Lecture Series **Heterogeneous Catalysis**

Fritz-Haber-Institute (Max Planck Society)
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Micro-Structured Reactors and Catalysis

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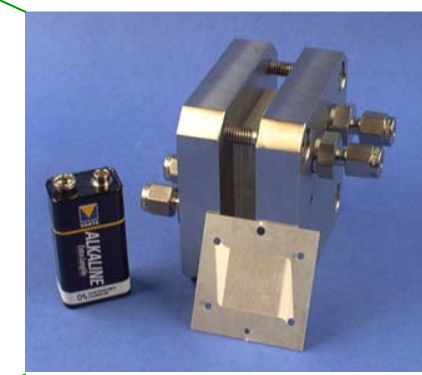
Principles of Micro-Structured Reactors: Application in Catalysis & Process Engineering

$$1 : 10^{-12}$$



Institut für Mikrotechnik Mainz

Subjects of Presentation

1. Principles of **M**icro-**S**tructured **R**eactors (MSR)

2. MSR as Tool in Catalysis

   2.1 Provision of kinetic data

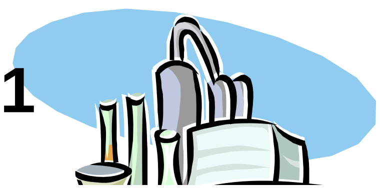
   2.2 (in-situ) Characterization of catalytic materials

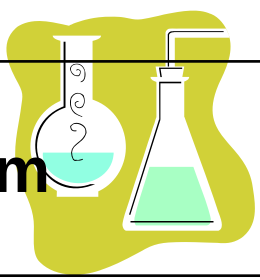
   2.3 Application of MSR in industrial catalysis

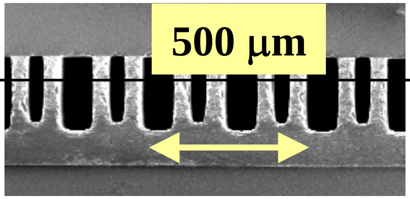
   - Hydrogen-driven fuel cells
   - Propene oxidation by H_2O_2 vapor

Scales of chemical reactors

	Industry	Laboratory	Microsystem
Volume	30 m^3	10^{-3} m^3	3 10^{-11} m^3
Scale-down	1	1:3 10^{-5}	1: 10^{-12}
Diameter	2 m	2 cm	20 μm
Surface / Volume	$2\frac{m^2}{m^3}$	$200\frac{m^2}{m^3}$	$200'000\frac{m^2}{m^3}$



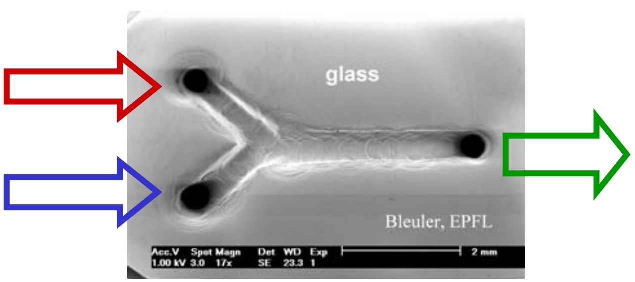




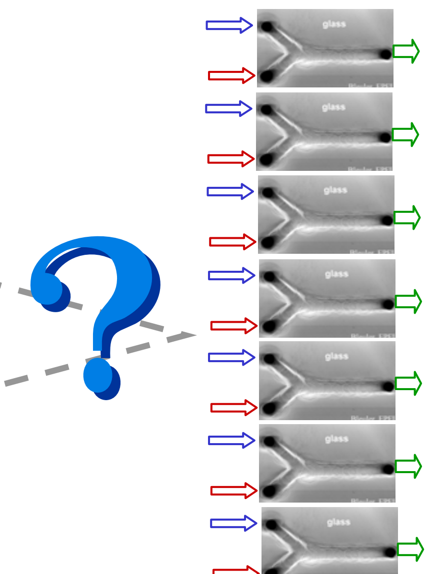
Process Development

scale-up

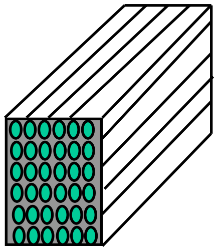
Laboratory **Pilot-plant** **Production**

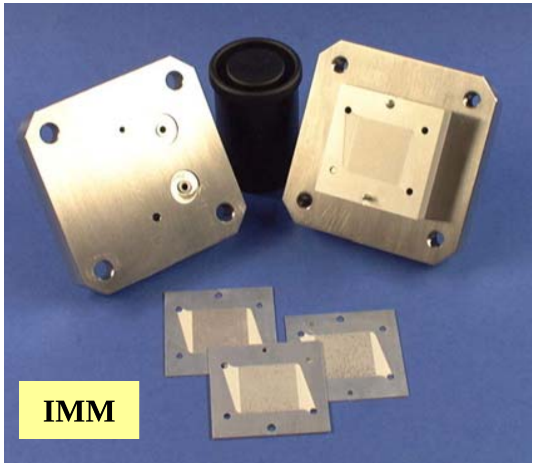


« scale up »



Micro-structured multichannel reactors



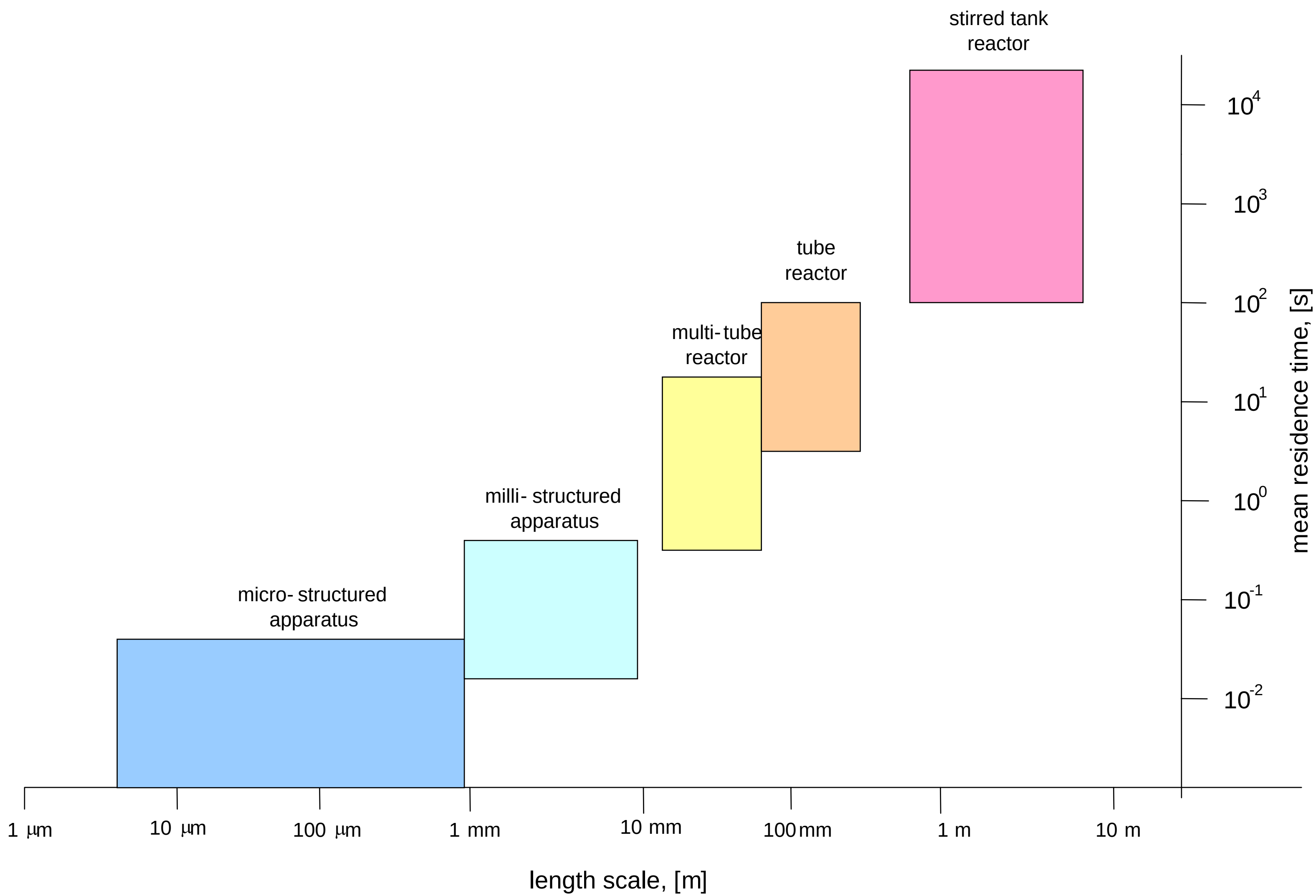


Volume: $V_R = 5\ cm^3$

Pressure drop: $\Delta p = 1$ bar

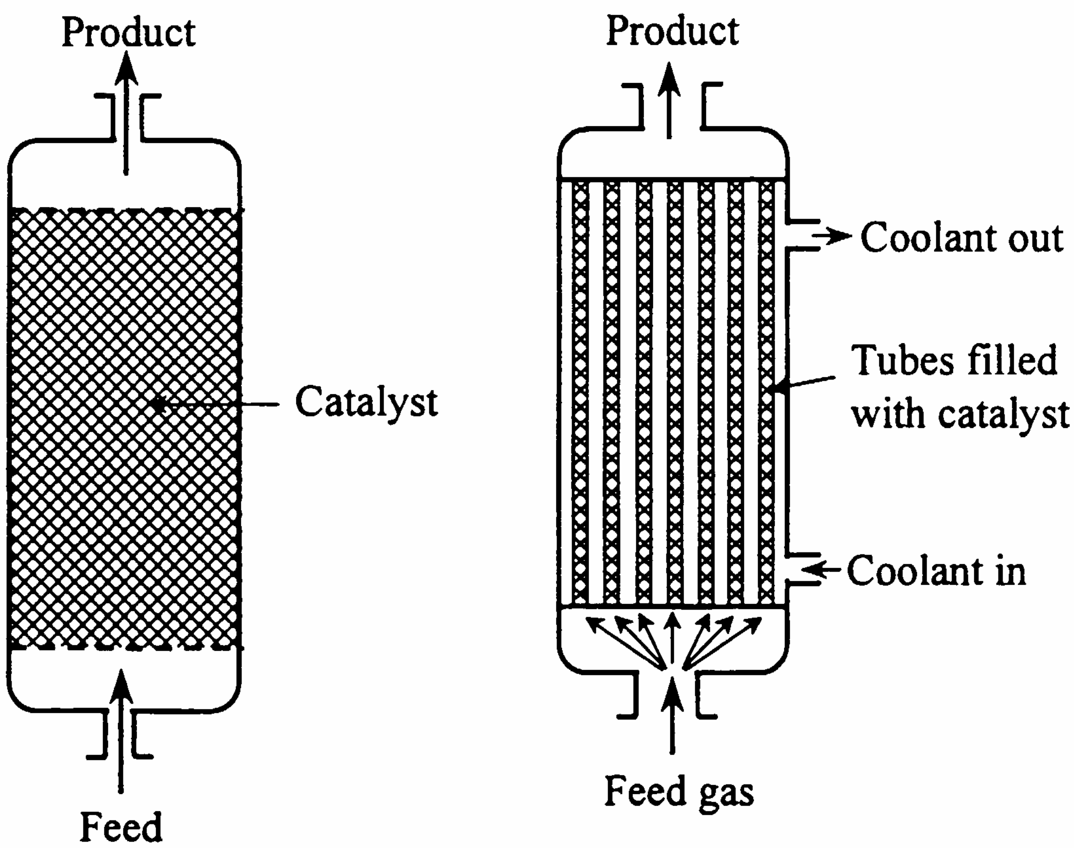
length:	L =	5.	cm
diameter:	d =	100.	µm
Number of channels:	N =	12,740.	
Specific surface:	a =	40,000.	m^2/m^3
Flow velocity:	u =	0.63	m/s (H_2O)
		35.	m/s (air)
Mass flow:	Q_m=	225.	kg/h (H_2O)
		15.	kg/h (air)

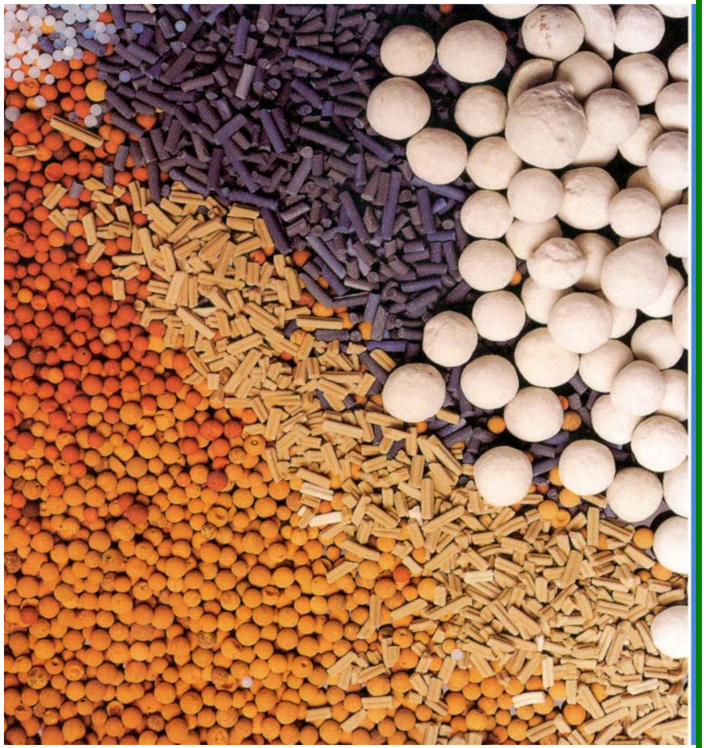
Typical time and length scale of chemical reactors



EPFL LGRC

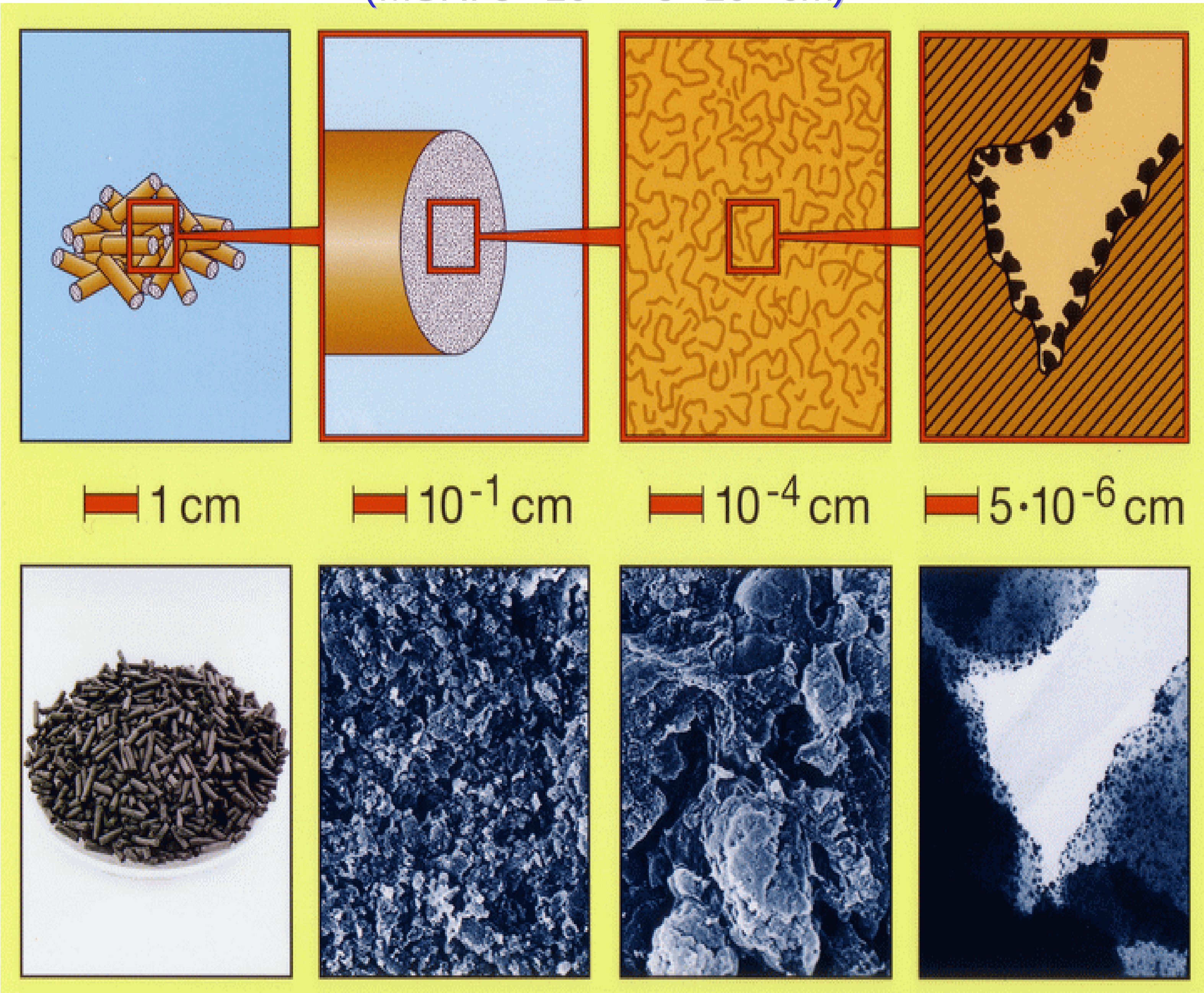
Mass transfer in heterogeneous catalysis



