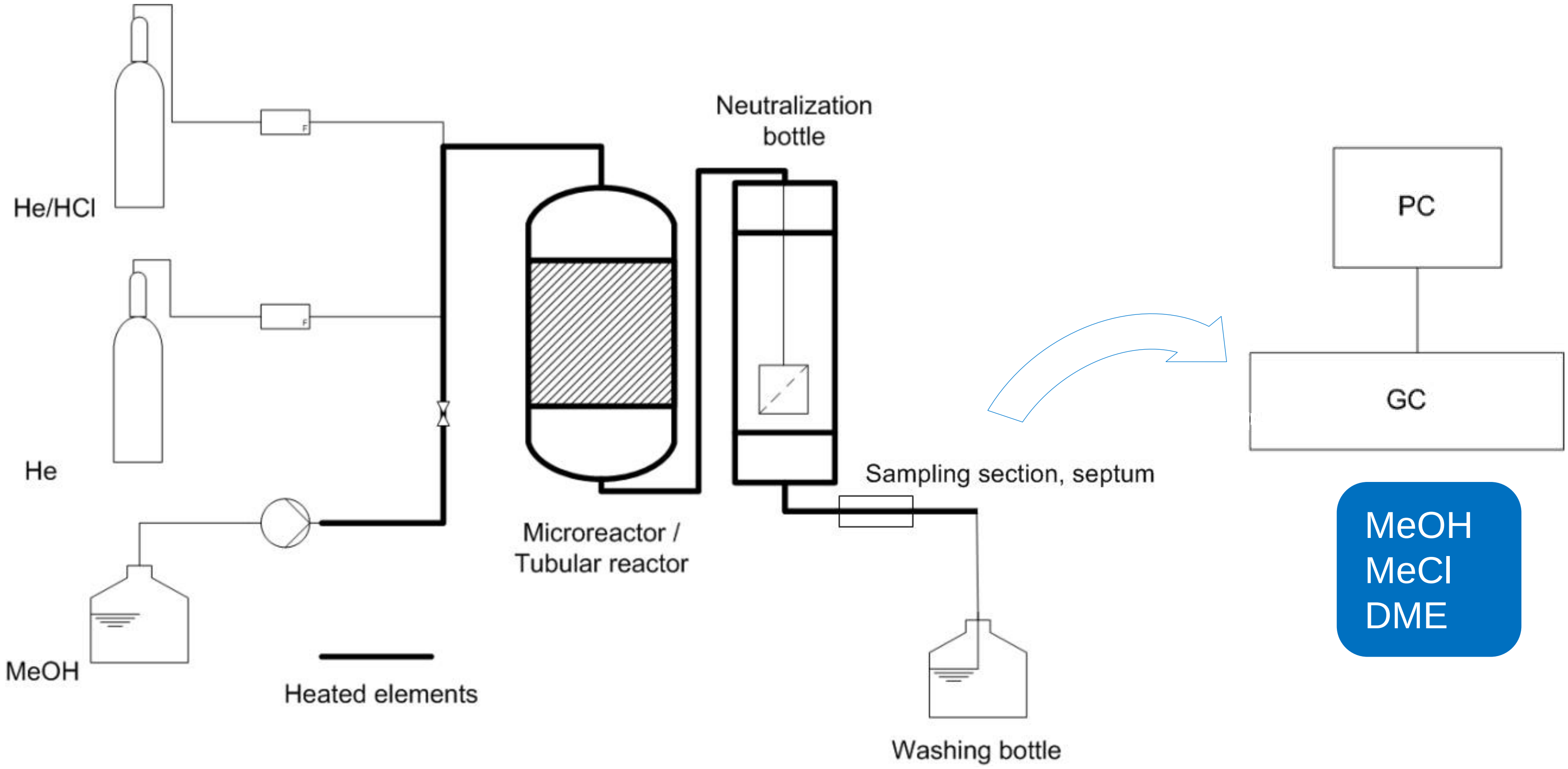
The experimental setup

The microreactor



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

Experimental setup: microreactor and tubular reactor

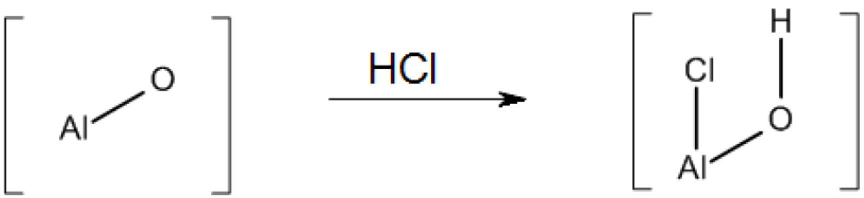


MeOH
MeCl
DME

Catalysts

The catalyst

- Industrially pure Alumina and $ZnCl_2$/Alumina
- Active sites: Lewis acid sites (Al^{3+} centers)



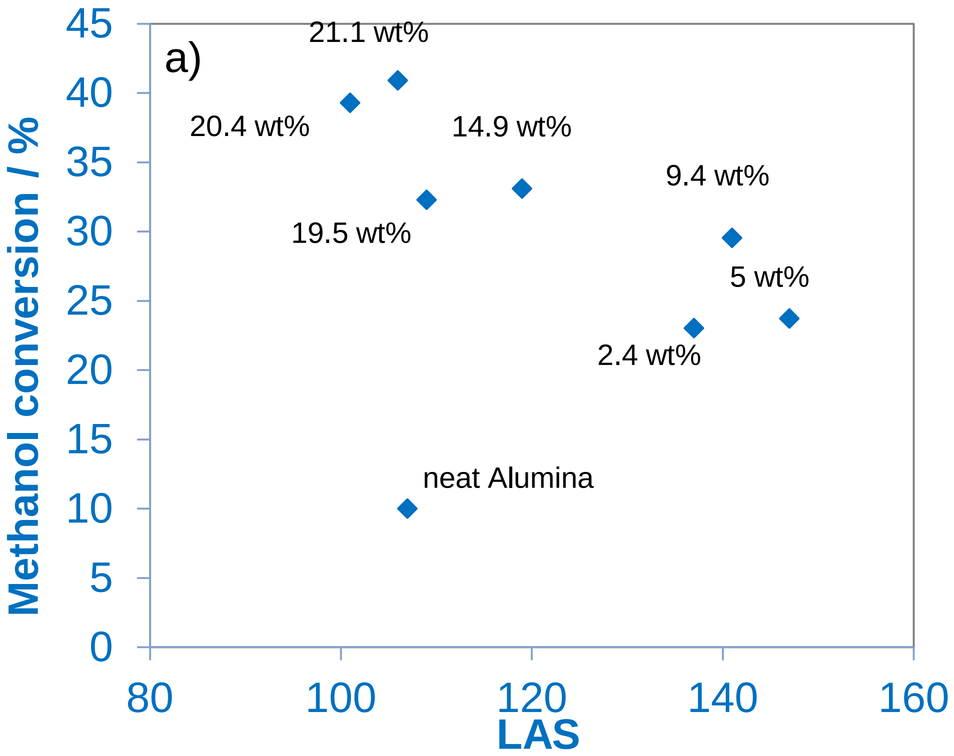
- Activity and selectivity can be improved by addition of zinc chloride
  - Formation of highly active and selective molecular zinc sites on the support from BAS (zeolites) and surface hydroxyl groups (alumina)
  - Formation of bulk species starting at 5-10 wt% zinc

