Turku/Åbo – the oldest city of Finland

The only medieval city of Finland
Around 300000 inhabitants in the Turku metropolitan area
Bilingual city
Two universities; more than 30000 university students
Big industrial centre: metal, process, pharmaceutical and alimentary industry, ship building
Cultural Capital of Europe 2011



Åbo Akademi

The university Åbo Akademi was established
1640 by the Swedish Queen Kristina

Closed by Russian emperor after
the Turku fire 1827

Åbo Akademi was re-established in 1918 after the
Finnish independence
University of Turku was founded 1920

Åbo Akademi

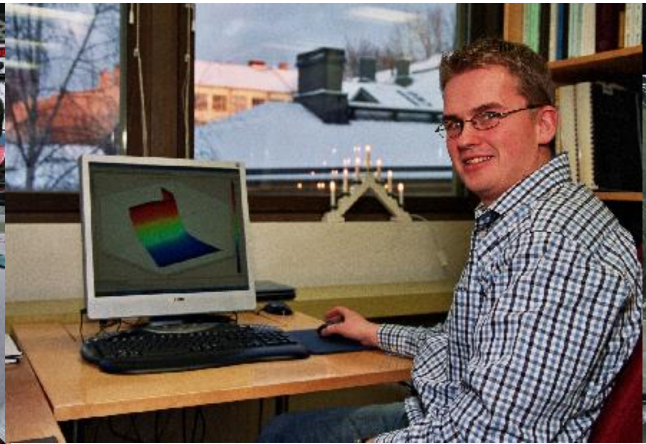
Today Åbo Akademi is classical, florishing university
-from humaniora to science,
-from theology to technology
-teaching language: Swedish
-English is used much in master’s
-and postgraduate level

- Close collaboration with University of Turku
-International
-Multicultural

TRADITIONS ARE HIGHLY APPRECIATED BY US – DOCTORAL PROMOTIONs EACH 2-3 YEARS

CHEMICAL AND PROCESS ENGINEERING
Åbo Akademi

- The activities of Chemical Engineering cover chemistry, chemical engineering, process and system engineering, pulp and paper technology, industrial management
- We follow the Bologna reform in studies (B.Sc & M.Sc. (diplomingenjör)
- International Master's Programme in Sustainable Chemical Engineering
- A very research-oriented Department – Dr.Degrees: Master's Degrees = 0.25 – about 15 Dr degrees per year
- Chemical Engineering Education was commenced in1920 – The Nobel Laureate Svante Arrhenius was consulted in the establishment of the curriculum


Industrial Chemistry Reaction Engineering at ÅA

around 35 scientists, around 15 languages

Towards new reactor technologies

Tapio Salmi

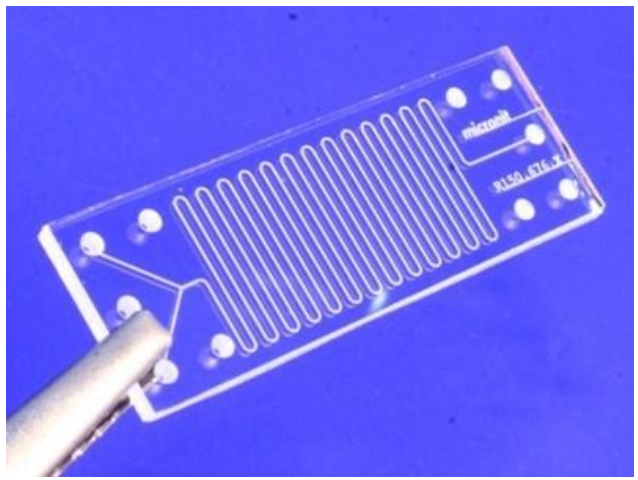
Åbo Akademi

Johan Gadolin Process Chemistry Centre,

Laboratory of Industrial Chemistry and Reaction Engineering

FI-20500 Turku / Åbo
Finland

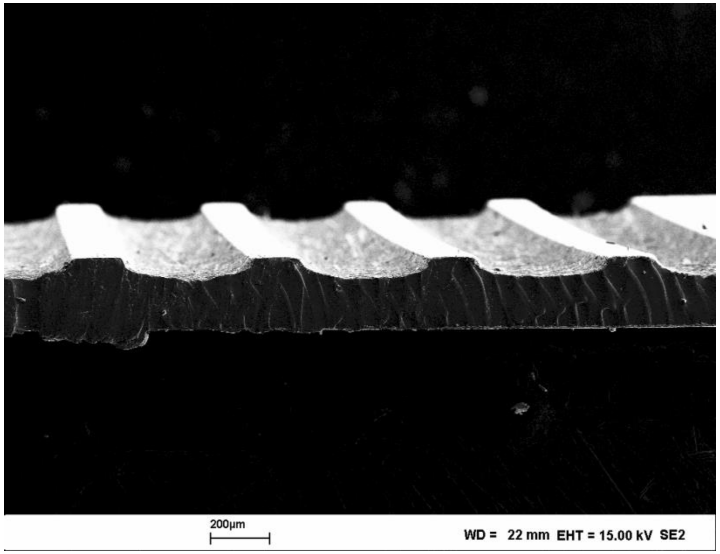
Gas-phase microreactor technology – some experiences



Tapio Salmi, Dmitry Murzin, Kari Eränen
José R. Hernández Carucci, Sabrina Schmidt, Ville Halonen
Åbo Akademi, Teknisk kemi och reaktionsteknik

Microreactors

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

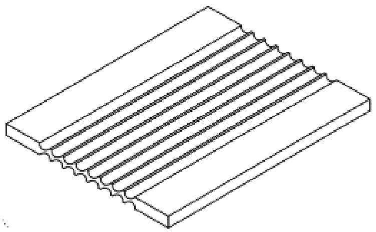


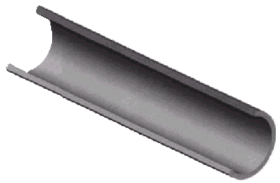
- Benefits of microreactors:
  - ✓ High heat transfer rates
  - ✓ Short diffusion distances
  - ✓ Small inner volume: Safety
  - ✓ Efficient kinetic investigation and catalyst screening

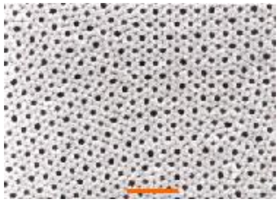
Microreactor - advantages

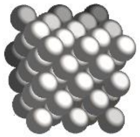
- Faster transfer of research results into on-site production
- High safety – small amounts of components
- Easy *number-up* to production capacity
- Smaller plants for production at distributed sites
- Smaller consuption of chemicals
- High surface-to-volume ratio
- Narrow residence time distribution (RTD)

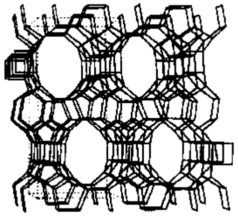
Microreaction technology: total reaction control at all length scales