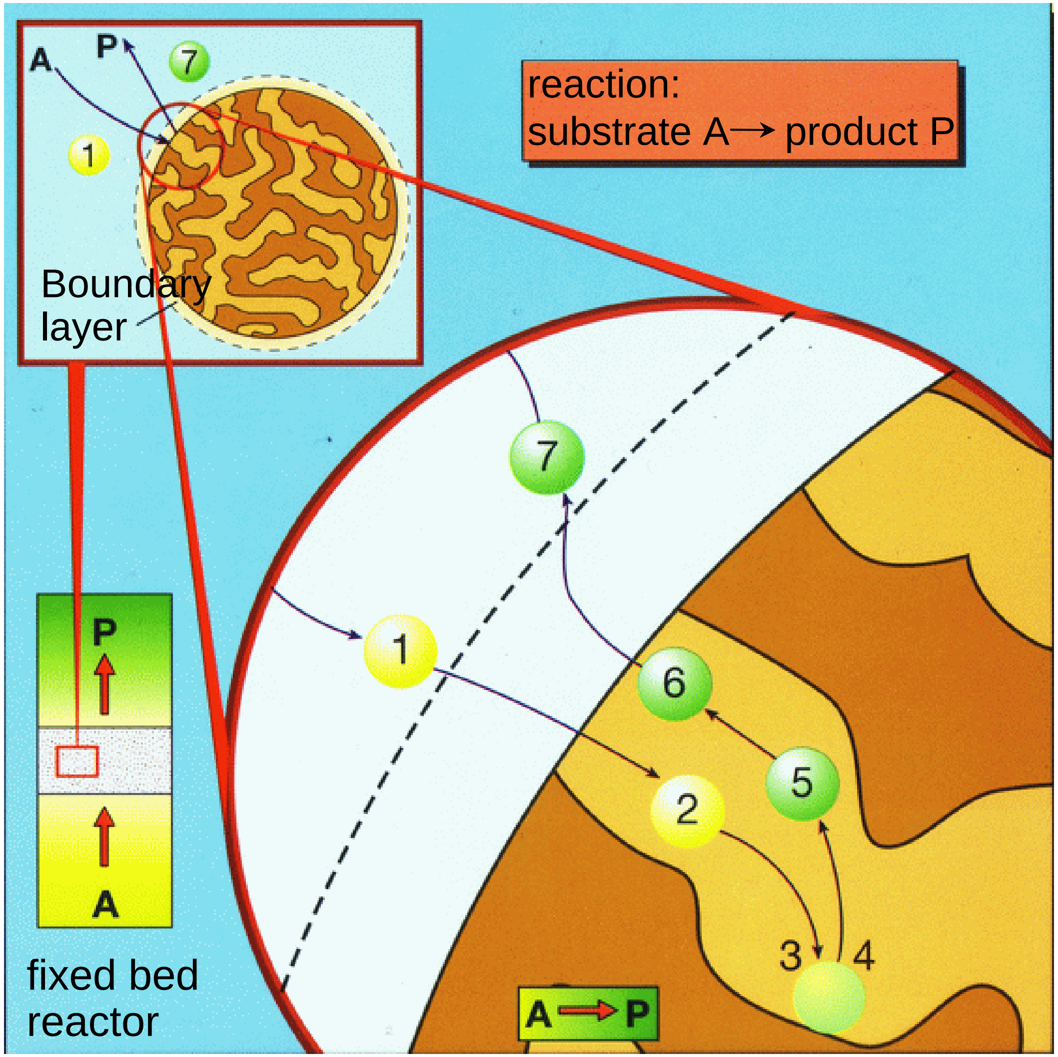


Scales of Heterogeneous Solid Catalysts

(MSR: $5 \cdot 10^{-3} - 5 \cdot 10^{-2}$ cm)



Process Steps in Heterogeneous Catalytic Reactions



Agar, 2003

Steps during the course of the reaction

① External diffusion

② **Internal diffusion**

③ Adsorption on the active sites

④ Surface reaction forming the products

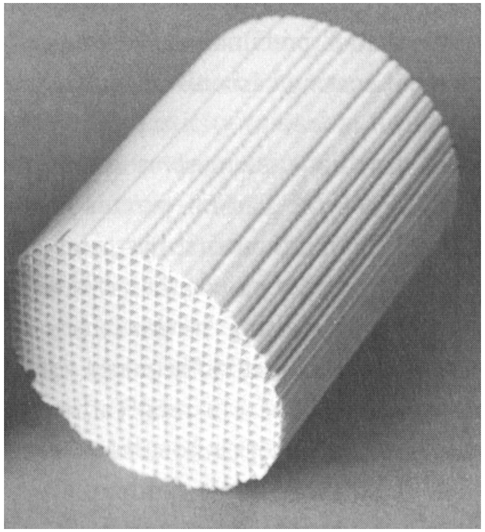
⑤ Desorption of the products

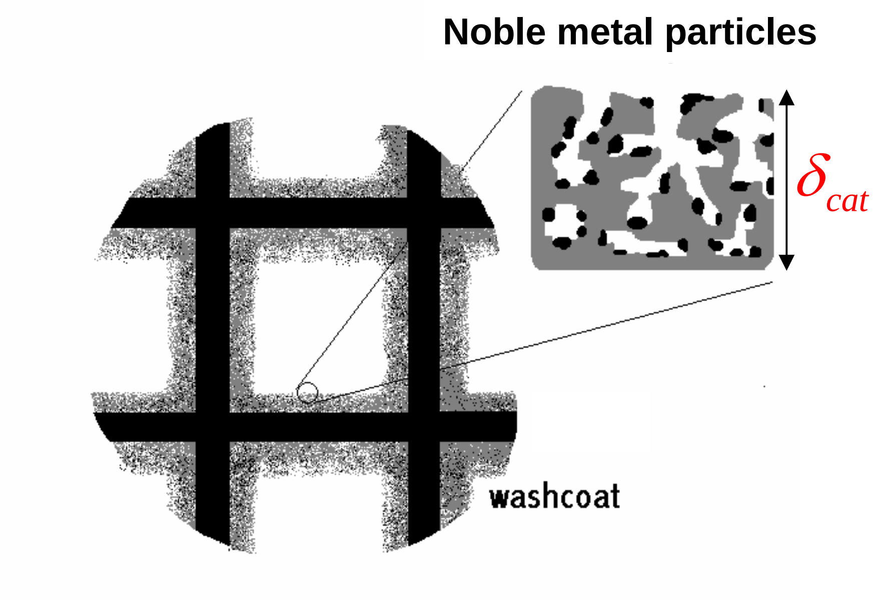
⑥ **Internal diffusion**

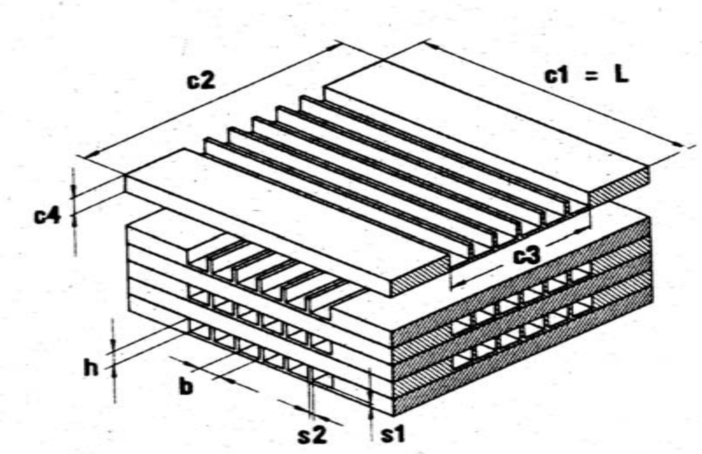
⑦ External diffusion

Internal mass transfer

- Internal mass transfer resistance can be reduced by
  - small particles
  - thin catalytic layers







Internal mass transfer

$$\phi = \delta_{cat}\sqrt{\frac{r_V}{D_{eff}\cdot c_{1,s}}}; \qquad \psi = \frac{\delta_{cat}^2 \cdot r_{V,eff}}{D_{eff}\cdot c_{1,s}}$$

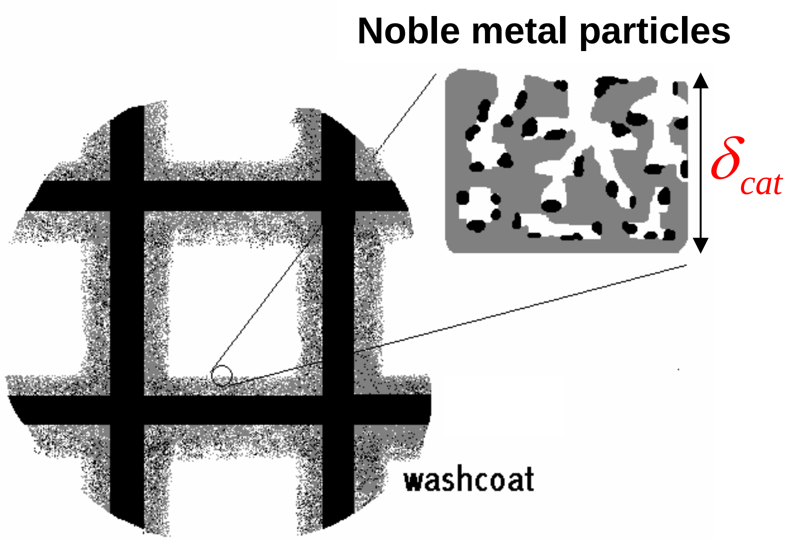
Thiele-modulus   Weisz-modulus

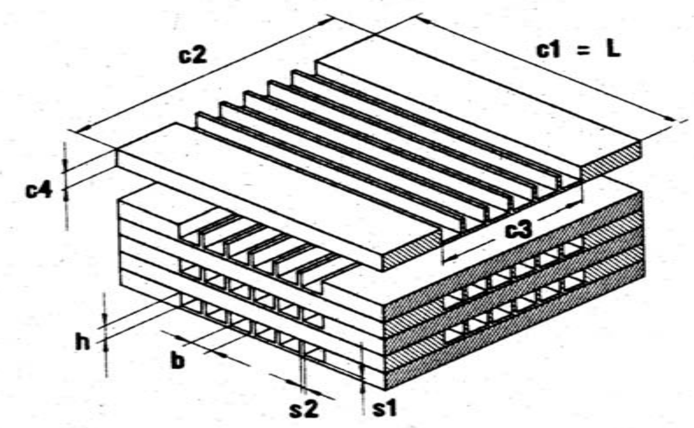
- Internal mass transfer resistance can be reduced by
  - small particles
  - thin catalytic layers

internal mass transfer can be neglected, if

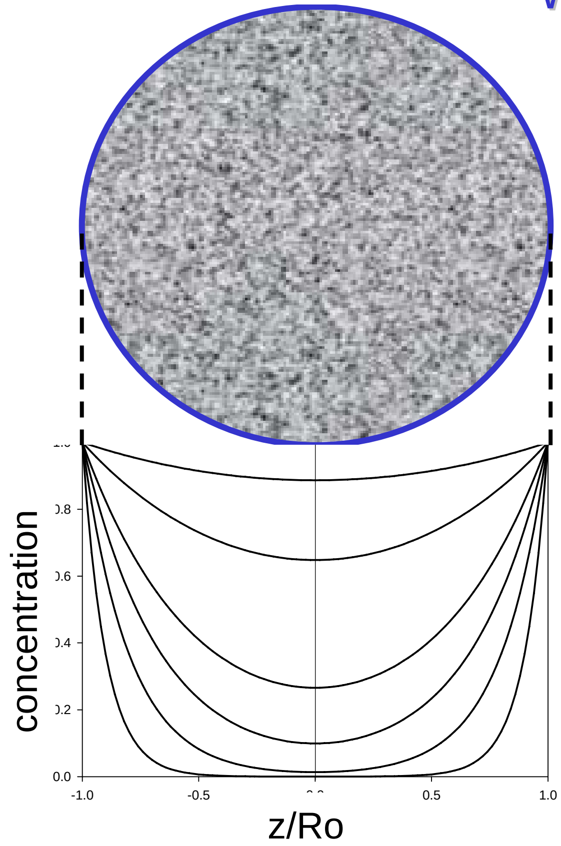
$$\psi = \frac{\delta_{cat}^2 \cdot r_{V,eff}}{D_{eff}\cdot c_{1,s}} < \begin{cases} 0.7; & n=0 \\ 0.07; & n=1 \\ 0.03; & n=2 \end{cases}$$

Internal mass transfer can be neglected for catalytic layers δ<20μm





Transport simultaneous with reaction: internal mass transfer within a spherical particle



The concentration profile established in the particle depends on the ratio between the characteristic diffusion time t_D and the characteristic reaction time t_r

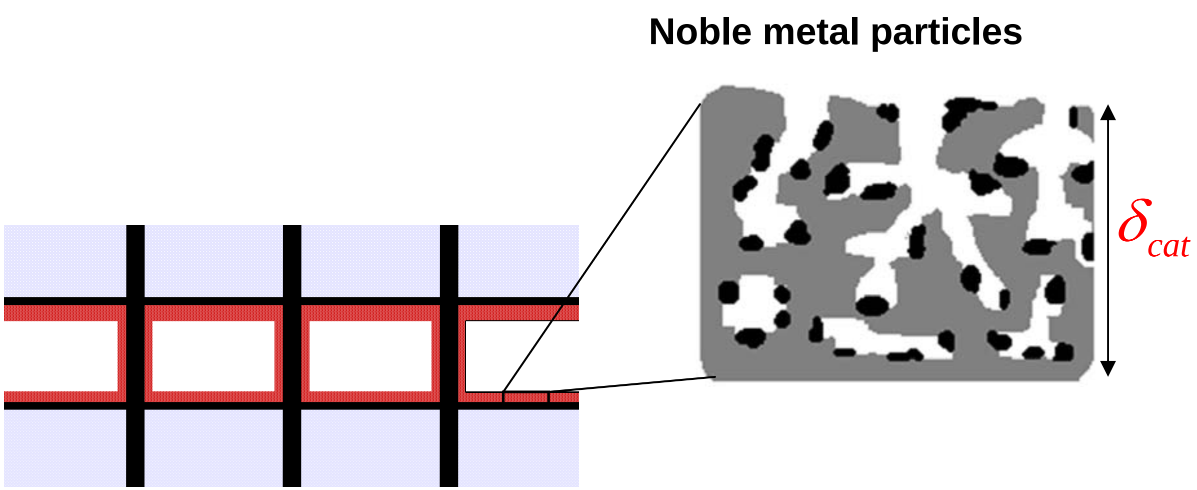
$$\frac{t_D}{t_r} = \frac{L^2}{D_e} k_r$$

First order reaction

$$\phi = L\sqrt{\frac{k_r}{D_{eff}}},$$

L is a characteristic length (the radius for the sphere particle), and ***D_e* is effective diffusivity** of a species A in the particle

Temperature control in catalytic wall reactors



•Heat production near the channel wall;
•main resistance to heat transfer in the catalytic layer;

Near isothermal conditions, if

$$\frac{\left|\Delta H_R\right| \cdot r_{V,eff} \cdot \delta_{cat}^2}{\lambda_{cat} \cdot T_w} < 0.15 \frac{RT_w}{E_a}$$

Properties of Micro-Structured Reactors

- High surface area per reactor volume (beneficial for heat exchange)
- Short contact (reaction) time
- Internal (and external) mass transport of reactants can be neglected
- Negligible resistance to heat transport from the catalyst layer to the wall
- Low pressure drop as compared to a packed bed
- Suppression of danger of explosion

Use of MSR as a Tool in Catalysis

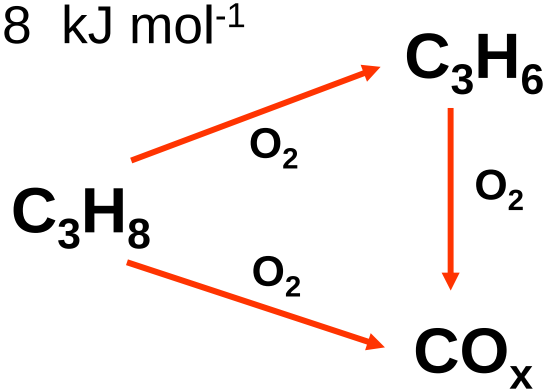
Determination of isothermal kinetic data

