Membrane reactors for improved processes: How to integrate reaction and separation in one apparatus

Reinhard Schomäcker

Fachgruppe Technische Chemie
Institut für Chemie der TU Berlin

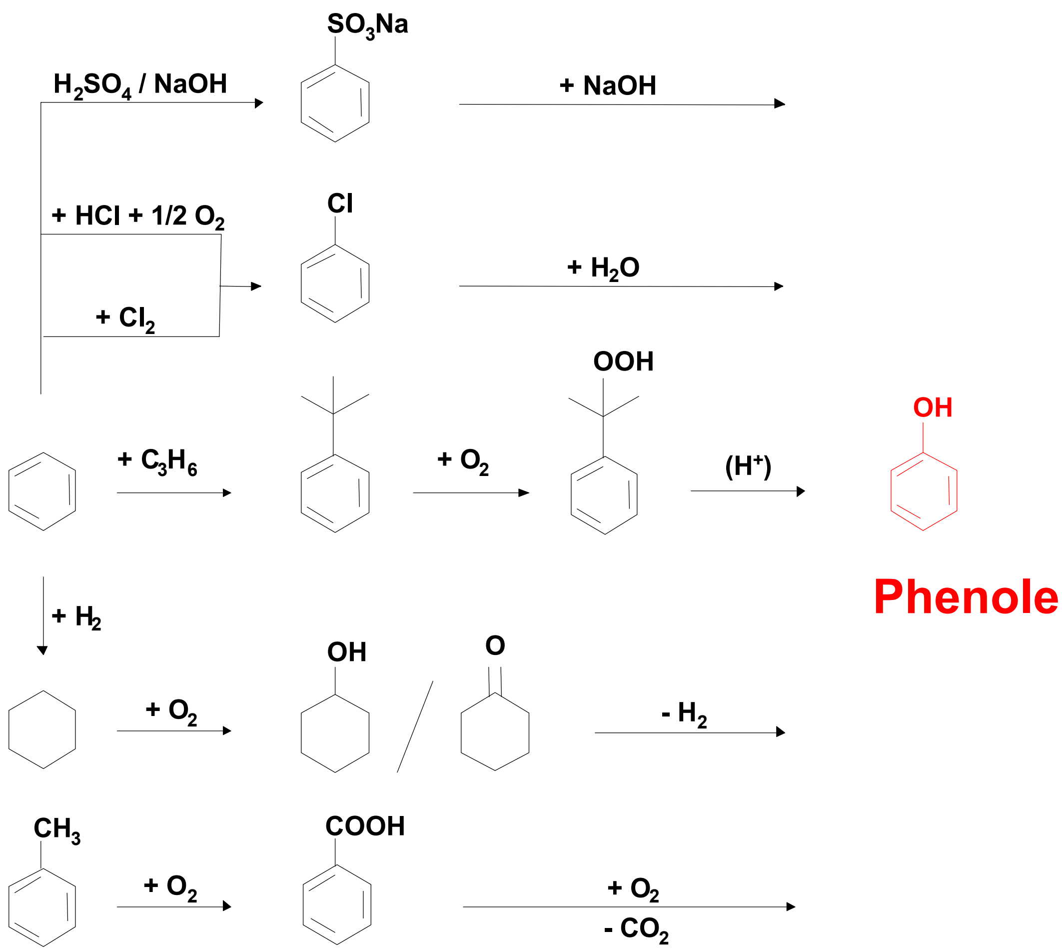
1. Classical concepts

2. Concepts for membrane reactors

3. Examples for reactions in membrane reactors

4. Problems to be solved before industrial scale application

Routes for Phenole Production



Benzene sulfonate-Route

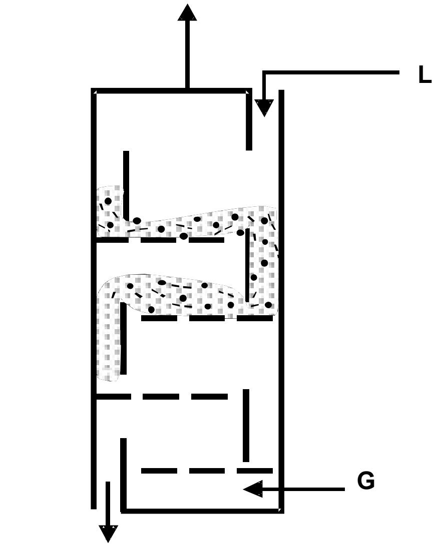
Chlorobenzene-Route

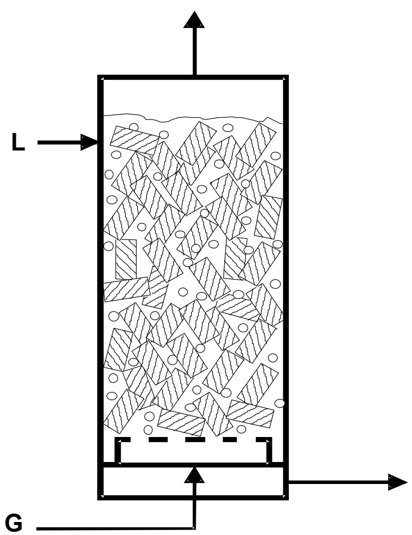
Cumene-Process

Anol/Anon-Dehydrogenation

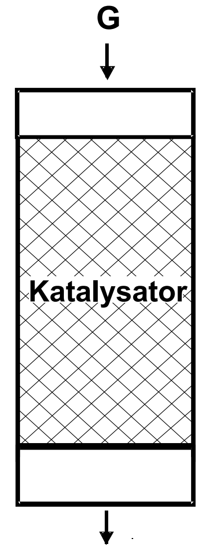
Toluene-Oxidation

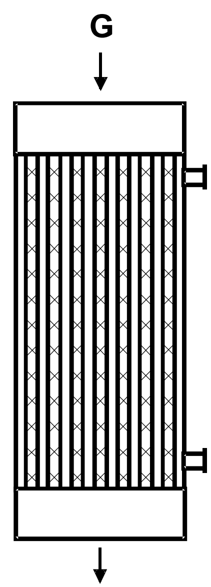
Gas-Liquid-Reactors



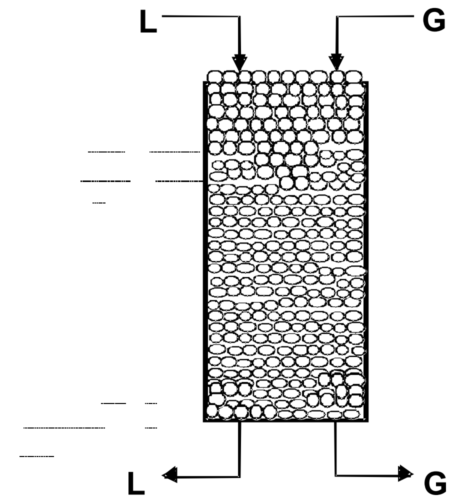


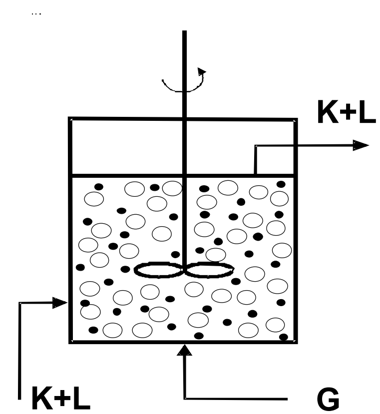
Fixed Bed Reactors





Three Phase Reactors





Typical Problems

A) Equilibrium "problems"

$$A + B \rightleftharpoons C + D$$

Complete conversion of A requied
Removal of C or D favourale

B) Selectivity "problems"

$$A + B \rightleftharpoons C$$

Main product C, By product D

$$A + C \rightleftharpoons D$$

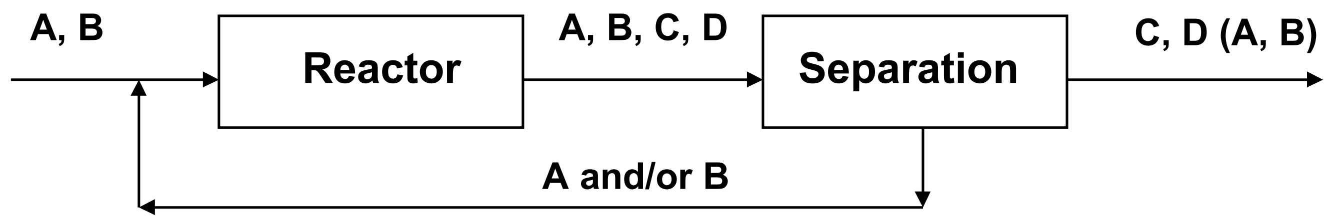
Solutions

- **Search for another chemistry (other reactants or reaction conditions)**
- **Optimimized process**
- **Improved process parameter (Temperature control)**
- **Combination of reaction and separation**