10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} m

Reactor plates **Microchannels** **Coatings** **Clusters** **Micropores**

Level 1 Level 2 Level 3

Chemical engineering

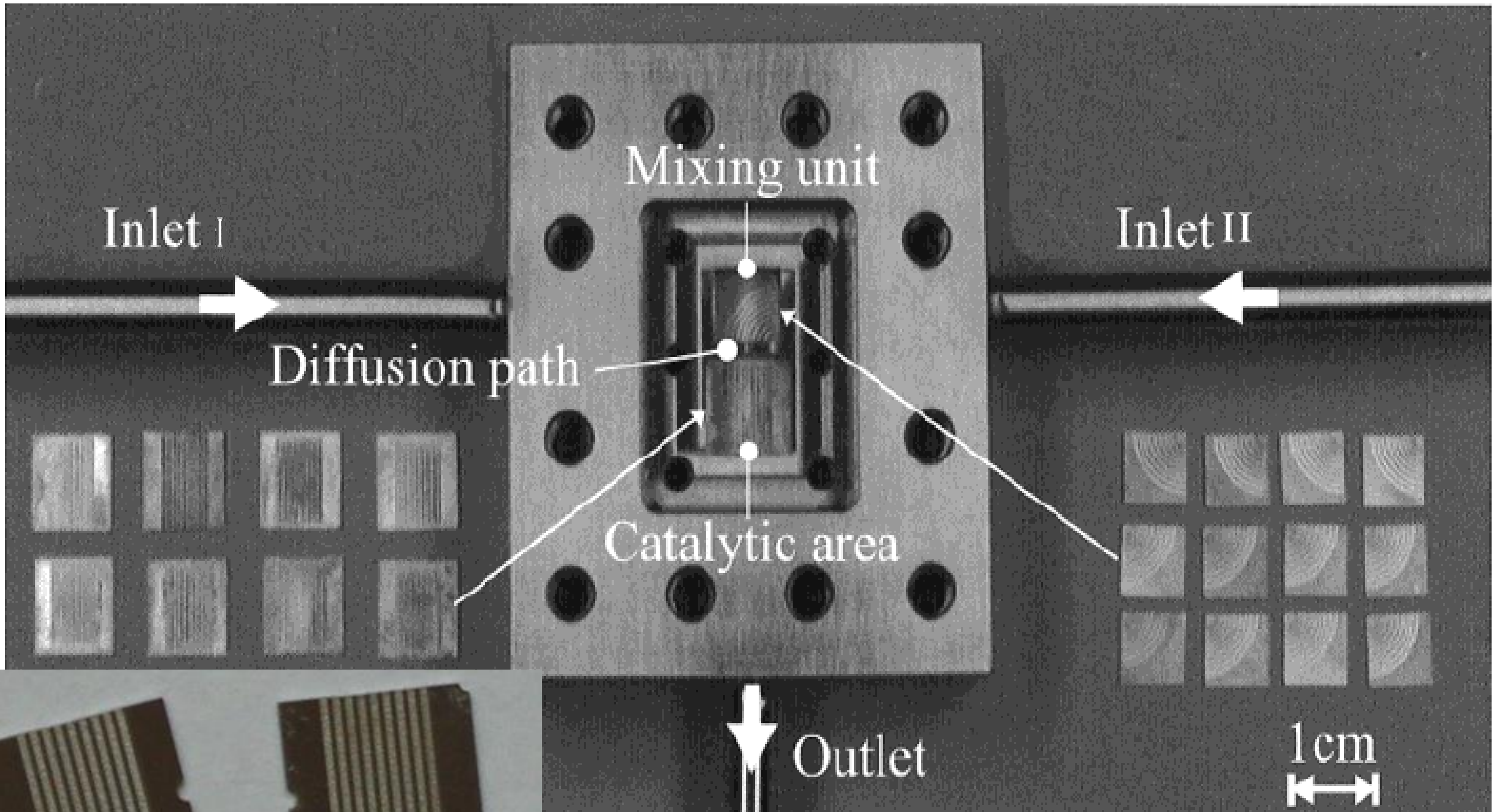
Materials science

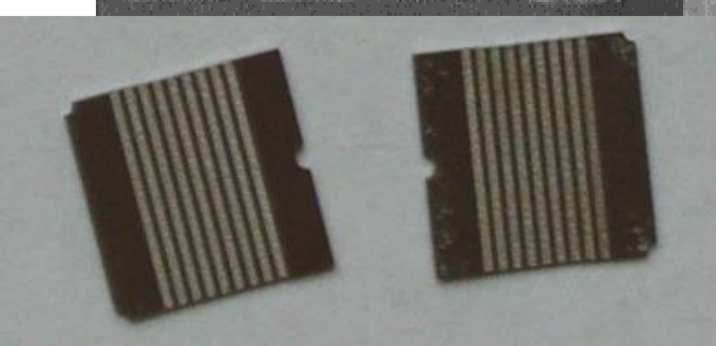
Organic chemistry

Mechanical engineering

Catalysis

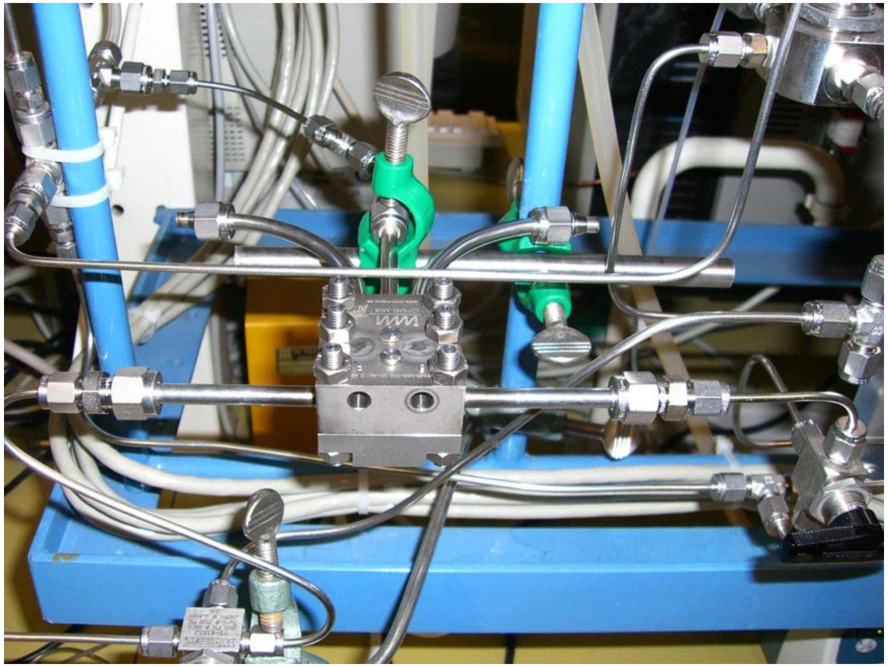
Gas-phase microreactor





Microreactors

– 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

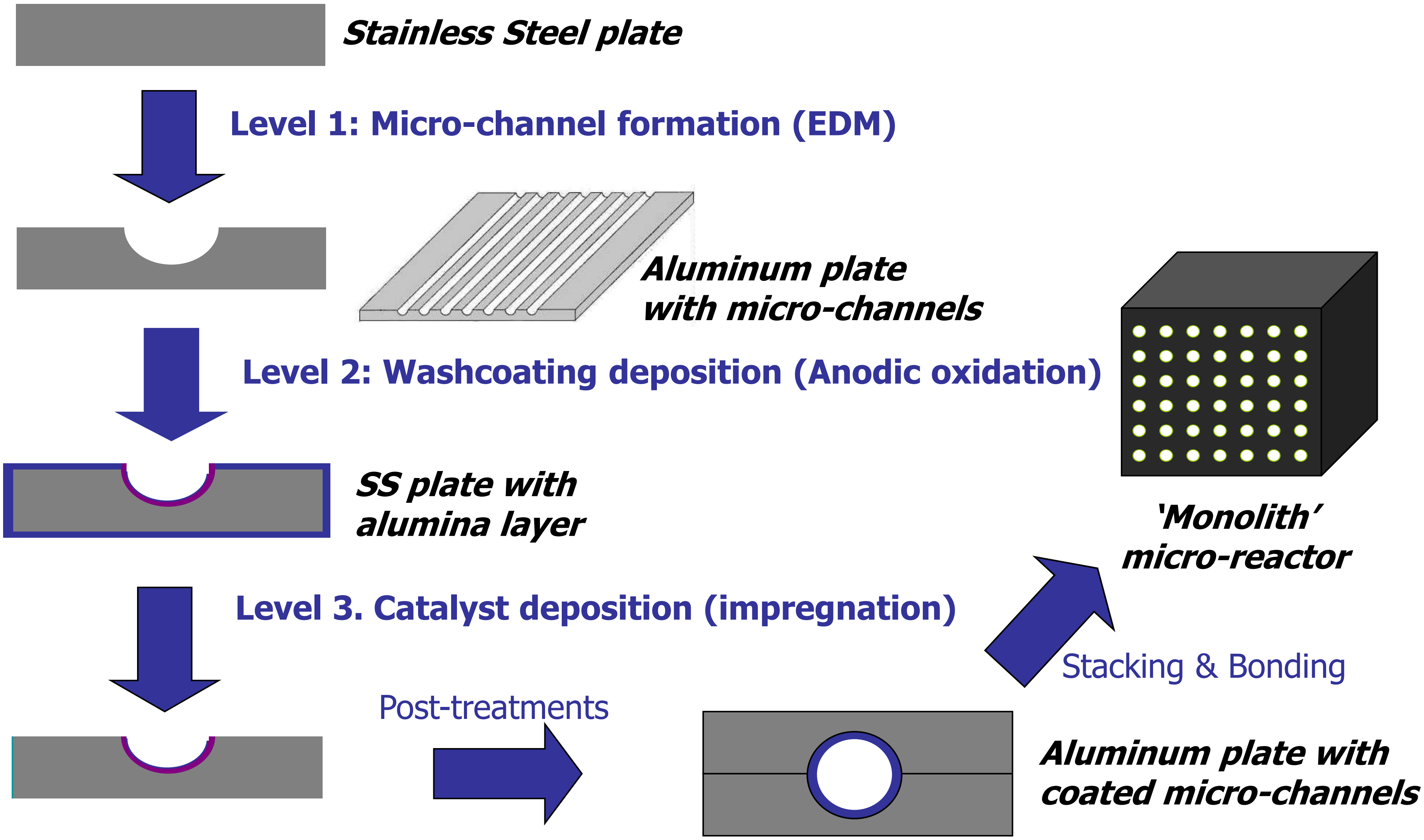


Microstructures = 100 – 500 μm
1 μm = 10^{-6} m

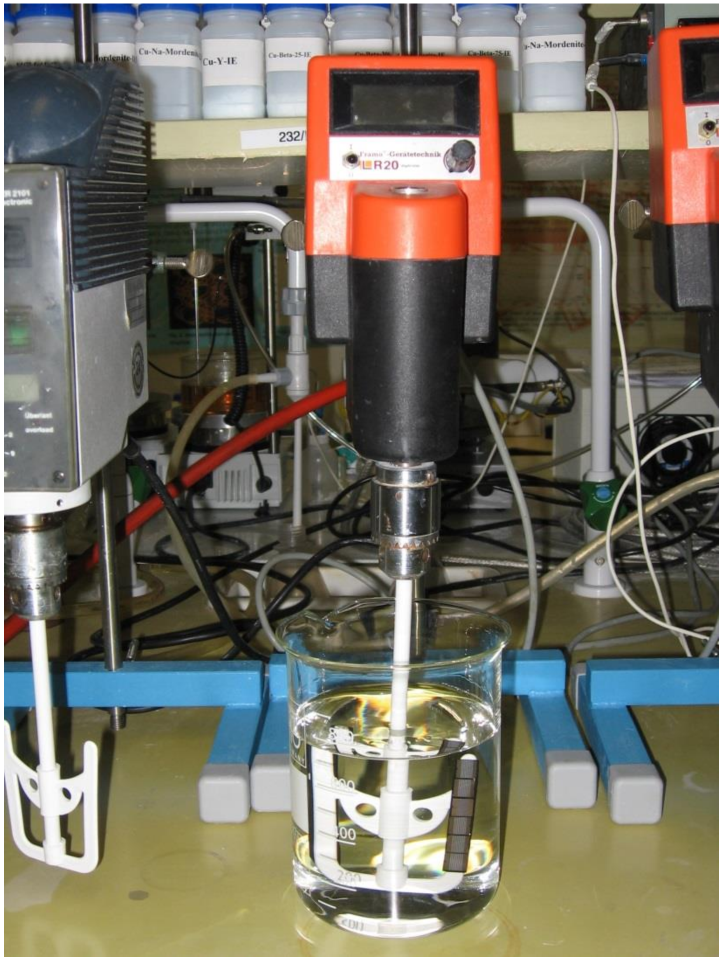
Research strategy

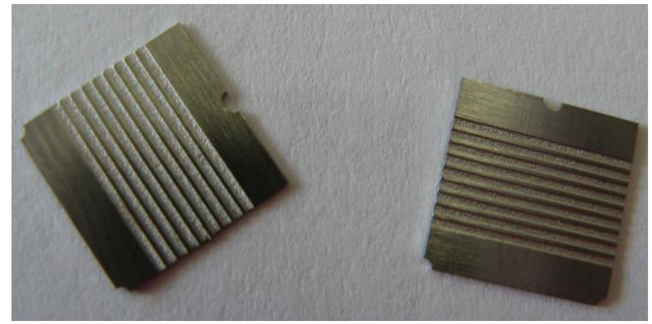
- To design and build the equipment