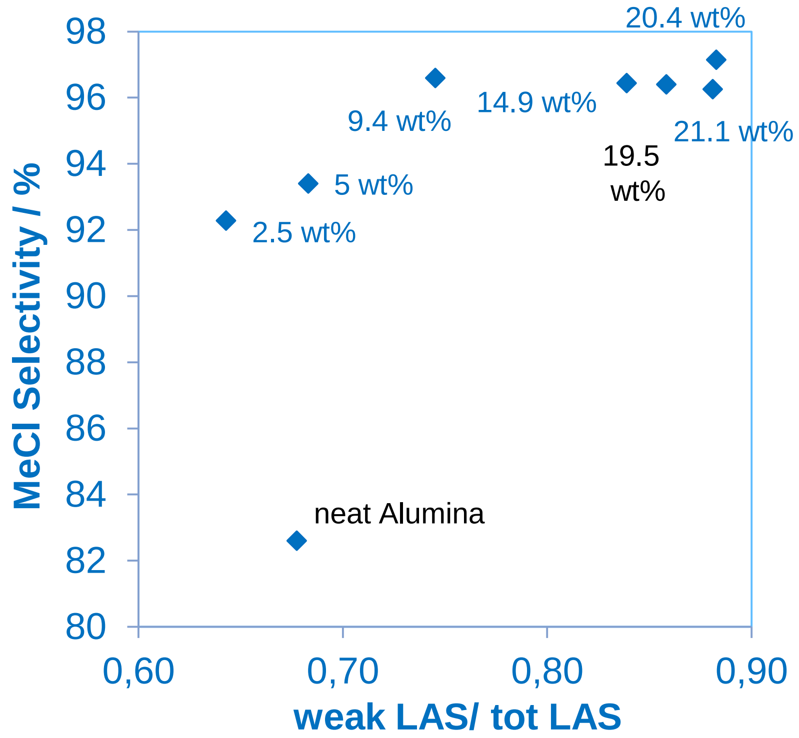
Catalysts for methanol hydrochlorination

- Tested catalysts:
  - Neat alumina
  - Zinc chloride modified alumina
  - Zinc chloride modified zeolites