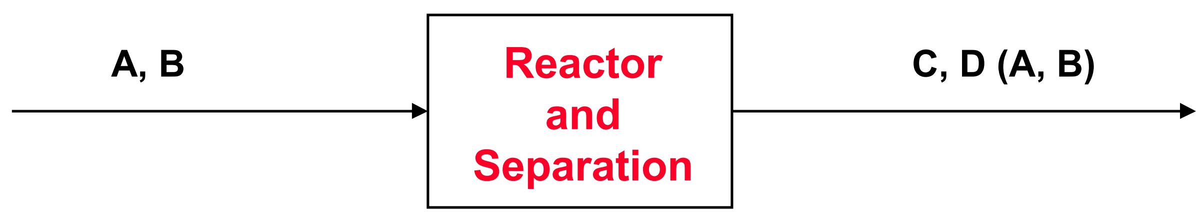
Thermodynamically controlled reactions

$$A + B \rightleftharpoons C + D$$

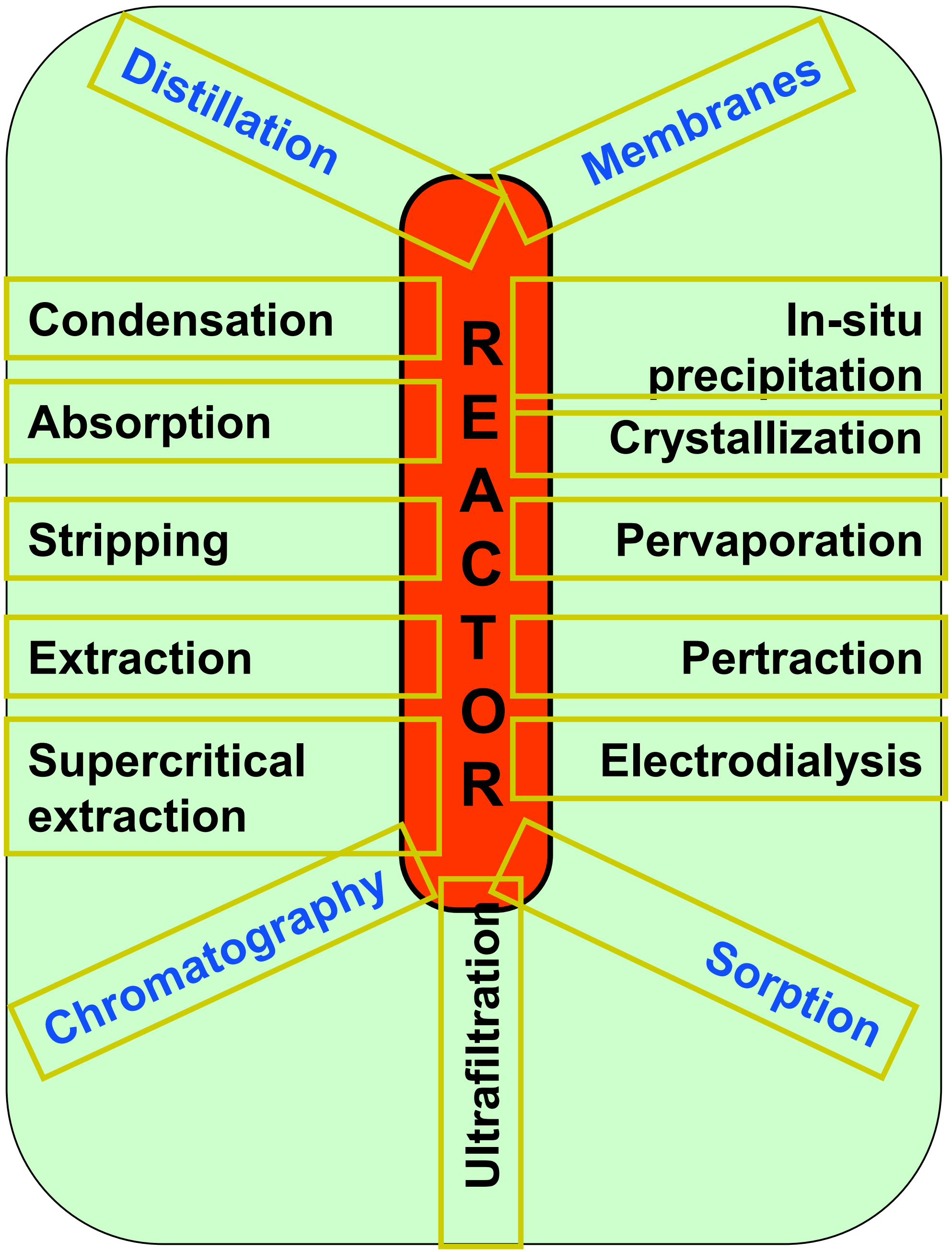
Conventional Process



Integrated Process



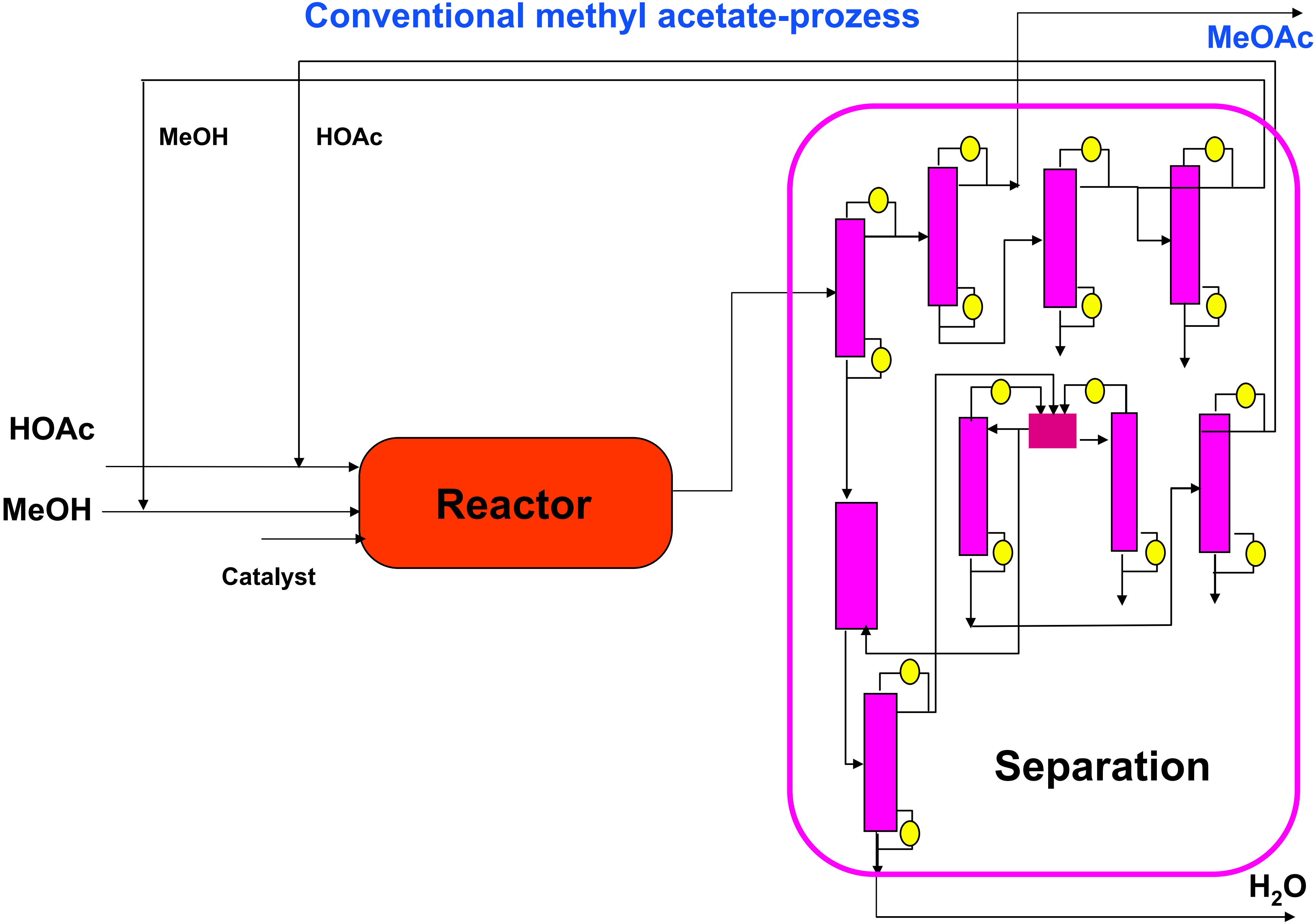
Posssible combinations of reaction and separation processes



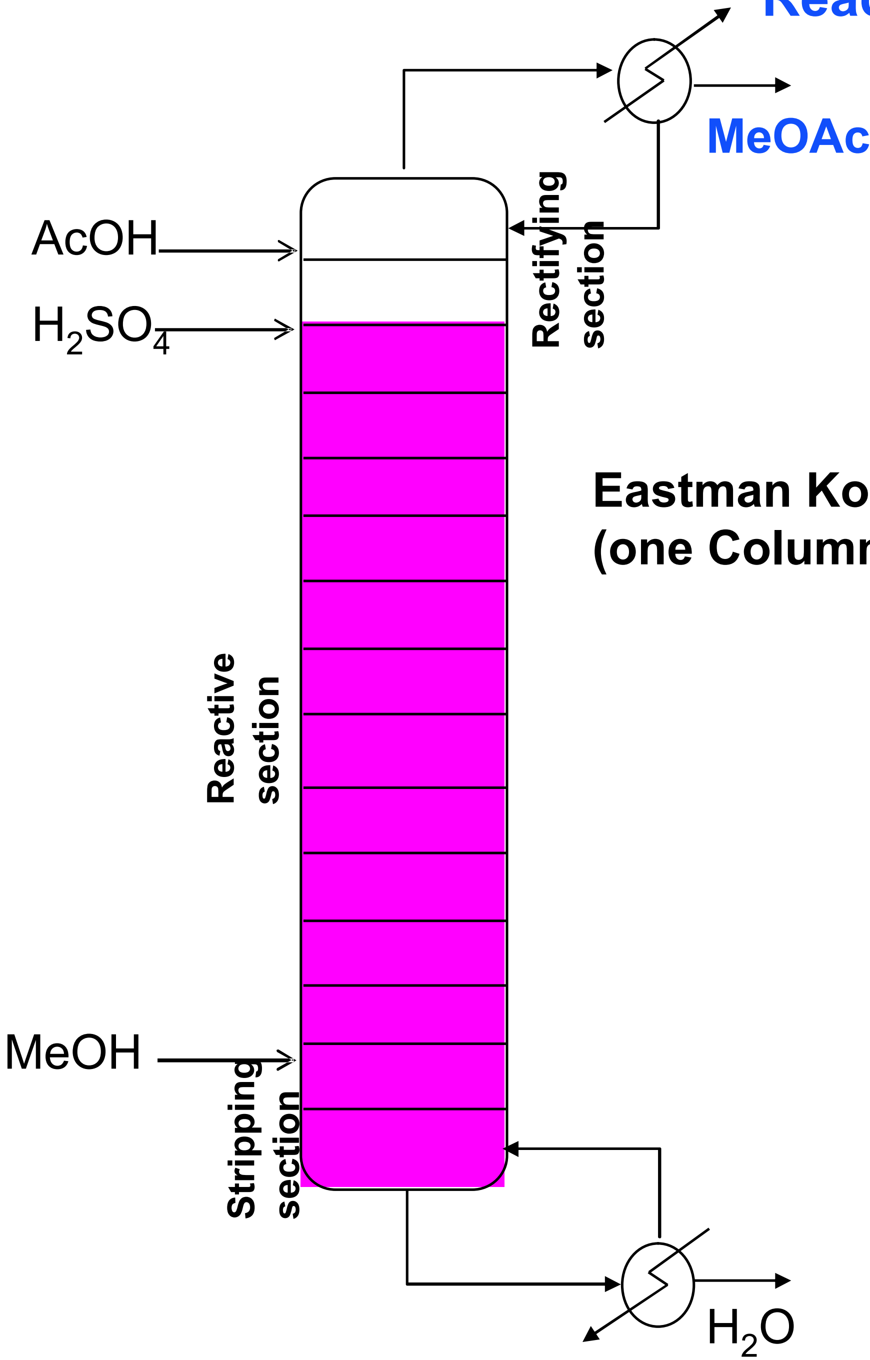
Literature

- Krishna, R. *'Reactive Separations: more ways to skin a cat'* Chem. Engng. Sci. (2002)
- Agar, D. W., W. Ruppel *'Multifunctionale Reaktoren für die heterogene Katalyse'* Chem.-Ing.-Tech. 60(10): 731-741 (1988)
- Westerterp, K.R. *'Multifunctional reactors'* Chem. Engng. Sci. 47(9-10):2195-2206 (1992)
- Krishna, R. *'A systems approach to multiphase reactor selection'* Adv. Chem. Engng 19:201-249 (1994)
- Lerou, J.J., K.M. Ng *'Chemical Reaction Engineering: A multiscale approach to a multiobjective task'* Chem. Engng. Sci. 51(10): 1595-1614 (1996)
- Hoffmann, U., K. Sundmacher *'Multifunktional Reaktoren'* Chem.-Ing.-Tech. 69(5):613-622 (1997)
- Agar, D.W. *'Multifunctional Reactors - old preconceptions and new dimensions'* Chem. Engng. Sci. 54(10):1299-1305 (1999)