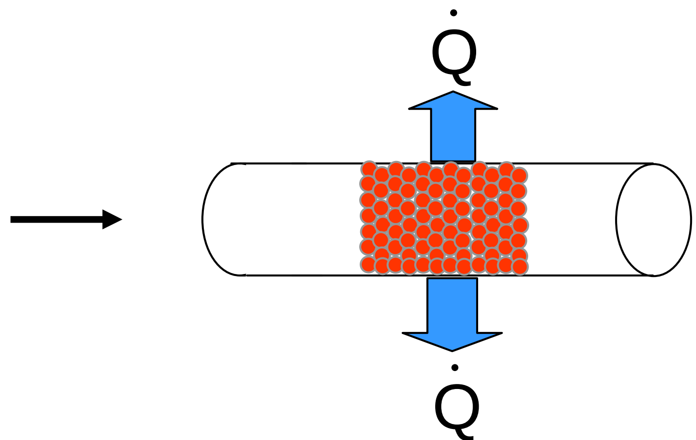
A. Oxidative dehydrogenation of propane on VO_x catalysts

Oxidative Dehydrogenation of Propane (ODP)

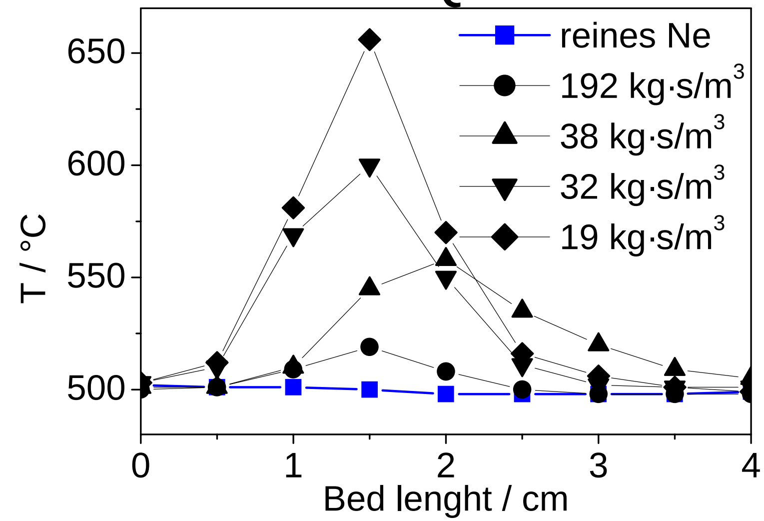
conventional fixed-bed reactor

$\Delta_R H_{873K}$ = -118 kJ mol^{-1}



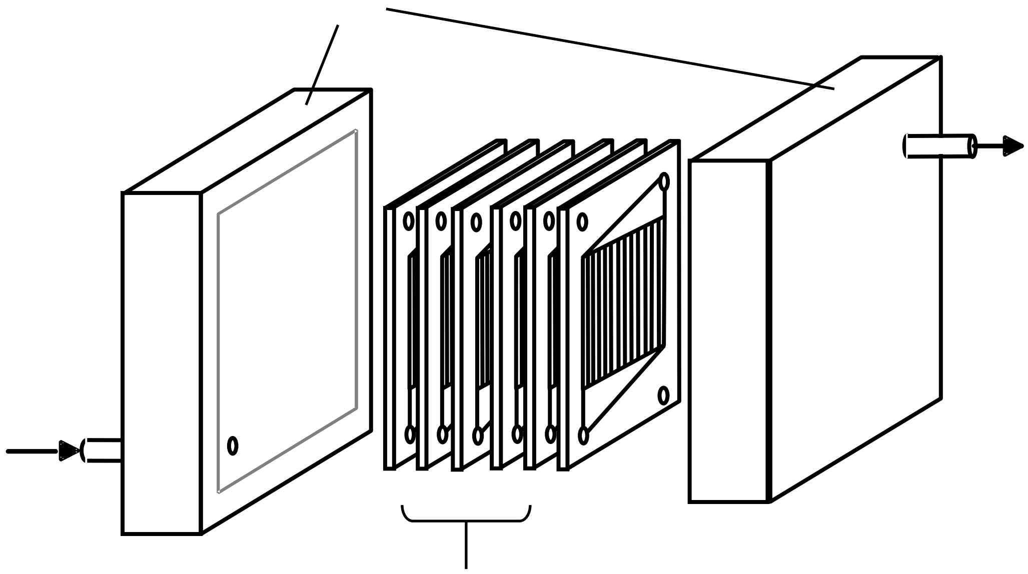


$\Delta_R H_{873K}$ = - 1195
to - 2045 kJ mol^{-1}

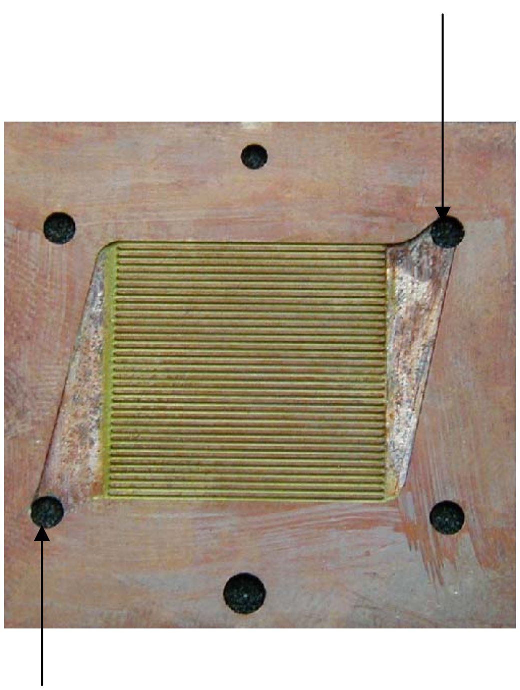


Assembly of the micro-channel reactor

Micro-channel reactor (IMM)



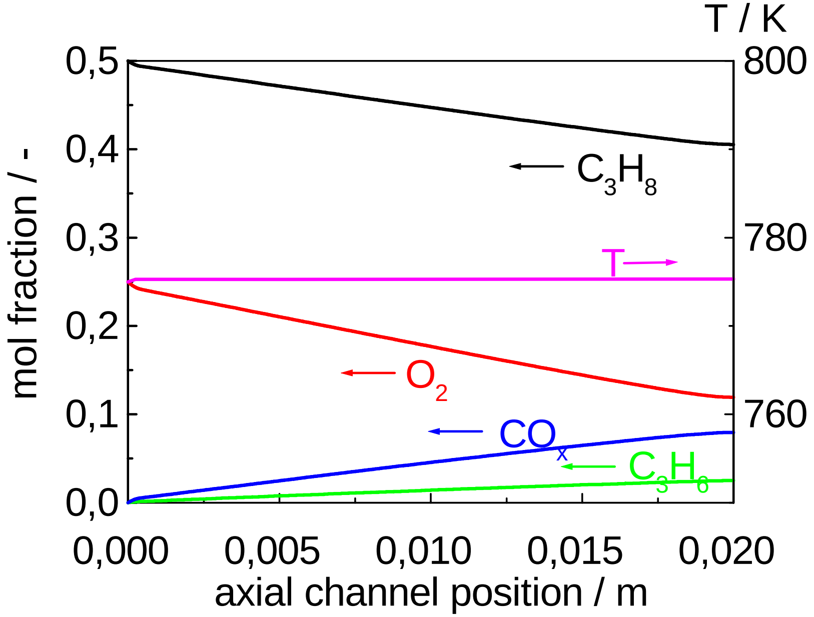
Single plate with deposited catalytic material (VO_x/Al_2O_3)

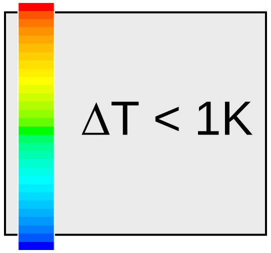


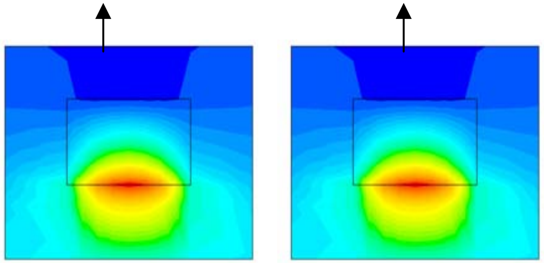
Channel dimension: 20 mm x 500 µm x 100 µm

CFD simulation of temperature profiles for ODP in a single micro-channel (T = 773 K)

$C_3H_8/O_2/Ne$ – 0.5/0.25/0.25





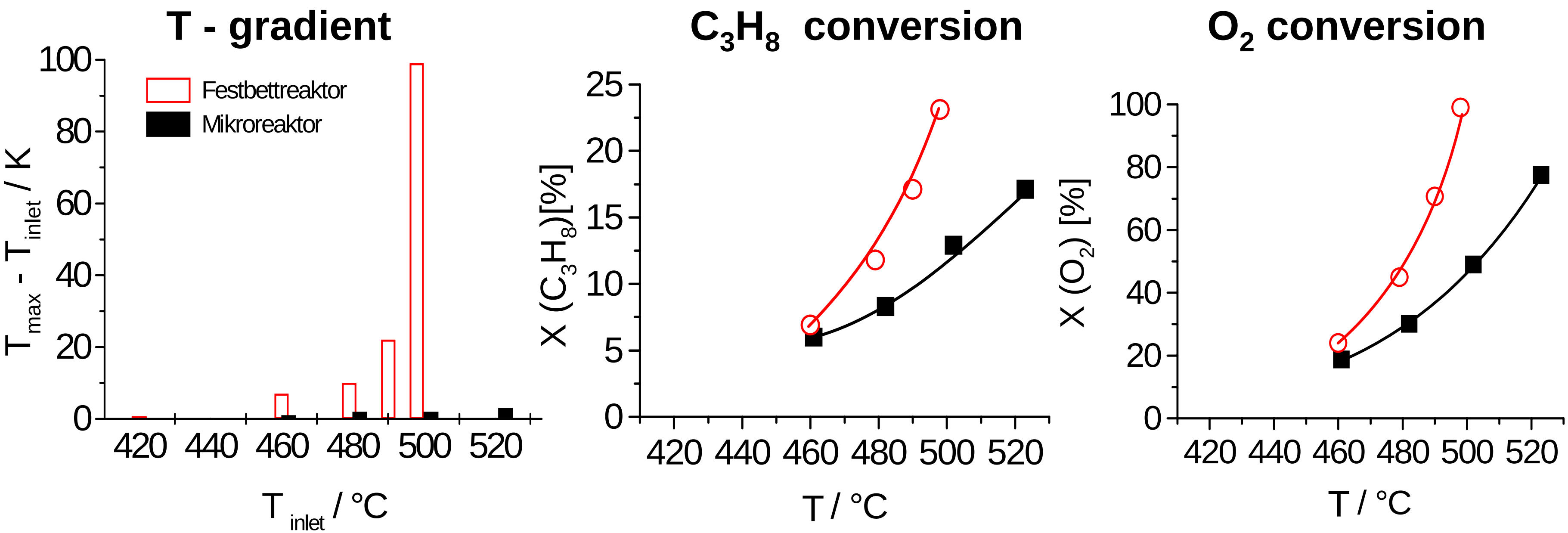


Heat conductivity of the wall = 15 W/m/s
Wall thickness: 125/150 µm

Isothermal condition within the channels when a reactor material is used with high heat conductivity and thick walls

Comparison of a micro-structured and a packed-bed reactor

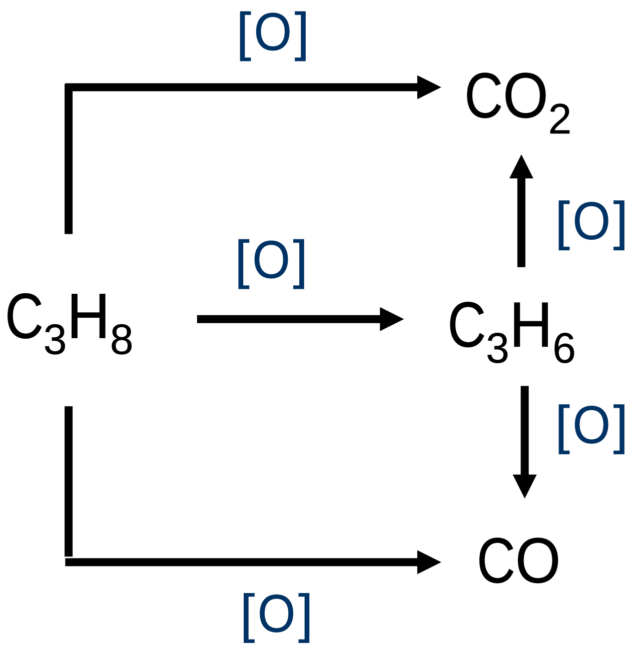
■ micro-structured wall reactor ○ packed-bed reactor



$p_{C3H8} = 51{,}2$ kPa, $P_{O2} = 25{,}6$ kPa , $p_{ges} = 101{,}2$ kPa

packed-bed reactor:	severe temperature gradients
micro-structured wall reactor:	almost no temperature gradients

Reaction network in ODP reaction



Model 2	Reaction rate
$C_3H_8 \rightarrow C_3H_6$	$k_1\ p_{C3H8}\ [O]$
$C_3H_6 \rightarrow CO$	$k_2\ p_{C3H6}\ [O]$
$C_3H_6 \rightarrow CO_2$	$k_3\ p_{C3H6}\ [O]$
$C_3H_8 \rightarrow CO$	$k_4\ p_{C3H8}\ [O]$
$C_3H_8 \rightarrow CO_2$	$k_5\ p_{C3H8}\ [O]$
$O_2 \rightarrow [O]$	$k_6\ p_{O2}\ [\ ]$

Re-oxidation

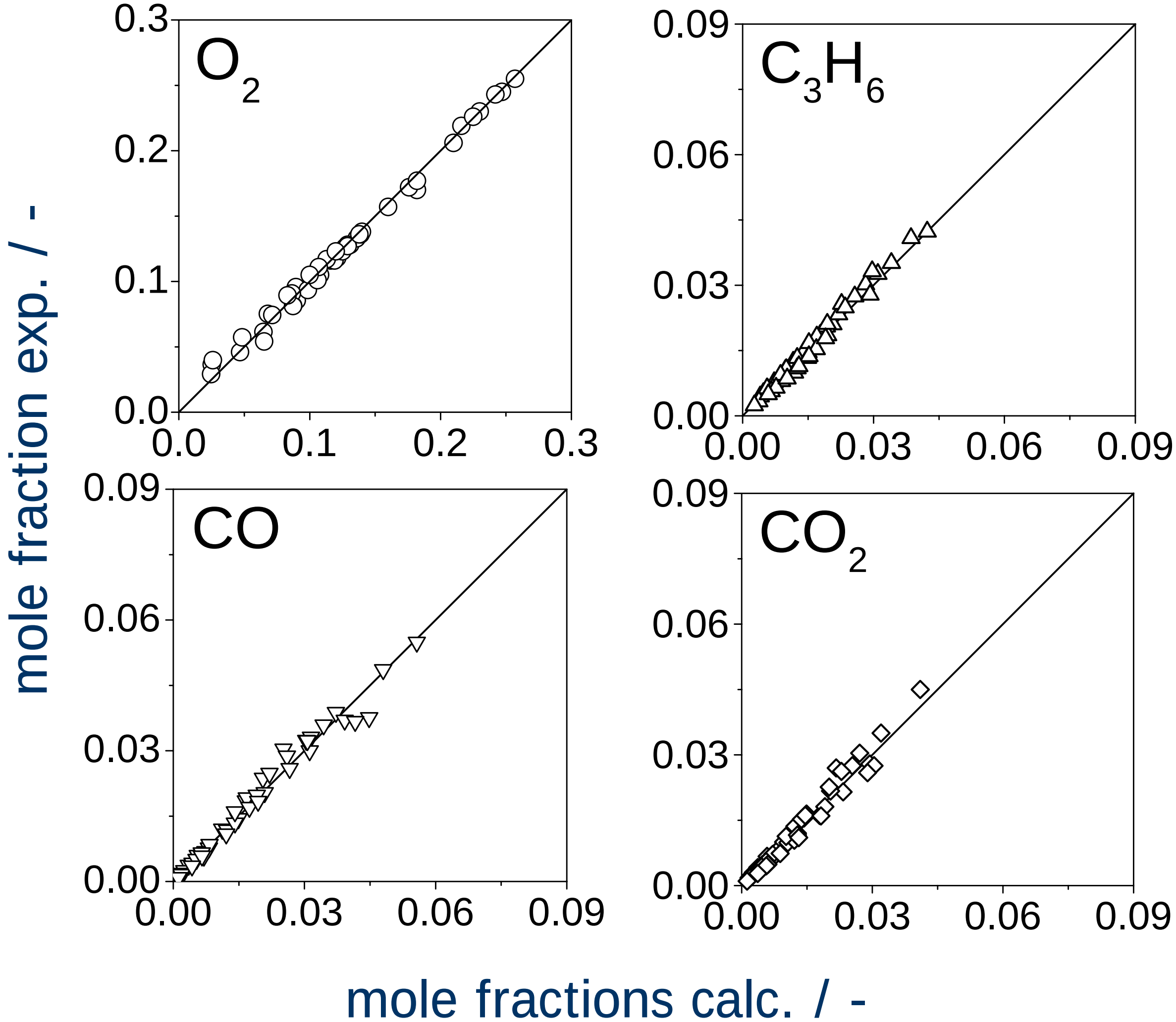
$2\ [\ ] + O_2 \rightarrow 2\ [O]$

[O] – lattice oxygen   [ ] – reduced VO_x-site

Kinetic parameters
(formation rates of C_3H_6 and $CO_x \propto [O]$)