Effects of zinc modification

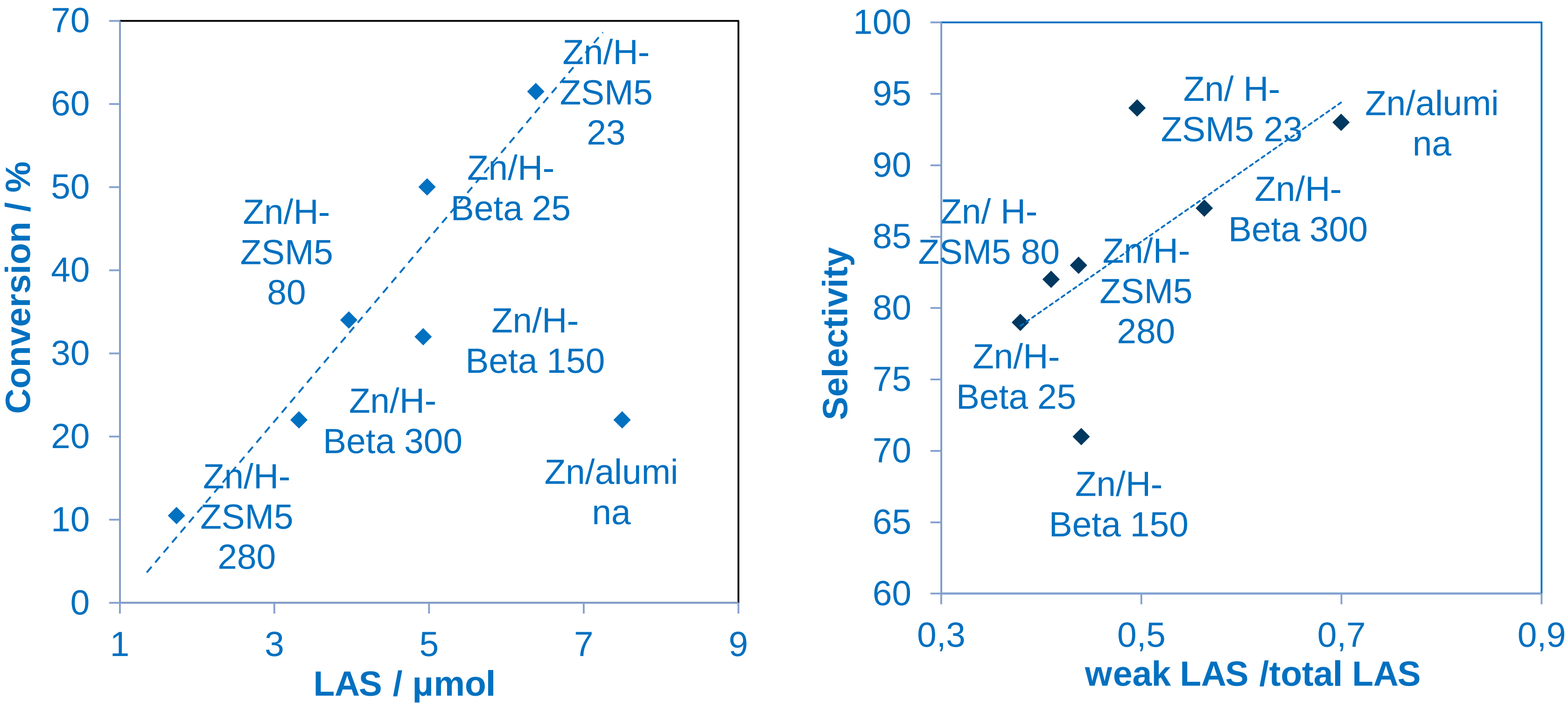
- Loading: 0-21 wt% Zn on alumina





Effects of zinc modification

- Support: 5 wt% Zn on alumina and zeolites

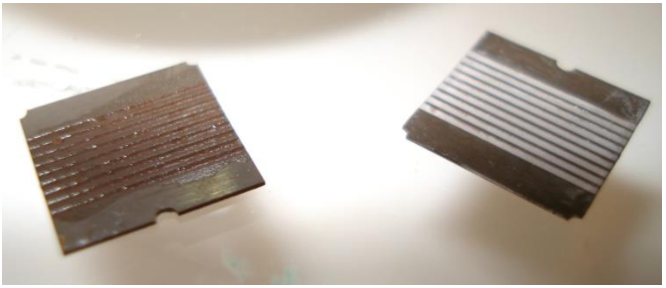


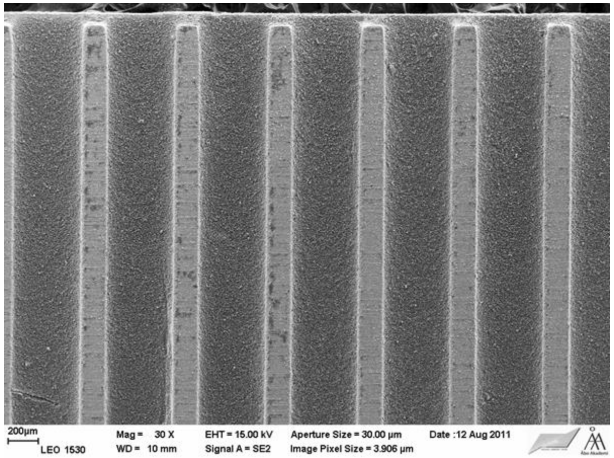
Catalyst of choice

- 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 selectivivity 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

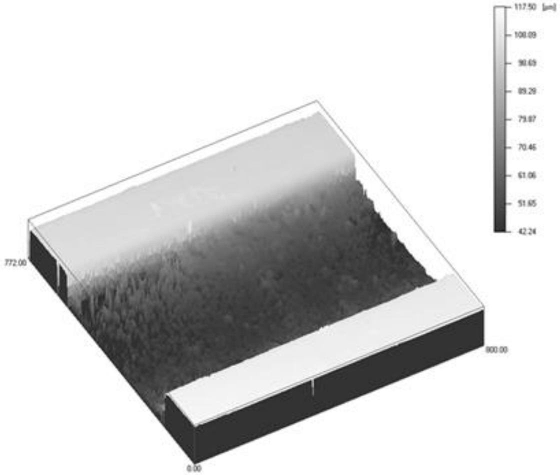


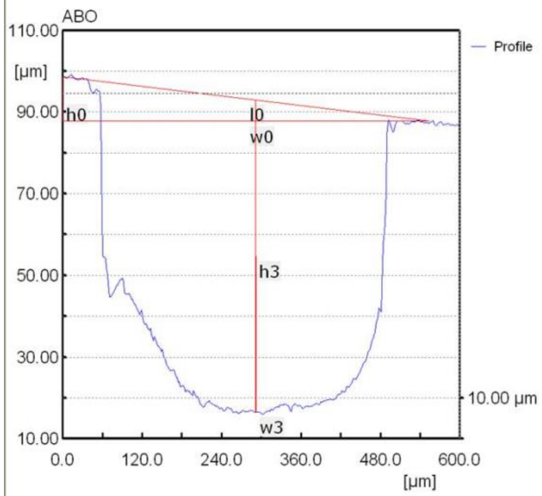


S. A. Schmidt, N. Kumar, B. Zhang, K. Eränen, D. Yu. Murzin, and T. Salmi, Preparation and Characterization of Alumina-Based Microreactors for Application in Methyl Chloride Synthesis, *Ind. Eng. Chem. Res*. **2012**, 51, 4545

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

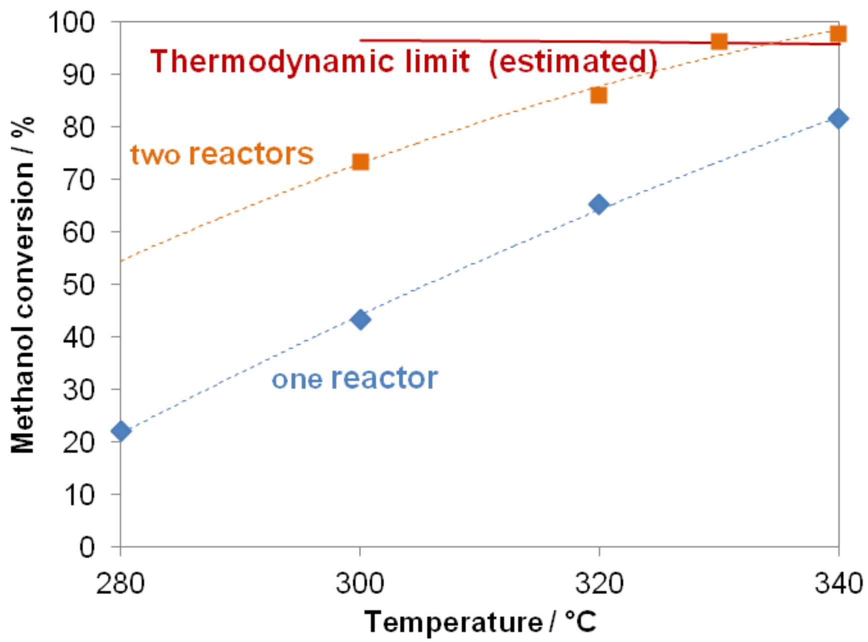
- Hydrochlorination of methanol at 300 °C

