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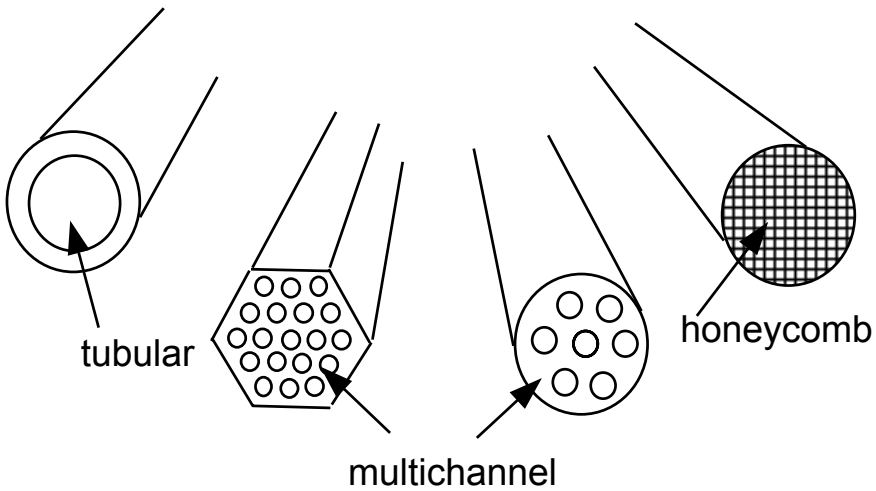
Membranes: On the interplay of Diffusion and Permeation and the Technical Consequences

1. Zeolite membranes – state of the development
2. Mass transport through zeolite membranes
3. Dehydrogenation of propane in a membrane reactor with MFI membrane
4. Separation of xylene isomers by zeolite MFI membrane
5. Semi-technical application of zeolite LTA membranes in water/alcohol pervaporation pilote plants
6. Outlook

1. Zeolite membranes – state of the development



Commercially available:

Nanofiltration membranes (< 2 5 nm) on basis of SiO_2, TiO_2, ZrO_2 (sol-gel) allow the separation of colloids, dust, bacteria… but not molecular gas separation!

There is a technical need for

→ Shape selective separations

→ High-T separations (T> 200°C)

Polymer membranes and sol-gel derived membranes fail, only zeolites can solve it.

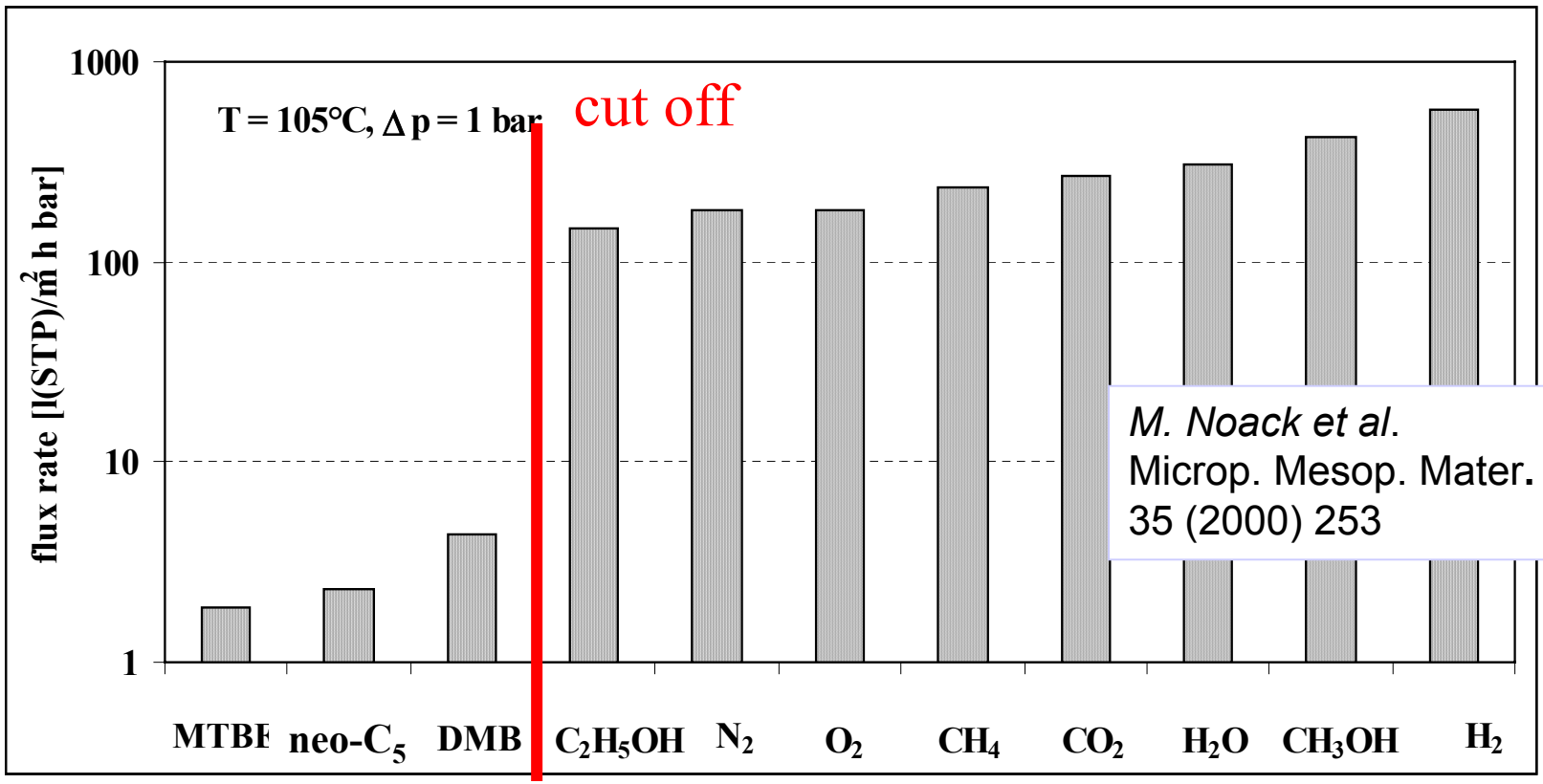
Main strategy of zeolite membrane preparation after 10 years development:

→ Crystallize a thin (some µm) zeolite layer on a mesoporous support (ceramic or metal)

→ Use a two-step crystallization with seed crystals to de-couple the aggregation (at high super-saturation) from crystal-growth (at low super-saturation)

1. Zeolite membranes – state of the development

Single component fluxes through a MFI-membrane (Silikalite I)

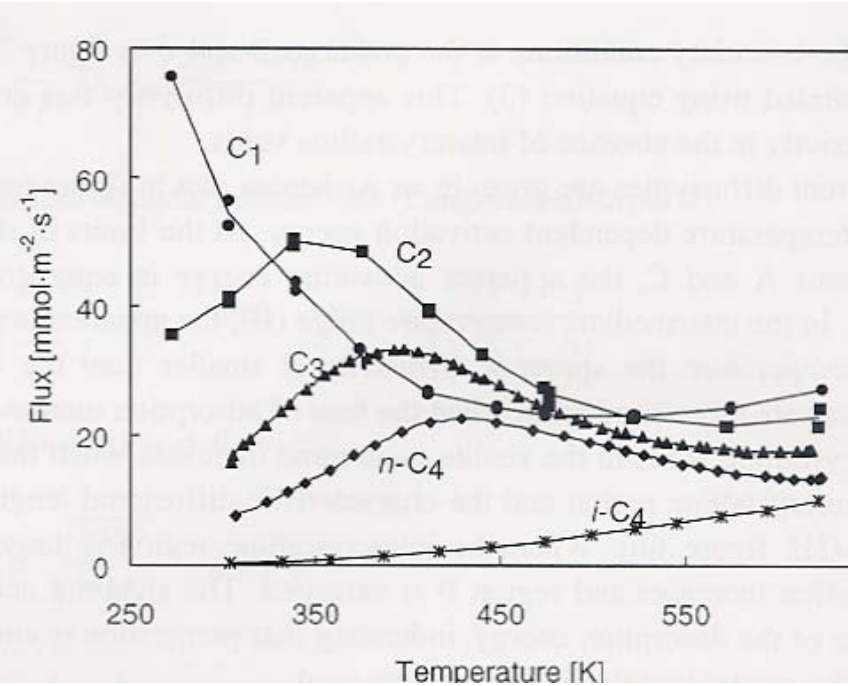


Membrane can discriminate molecules < and > 5,5 Å

The flux of the bulky gases is not zero → defect sites

Membrane allows the study of molecular diffusion

2. Mass transport through zeolite membranes



Flux of methane, ethane, propane and butanes as single components through a MFI (Silicalite-1) membrane as function of temperature.
Measurement by Wicke Kallenbach technique, feed pressure 1 bar

Thesis, J. van de Graaf, Delft, 1999

The maximum of flux as a function of T indicates:
There must be at least two molecular processes of opposite T influence