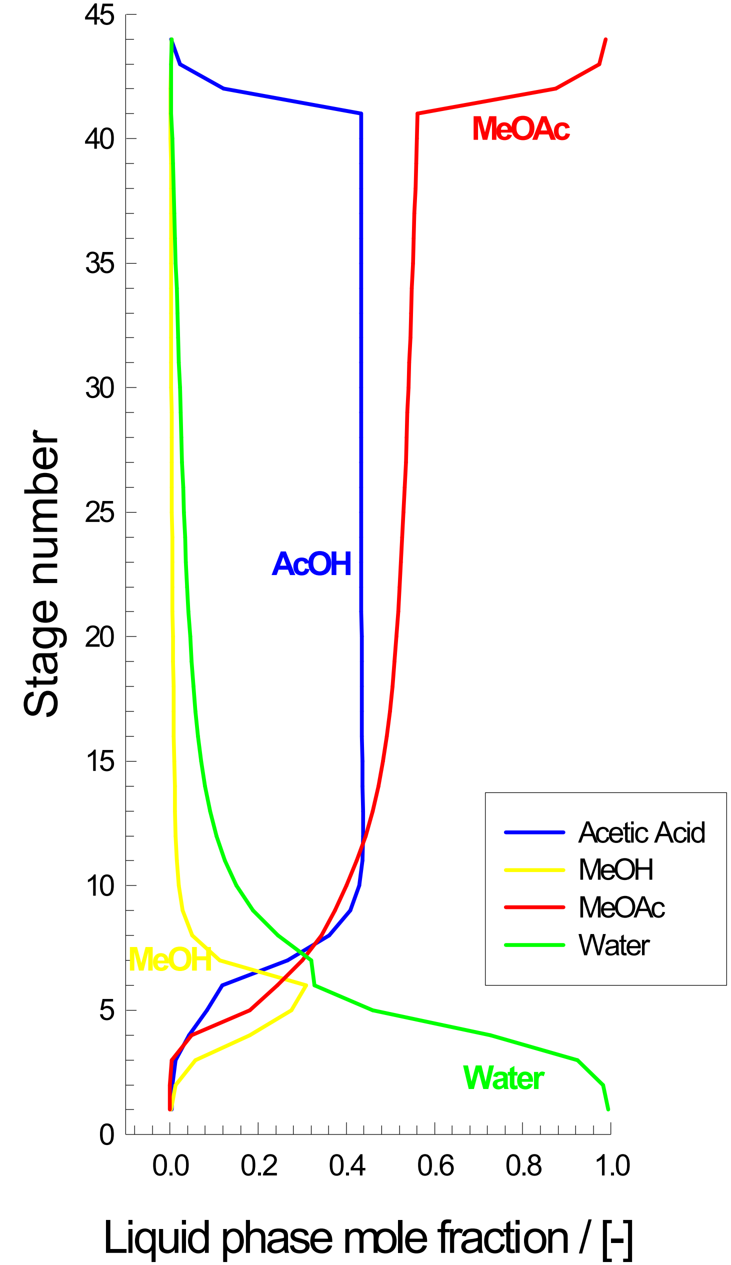
Conventional methyl acetate-prozess



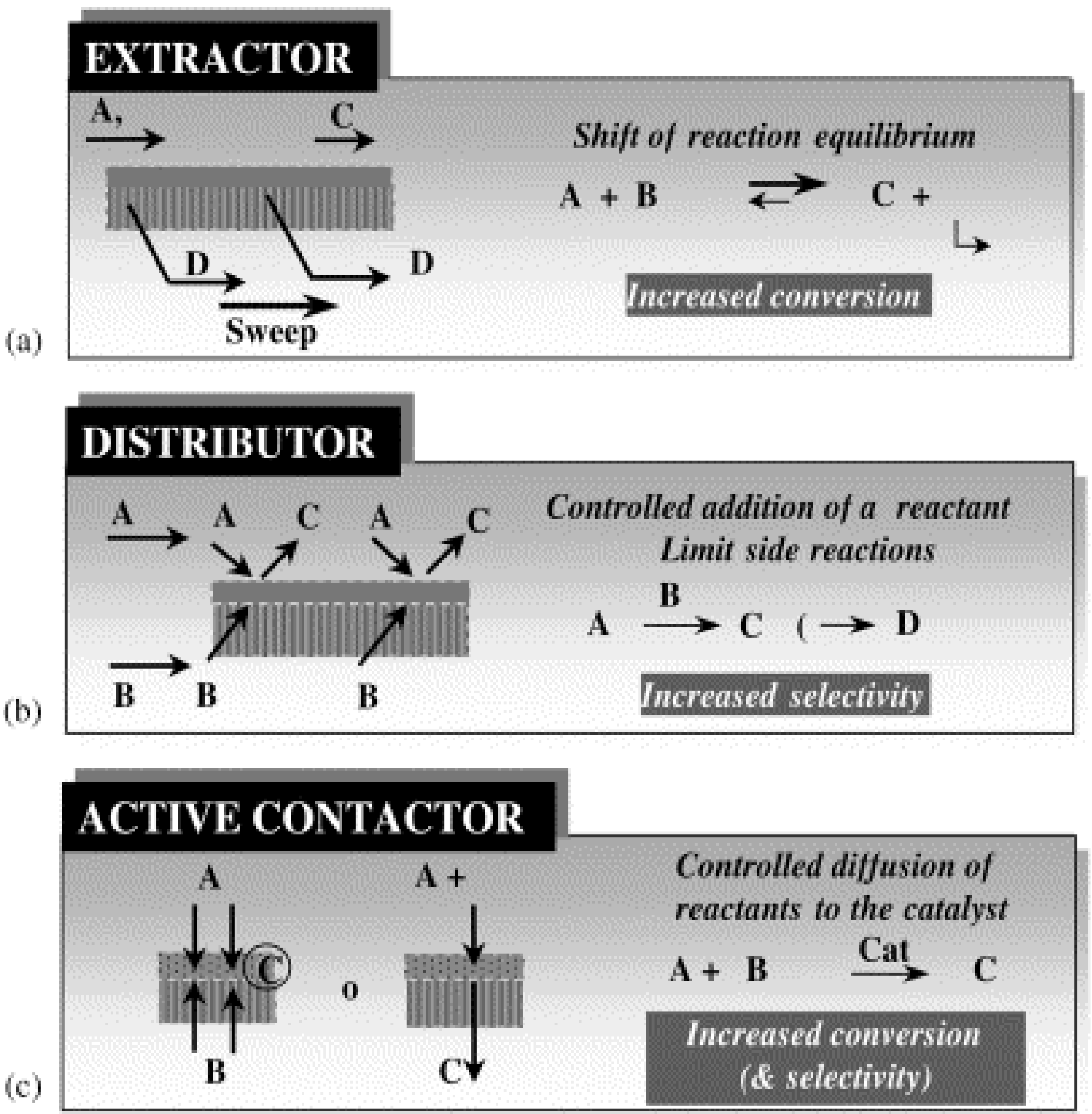
Reactive destillation



Eastman Kodak Process (one Column !)



Concepts for membrane reactors



<u>IUPAC</u>

A membrane reactor is an apparatus that integrates chemical reaction (catalysis) And separation

Concepts for membrane reactors

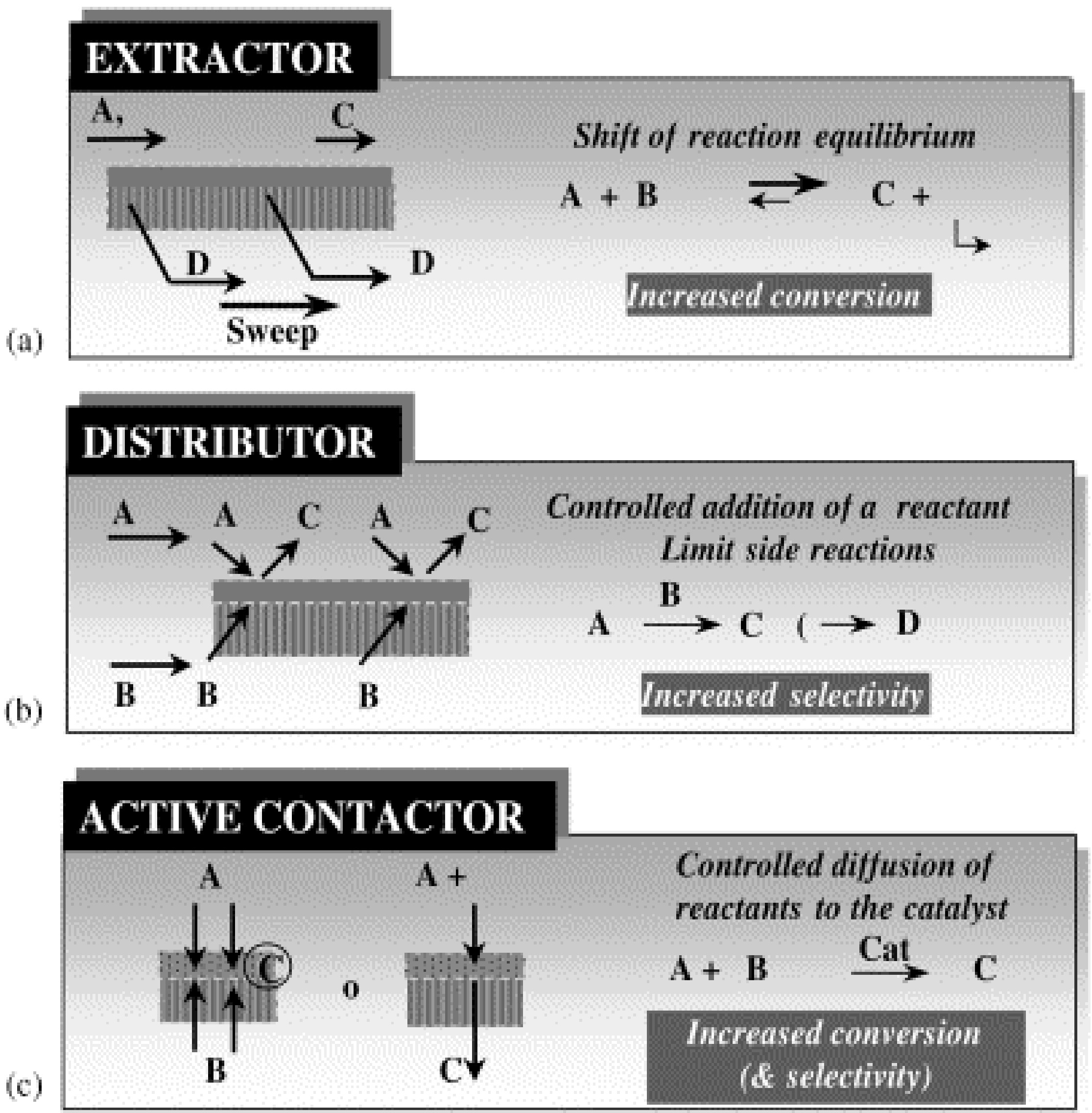
Advantages:

- Reduced investment because of different unit operations in one apparatus
- Increased conversion for equillibrium reactions
- Improved selectivities for partial oxidations and hydrogenations
- Avoid/Reduce high volume circuits of solvents and feeds

Disadvantages:

- Reactions and separations at the same conditions (p,T)
- Availability of required materials for construction of membrane reactors
- Extended process development for integrated chem. processes