	Reaction rate	$k_{733\ K}$ / mol kg^{-1}s^{-1} Pa^{-b}	E_A / kJ mol^{-1}
$C_3H_8 \rightarrow C_3H_6$	$k_1\ p_{C3H8}\ [O]$	$2.9 \cdot 10^{-6}$	121
$C_3H_6 \rightarrow CO$	$k_2\ p_{C3H6}\ [O]$	$9.7 \cdot 10^{-6}$	102
$C_3H_6 \rightarrow CO_2$	$k_3\ p_{C3H6}\ [O]$	$8.3 \cdot 10^{-6}$	98
$C_3H_8 \rightarrow CO$	$k_4\ p_{C3H8}\ [O]$	$3.7 \cdot 10^{-7}$	155
$C_3H_8 \rightarrow CO_2$	$k_5\ p_{C3H8}\ [O]$	$3.2 \cdot 10^{-7}$	126
$O_2 \rightarrow [O]$	$k_6\ p_{O2}\ [\ ]$	$3.7 \cdot 10^{-6}$	87

Parity Plot (rates of formation of C_3H_6 and $CO_x \propto [O]$)



Open symbols:

T = 693-796 K

$C_3H_8/O_2/Ne$

0.3/0.15/0.55

0.50/0.25/0.25

0.15/0.15/0.70

Simulation of the lab-scale fixed-bed reactor

T_{Inlet} / K	ΔT / K	$X(C_3H_8)$ / %	$X(O_2)$ /%	$S(C_3H_6)$ /%	$S(CO)$ /%	$S(CO_2)$ /%
693	1	3.0	8.5	77	13	10
	3	2.9	9.0	76	12	12
773	20	17.1	82.4	47	35	18
	28	14.8	58.3	57	25	17

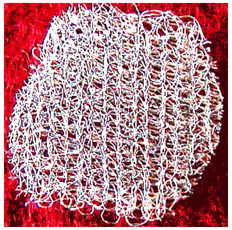
blue – simulated values

Use of MSR as a Tool in Catalysis

Determination of isothermal kinetic data

B. Ammonia oxidation on a thin Pt foil

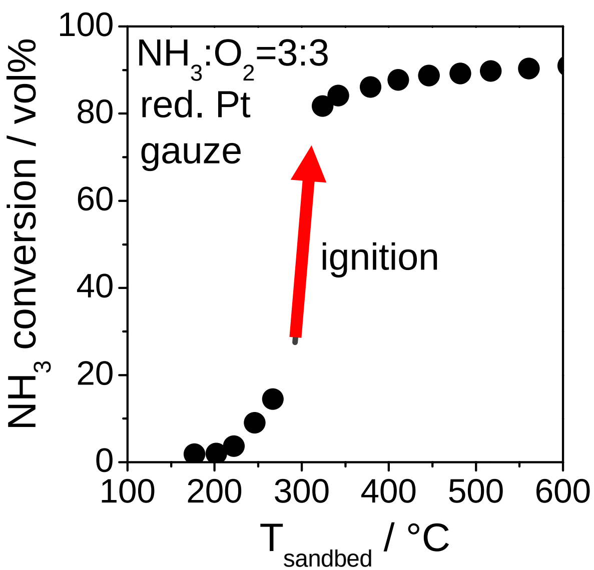
Ammonia oxidation on Pt
Temperature control during Reaction

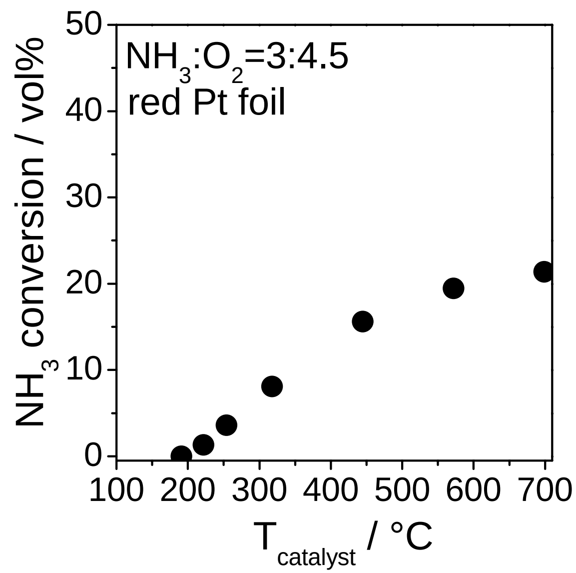


Temperature-programmed reaction over:

Pt gauze in tubular reactor	Pt foil in the micro-structured reactor

400 ml/min
101 kPa
3% NH_3
3% O_2



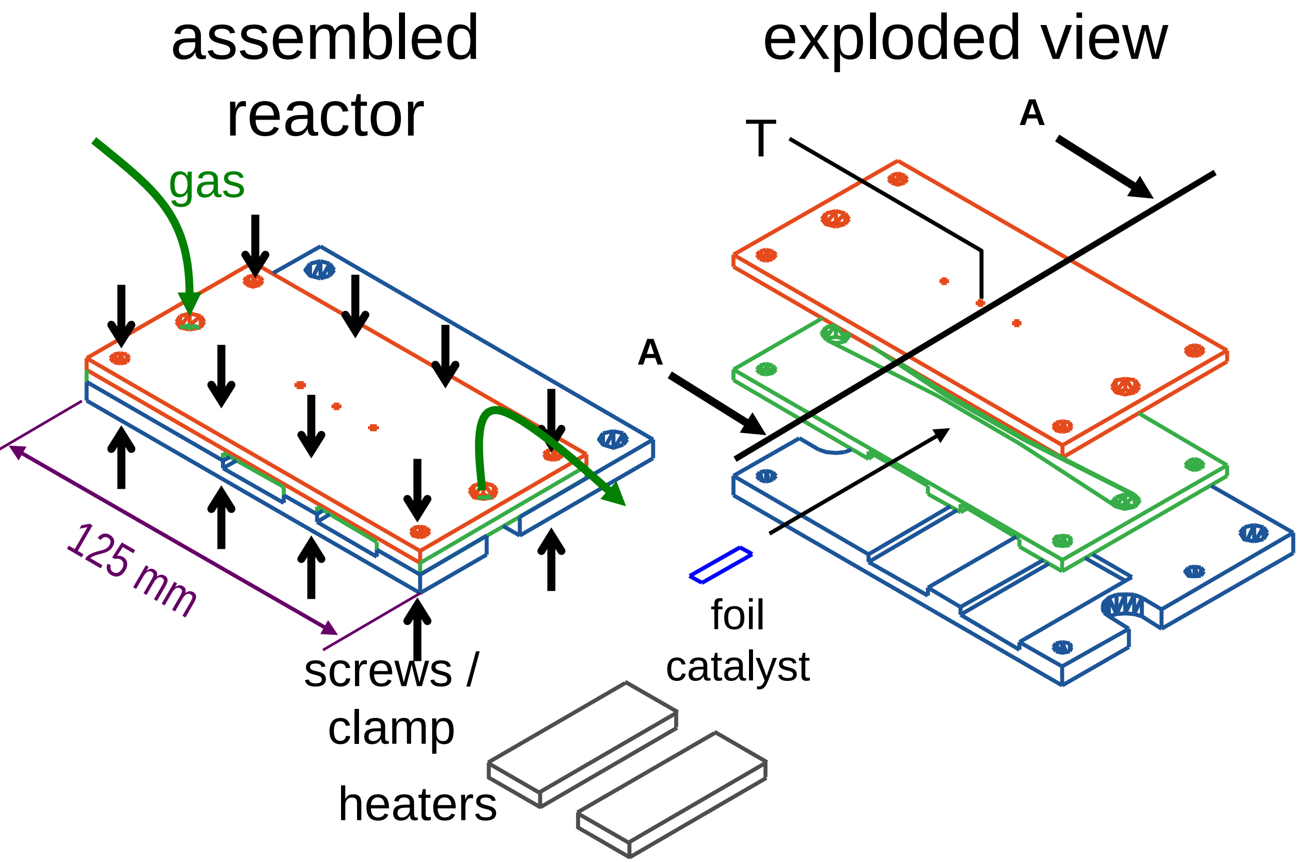


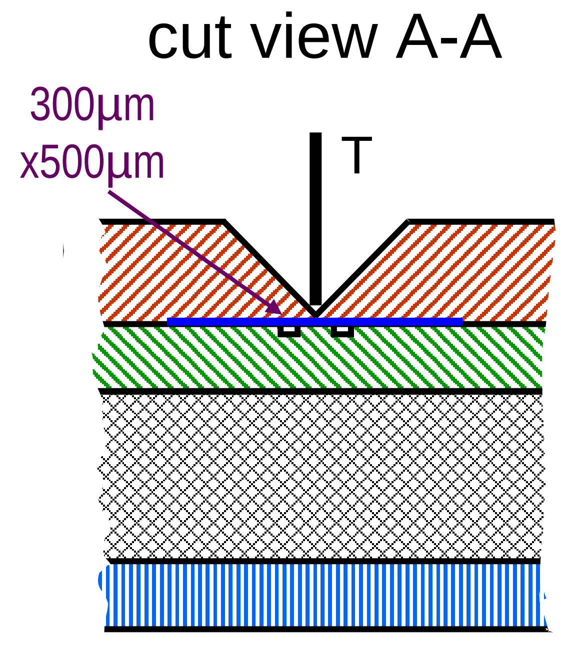
250 ml/min
101 kPa
3% NH_3
4.5% O_2

poor heat transfer leads to ignition
= loss of temperature control

micro reactor provides tem-
perature control up to 700°C

Surface reconstruction of thin-foil Pt catalyst





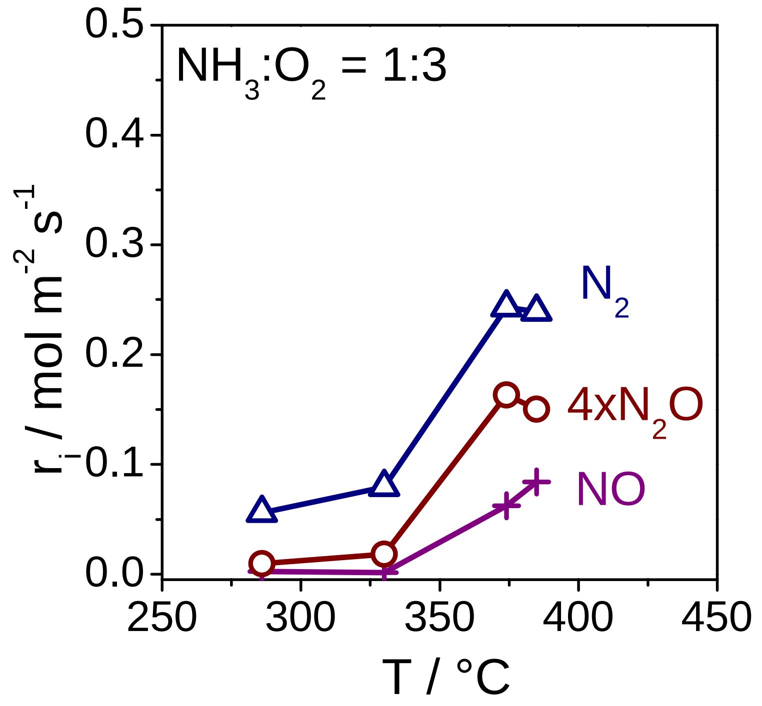
operates without
gaskets upto 130 kPa !

+ simple flat catalyst in optimal contact with the wall
+ fast catalyst exchange and protected thermocouple
+ short contact time (for fast reactions)

Measured influence of temperature on rates of product formation

NH_3
O_2
Ar+Ne

$r_i = f(T)$



400 ml/min
101 kPa
X<11%
TOS>14h

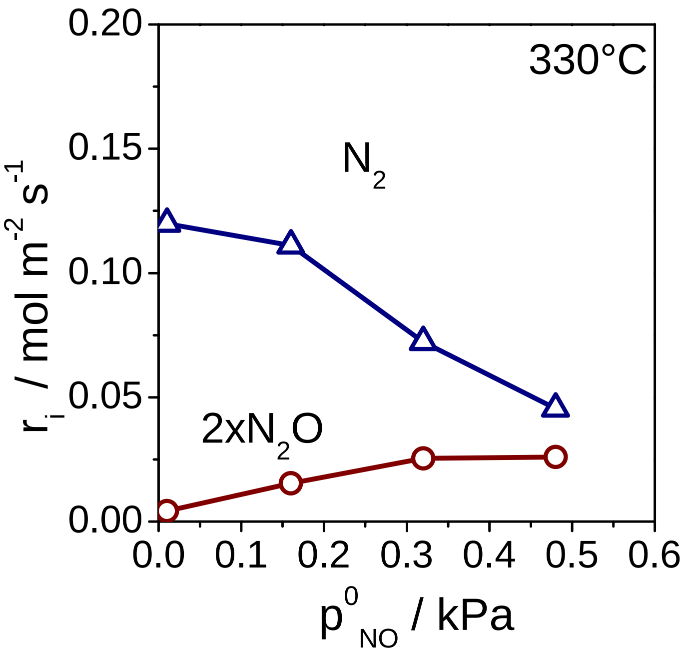
- N_2, N_2O, and NO are formed as products
- product formation increases with temperature
- NO formation requires T > 330°C

Measured influence of adding products NO and N_2O on rates of product formation

400 ml/min
101 kPa
X<11%
TOS>14h
3 kPa NH_3
3 kPa O_2

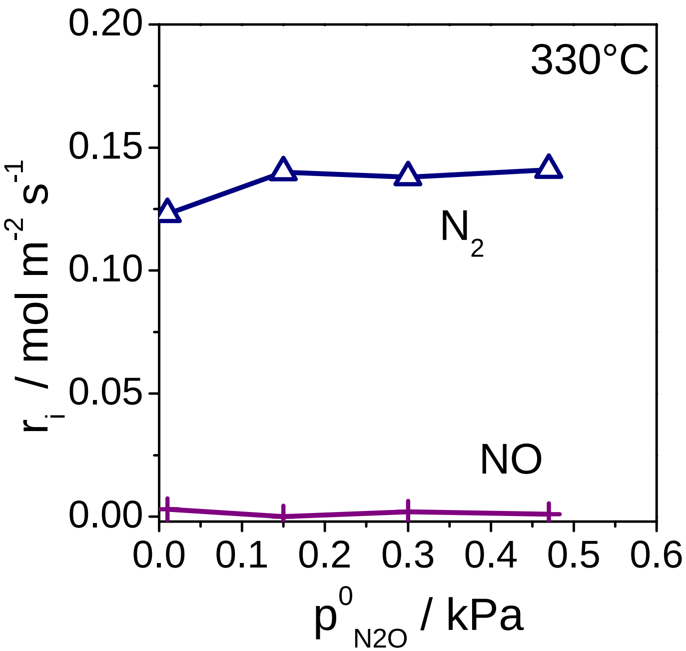
(NH_3+O_2) + NO

$r_i=f(p_{NO})$



(NH_3+O_2) + N_2O

$r_i=f(p_{N2O})$



400 ml/min
101 kPa
X<11%
TOS>14h
3 kPa NH_3
3 kPa O_2

➡ NO reduces rate of nitrogen formation, but increases it slightly for N_2O formation

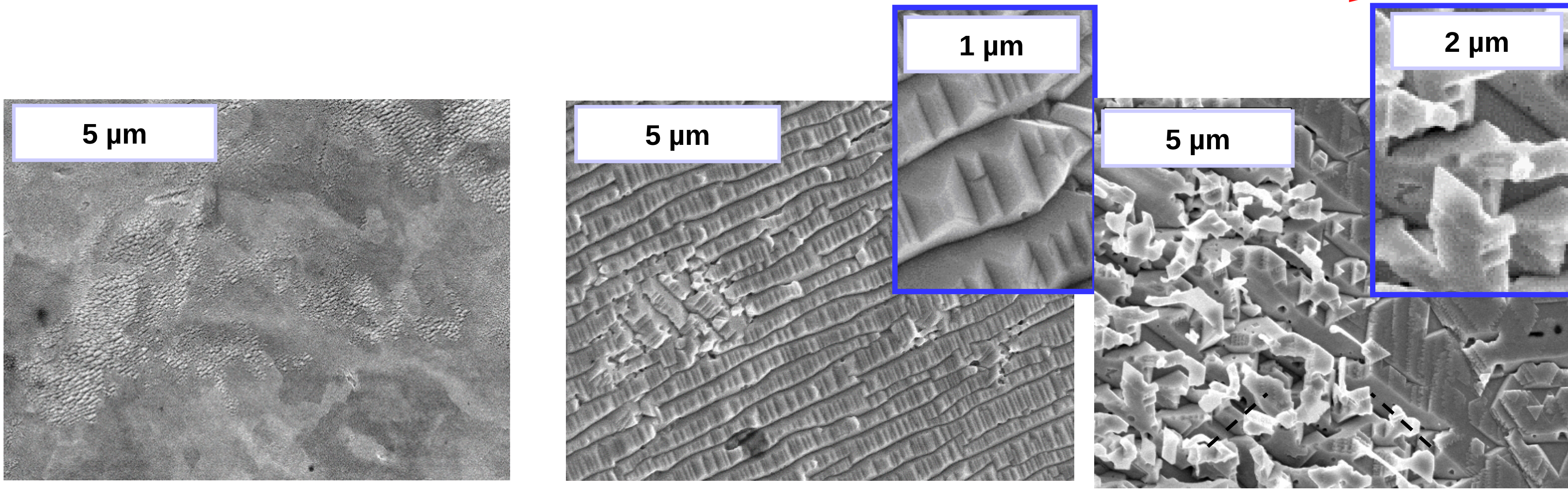
➡ N_2O has hardly any influence on rate of product formation