Adsorption influence, which goes back with increasing T, since the amount Adsorbed decreases with increasing T

Diffusion influence, which increases with T, since diffusion is activated

2. Mass transport through zeolite membranes

Simple Model

$$\frac{\partial \ln p}{\partial \ln c} = \frac{c}{p}\frac{\partial c}{\partial p} = \frac{1}{1-\Theta_{Langmuir}}$$

$$K = K_0 e^{H_{ads}/RT}$$

$$D' = D_0' e^{-E_a/RT}$$

$$c = c_{sat}\frac{Kp}{1+Kp}$$

$$D = D'\frac{\partial \ln p}{\partial \ln c}$$

$$grdc \approx \frac{\Delta c}{d}$$

First Fick's Law

$$J = -D\ grdc$$

Diffusion contribution to J increases with T

Adsorption contribution to J decreases with T

2. Mass transport through zeolite membranes

More sophisticated models

The General Maxwell-Stefan equations describing the multi-component mass transfer in porous media by a balance of the „driving force“ by the friction experienced by that species (Krishna)

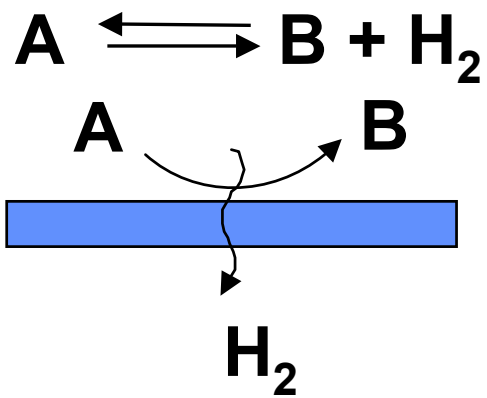
Solid vibration model for strongly adsorbed molecules who loose their gaseous entity: molecules vibrate together with the host lattice before an activated jump (Wei)

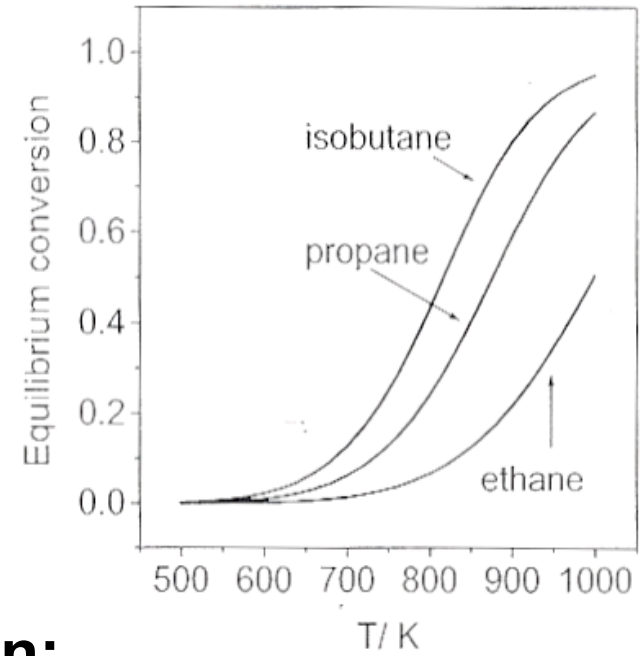
Gas translation model for weakly adsorbed molecules who retain their gaseous characteristics: jump from site to site is restricted by an energy barrier imposed by the potential field (Wei)

3. Dehydrogenation of i-butane in a membrane reactor with MFI membrane

The problem:

De-hydrogenations are equilibrium-controlled reactions

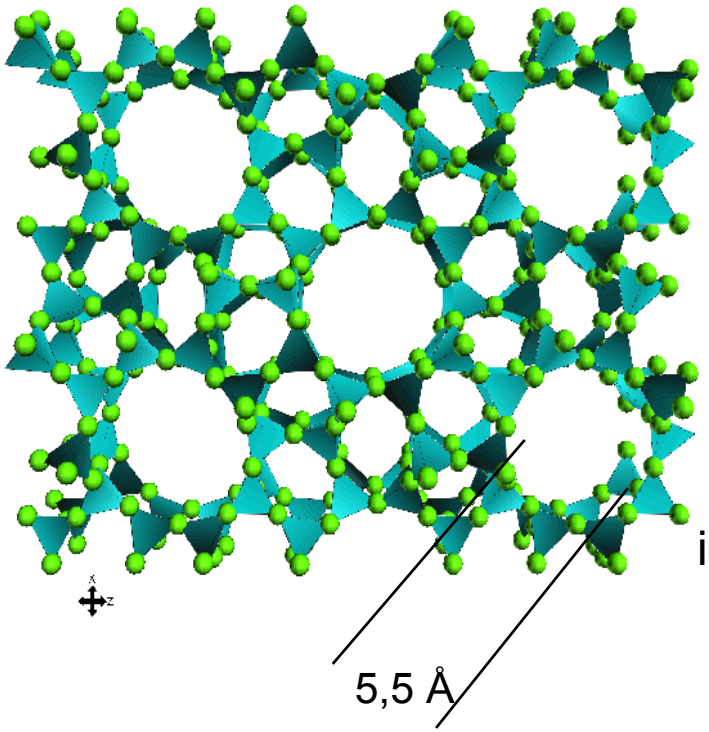


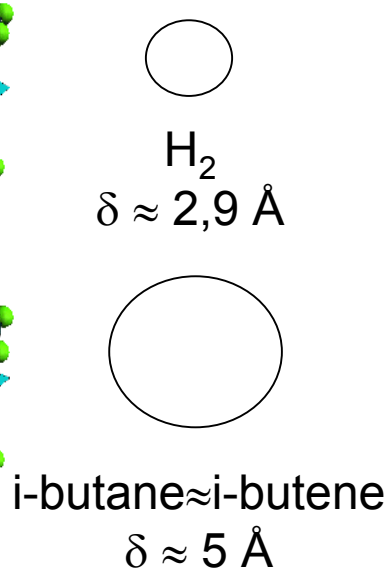


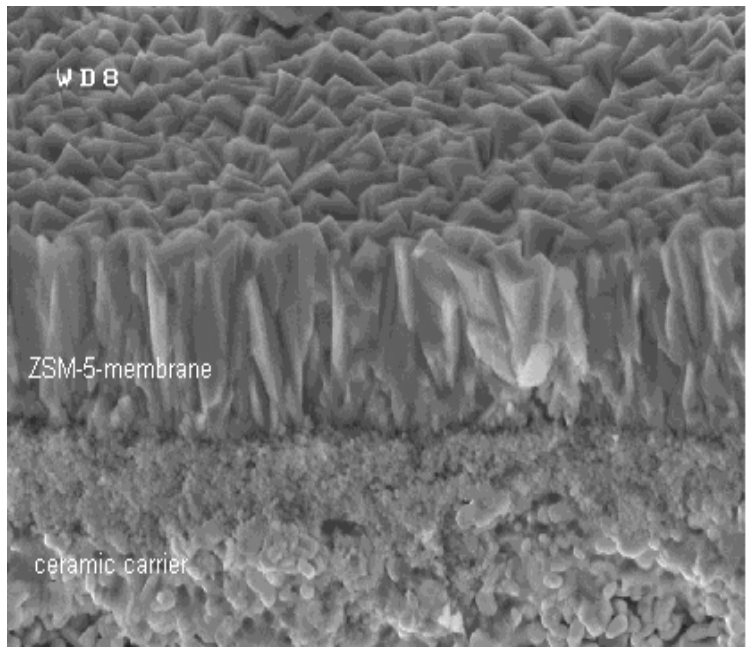
Concept for membrane application:

Increase of the i-butane conversion by continuous removal of H_2 at 500°C via a H_2-selective membrane!