Concepts for membrane reactors



<u>Membrane properties</u>

- Permselectivity for product D

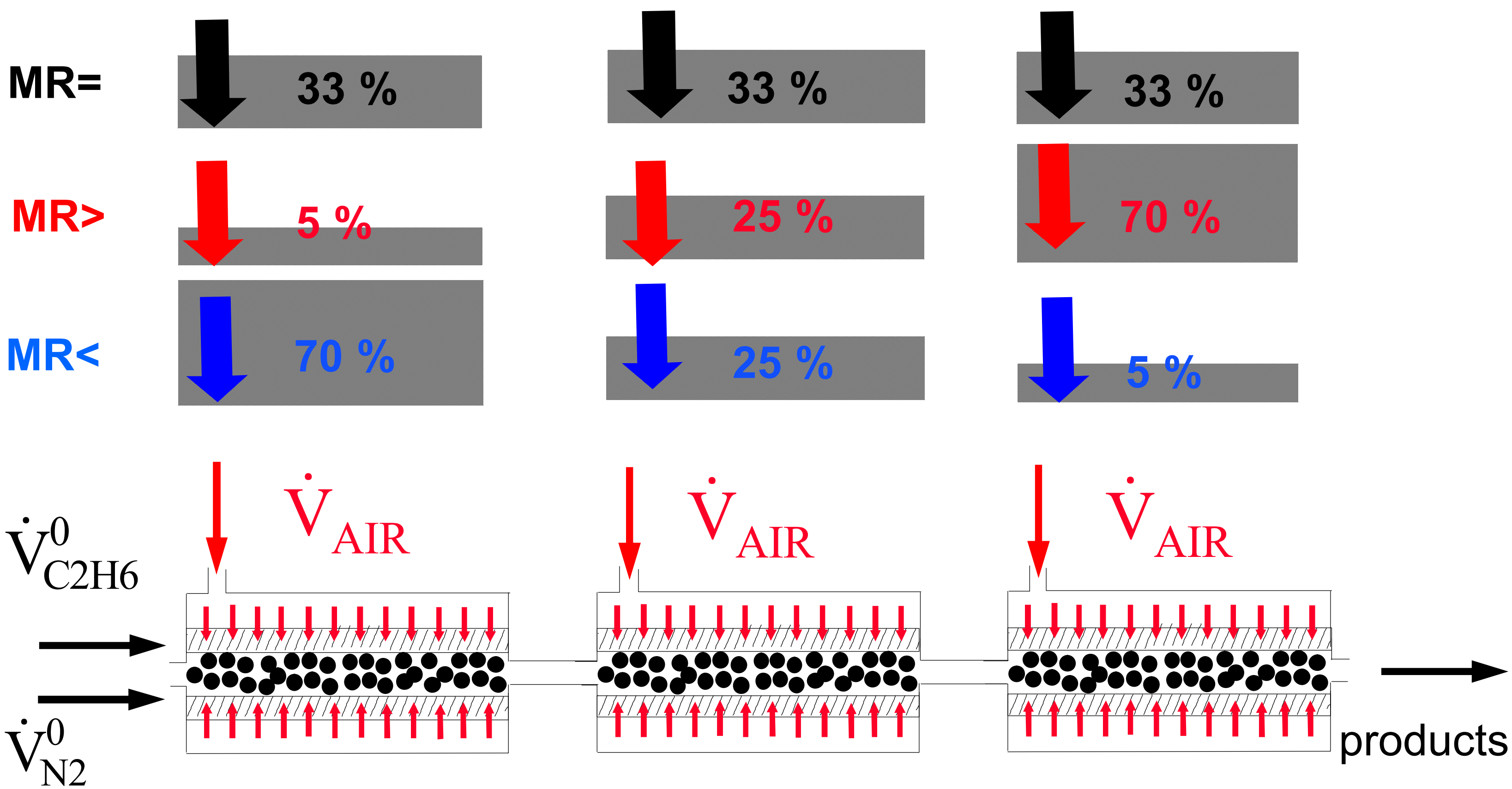
- Permeability für reactant A

- Permeability for reactant
  und catalytic activity

- chemical und thermal
  stability

Example 1: Controlled Feed

$$\left(\dot{V}_{AIR}^{total} = const\right)$$



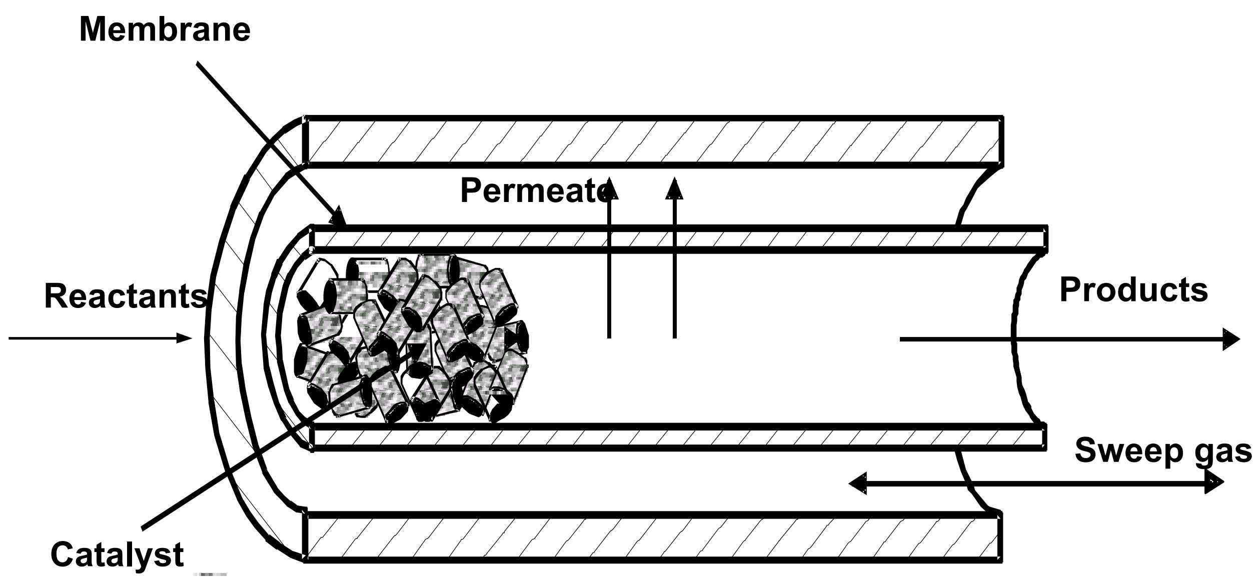
Seidel-Morgenstern, MPI Magdeburg

Example 2: Selektive Product removal

C_6H_{12} ®¬ $C_6H_6 + 3\ H_2$ $\Delta\ H_R = 205$ kJ/mol

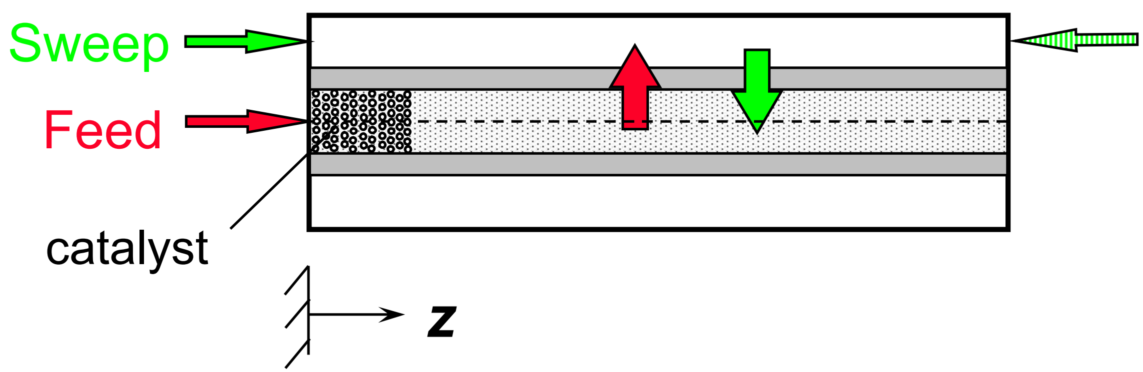
Catalyst: 1% Pt on $\gamma - Al_2O_3$

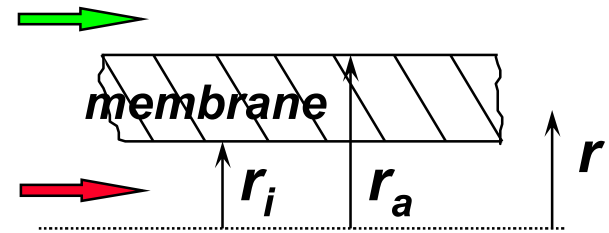
Membrane: Vycor-Glas (Na_2O-B_2O_3-SiO_2)
L = 25 cm, D = 0,46 cm



Seidel-Morgenstern, MPI Magdeburg

Assumptions - isothermal conditions
- one dimensional model satisfactory





Mass balance for Feed- side:

$$0 = -\frac{p_f}{RT}\frac{1}{q_f}\frac{\partial\left(\dot{V}_f\, x_{f,i}\right)}{\partial z} + D_{ax}\frac{p_f}{RT}\frac{\partial^2 x_{f,i}}{\partial z^2} - \frac{2\pi\, r_i}{q_f}\, J_i\Big|_{r=r_i} + R_i$$

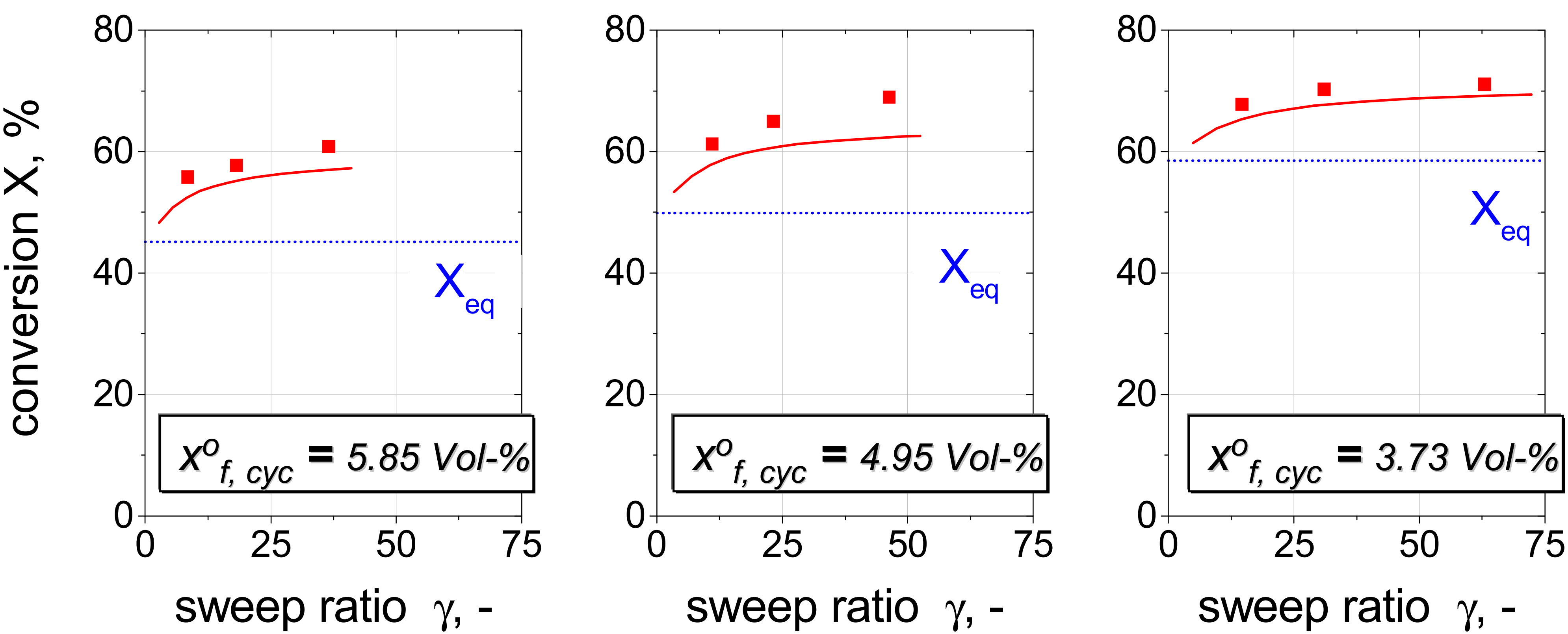
Mass balance **for membrane:**

$$0 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\, J_i\right)$$

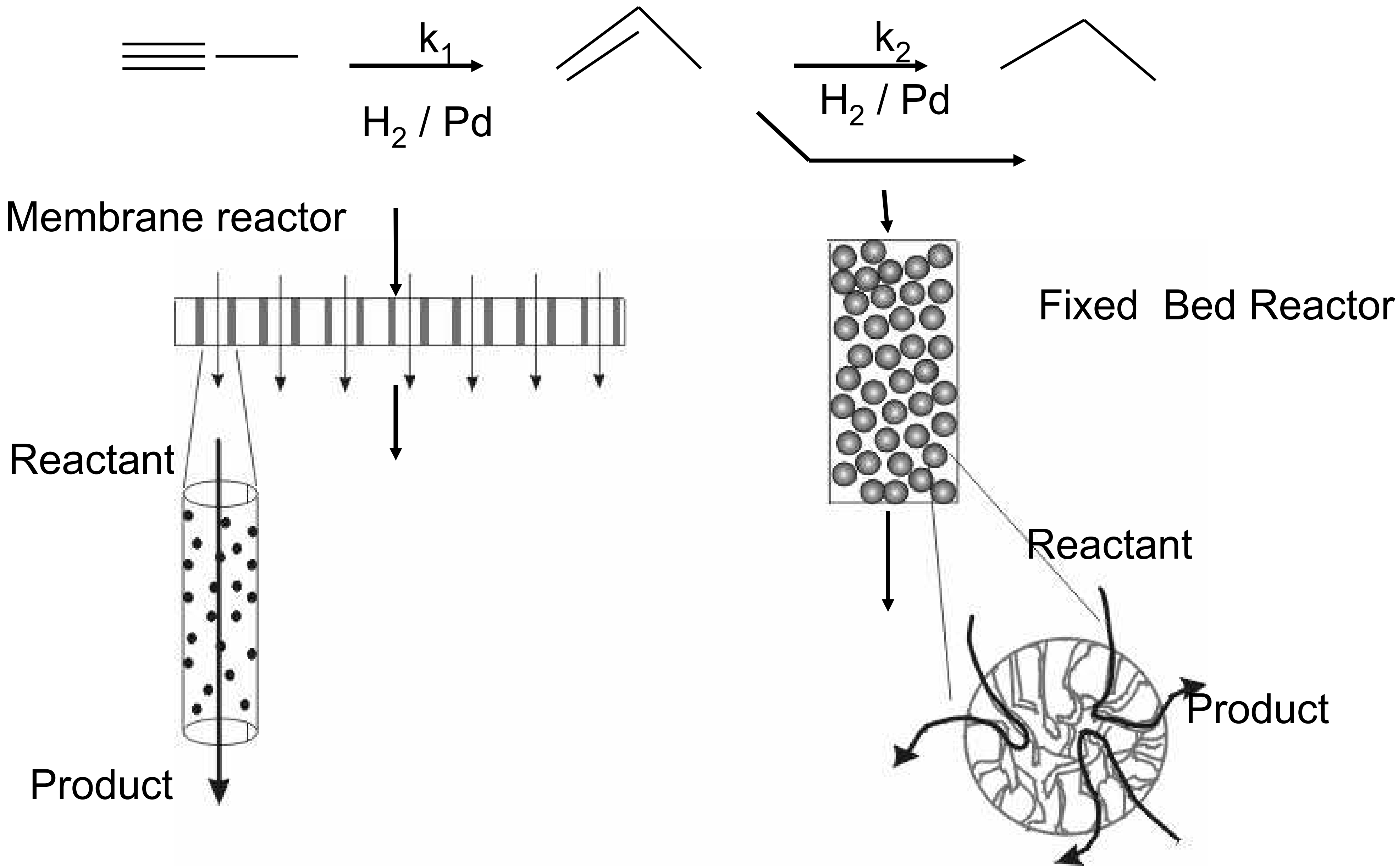
Mass balance für Sweep-side:

$$0 = \pm\frac{p_s}{RT}\frac{1}{q_s}\frac{\partial\left(\dot{V}_s\, x_{s,i}\right)}{\partial z} + D_{ax}\frac{p_s}{RT}\frac{\partial^2 x_{s,i}}{\partial z^2} + \frac{2\pi\, r_a}{q_s}\, J_i\Big|_{r=r_a}$$

pressure conditions	$p_f = p_s$	= 1 bar
temperature	T	= 473 K
mole fraction (feed side)	$x^0_{f,cyc}$	= 3.73 ... 5.85 Vol-%
mole fraction (sweep side)	$x^0_{s,cyc}$	= 0.0 Vol-%
flow rate (feed side)		V^o_f = 25 ml/min
sweep ratio	γ	$= V^o_s / (x^0_{f,cyc} V^o_f)$