- To develop a catalyst (preparation, screening, characterization)
- To study the selected chemical systems in microreactors
- To develop kinetic and reactor models

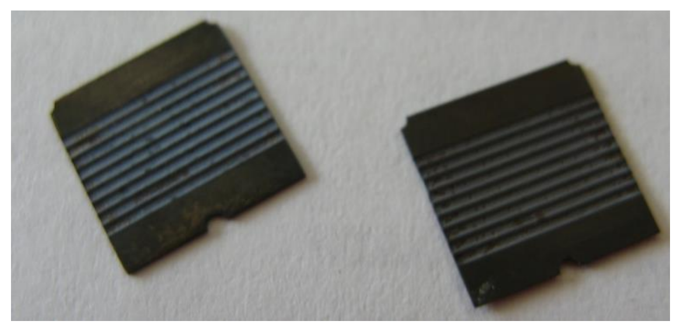
Plates manufacture



Plates impregnation (ÅA)

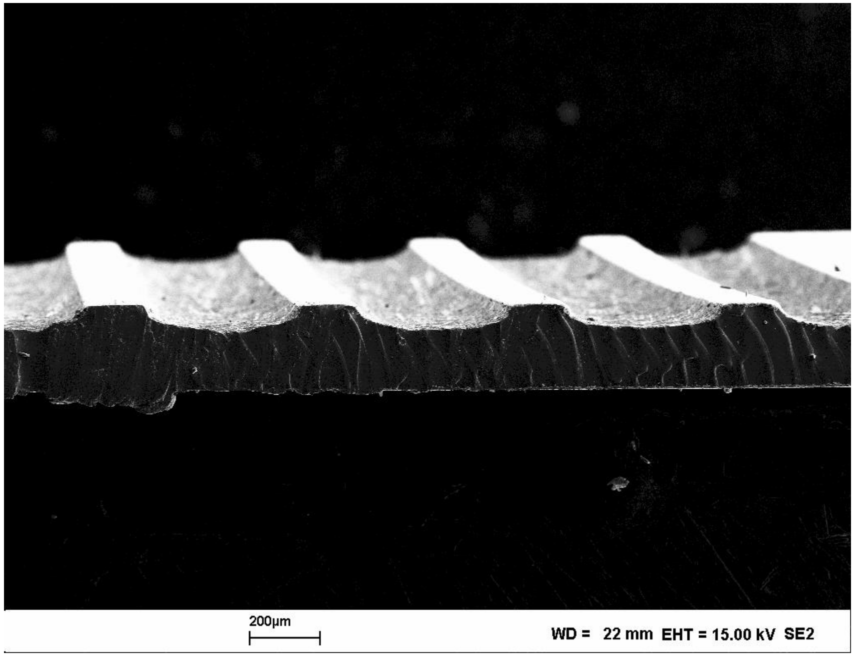


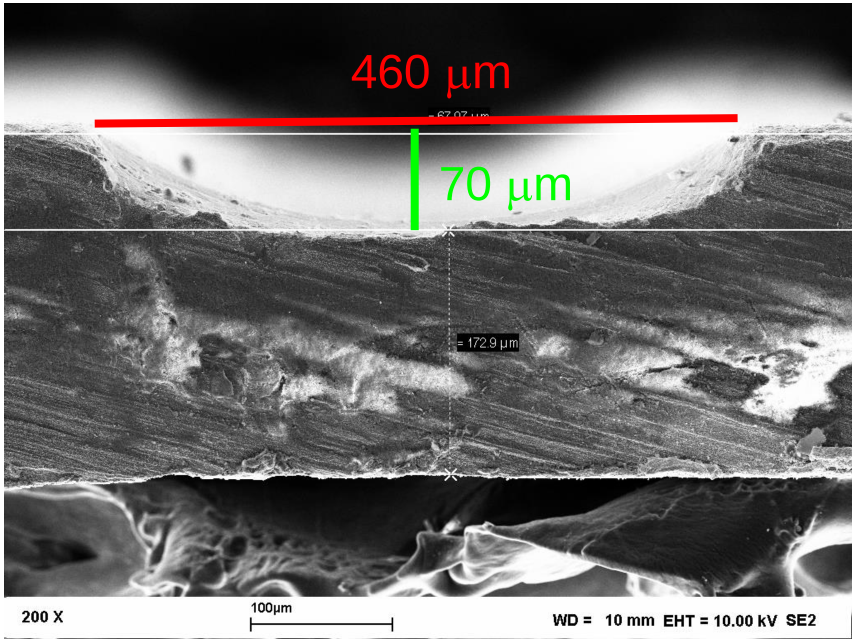




Characterization
SEM pictures of the plates

SEM pictures of raw platelet – 50X



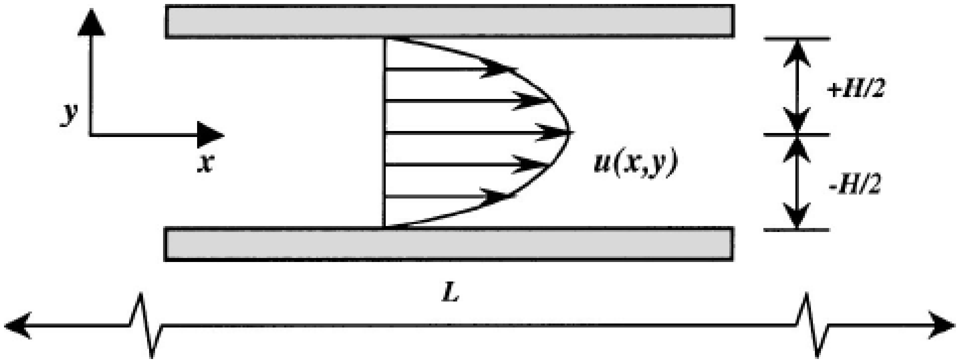


SEM pictures of raw platelet – 200X

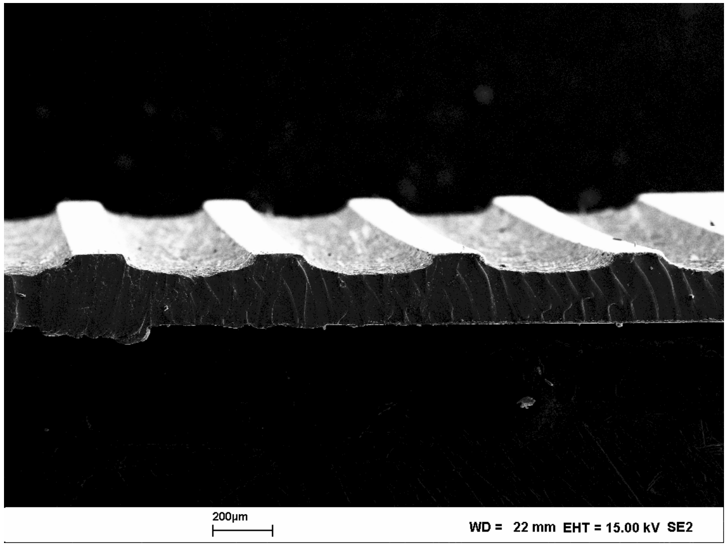
Modelling of microchannels

- Modelling of microreactors still slightly inmature.
- 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