Ammonia oxidation on thin-film Pt catalyst

Temperature-dependent surface reconstruction

SEM after reaction at:

330°C **374°C** **~700°C**

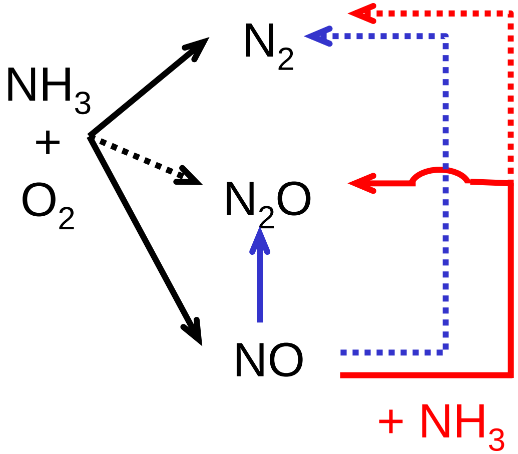


250 ml/min
101 kPa
3% NH_3
4.5% O_2

- temperature-dependent surface faceting
- different Pt morphology at low- and high-T <=> diiferent transport mechanism?
- T-controlled reaction below 500°C made it possible to study faceting & kinetics

Building models:
Set of Reactions and Rate equations

simplified
reaction network



NH_3 adsorption	$NH_3 + s$	$\longrightarrow$	$NH_3\text{-}s$
	$NH_3\text{-}s$	$\longrightarrow$	$NH_3 + s$
O_2 adsorption	$O_2 + 2s$	$\longrightarrow$	$2\ O\text{-}s$
	$2\ O\text{-}s$	$\longrightarrow$	$O_2 + 2s$

NH_3 activation + H_2O formation

$$NH_3\text{-}s + {}^3/_2 O\text{-}s \rightarrow N\text{-}s + {}^3/_2\, H_2O + {}^3/_2\, s$$

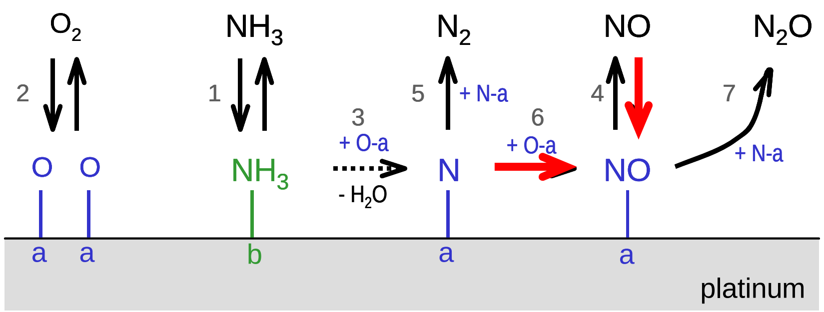
$$r = k_i\, (NH_3\text{-}s)\, (O\text{-}s)$$

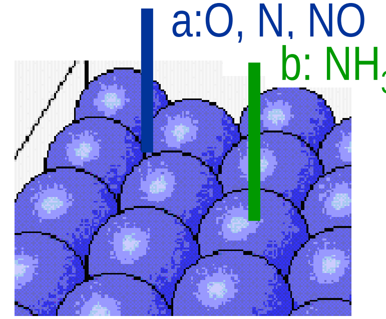
N_2 formation reactions	$2\ N\text{-}s$	$\longrightarrow$	$N_2 + 2\ s$
NO formation	$N\text{-}s + O\text{-}s$	$\longrightarrow$	$NO\text{-}s + s$
NO desorption adsorption	$NO\text{-}s$	$\longrightarrow$	$NO + s$
	$NO + s$	$\longrightarrow$	$NO\text{-}s$
N_2O formation reactions	$NO\text{-}s + N\text{-}s$	$\longrightarrow$	$N_2O + 2s$

Mechanistic indications from kinetic fitting

best-fitting model

286-385°C
$p_i < 6$ kPa





dual / Pt(111)

- re-adsorption of NO must be considered
- decomposition of NO is not significant
- adsorption sites and reactions are consistent with literature on Pt(111)

A kinetic model on pc Pt describes the formation of N_2 and N_2O and NO

The Pt surface is reconstructed already at mild conditions (374°C); this knowledge is essential for evaluation of kinetic data!

Conclusions

Micro-structured reactors are suited for obtaining isothermal kinetic data

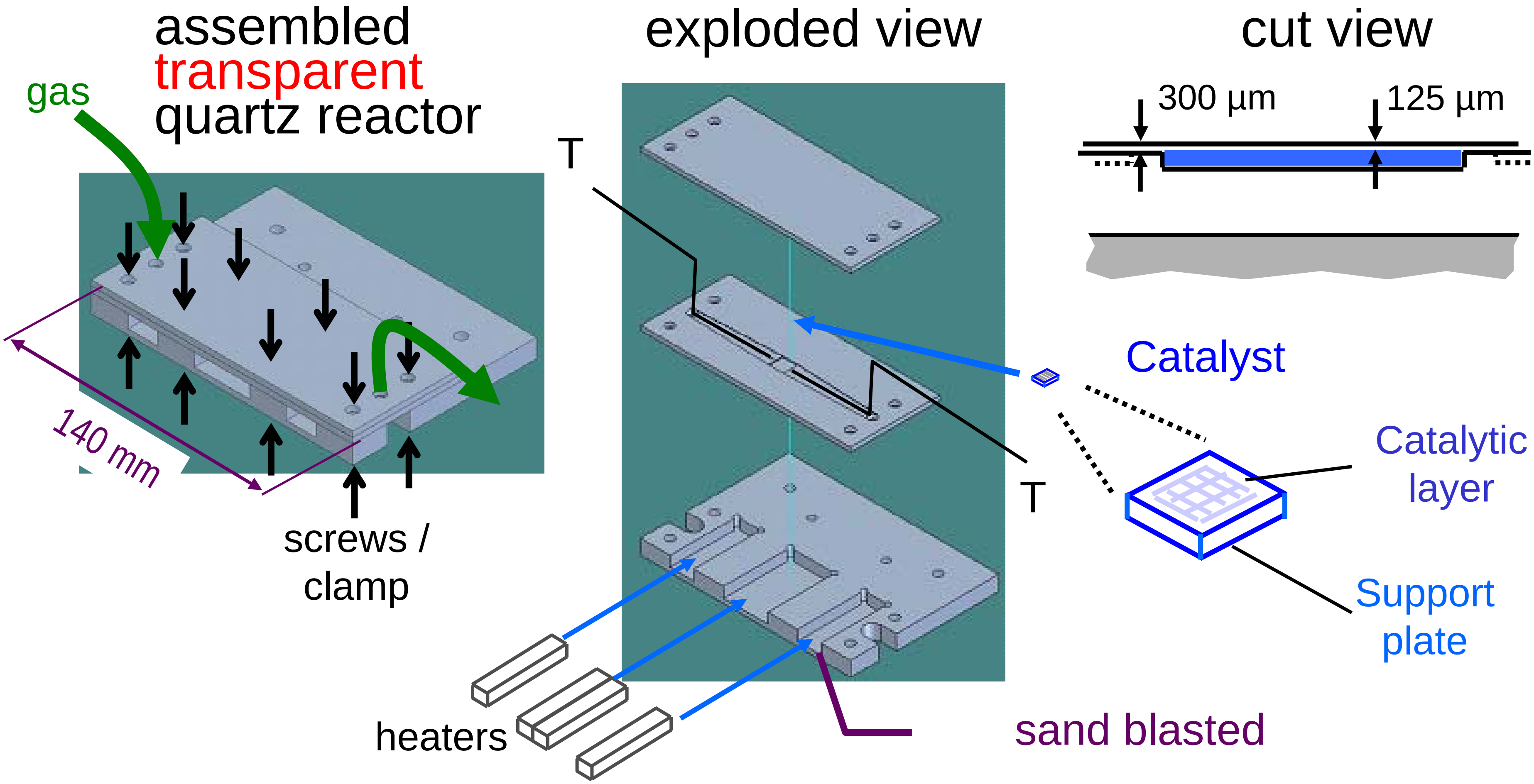
A.) for simulation of catalytic fixed-bed reactor performance and

B.) for deriving indications on possible reaction mechanisms

Use of MSR as a Tool in Catalysis

- Surface restructuring in ammonia oxidation on a Pt foil as catalyst at defined T (remember previous section)
- Identification of surface oxides of a Mo/V/W-O_x on silica catalyst by Laser-Raman spectroscopy

In-situ Laser Raman Catalyst Characterization
- C_3H_6 oxidation by catalyst on carrier plate -

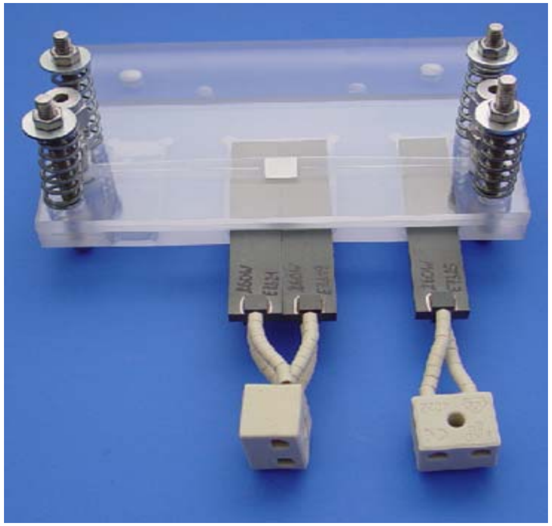


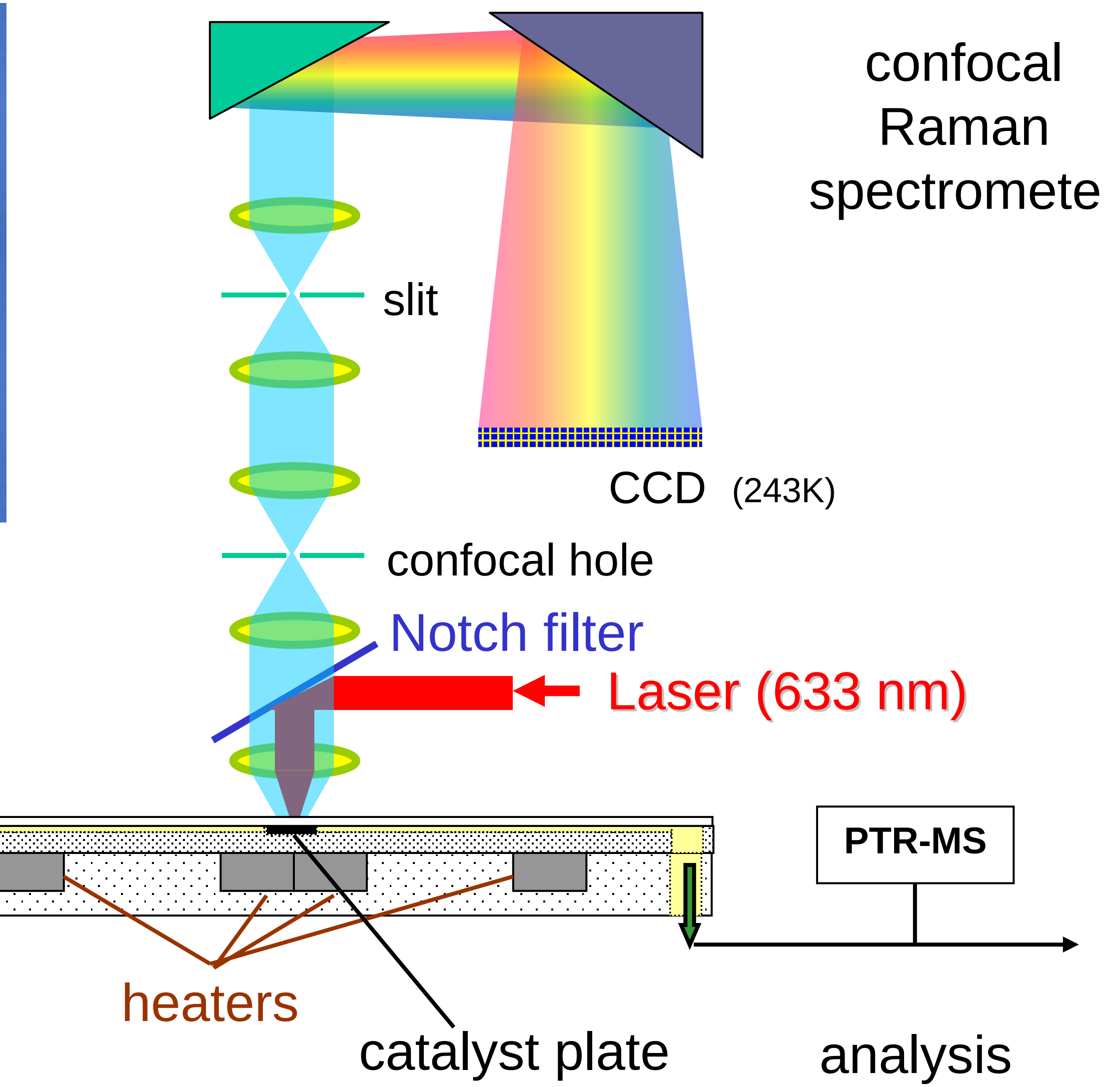
+ cheap simple support plates
+ defined catalyst film

+ fast catalyst exchange
(high contact time)

FHI

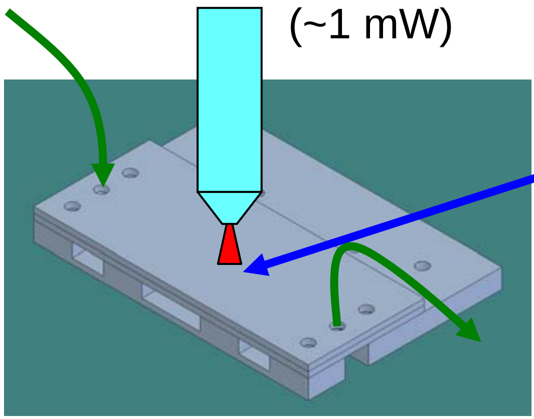
Laser-Raman Setup





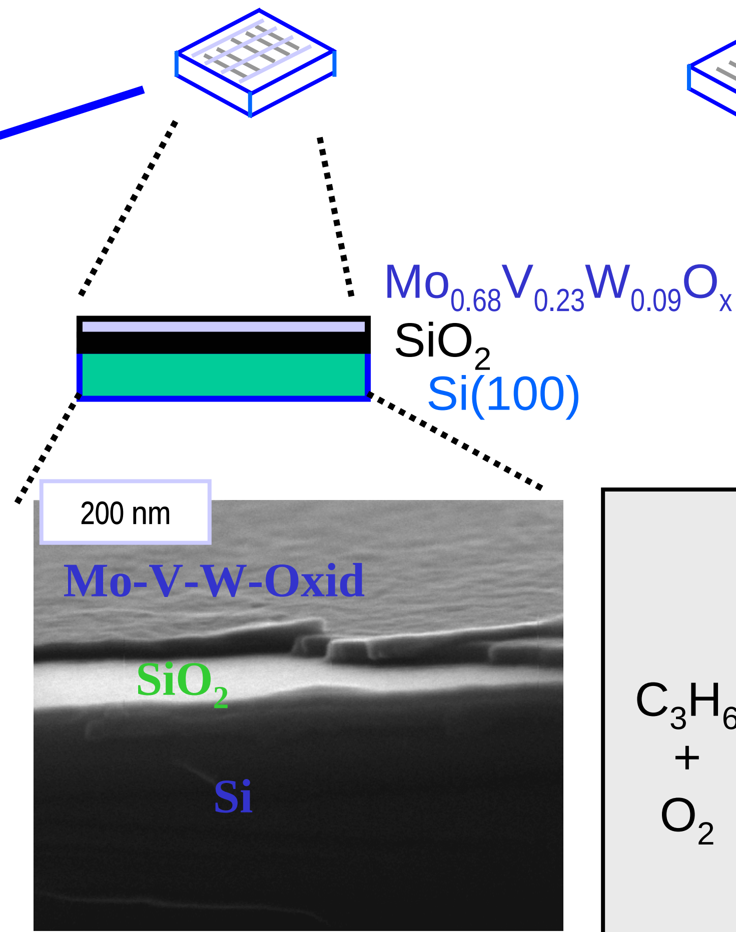
Propene oxidation / Experimental

Reactor A + Raman

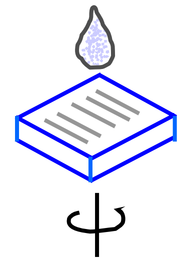


A	1 cm^2
flow	1 ml/min
tau	< 500 ms
Re	< 1
T	< 400°C
p	101 kPa
p_i	< 20k Pa

Catalyst



Catalyst preparation



*solution (Mo, W, V)
*spray drying (powder)
*add water-gelatine
*spin-coat at 37°C, dry
*calcine 3h@300°C in air