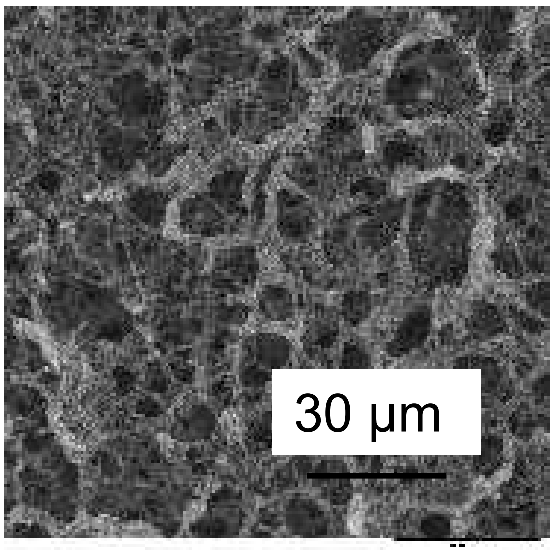


Example 3: Catalysis in porous membranes



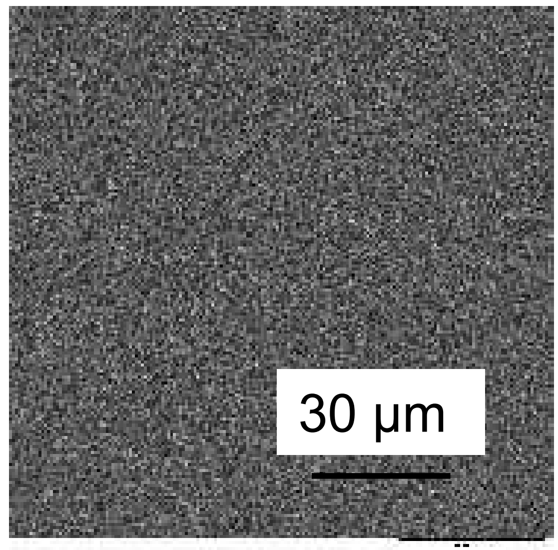
Example 3: Characterisation of membranes

Φ = 2 wt.% Polymer



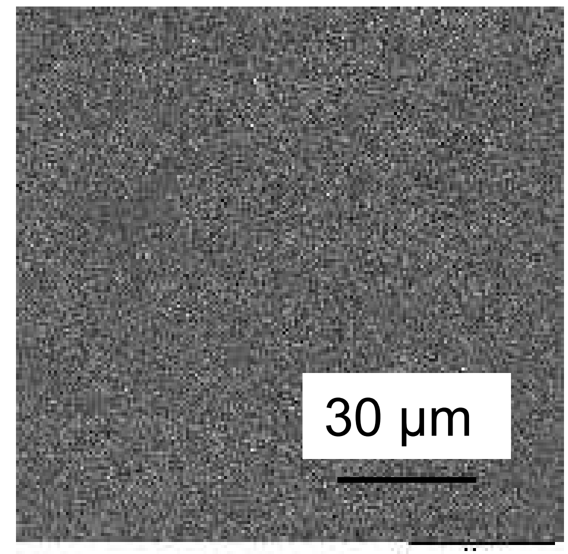
S = 52 m^2/g
r_P= 1800 nm

Φ = 10 wt.% Polymer



S = 17 m^2/g
r_P= 380 nm

Φ = 20 wt.% Polymer

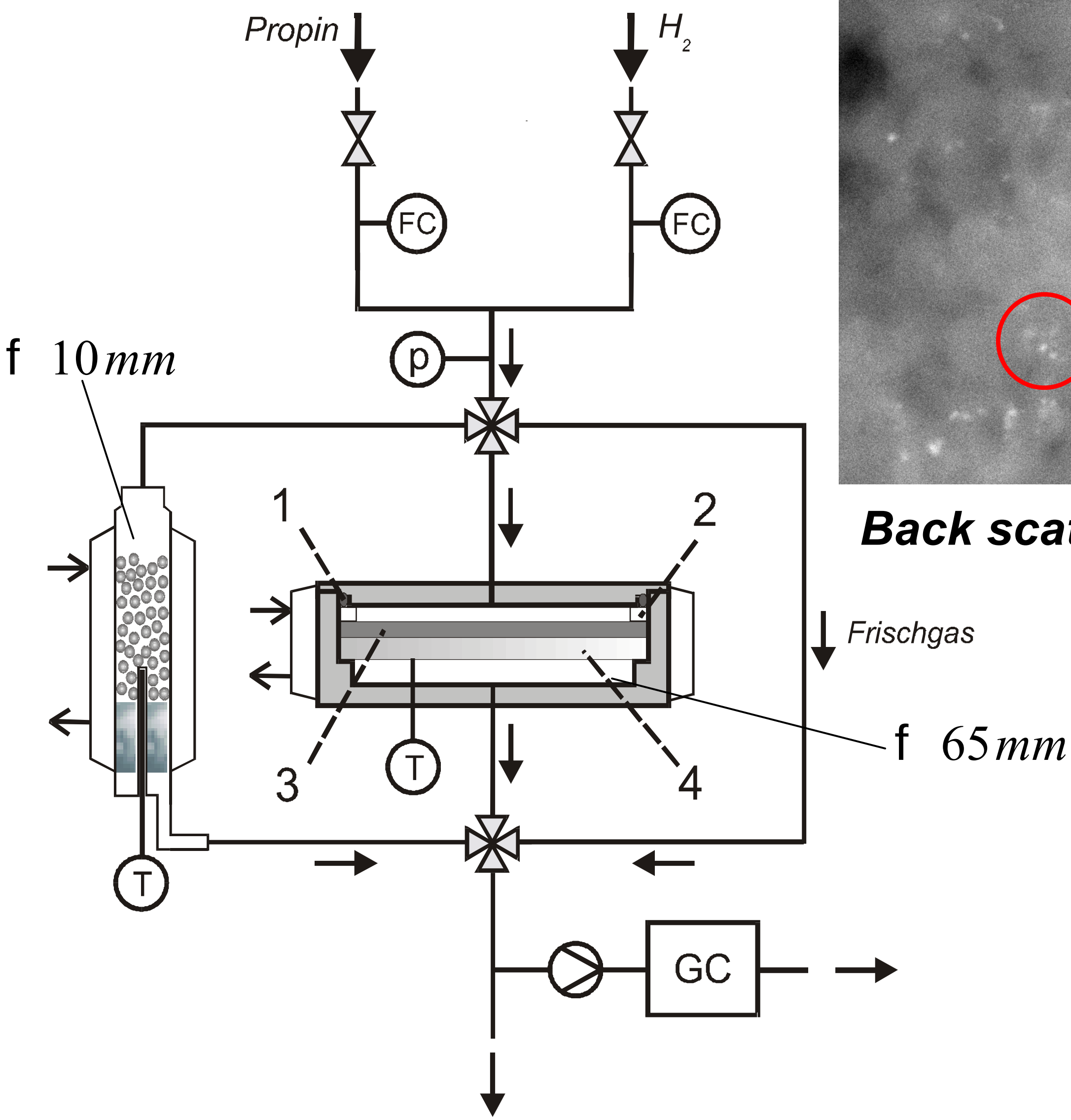


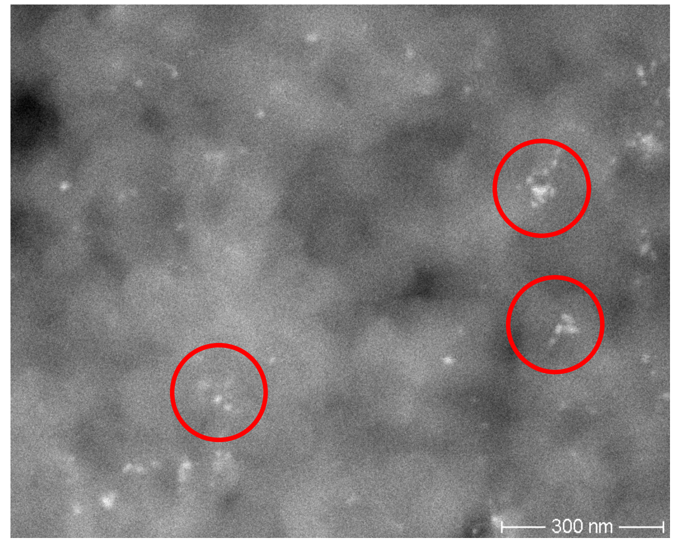
S = 12 m^2/g
r_P= 250 nm

Charakterisation of structure by:

- BET-measurements, Hg-Porosimetry
- Gas permeation experiments

Example 3: Experimental Set-Up (gas phase)





Back scattering mode

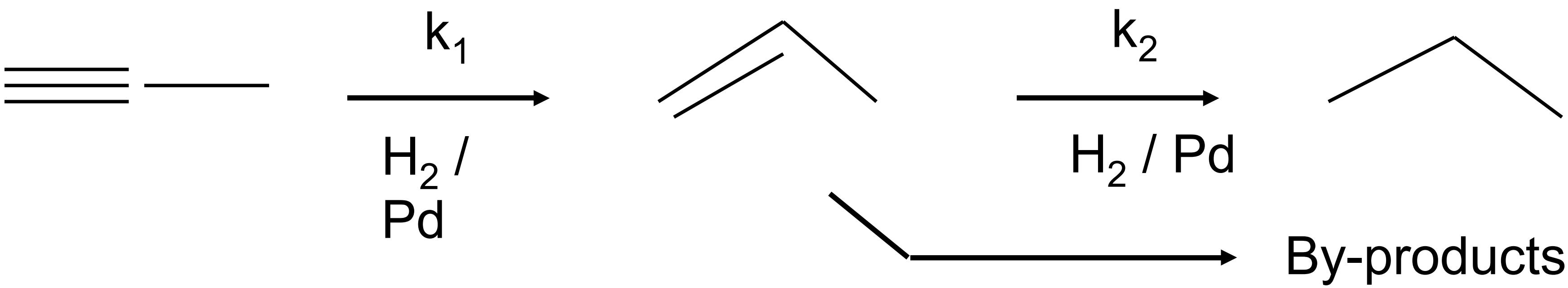
5 ml 10 % PAA.-Disp. (450 mg PAA)