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

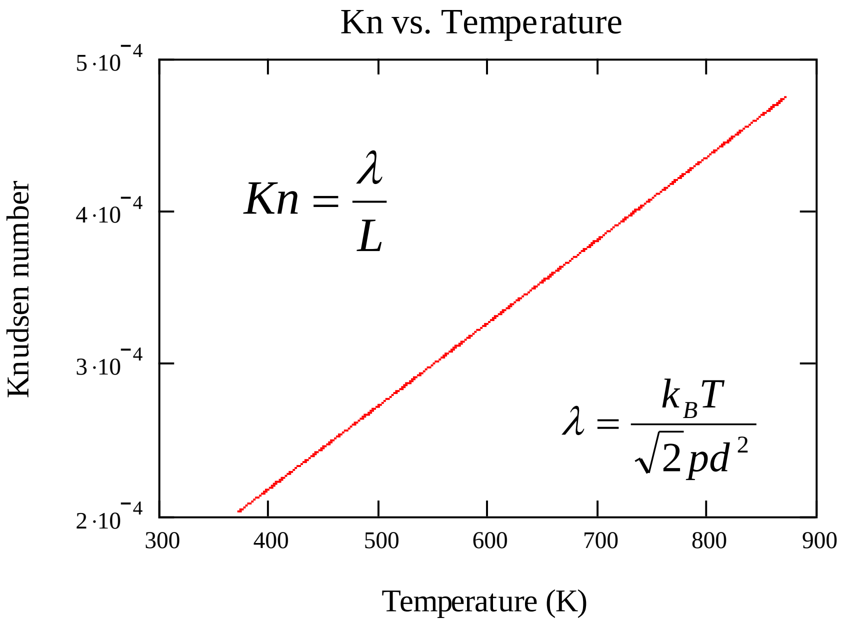
Kn all the time in non-slip domain, usual continuum description and all the components of the velocity are zero close to the walls

Flow in microchannels

Gas-phase microreactor system with spare parts

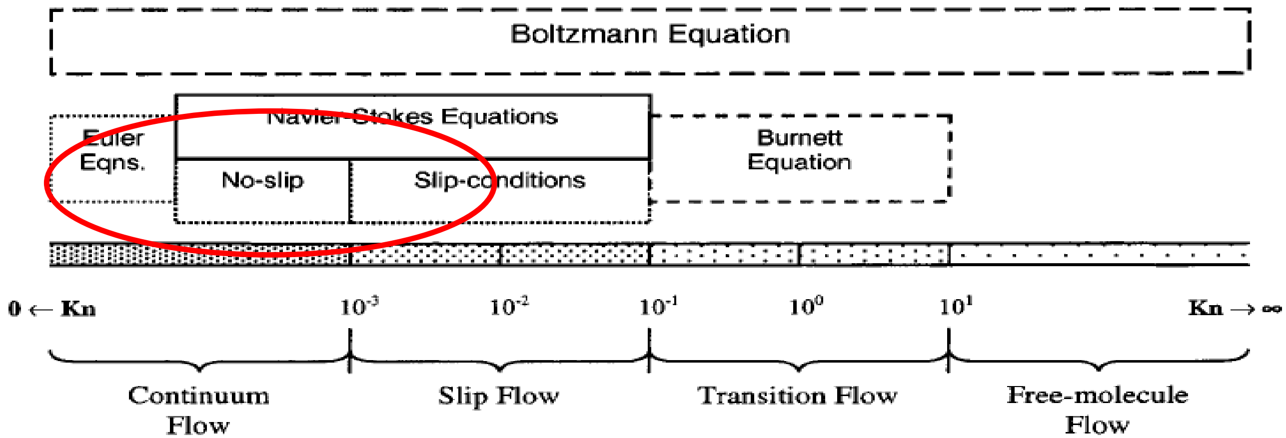
- What are the boundaries?
- What is microscale?
- Are the classical equations valid?

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 ($Kn > 10$)

Macroflows relationships are valid!



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

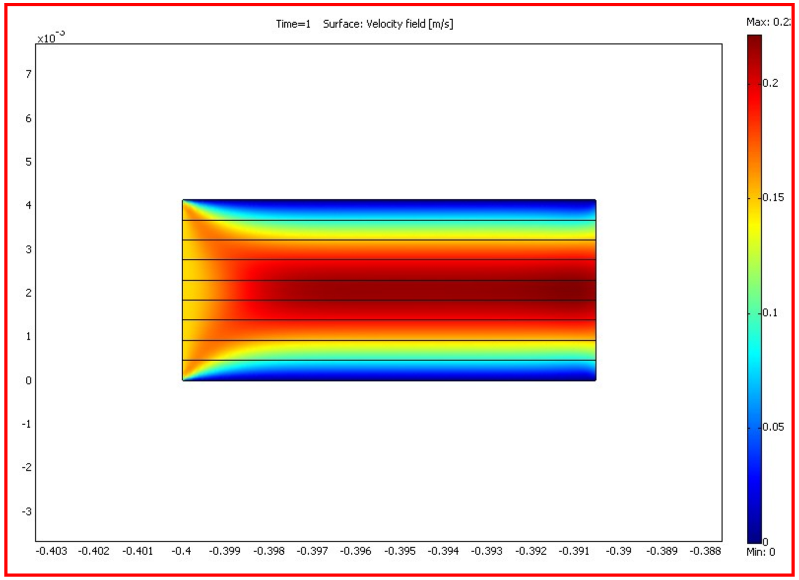
Convection

Pressure difference

Gravity

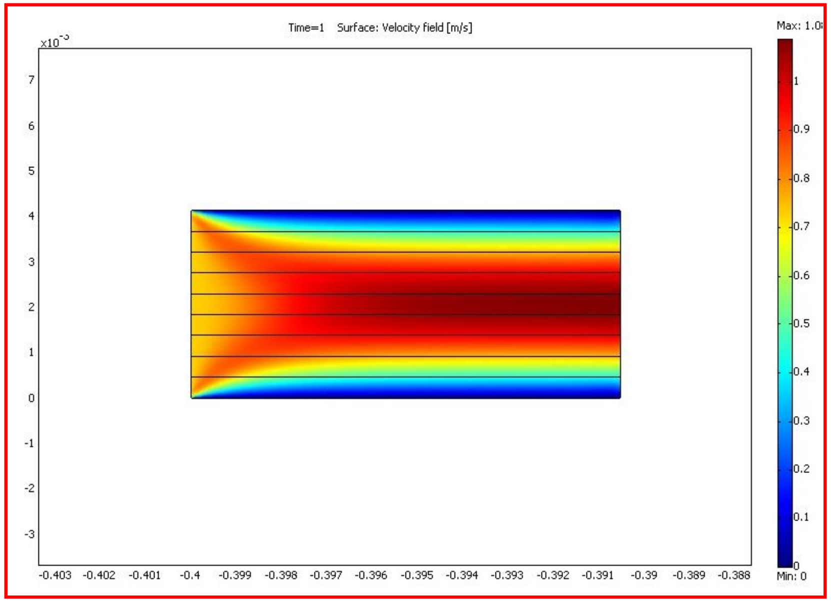
Viscous dissipation

CFD modelling



Volumetric Flow = 20 mL/min

Volumetric Flow = 100 mL/min



Reactor modelling

Typical 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

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

Mass balance in the **microchannels**:

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

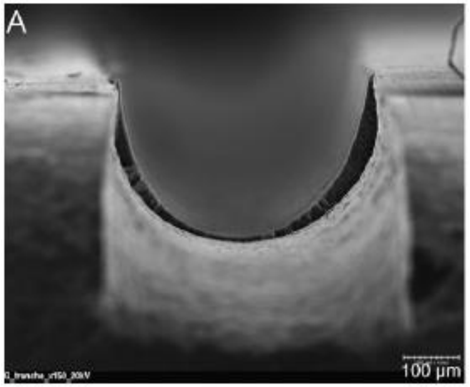
Boundary conditions:

$$\frac{dc_i}{dr} = 0, r = 0 \qquad \frac{D_e}{\delta}\left(\frac{dc_i^{'}}{dx}\right)_{x=0} = D_i\left(\frac{dc_i}{dr}\right)_{r=R} \qquad \left(\frac{dc_i^{'}}{dx}\right)_{x=1} = 0$$

Layer thickness

A distribution function ω(δ) as a function of the thickness δ:

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



Equation to be solved:

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

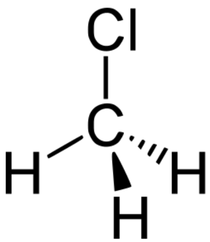
$$w = \left(1 - \left(\frac{r}{R}\right)^2\right)\cdot w_0$$

Synthesis of chemical intermediates in microreactors

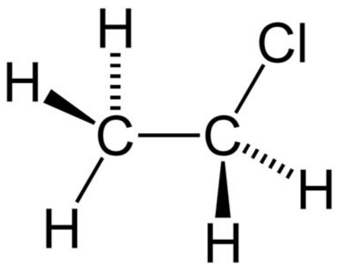
Sabrina A. Schmidt, Tapio Salmi, Dmitry Murzin,
José Hernández Carucci, Narendra Kumar, Kari Eränen

Teknisk kemi & reaktionsteknik
Åbo Akademi

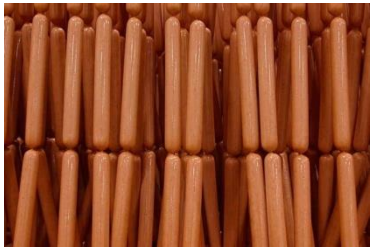
Methyl and ethyl chloride

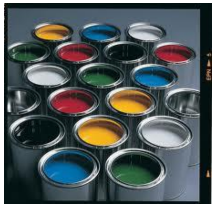


~10^6 tons/year to important everyday products



~100.000 tons/year direct use and ethyl cellulose production





ICIS Chemical Business Americas; 3/19/2007, Vol. 271 Issue 11, p50-50, 1p;
Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, New York, 2004.
Pictures: Wikipedia

Production

- Hydrochlorination of ethanol and methanol
- **R-OH + HCl → R-Cl + H_2O**
  - Ether as side-product formed
  - In case of ethanol also ethylene, acetaldehyde
  - T ~ 300 °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!”