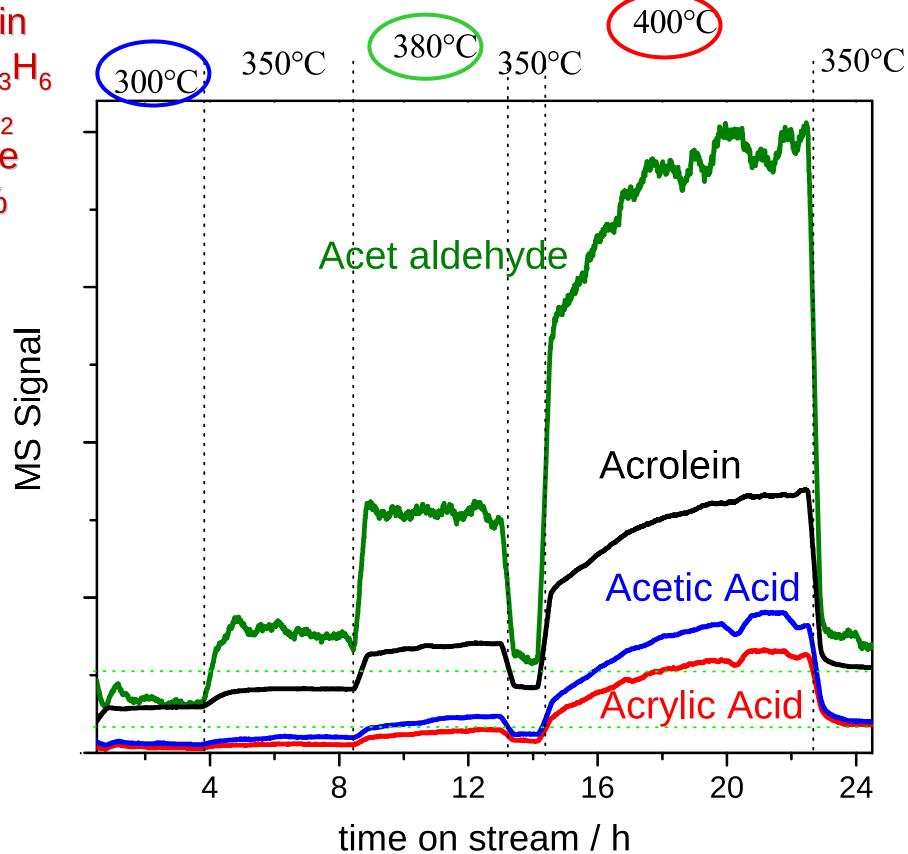
Reactants

$C_3H_6 + O_2 \rightarrow$
- acrolein
- acrylic acid
- acetaldehyde
- acetic acid
- CO CO_2

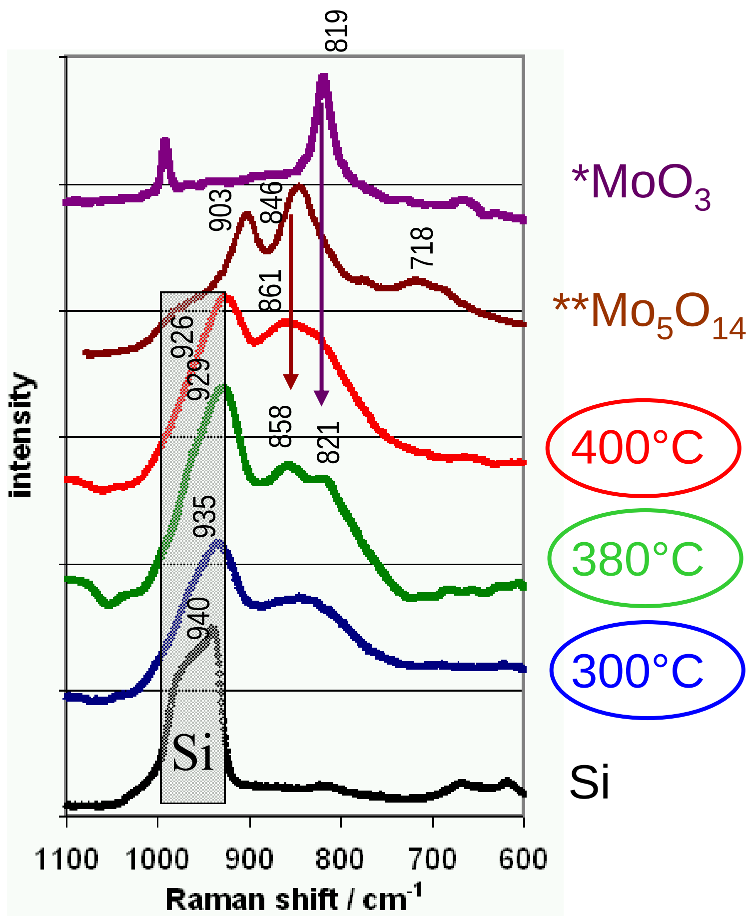
FHI **Propene oxidation** (in-situ Laser-Raman cat.char.)

T-programmed reaction

1 ml/min
10% C_3H_6
20% O_2
70% He
X < 5%



in-situ Raman



* active catalyst / all products
* activation + change of Raman
= structure vs. activity in parallel

** A. Brückner / ACA*
***G. Mestl, J. Raman Spectrosc. 33 (2002) 333*

Use of MSR as a Tool in Applied Catalysis

A. Hydrogen-driven fuel cells
B. Partial oxidation of propene by H_2O in the vapor phase

Aspects of micro-structured reactor applications for mobile fuel cells

- choice of hydrogen carrier for hydrogen-driven fuel cells
- for maximizing hydrogen selectivity in steam reforming of methanol, low temperatures are required for thermodynamic reasons
- coating of ceramic walls with catalytic material

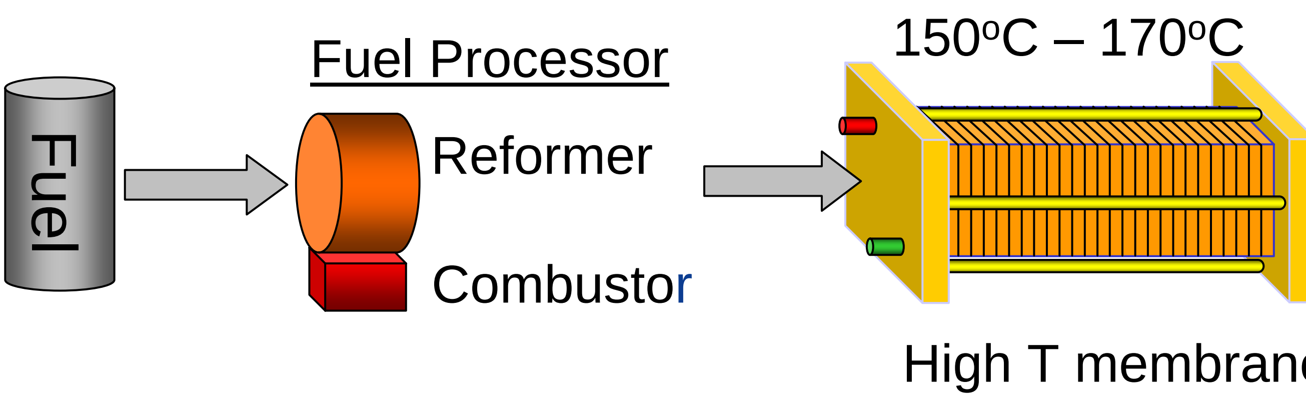
Fueling fuel cells for mobile applications

Prototype reformer and PEMFC for a laptop from Casio, about 20 hr of operation.

Hydrogen storage is not ideal for portable devices.

A liquid fuel (hydrogen-carrier) is stored and reformed to produce on-demand hydrogen for the fuel cell.

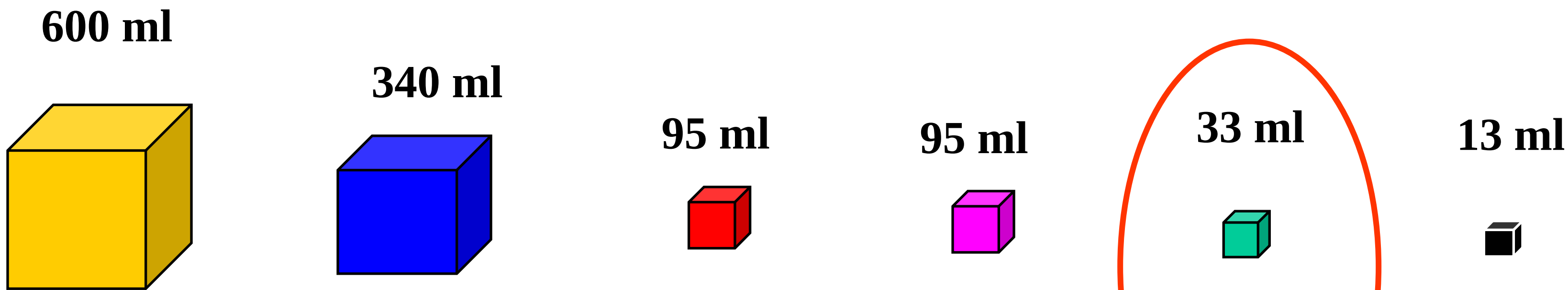
Which fuel should be used?



Kawamura et al., Chem. Eng. Sci. **61** 1092 (2006)

Energy densities for various "hydrogen-carriers"

Volumes and weights of different fuels equivalent to 150Wh of stored energy*



Li-ion Battery	H_2 Compressed (200 bar)	H_2 Liquid Hydrogen	H_2 Metal Hydride	Methanol	Diesel
600 ml	340 ml	95 ml	95 ml	33 ml	13 ml
1 kg	920 g		530 g	26 g	13 g

Why Methanol

- Low reforming temperature (220-250 ºC)
- Lower CO production compared to other fuels.
- High H_2 content in product stream
- Zero sulfur

* D. Browning et al./Journal of Power Sources 65 (1997) 187-195

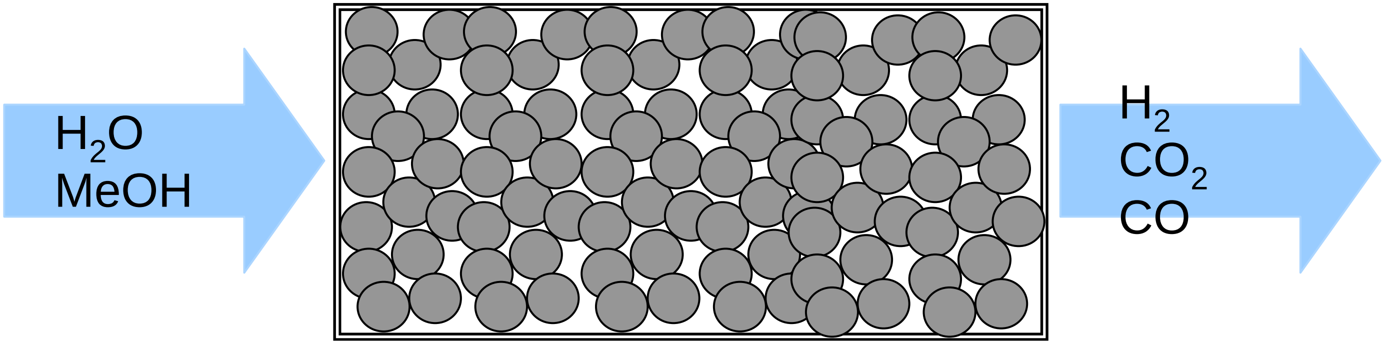
Steam reforming of methanol

$$CH_3OH + H_2O \longrightarrow 3H_2 + CO_2$$

$$CO_2 + H_2 \longleftrightarrow CO + H_2O$$

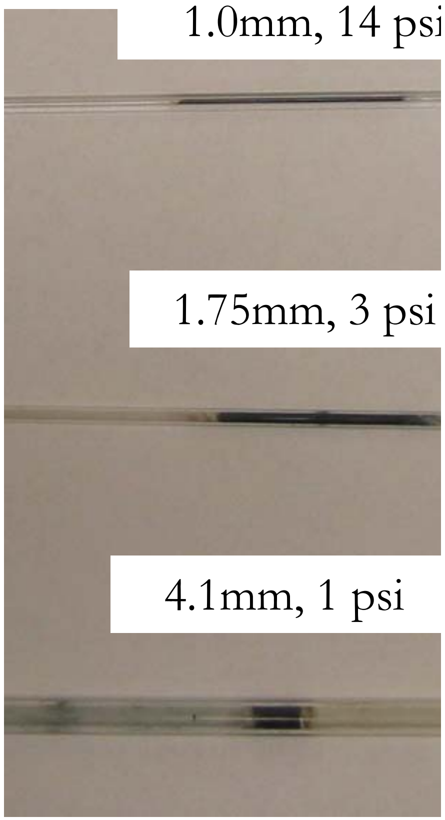
CO production must be minimized because it is a poison to the anode catalyst.

For a 20W fuel cell, assuming
a liquid flow of 15ml/hr and 98% MeOH conversion
approximately 4.8g of catalyst are needed.

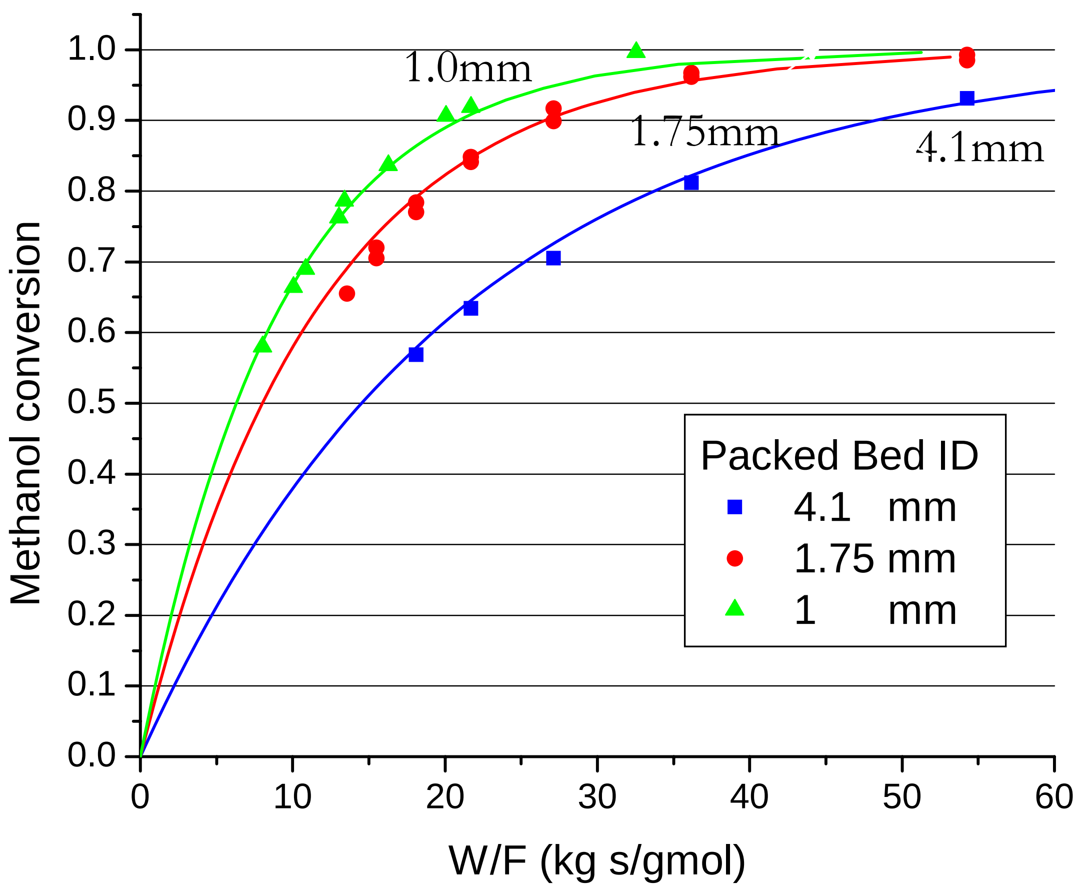


chemical nuclear ChNE department of chemical & nuclear engineering

Methanol Conversion for Different Fixed-Bed Reactor Dimensions



Steam/Methanol = 1.1, T= 230ºC, P = 640 Torr



Packed-bed reactors are far from isothermal

(Enthalpy of reforming reaction: ca. -41 kJ/mol)