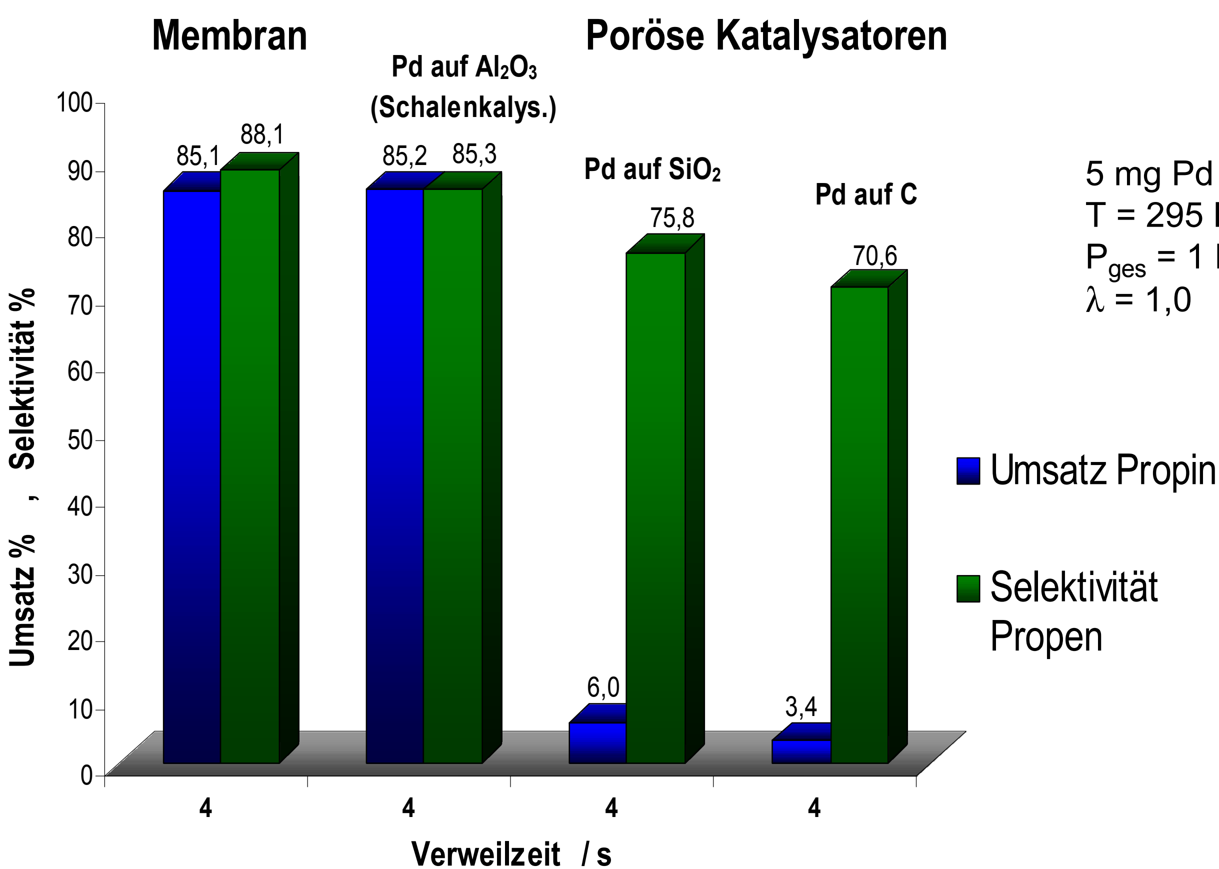
20 mg Pd

100 mg SE3010

0,5 ml $NaBH_4$

Example 3: Comparison of Catalysts



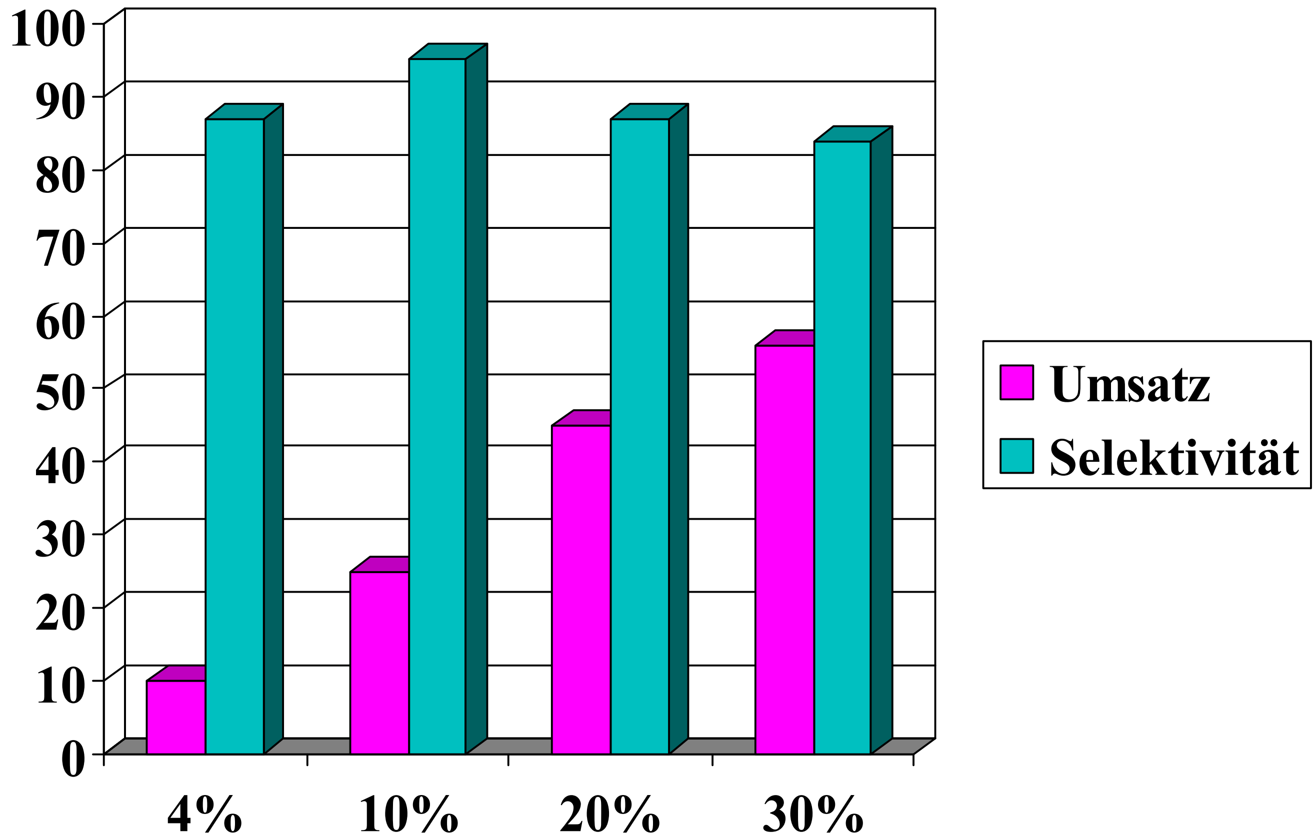


5 mg Pd
T = 295 K
P_{ges} = 1 bar
λ = 1,0

$$Umsatz = \left[1 - \frac{C_1}{C_{1,0}}\right] \times 100$$

$$Selektivität = \left[\frac{C_2}{C_{1,0} - C_1}\right] \times 100$$

Example 3: Variation of membrane structure



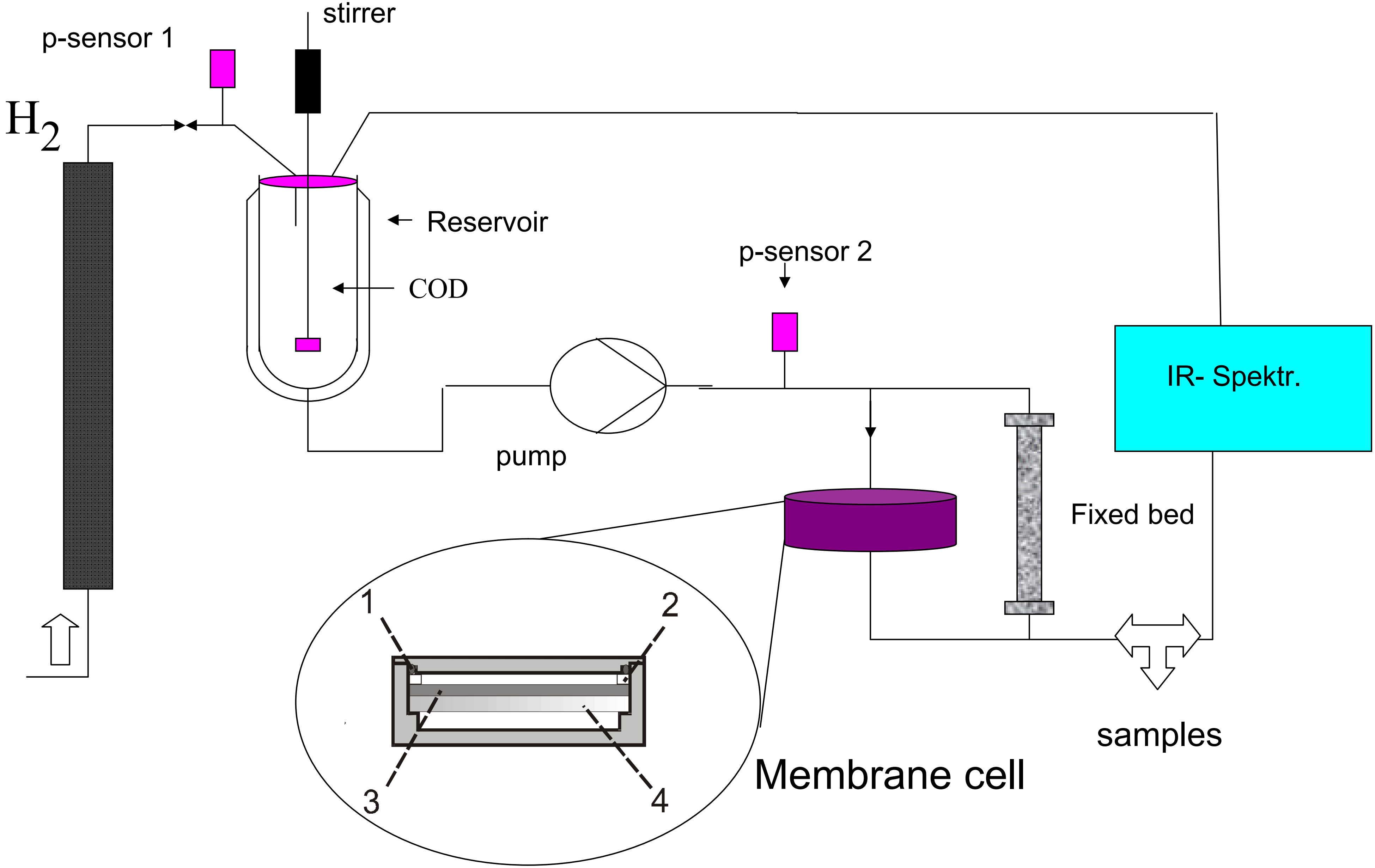
PAA in cross-linked dispersion

ε /%	94	85	70	55
r_p /mm	1,5	0,4	0,25	0,18

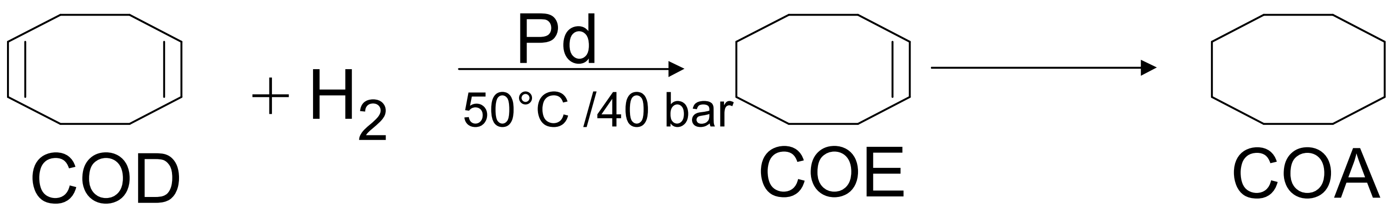
T = 25 °C
H_2/Propin = 1/1
40 ml/min

2 mg Pd
$NaBH_4$
SE3010

Membrane test cell (liquid phase)