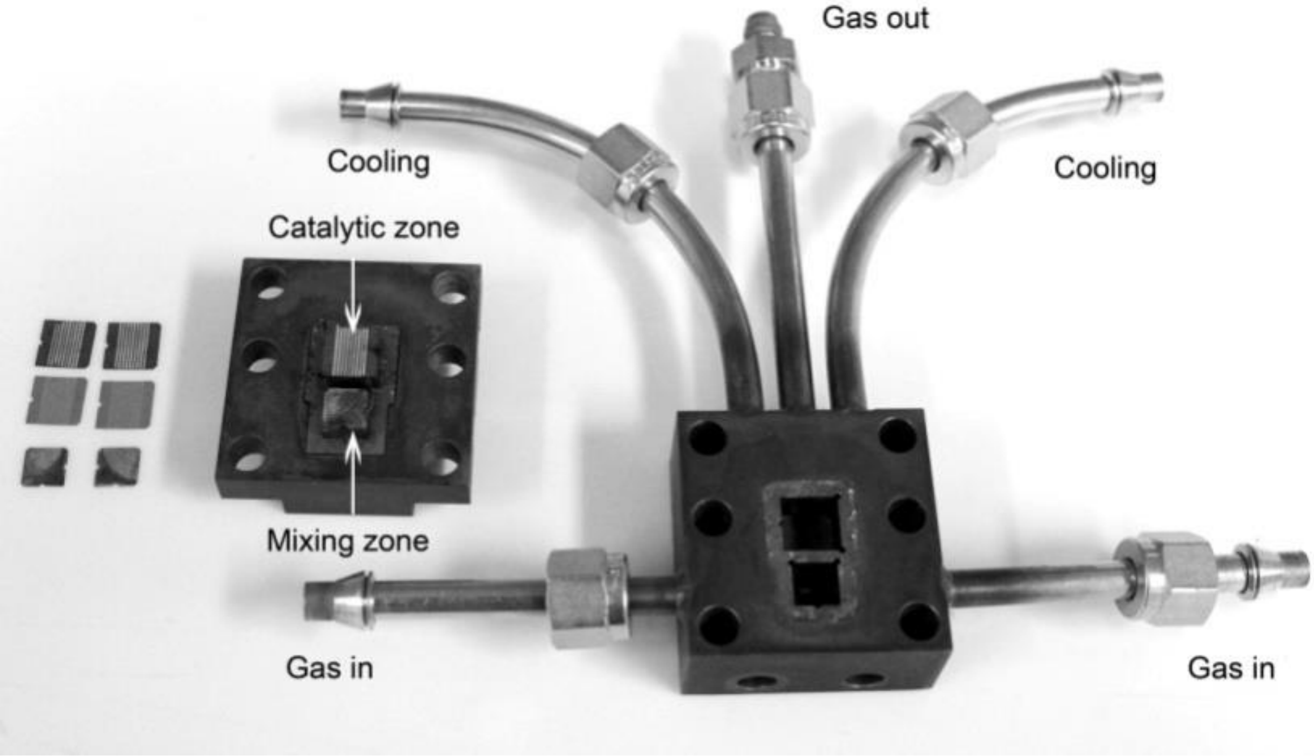
Why microreactor: diffusion

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

Research strategy

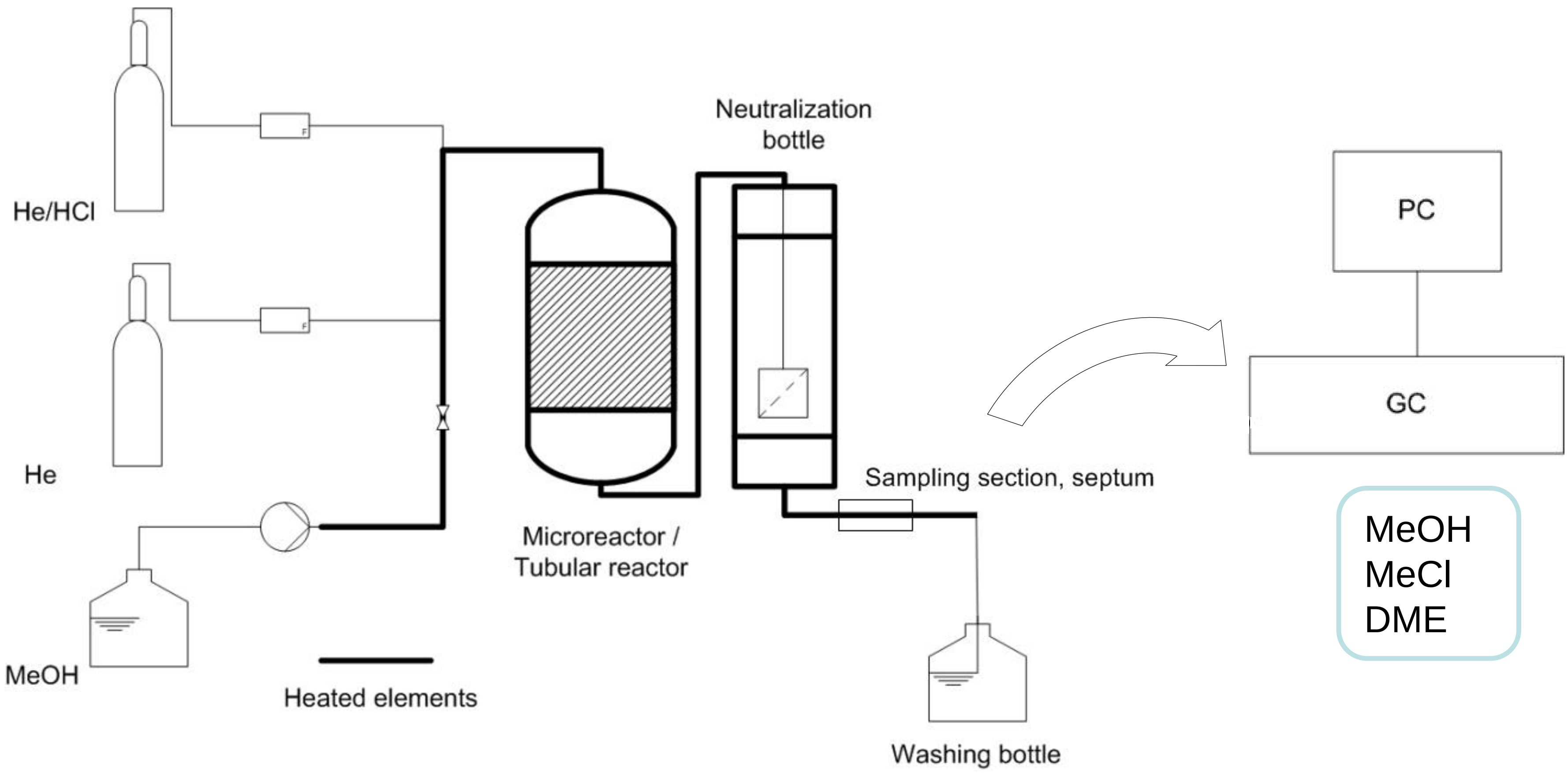
- Catalyst studies
- Catalyst coating technique for microchannels
- Kinetic and thermodynamic investigations
- Mathematical modelling