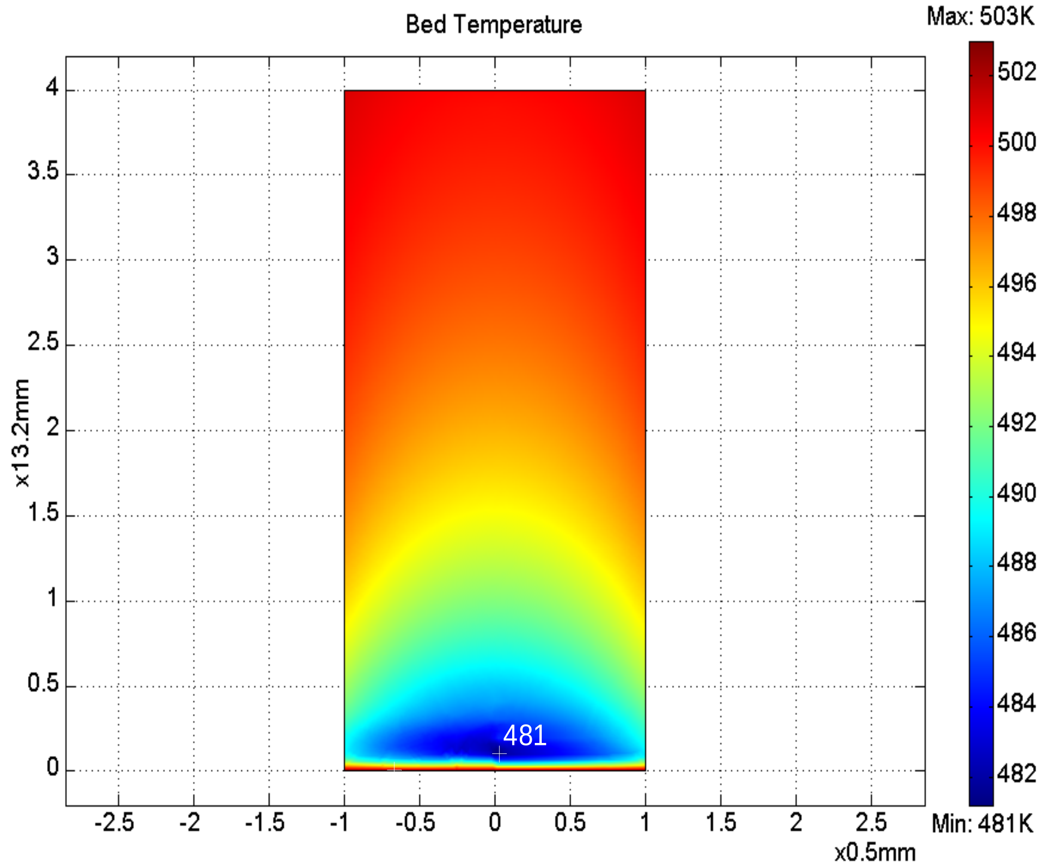
Reactor: 1mm ID

U_0 = 0.26 m/s

W/F = 16 kg s/gmol

Methanol Conversion = 0.86

ΔT is 20K for such a small-diameter reactor



Karim *et al*., App. Cat. A. **282** 101 (2005)

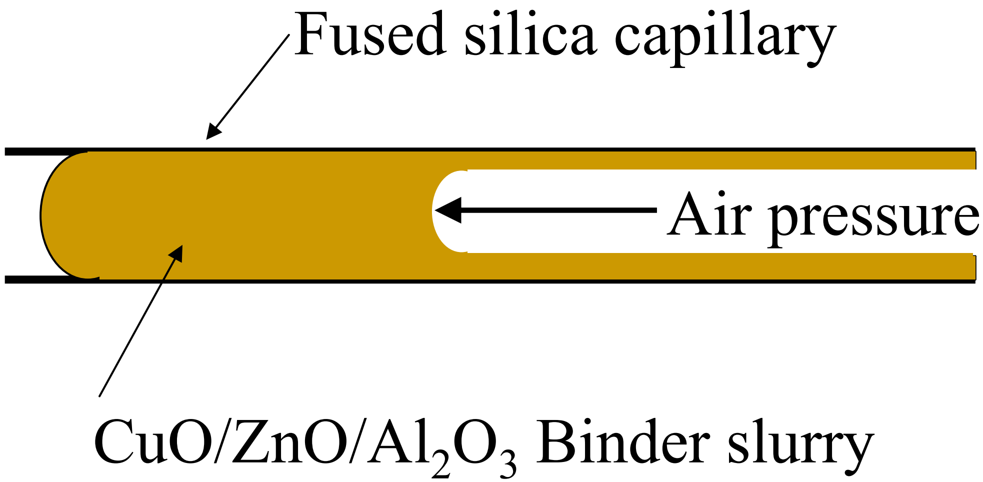
Solution:

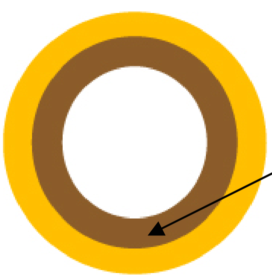
micro channel reactors

(ca. 500 to 100 μm)

Coating of micro-structured ceramic tubes

Gas-Assisted Fluid Displacement





$$m = \frac{(coated\ mass) - (empty\ mass)}{(full\ mass) - (empty\ mass)}$$

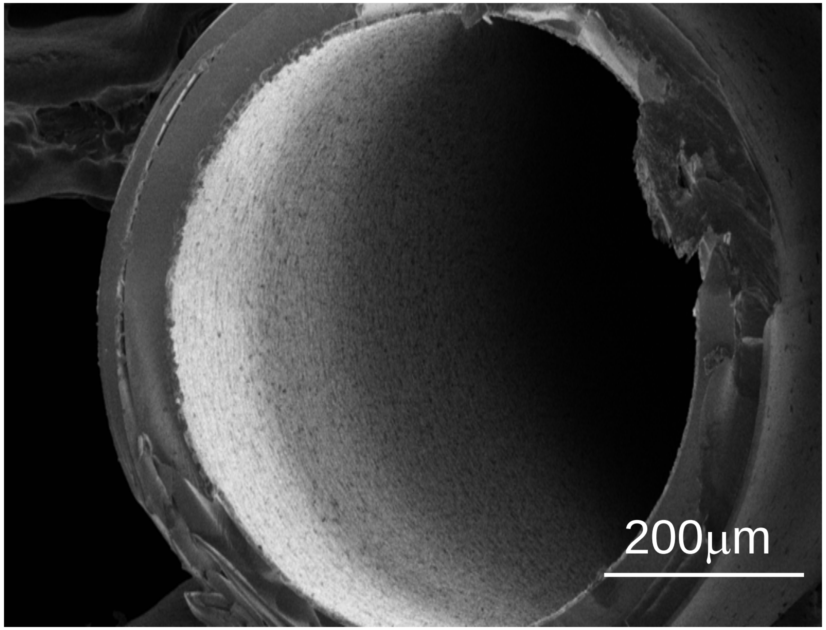
First, the fused-silica capillary is cleaned by etching, then rinsed with water and subsequently with ethanol; finally it is dried in air.

Afterwards, the capillary is filled with the coating fluid.

Purging the tube with air causes a thin film of liquid to be left behind

Wall coated reactor represents superior geometry

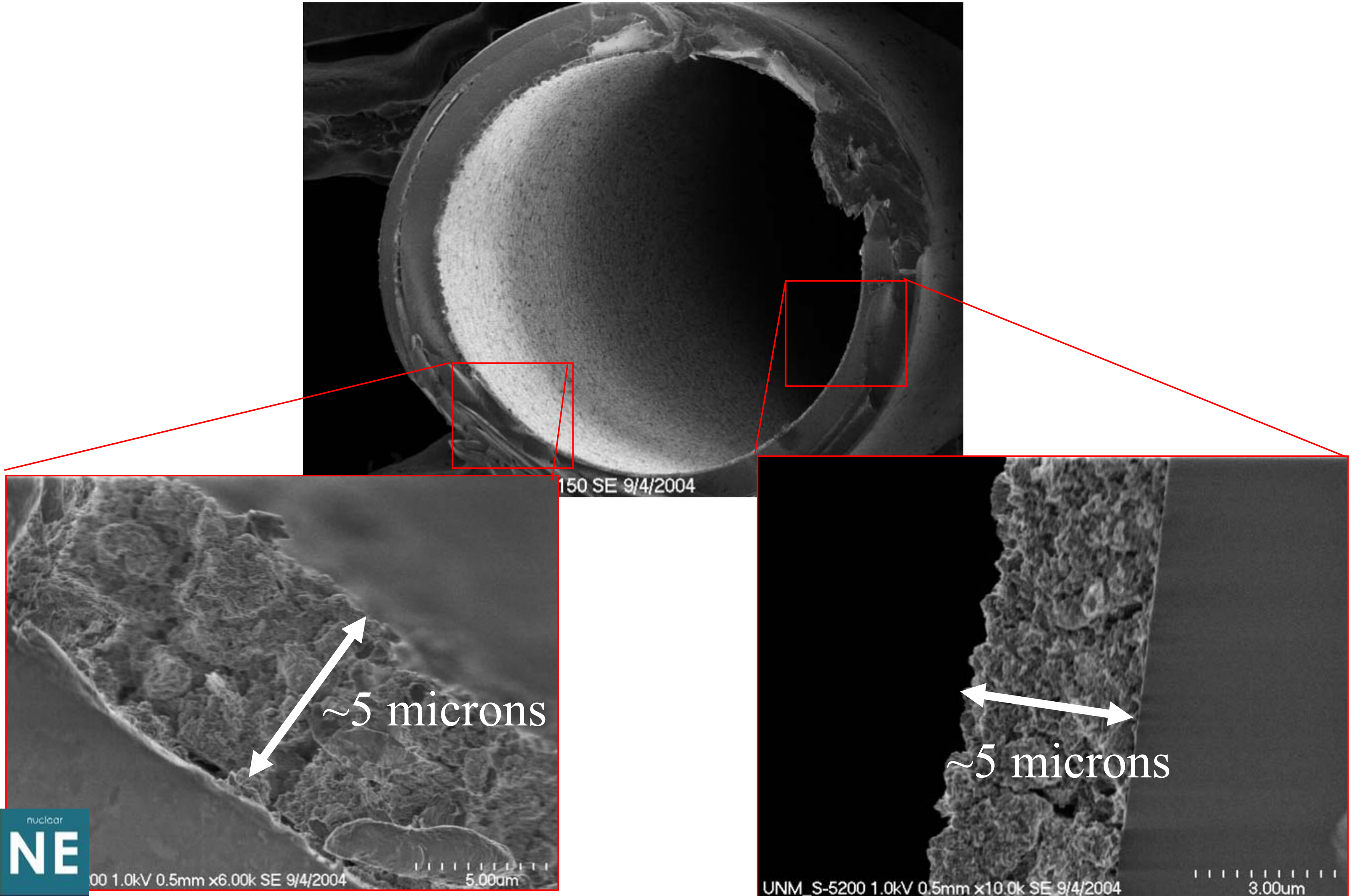
530μm capillary showing a dried 15μm thick $Cu/ZnO/Al_2O_3$ catalyst coating.



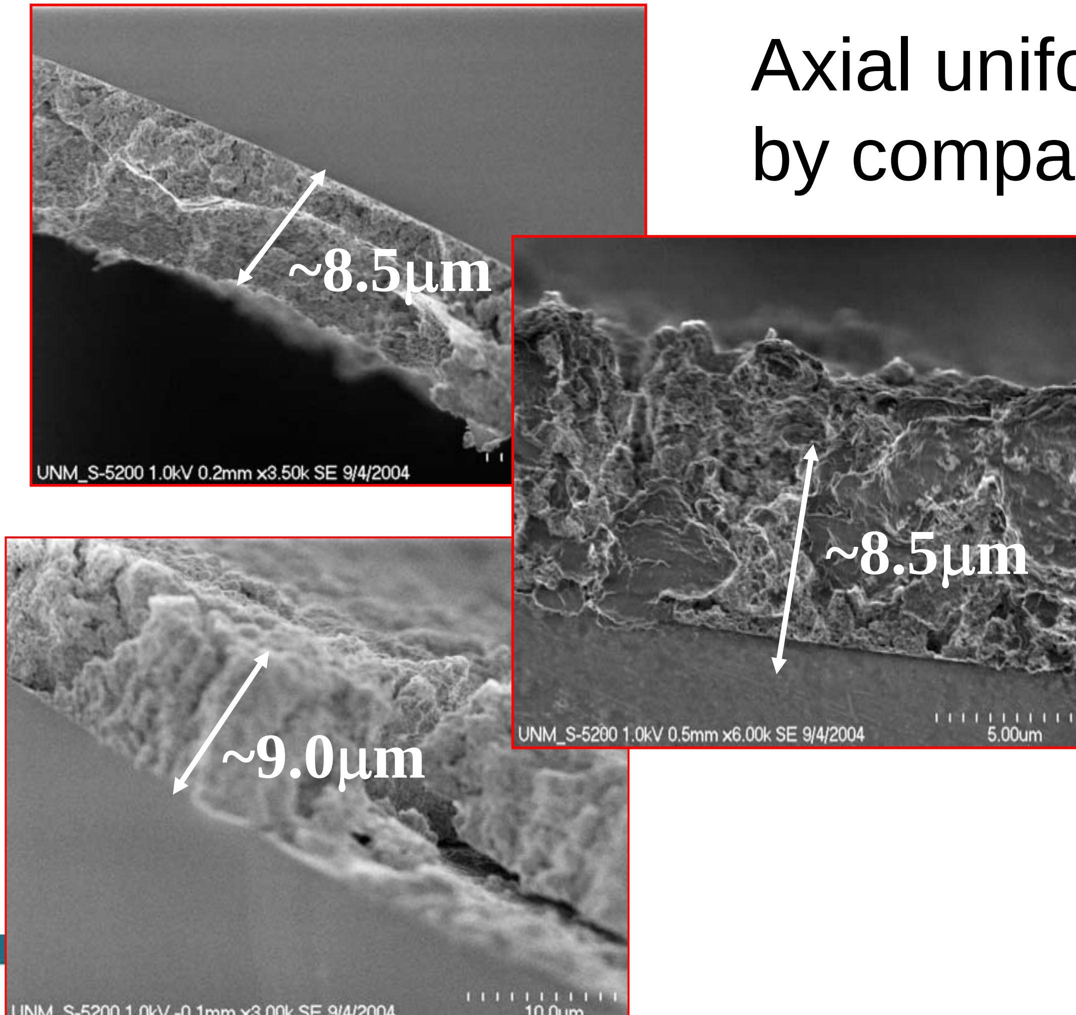
Wall coated reactors are better than micro-packed bed reactors for catalyst incorporation:

- Inherently low pressure drop.
- Short diffusion/conduction lengths lead to isothermal operation.
- More stable and reliable than packed bed for long-term portable use.

Radial Uniformity



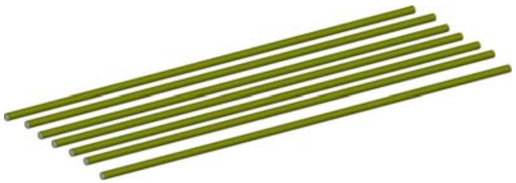
Axial Uniformity



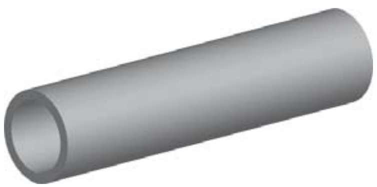
Axial uniformity is determined by comparing points on the **ends** and in the **middle** of the coated capillary.

Multi-channeled structure fabrication

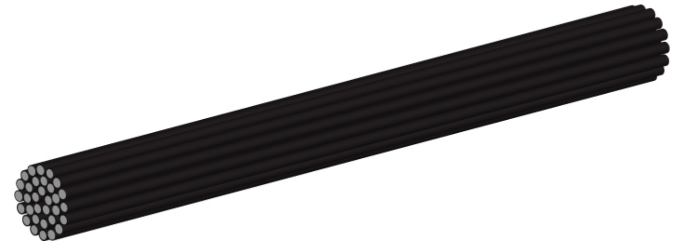
Fused-silica capillaries



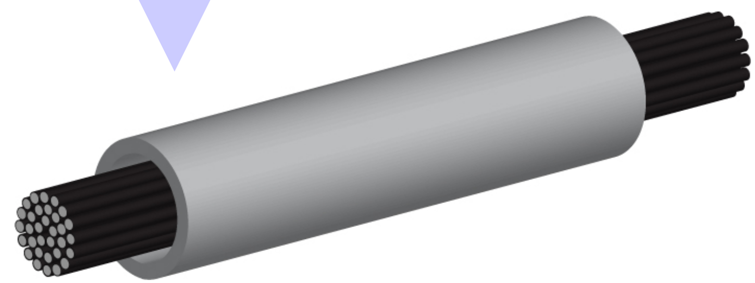
¼" OD stainless steel tube



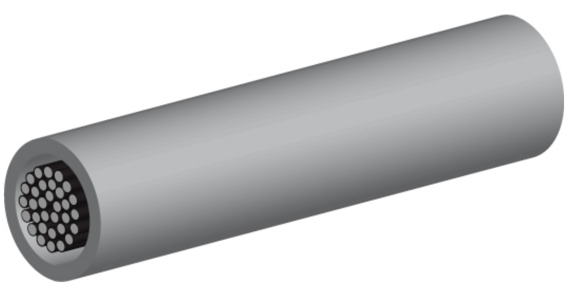
Capillaries bundled and set with high T epoxy.