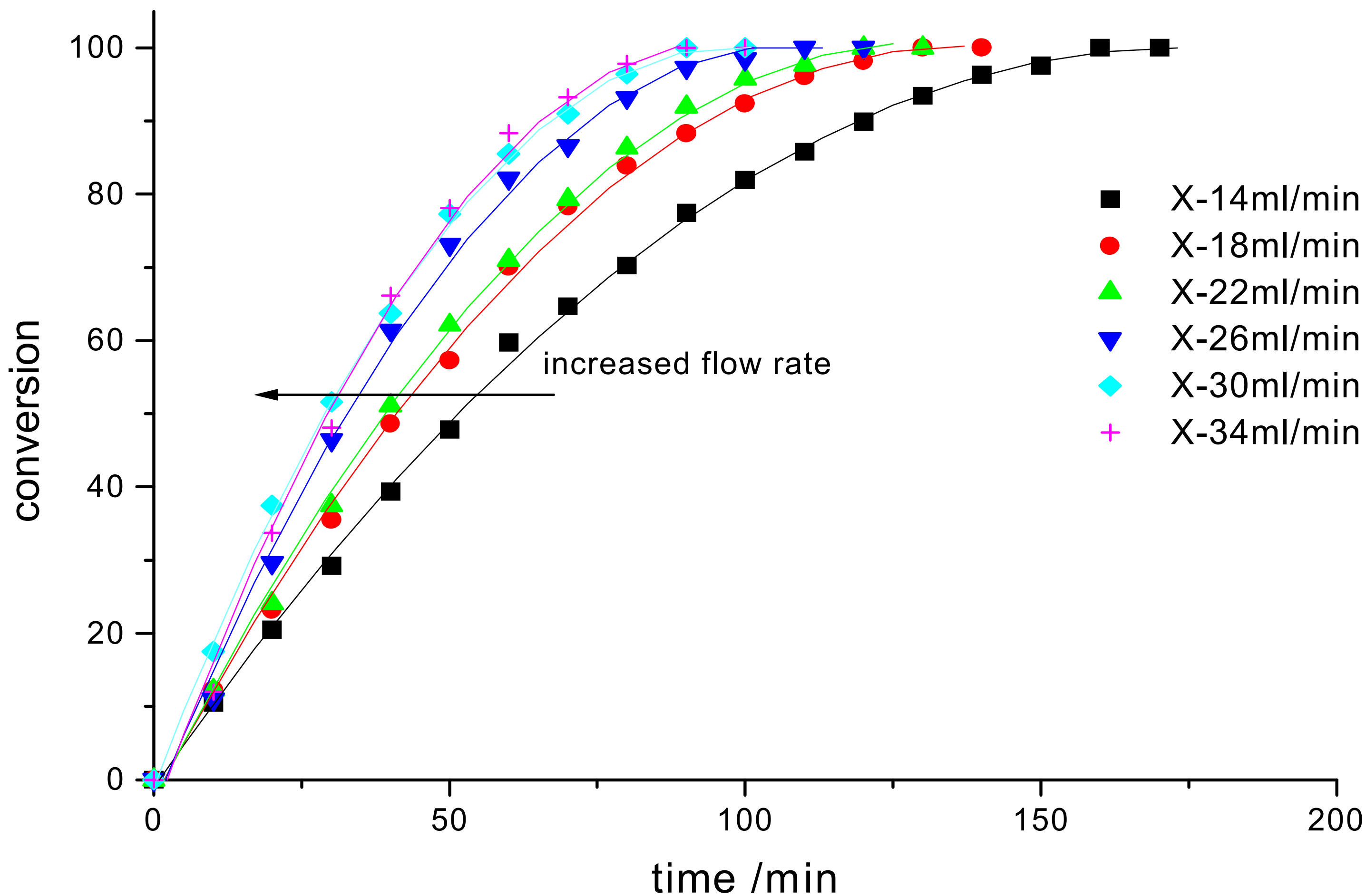
Selectivity of partial hydrogenation



PAA-Pd membrane, ε = 50%, r_P= 250 nm
T= 50 °C, p = 40 bar

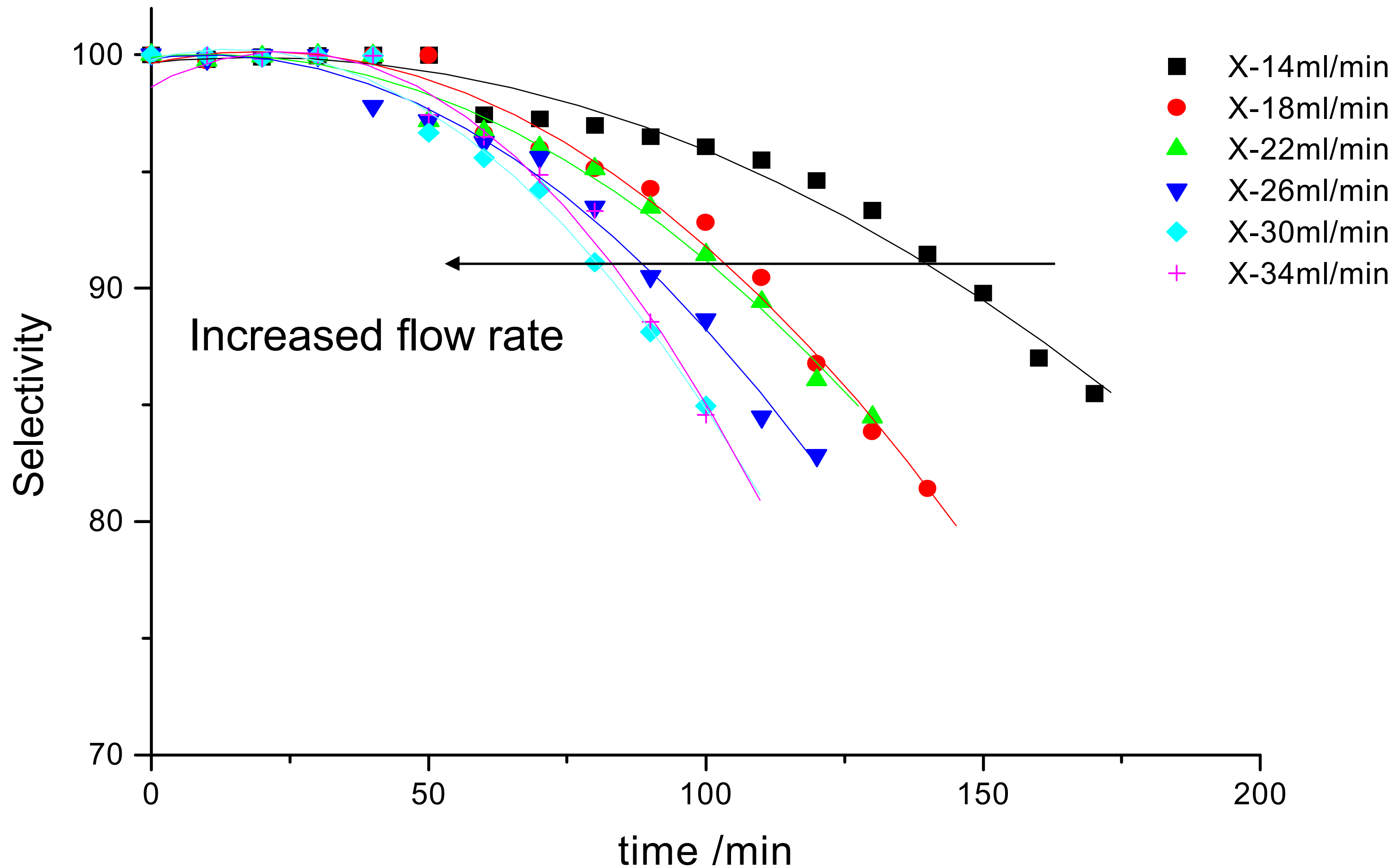
Conversion vs. time at different flow rates