The microreactor



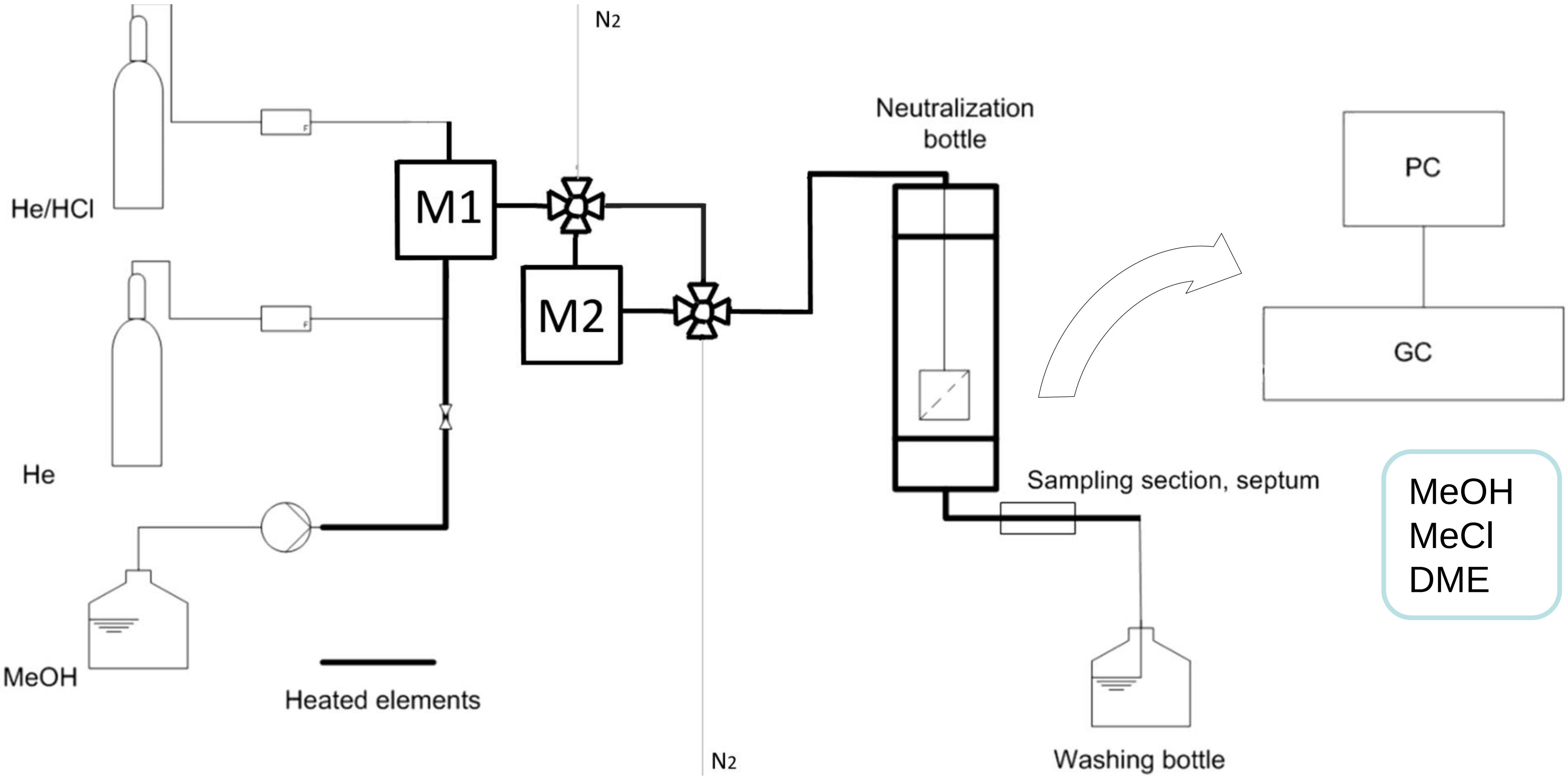
- IMM GPMR-mix : Gas phase microreactor with mixing and catalyst zone
- Material: stainless steel

Microreactor and tubular reactor



MeOH
MeCl
DME

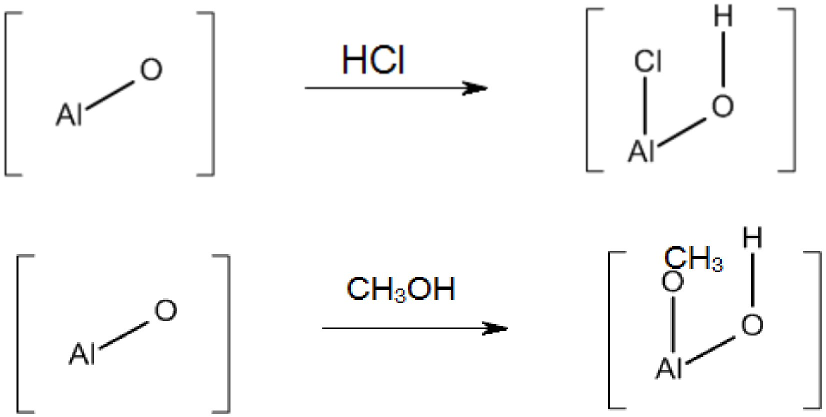
Two microreactors



MeOH
MeCl
DME

Catalysts

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



- Alternatively: $ZnCl_2$/Alumina
  - Introduction of zinc based LAS
- $ZnCl_2$/ Zeolites
  - Tunable acidity

Catalyst of choice

- Activity and selectivity can be improved by addition of zinc chloride

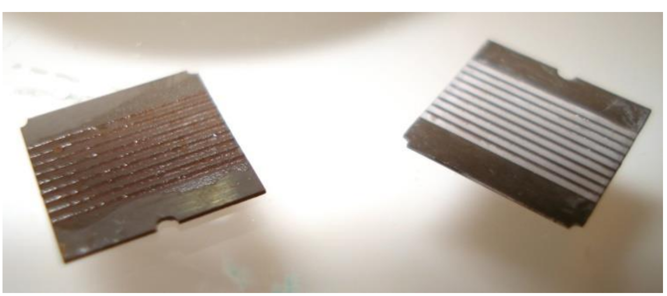
- Zeolites are the most active but least stable and selective catalysts

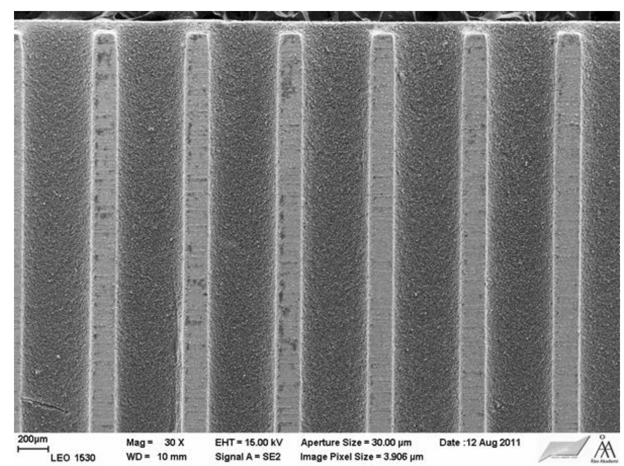
- Zinc modified alumina is stable in the tubular reactor but selectivity decreases in the microreactor

- 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

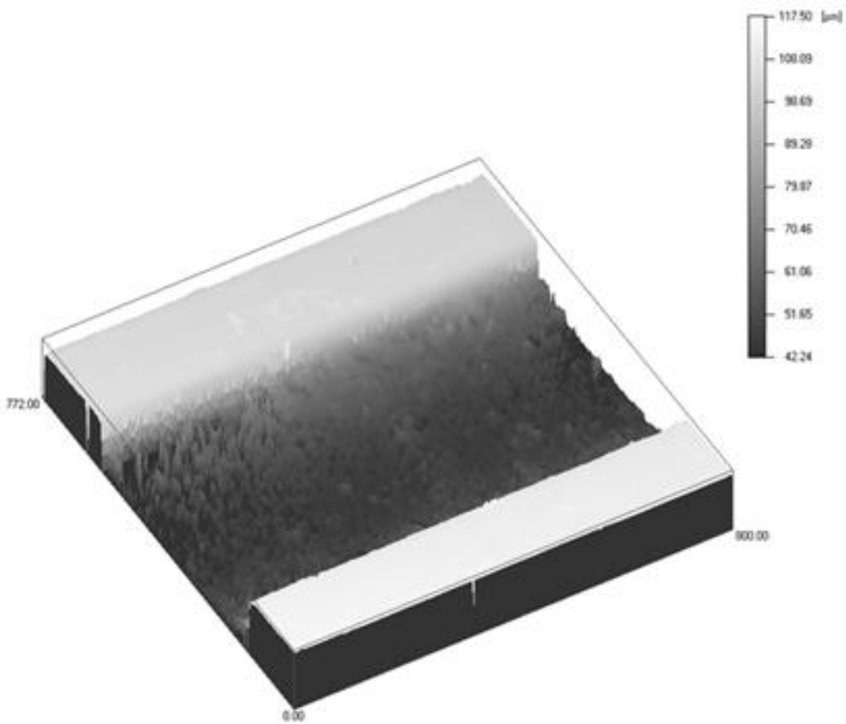


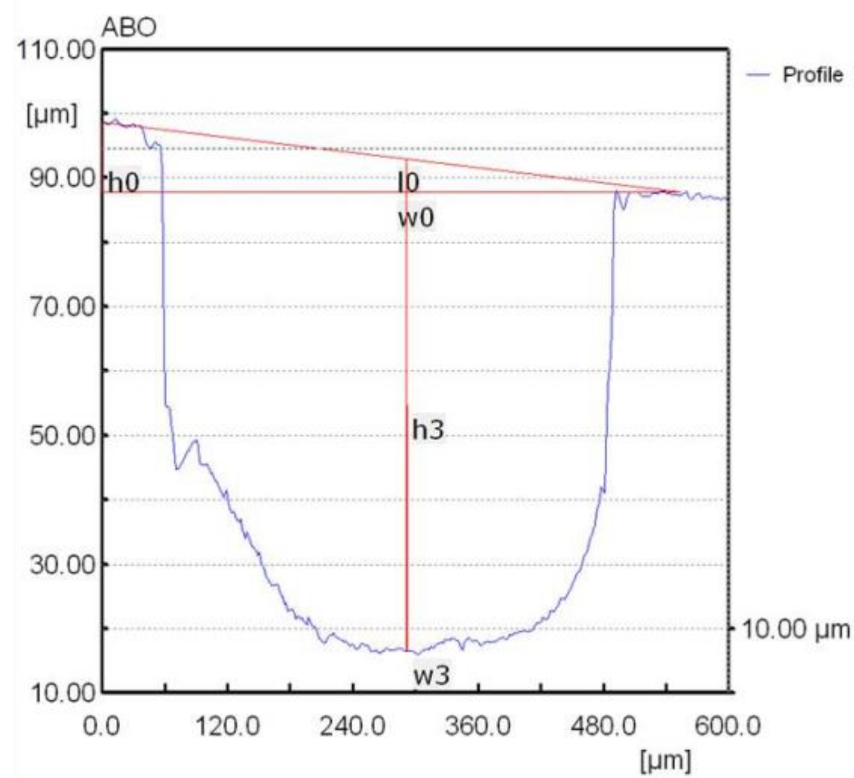


S. A. Schmidt, N. Kumar, B. Zhang, K. Eränen, D. Yu. Murzin, and T. Salmi, Preparation and Characterization of Alumina-Based Microreactors for Application in Methyl Chloride Synthesis, *Ind. Eng. Chem. Res*. **2012**, 51, 4545