Capillary bundle inserted into s.s. housing and sealed with epoxy.



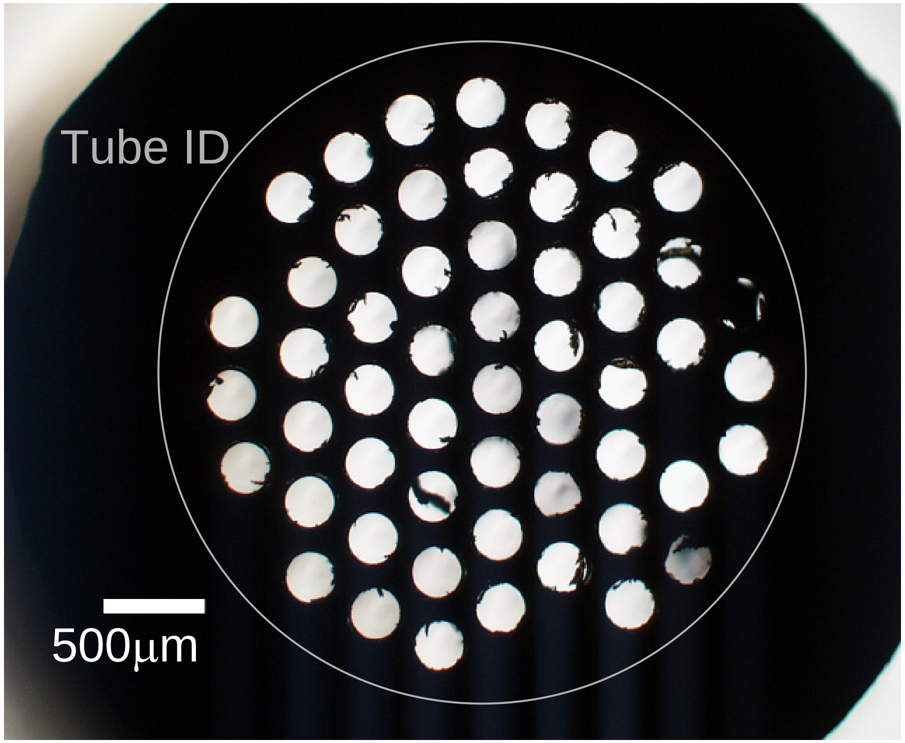
Ends cut with ceramic saw.



Multi-Channeled Structures

Transmitted-light optical microscope image of an un-coated M.R. with about 60 250μm capillaries.

The channels are regularly spaced and the epoxy has filled in all of the voids between the tubes creating an air-tight seal.



Micro-structured fuel-cell processor

Y. Men, G. Kolb, R. Zapf, D. Tiemann, M. Wichert, V. Hessel, H. Löwe,
submitted to Intern. J. Hydrogen Energy (2006)

Complete Microstructured Fuel Processor for Methanol Steam Reforming – (Running for 5 Days at Hannover Fair 2005)

Methanol + Water

Micro-structured Evaporator (250° C)

Catalyst: Industry

Reformer (270° C)

≈1% CO

Oxygen $O_2/C = 4$

Preferential Oxidation Stage 1 (140° C)

< 100 ppm CO

Oxygen $O_2/C = 8$

Catalyst: Home-made

Preferential Oxidation Stage 2 (140° C)

< 15 ppm CO

Catalyst: Home-made

Condensation

IR-Sensor

Fuel Cell (30 W) (PEM)

Electrical Consumer

Catalytic Burner (200° C)

CO_2, Water

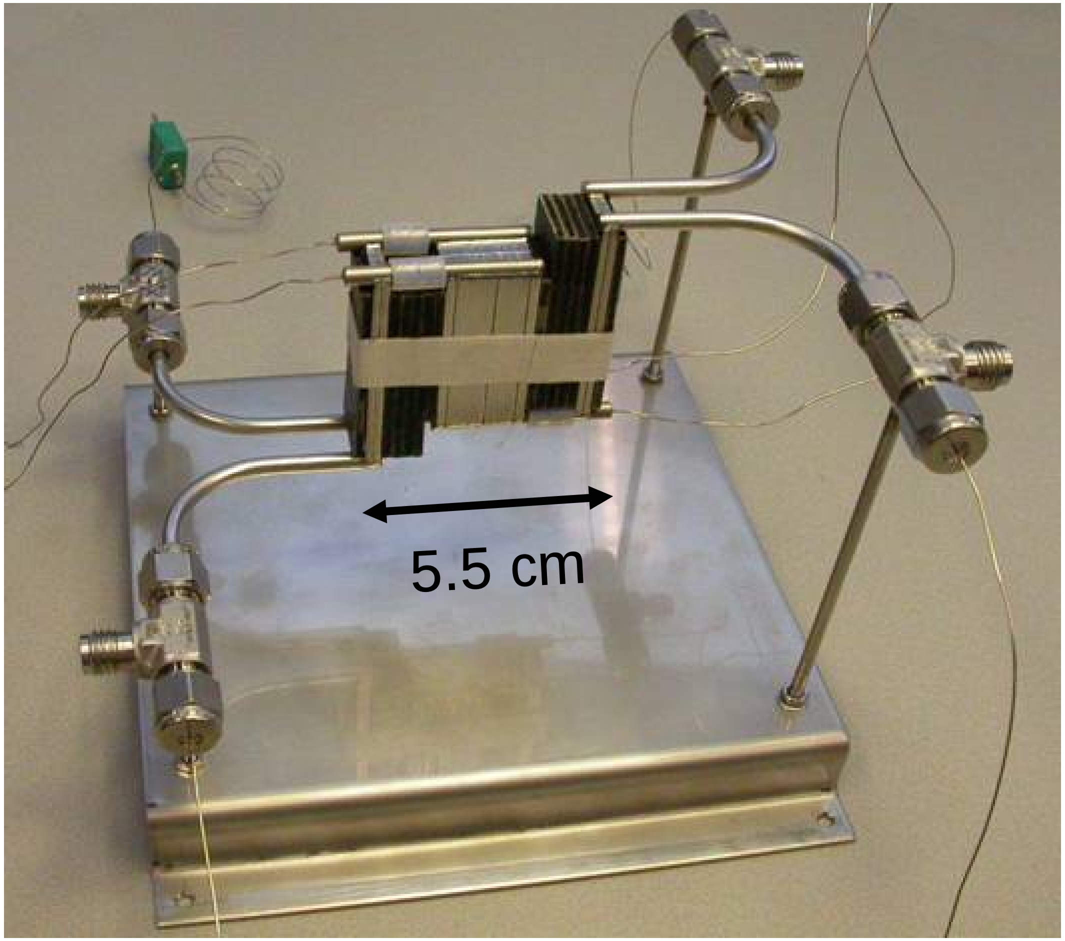
Catalyst: Pt (DEGUSSA)

All devices were externally heated

Reactor Size 7 x 2 x 1 cm³

400 ml/min H_2 produced

Preferential oxidation of CO (PrOX) in a micro-structured reactor



Specifications:

- 53 microstructured plates
- Volume: 60 cm^3
- Mass: 150 g
- 1.5 g $Pt/Ru/Al_2O_3$ catalyst
- coating thickness: 50 mm

Experimental conditions:

- simulated reformate gas:

  $H_2/CO_2/H_2O/CO/O_2$ =

  56/ 18 / 10 /0.5/0.9 %
- coolant gas: nitrogen

IChemE Chemistry Inno-vation KTN/Impact Award

TU/e award winner for TU/e-IMM development
(Whitehall, London)

Delsman, E. R., de Croon, M. H. J. M., Kramer, G. J., Cobden, P. D., Hofmann C., Cominos, V., Schouten, J.C. *Chem. Eng. Sci.* **59** *(*2004) 4795-4802.

Cominos V., Hessel V., Hofmann C., Kolb G., Zapf R., Ziogas A., Delsman E.R., Schouten J.C. *Catal. Today* **110**, 1-2 (2005) 140-153.

Testing rig for the steam-reforming reaction in micro-structured reactors

Demonstration plant reactor

consisting of

micro-structured catalytic modules

for epoxidation of

propene to propene oxide

by vapor-phase hydrogen peroxide

DEMIS Consortium:

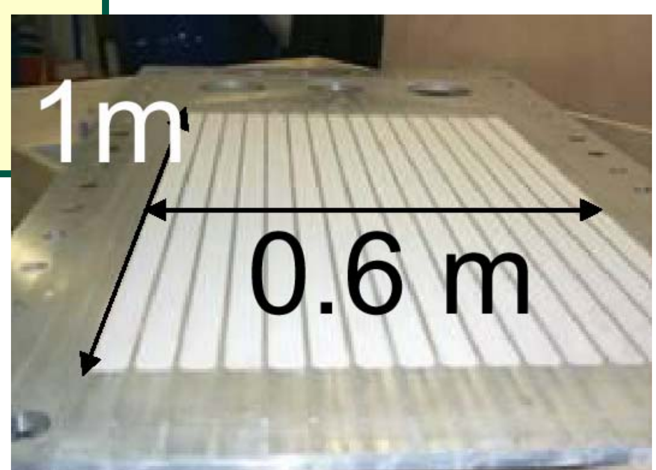
Degussa, Uhde/Thyssen-Krupp,TU Chemnitz und Darmstadt,

MPI-Mühlheim

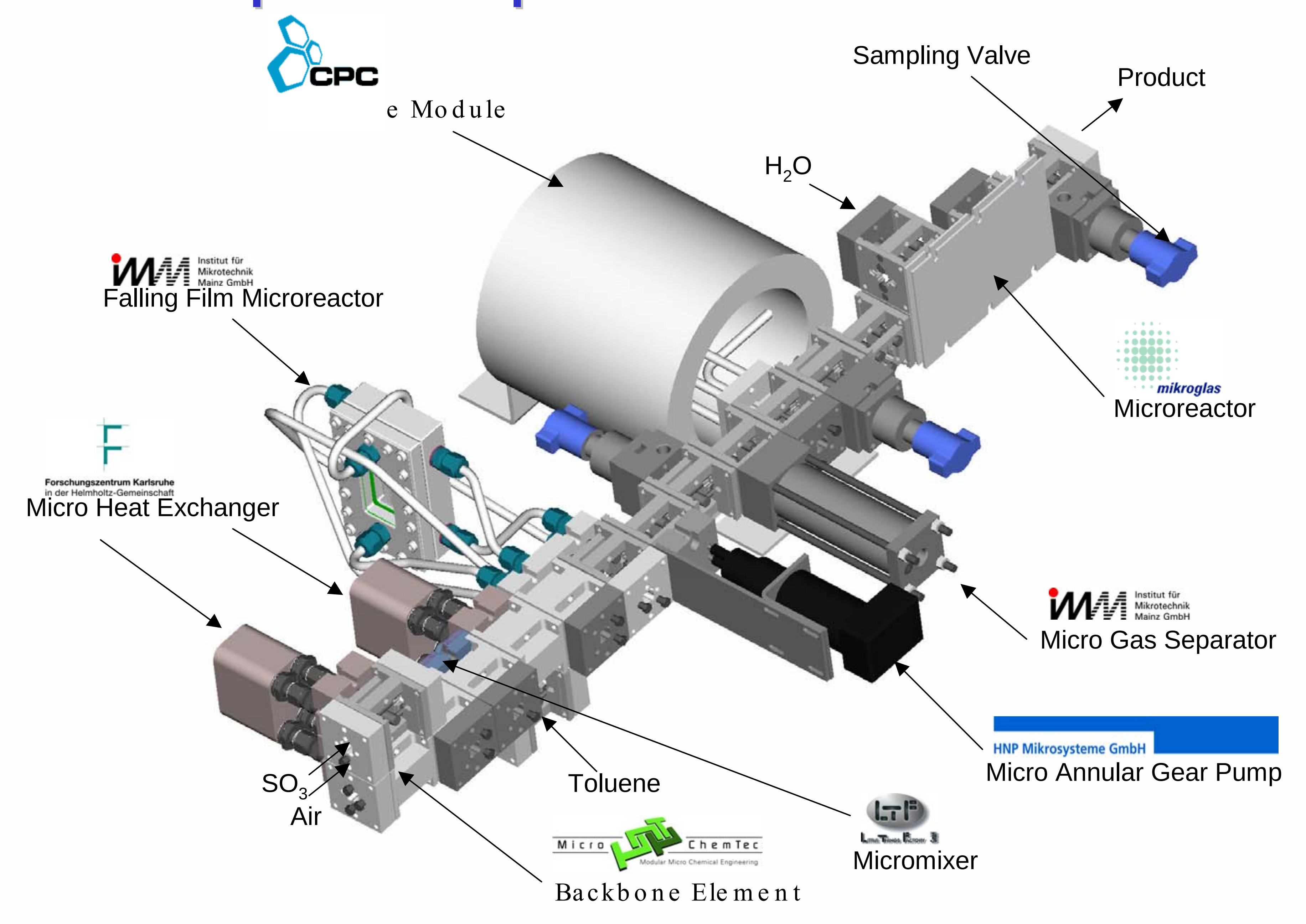
Gas-phase epoxidation of propene by hydrogen peroxide to propene oxide

Lab Scale

towards technical scale



Microplant Composed of Various Modules

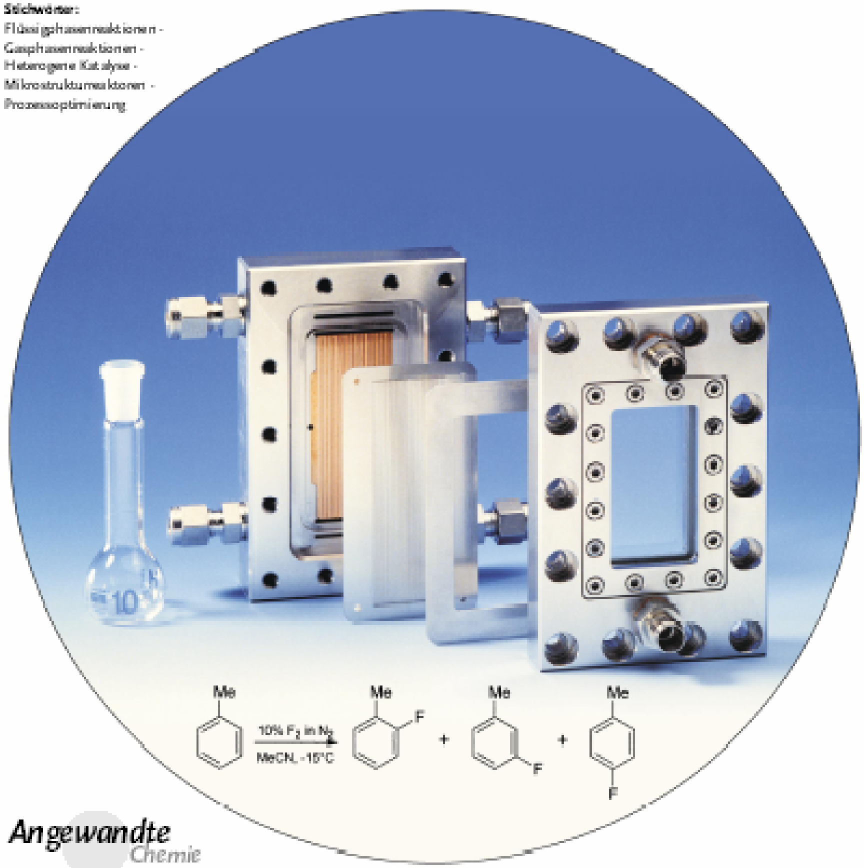


Mikroverfahrenstechnik

Chemie in Mikrostrukturreaktoren

Klaus Jähnisch, Volker Hessel,* Holger Löwe und Manfred Baerns*

Stichwörter:
Flüssigphasenreaktionen · Gasphasenreaktionen · Heterogene Katalyse · Mikrostrukturreaktoren · Prozessoptimierung



  DOI: 10.1002/ange.200300577

The End

References:

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K. Jähnisch, V. Hessel, H. Löwe, M. Baerns: Chemistry in Microstructured Reactors; Angew. Chem. Int. Ed. **2004**, 43, 406-446

G. Markowz, S. Schirrmeister, J. Albrecht, F. Becker, R. Schütte, K.J. Caspary, E. Klemm: Microstructured Reactors for Heterogenously Catalyzed Gas-Phase Reactions on an Industrial Scale; Chem. Engng. & Techn. **28**, no.4, 459-464 (2005)

L. Kiwi-Minsker, A. Renken: Microstructured Reactors for Catalytic Reactions; Catal. Today **110**, issues 1-2, 2-14 (2005)