Reaction		K_{eq}
$CH_3OH + HCl \leftrightarrow CH_3Cl + H_2O$	(I)	398
$2CH_3OH \leftrightarrow CH_3OCH_3$	(II)	12
$CH_3OCH_3 + HCl \leftrightarrow CH_3OH + CH_3Cl$	(III)	36

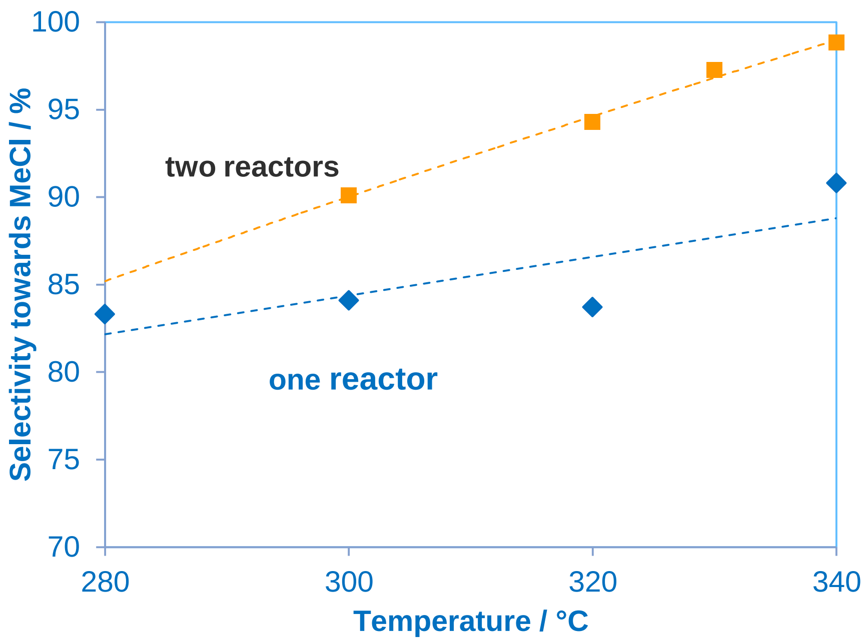
- Lightly exothermic, main reaction: -30 kJ/mol
- The reactions are not completely irreversible!

Performance of one and two microreactors

Methanol conversion



Selectivity towards methyl chloride



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

Reaction modeling inside the catalyst layer

- Kinetic model: Langmuir-Hinshelwood

$$r_1 = k_1 \frac{(c_{CH3OH} c_{HCL} - \frac{c_{CH3Cl} c_{H2O}}{K_1})}{D^2}$$

$$r_2 = k_2 \frac{(c_{MeOH}{}^2 - \frac{c_{DME} c_{H2O}}{K_2})}{D^2}$$

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

$$D = K_{HCl} c_{HCl} + 1$$

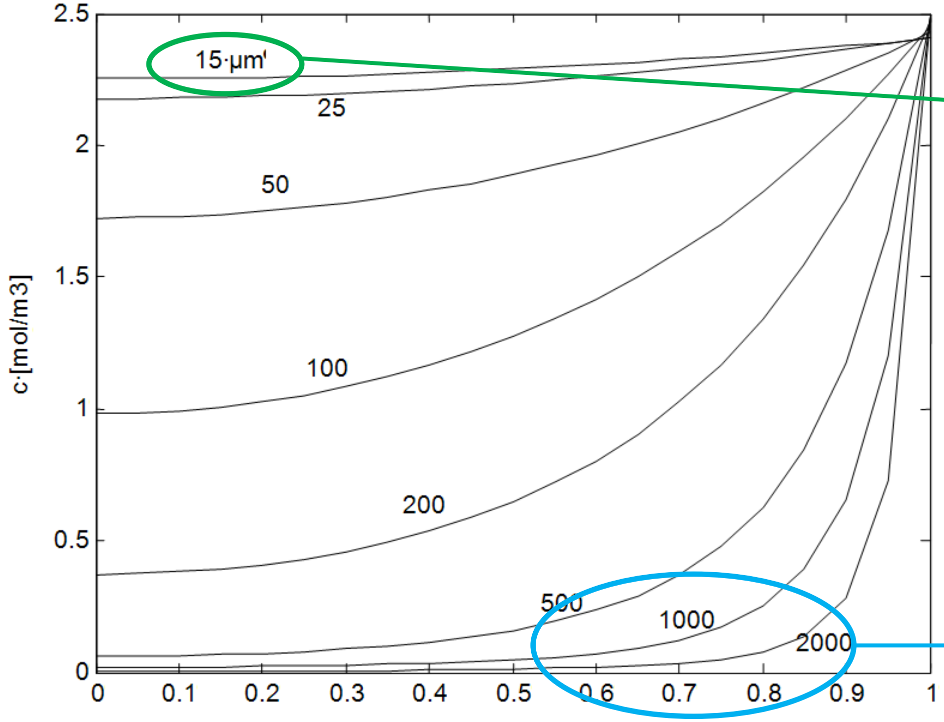
- Diffusion model: Mean transport pore model

$$D_{ei} = (\frac{\varepsilon_p}{\tau_p}) D_i$$

$$\frac{dc_i}{dt} \varepsilon_p^{-1} = \left(\rho_p \sum \nu_{ij} R_j a_j + D_{ei} \left(\frac{d^2 c_i}{dr^2} + \frac{s}{r} \frac{dc_i}{dr} \right) \right)$$