Characterisation of coating

- Confocal microscopy: Morphology, thickness and surface roughness





- Coating thickness : 15 µm, channel depth: 90 µm

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

Kinetic and thermodynamic investigations

-

Mathematical modelling

Methanol hydrochlorination

- Hydrochlorination of methanol at 300 °C

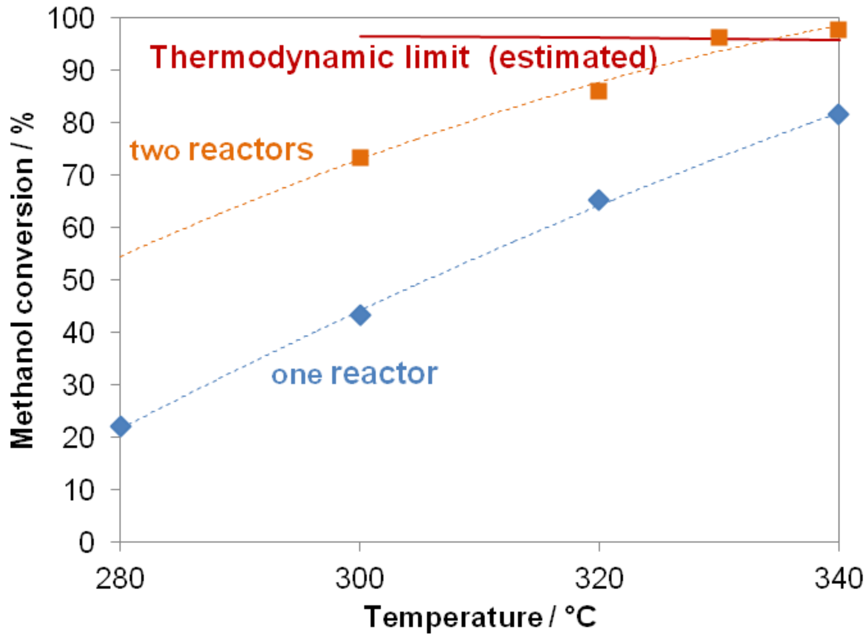
Reaction		K_{eq}
$CH_3OH + HCl \leftrightarrow CH_3Cl + H_2O$	(I)	398
$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$	(II)	12
$CH_3OCH_3 + HCl \leftrightarrow CH_3OH + CH_3Cl$	(III)	36

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

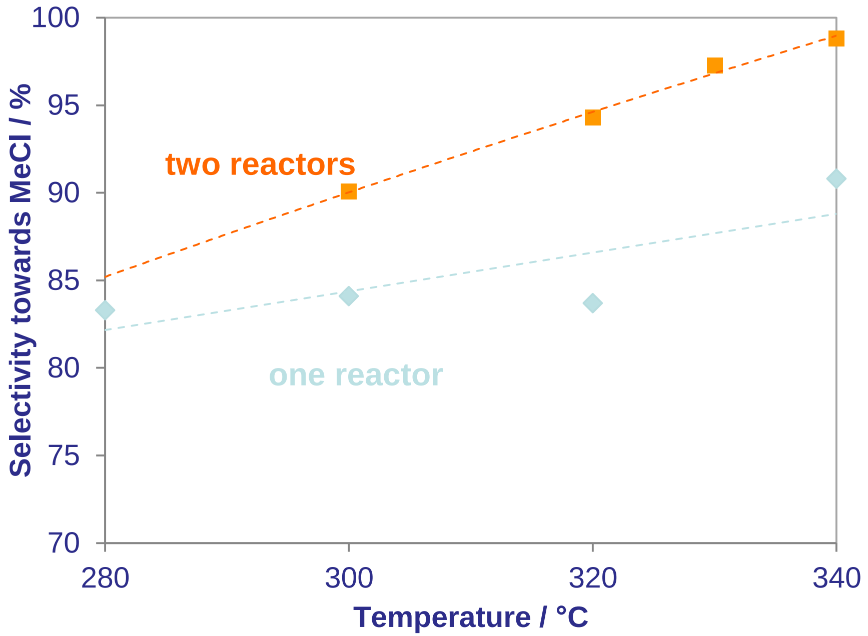
S. A. Schmidt, N. Kumar, A. Reinsdorf, K. Eränen, J. Wärnå, D., Murzin, T., Salmi, Methyl chloride synthesis on Al_2O_3 in a microstructured reactor – thermodynamics, kinetics and mass transfer, Chem. Eng. Sci 2013, 95, 232-245.

Performance of microreactors

Methanol conversion



Selectivity towards methyl chloride



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

S. A. Schmidt, Z. Vajglova, K. Eränen, D. Murzin, T. Salmi, Microreactor technology for on-site production of methyl chloride. Green Process. Synth. 2014, Advance online publication, DOI: 10.1515/gps-2014-0039

Reaction modeling -catalyst layer

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

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

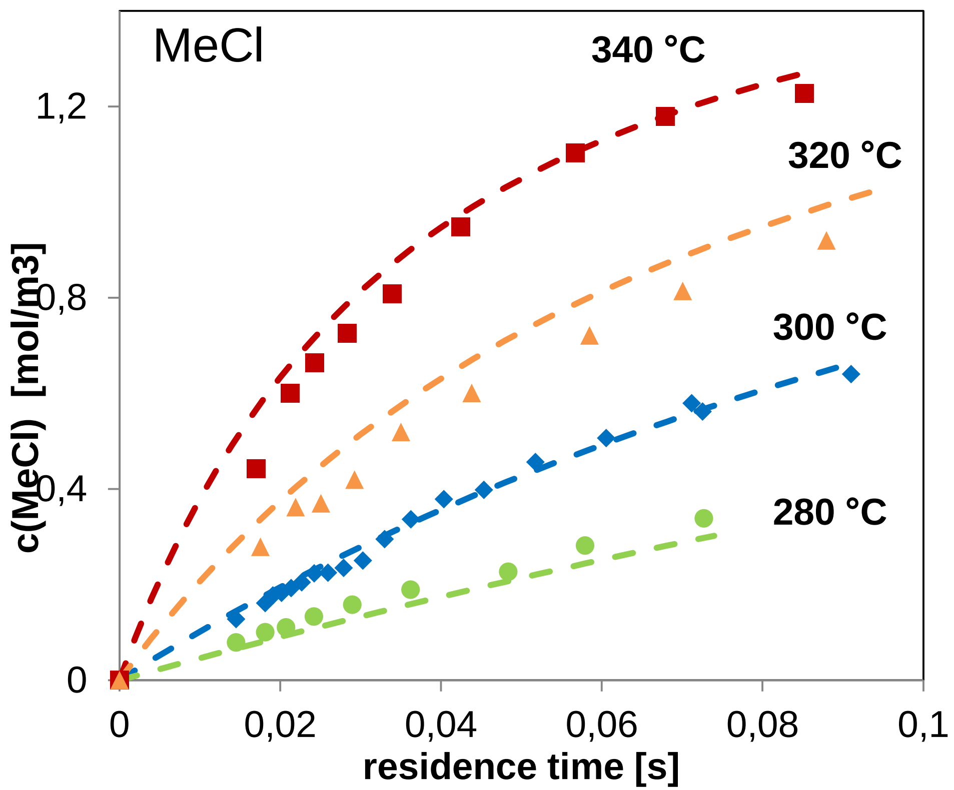
$$r_2 = k_2 \frac{(c_{MeOH}{}^2 - \frac{c_{DME} c_{H2O}}{K_2})}{D^2}$$