Membrane F =20%

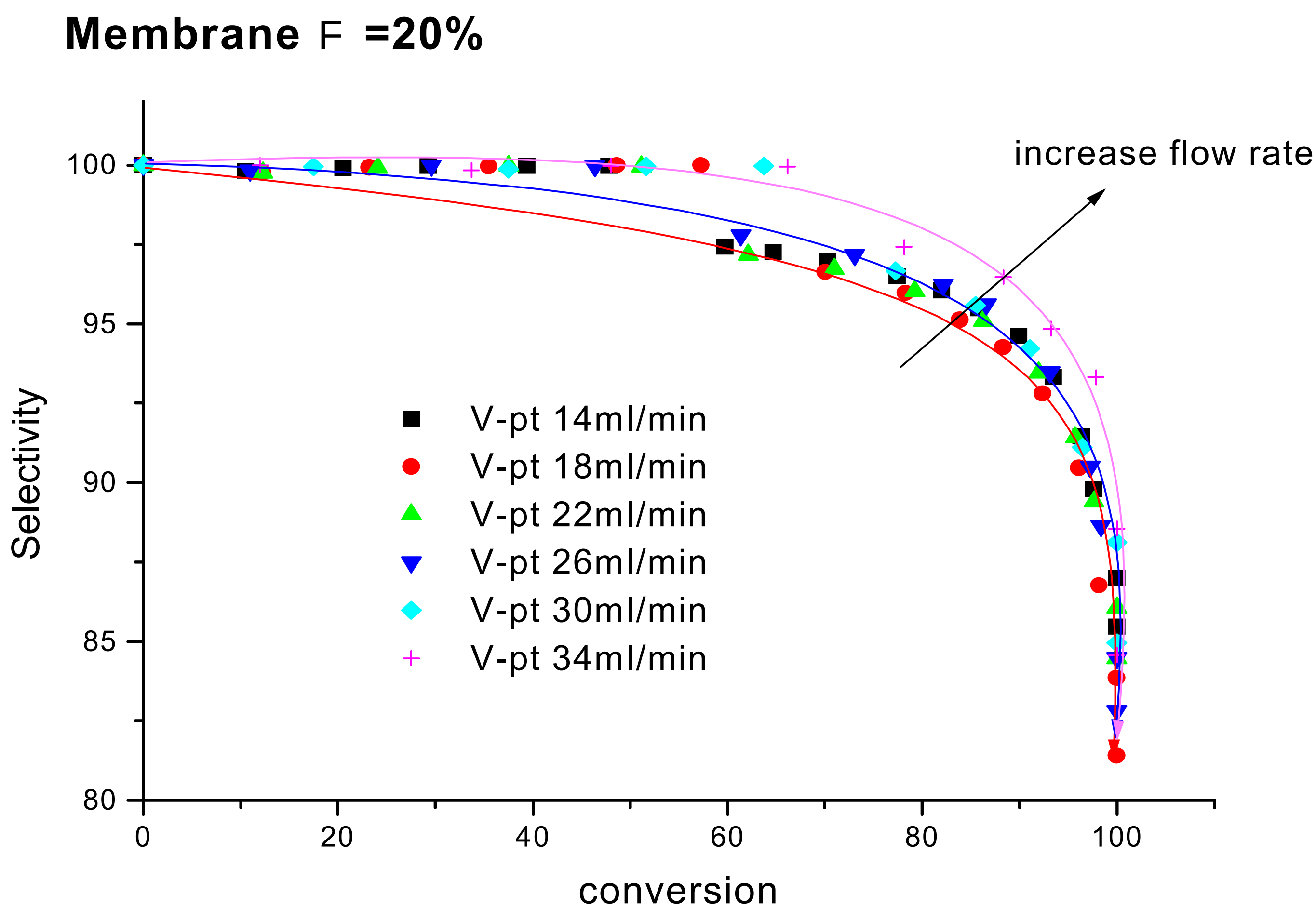


Selectivity vs. time at different flow rates

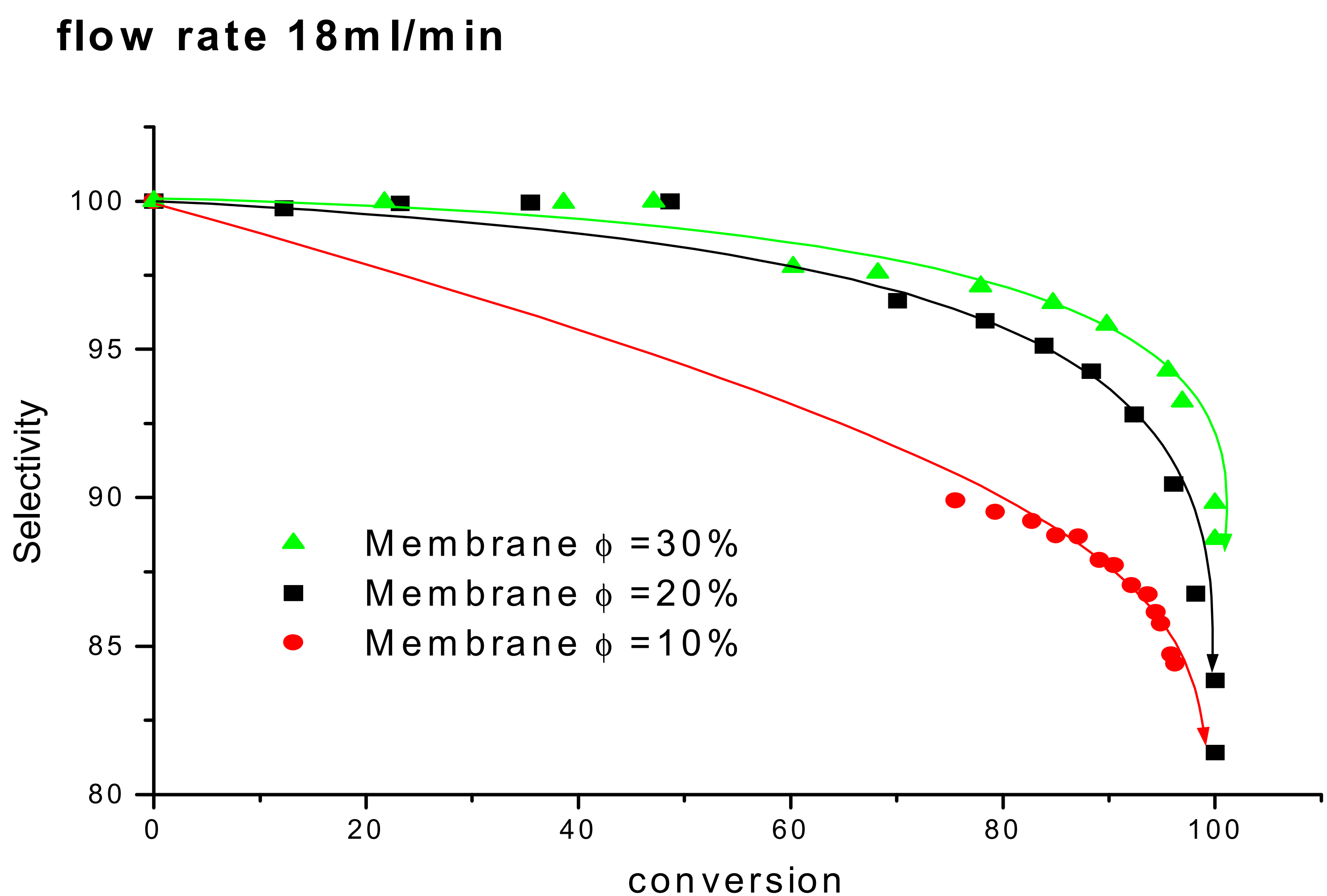
Membrane F **= 20%**



Selectivity vs. conversion at different flow rates

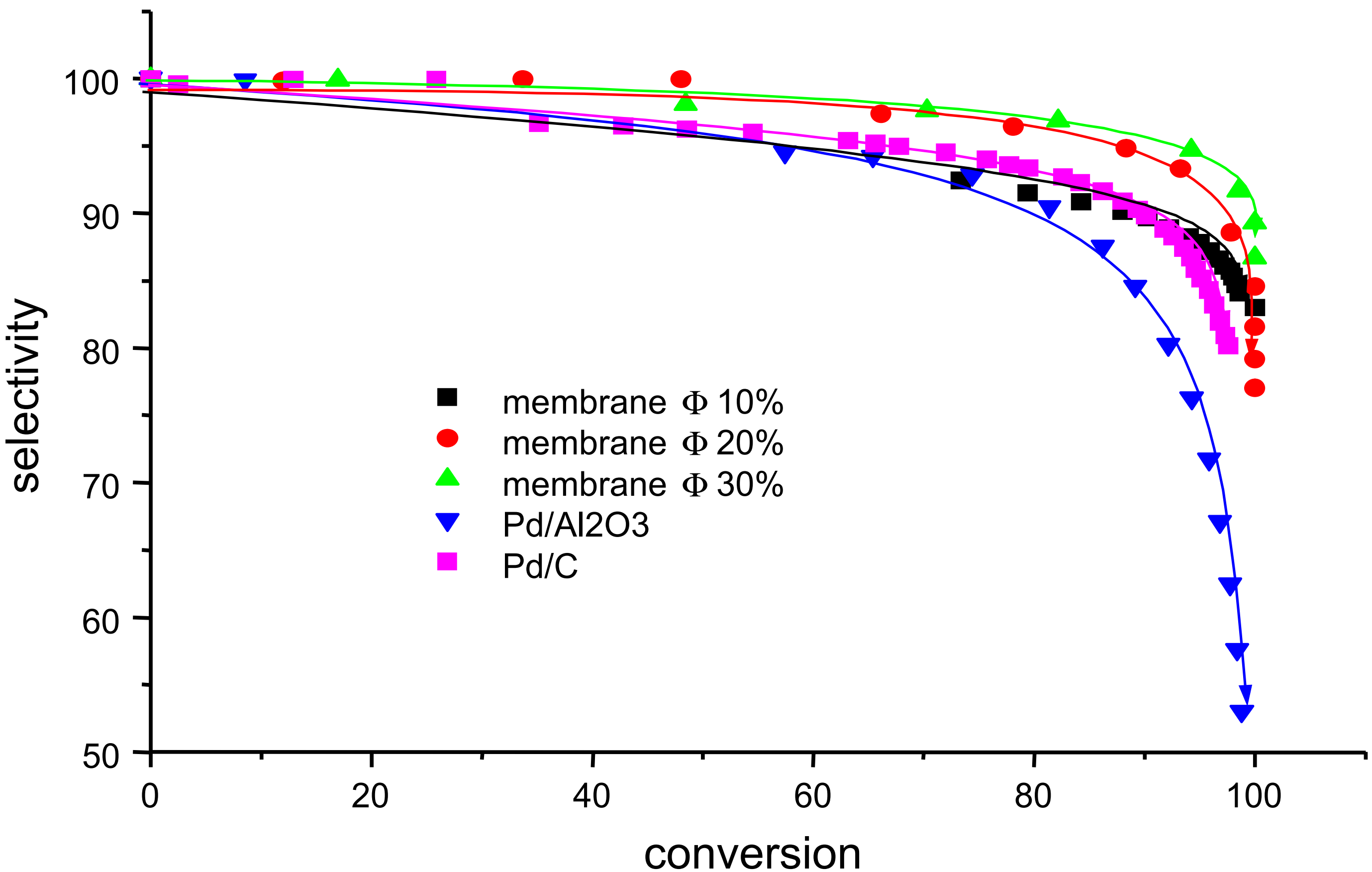


Selectivity vs. conversion for membranes at different pore size



Selectivity of different catalyts

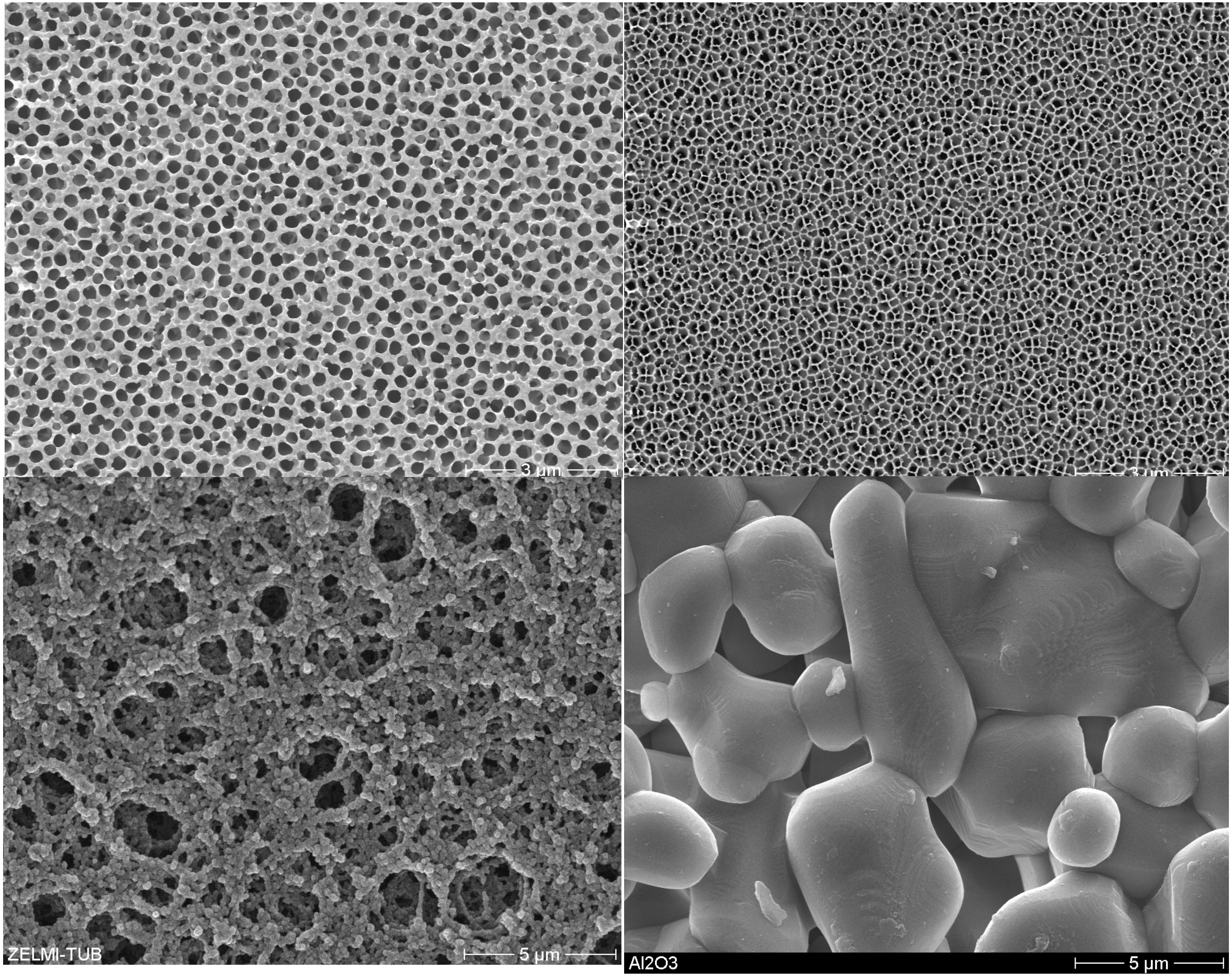
flow rate: 34ml/min



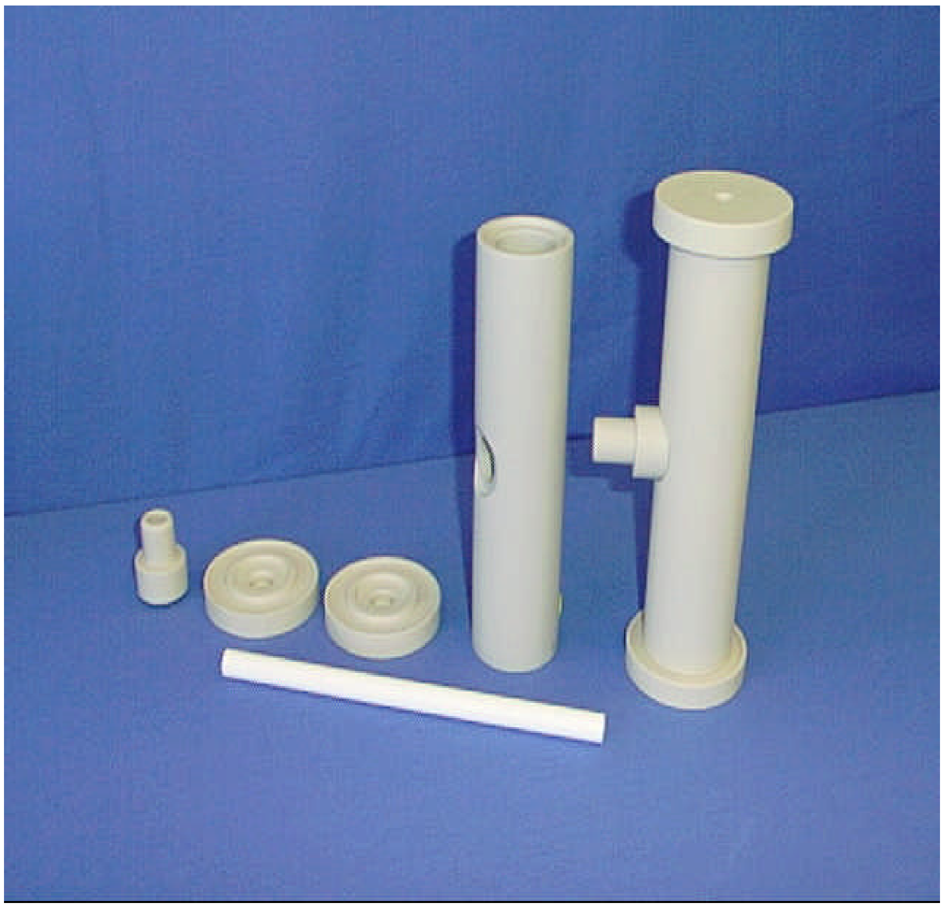
PAA-Pd membrane, ε = var. r_P= f(ε)

T= 50 °C, p = 40 bar

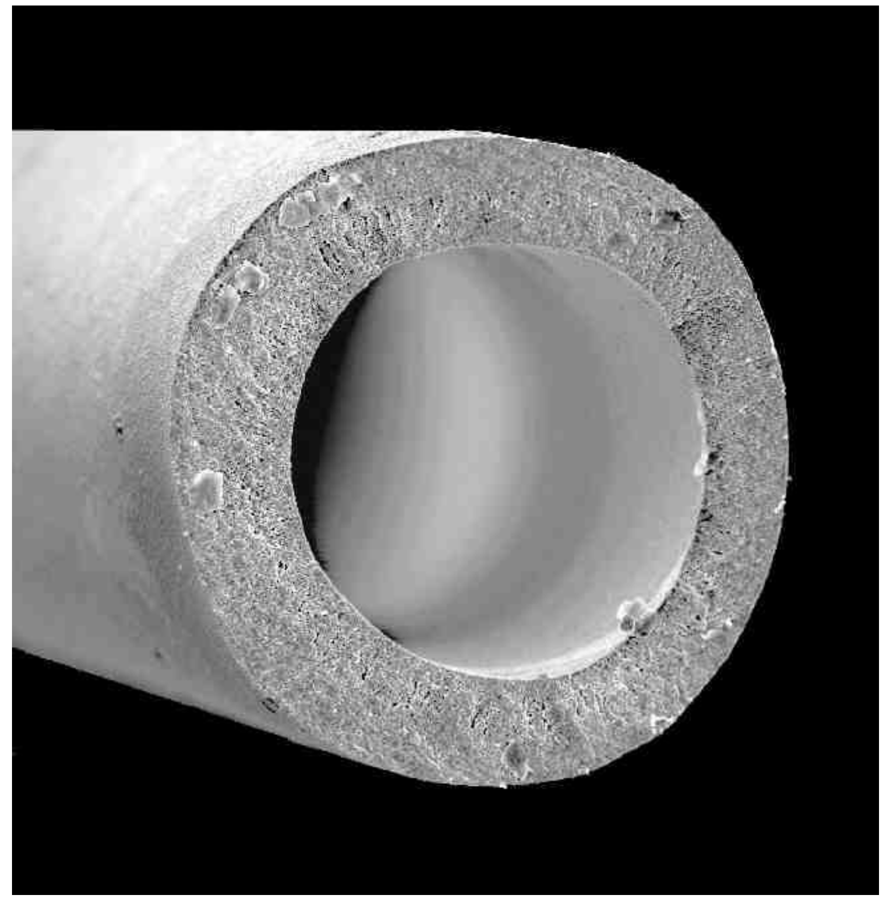
Ceramic membranes for membrane reactors



Construction of ceramic modules



Full ceramics test module (HITK)



Al_2O_3-hollow f bre 0,6 mm diam. (HITK)

Problems to be solved

Materials

- Membranes with adjustable properties
- Inpregnation with different active componentes
- Fitting of different materials
- Production of composite membranes
- Concept for a cooled membrane reactor

Methods

- Charakterisation of catalytically active membranes
-Two and three dimensional models for mass and heat balance

Approaches to solve the problems

Developement of materials and modules in interdisziplinary teams from chemistry, chemical engineering, process technology and material science.

Developement of models for scale up and process control of membrane reactors.