Reactant concentration profile inside the catalyst layer

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

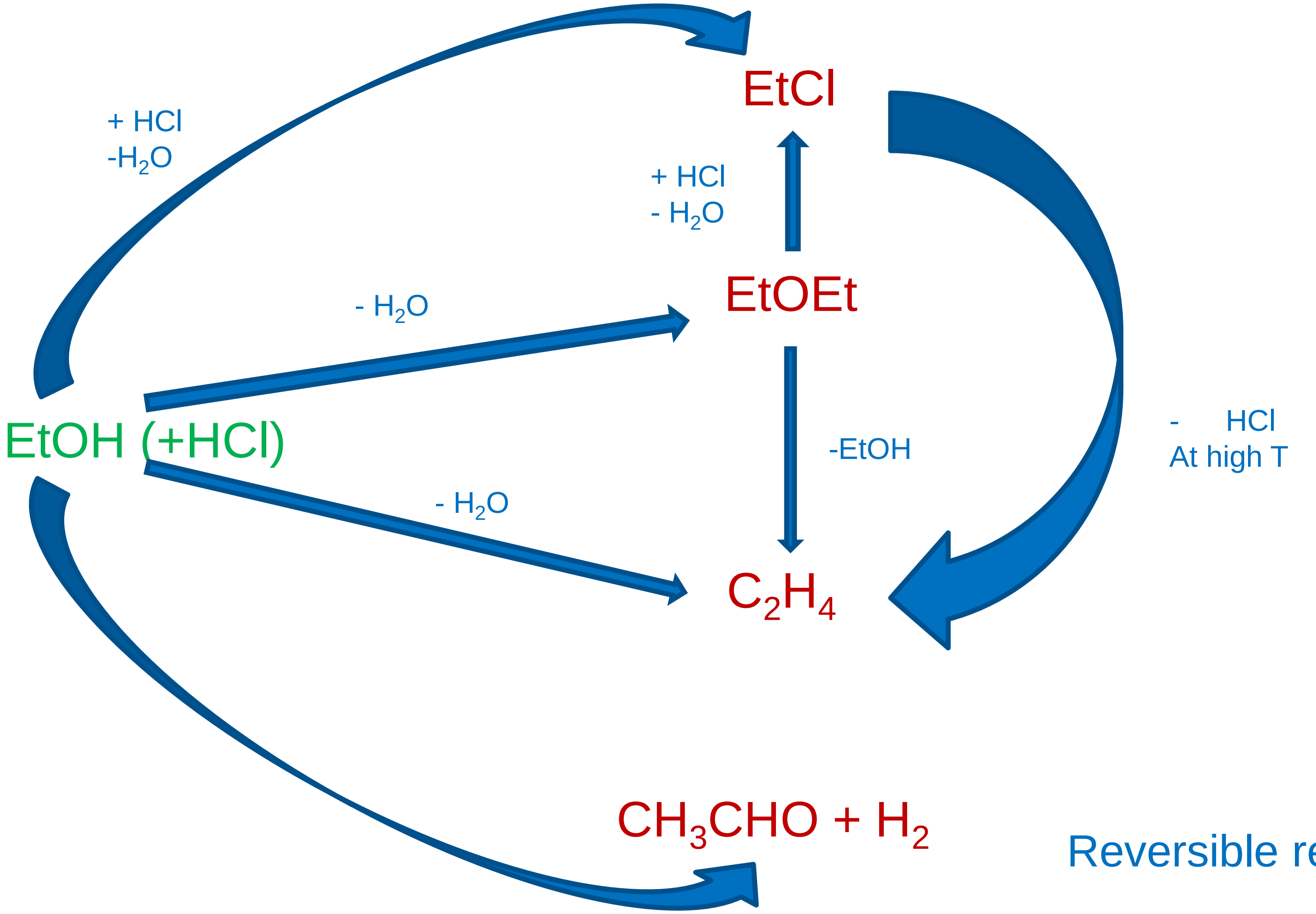


Microreactor
Effectiveness factor:
0.93

Conventional
fixed bed
Effectiveness factor:
0.1-0.06

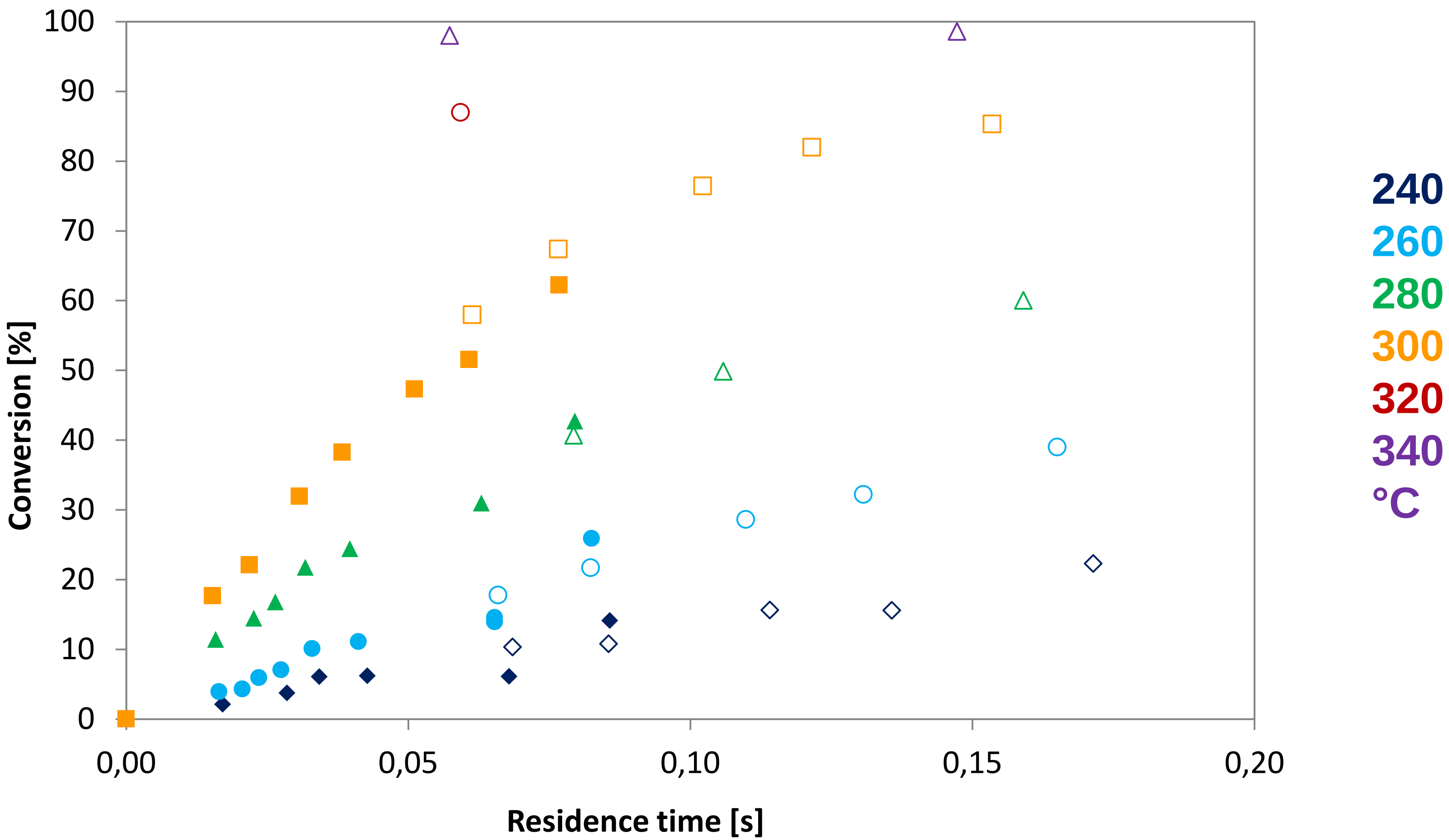
- Wrong activation energies reported in literature