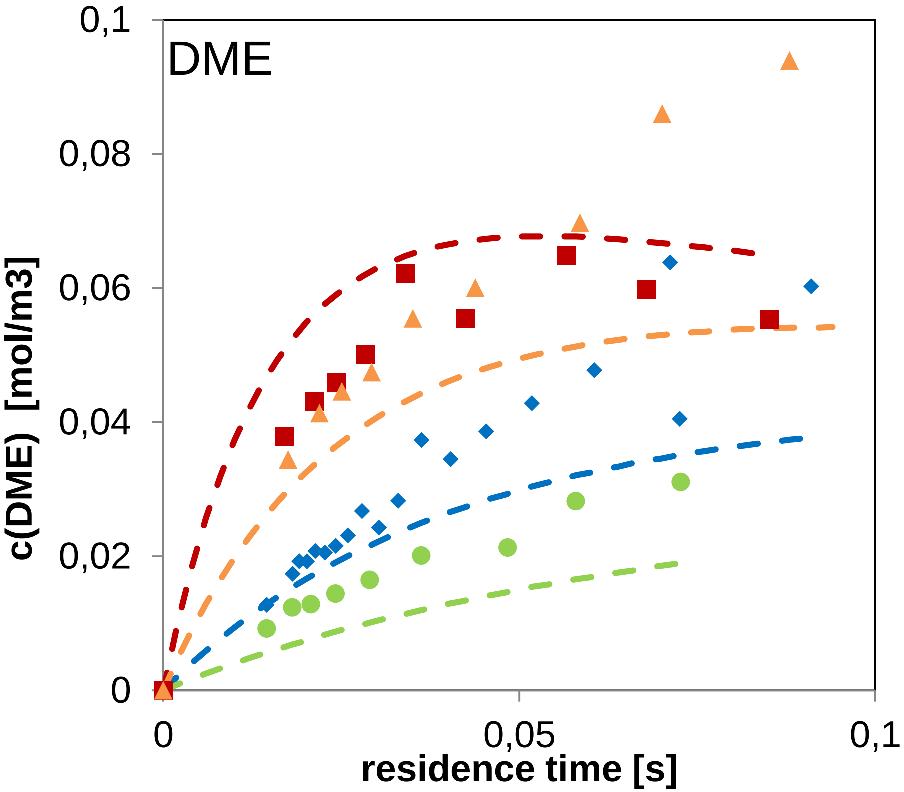
$$r_3 = k_3 \frac{(c_{DME} c_{HCl} - \frac{c_{MeOH} c_{MeCl}}{K_3})}{D^2}$$

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

S. A. Schmidt, N. Kumar, A. Reinsdorf, K. Eränen, J. Wärnå, D., Murzin, T., Salmi, Methyl chloride synthesis on Al_2O_3 in a microstructured reactor – thermodynamics, kinetics and mass transfer, Chem. Eng. Sci 2013, 95, 232-245.

Kinetic model





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

S. A. Schmidt, N. Kumar, A. Reinsdorf, K. Eränen, J. Wärnå, D., Murzin, T., Salmi, Methyl chloride synthesis on Al_2O_3 in a microstructured reactor – thermodynamics, kinetics and mass transfer, Chem. Eng. Sci 2013, 95, 232-245.

Reaction modeling - catalyst layer

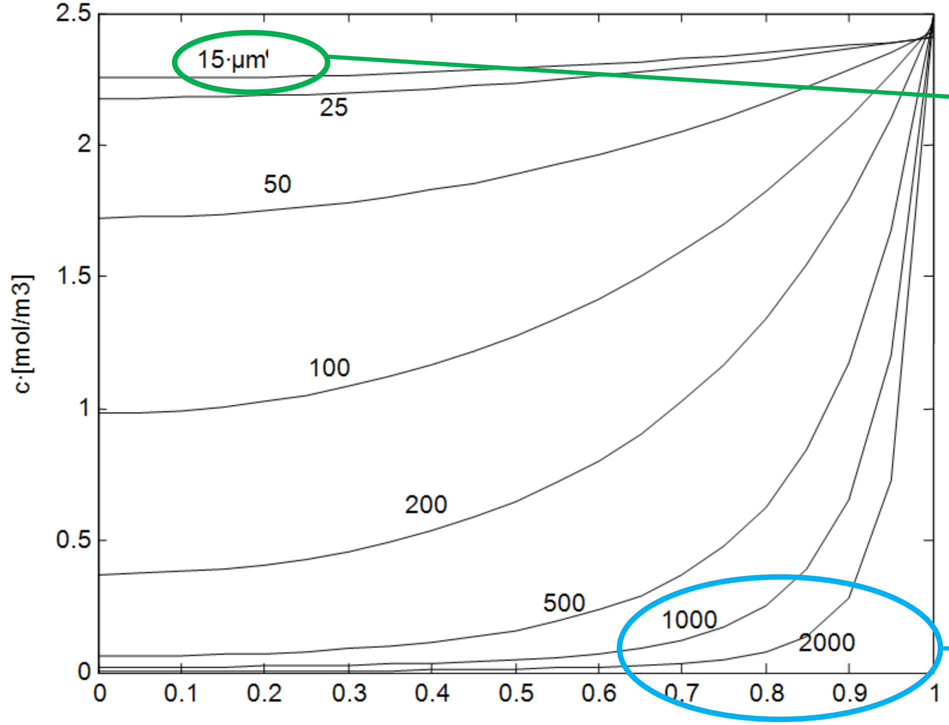
- Obtained activation energy for MeCl formation is double of previously published
  - Suggests internal diffusion limitations

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

$$D_{ei} = \left(\frac{\varepsilon_p}{\tau_p}\right) D_i \qquad \frac{dc_i}{dt} = \frac{1}{\varepsilon_p}\left(D_{ei}\frac{d^2 c_i}{dr^2} + r_i \rho_p\right)$$

S. A. Schmidt, N. Kumar, A. Reinsdorf, K. Eränen, J. Wärnå, D., Murzin, T., Salmi, Methyl chloride synthesis on Al_2O_3 in a microstructured reactor – thermodynamics, kinetics and mass transfer, Chem. Eng. Sci 2013, 95, 232-245.

Reactant concentration profiles inside the catalyst layer



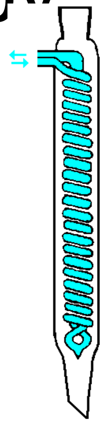
Microreactor
Effectiveness factor:
0.93 (high)

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

- Wrong activation energies reported in literature

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

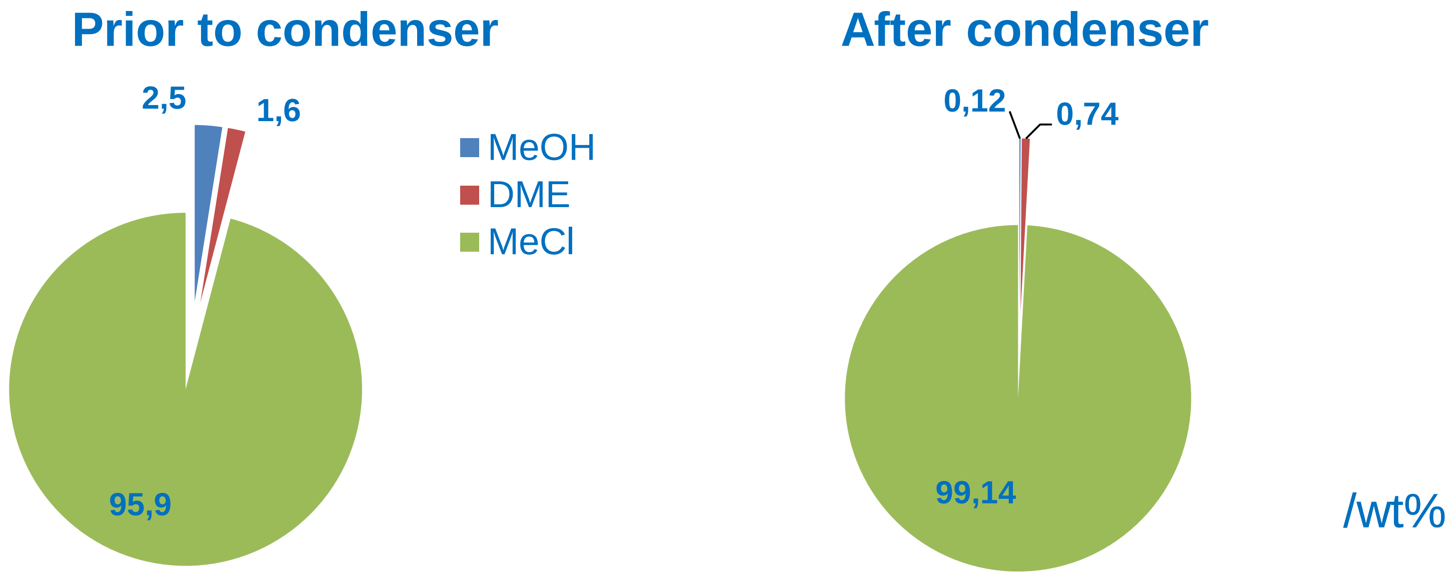


Cooling surface: 210 cm^2

S. A. Schmidt, Z. Vajglova, K. Eränen, D. Murzin, T. Salmi, Microreactor technology for on-site production of methyl chloride. Green Process. Synth. 2014, Advance online publication, DOI: 10.1515/gps-2014-0039.

Efficiency: gas phase

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



- MeCl and DME are efficiently separated from the liquid

S. A. Schmidt, Z. Vajglova, K. Eränen, D. Murzin, T. Salmi, Microreactor technology for on-site production of methyl chloride. Green Process. Synth. 2014, Advance online publication, DOI: 10.1515/gps-2014-0039.

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!

Financial support:

ACADEMY OF FINLAND

GSCE

Internship students: Arne Reinsdorf, Zuzana Vajglova and Quentin Balme