Ethanol hydrochlorination

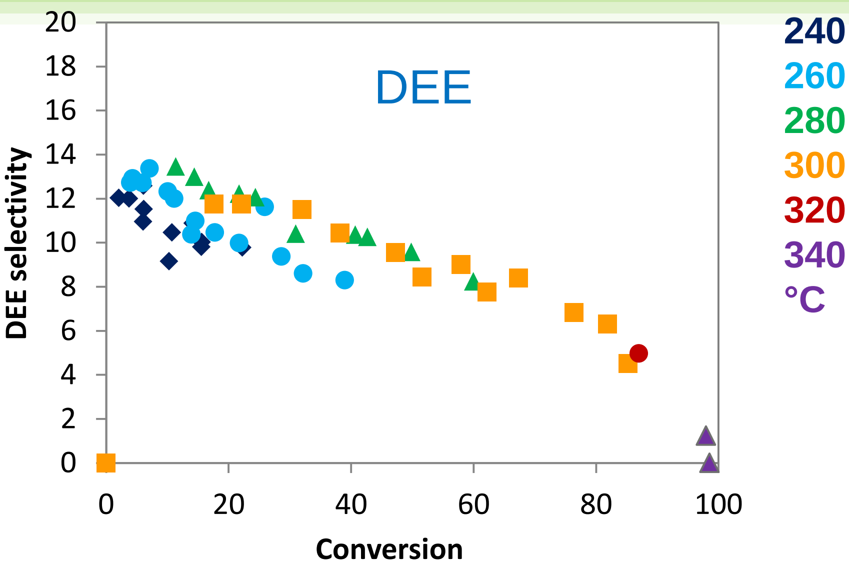


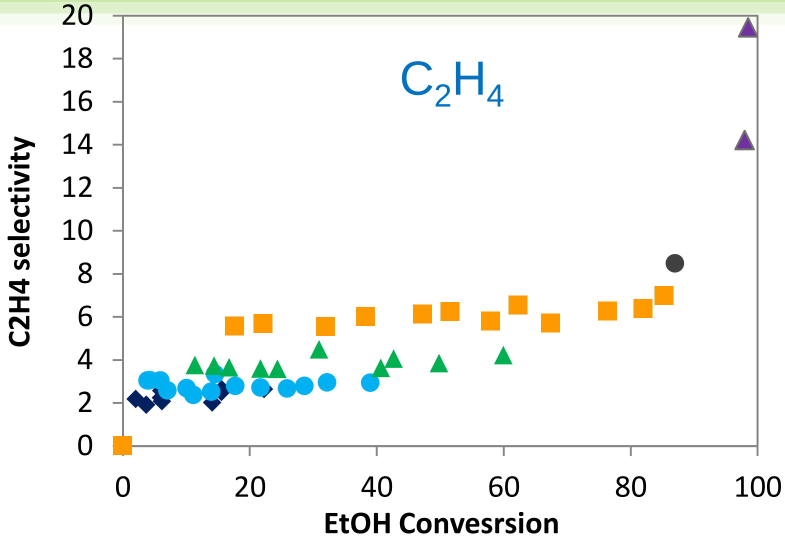
Reversible reactions

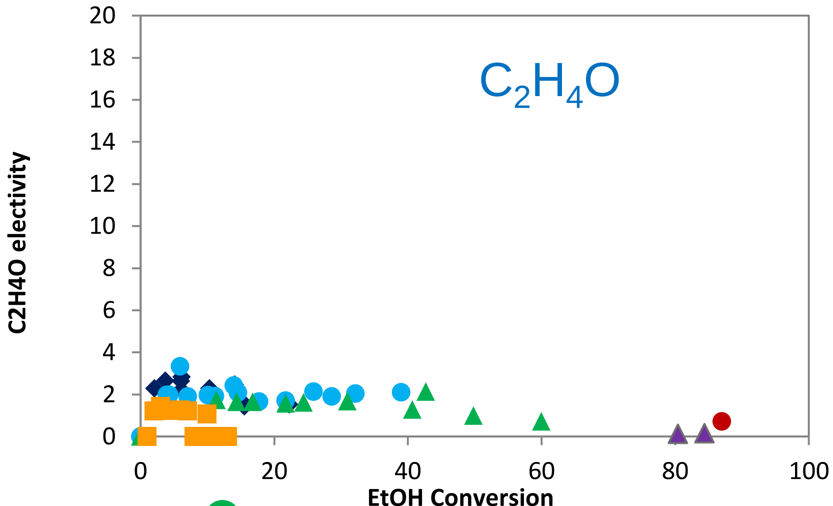
EtOH Conversion



Selectivity to side products







- DEE: decrease with time and temperature
- C_2H_4: increase with temperature and time (at t≥300°C

DEE + HCl → EtCl+ EtOH
DEE → C_2H_4 + EtOH
ETCl→ C_2H_4 + HCl (at 340 °C)

- Acetaldehyde: very low

Kinetic model

- Kinetic model :

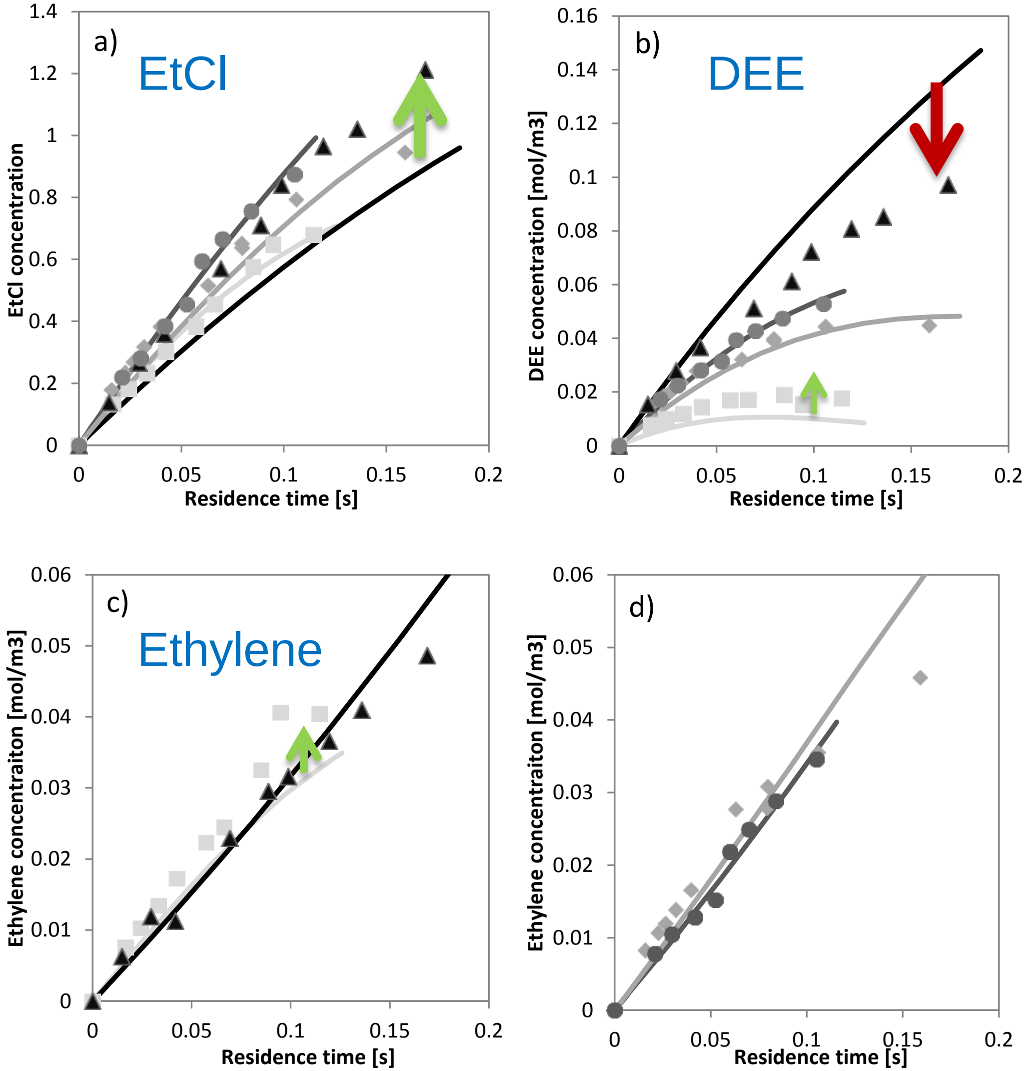
1) EtOH + HCl → EtCl + H_2O
2) 2 EtOH → DEE + H_2O
3) EtOH → C_2H_4 + H_2O
4) EtOH → CH_3CHO + H_2
5) DEE + HCl → EtCl+ EtOH

- Langmuir-Hinshelwood :

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

$$D = (1 + K_{EtOH} c_{EtOH} + K_{HCl} c_{HCl})$$

Product distribution at varying reactant concentrations



overestimated

underestimated

Influence of HCl on ether and ethylene formation

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

- Expression:

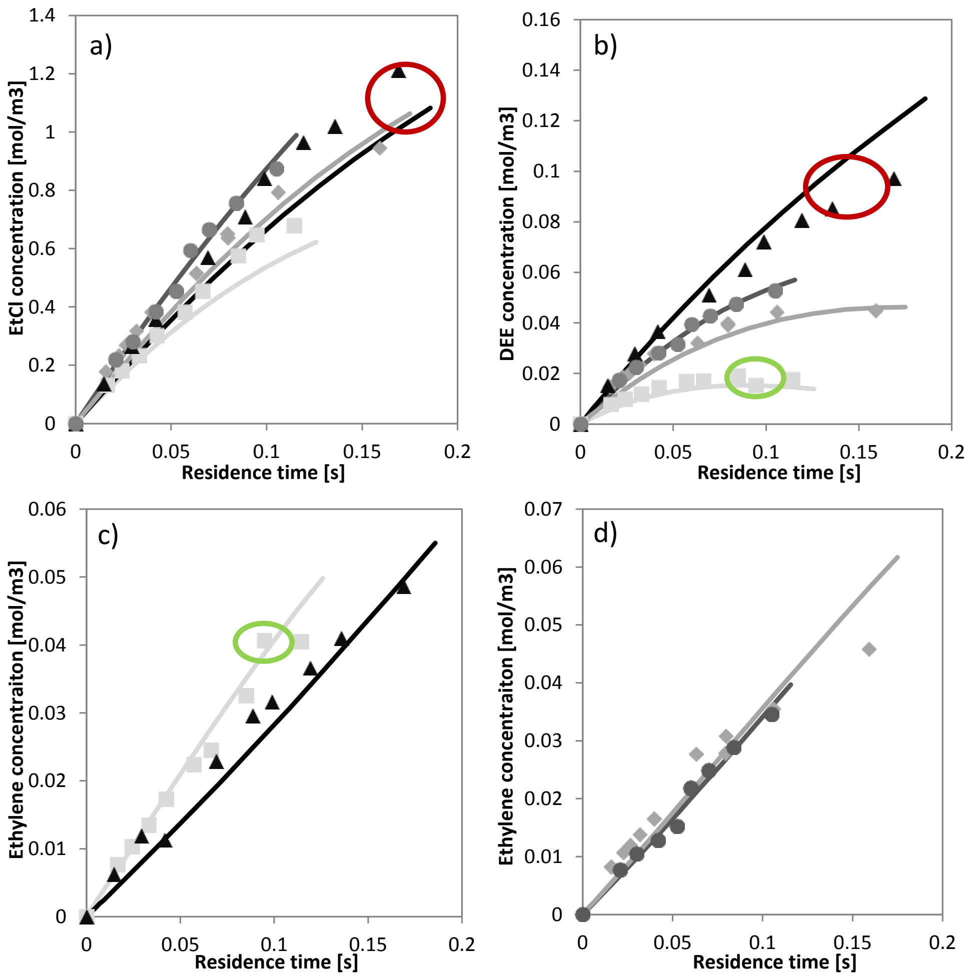
$$r_2 = k_2 \frac{c_{EtOH}^2 - \frac{c_{DEE} c_{H2O}}{K_{II}}}{D^2}$$

$$*(1 + c_{HCl}^*)^{\alpha * \frac{c_{HCl}^*}{c_{HCl}^* + c_{EtOH}^*}}$$

α: Parameter : impact of HCl catalysis

For c_{HCl} or $\alpha \rightarrow 0$ the term approaches 1

Improved kinetic model



Improved description

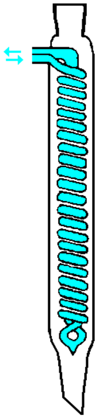
Precise description

- 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

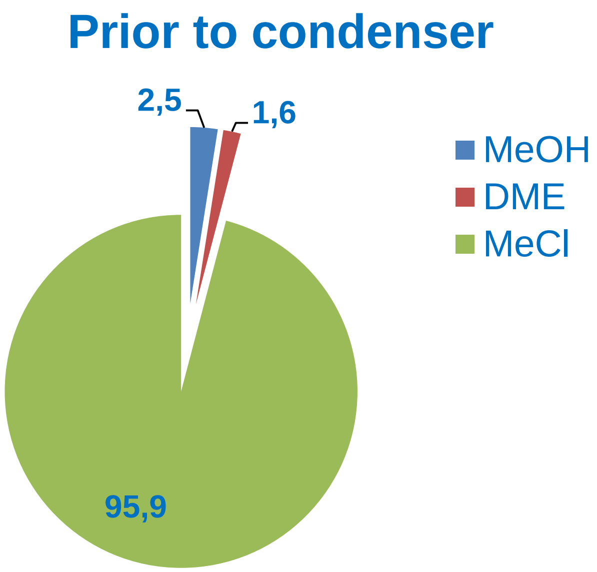
- Aim: At the outlet of the reactor: only traces of MeOH, HCL and DME due to maximum conversion
- Methanol and water separation by condensation
- Glass made condenser, coolant: glycerin -10 °C

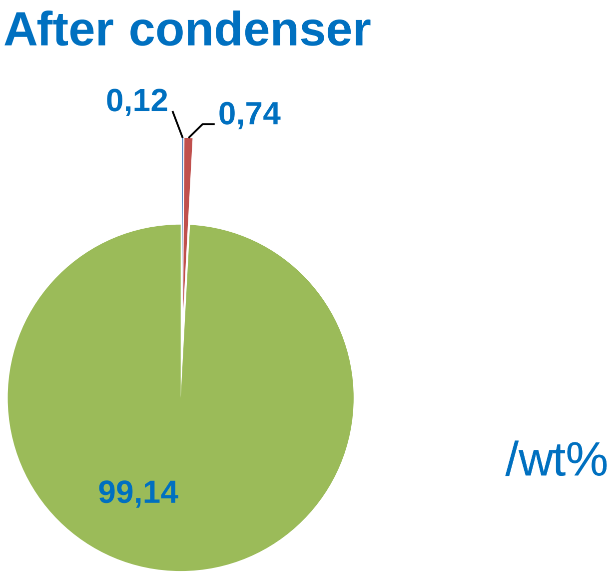


Cooling surface: 210 cm^2

Efficiency of separation: gas phase

- Composition of the gas phase at maximum conversion (97.6%)
- Composition comparable for all condensers at -10 °C

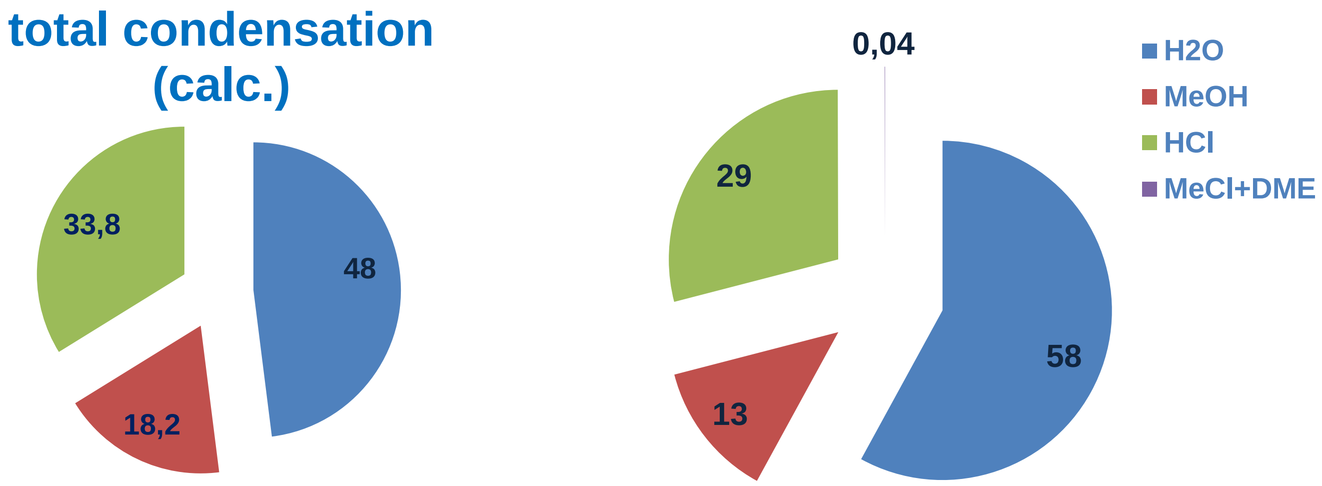




- MeCl and DME are efficiently separated from the liquid

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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