3. Dehydrogenation of i-butane in a membrane reactor with MFI membrane







Permeance: **1.1 m^3 H_2/m^2hbar**

Selectivity: **H_2 : i-C_4 = 70 : 1**

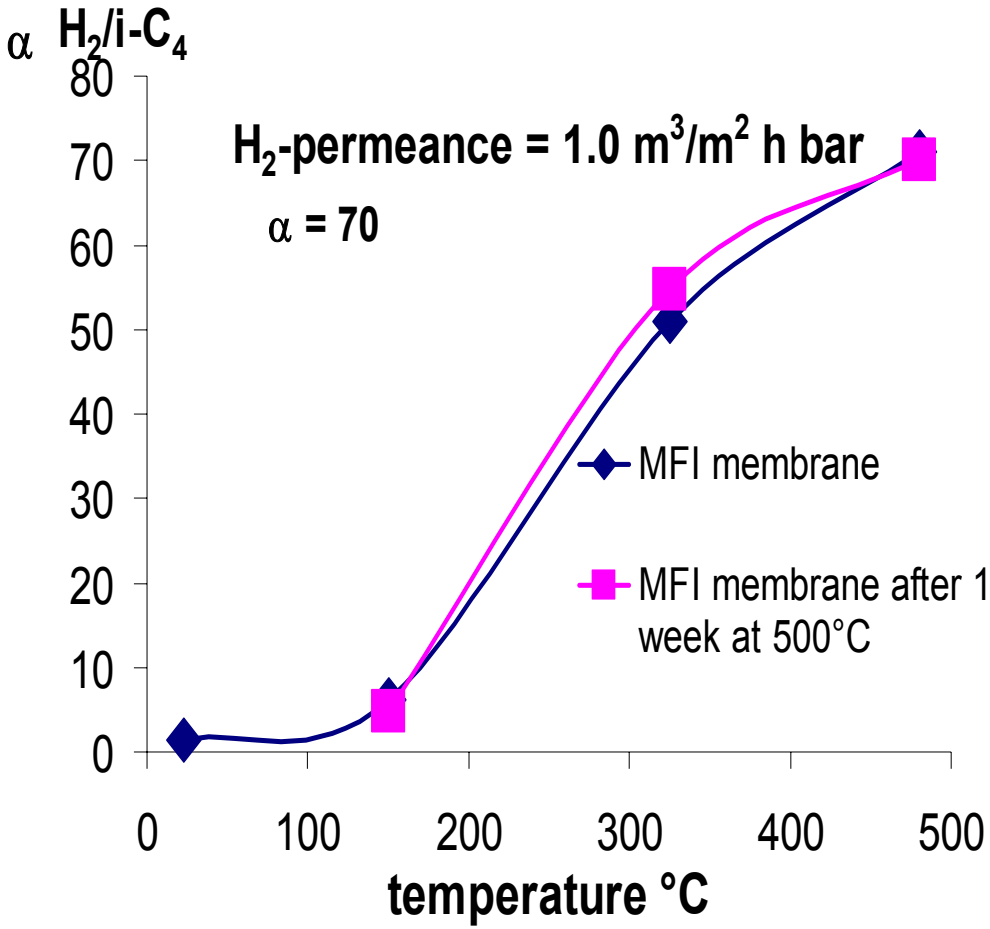
at 500°C!!!

- *M. Noack et al.*; Microp. Mesop. Mater. 35 (2000) 253
- *J. Caro et al.*; Microp. Mesop. Mater. 28 (2000) 3

Separation behaviour of an MFI-Silicalite I – membrane for a 50% / 50%-H_2/i-butane mixture as a function of temperature

Mixture separation factor: $\alpha_{i/j} = (y_i : y_j) / (x_i : x_j)$

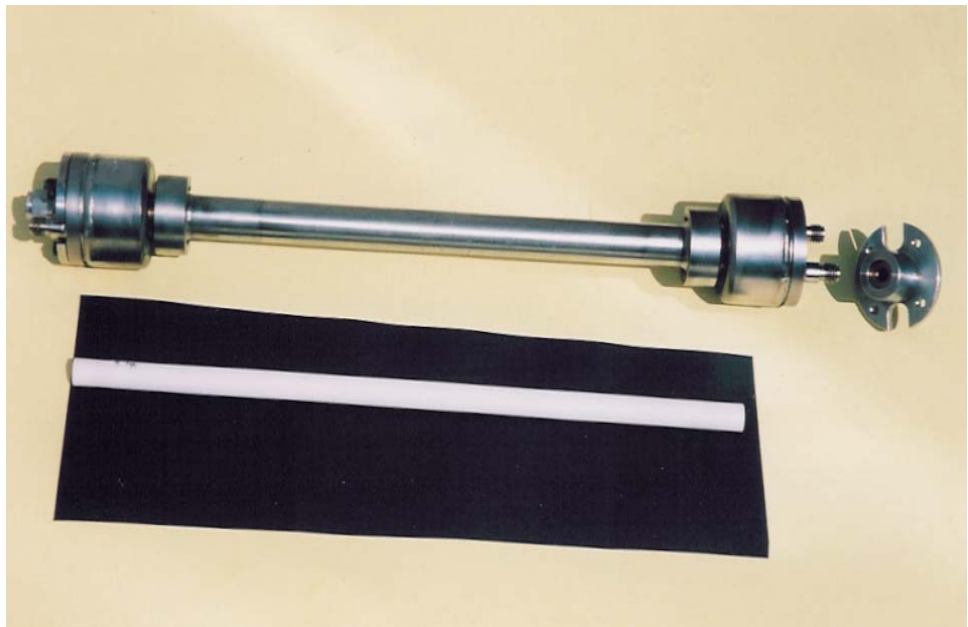
$\alpha_{i/j}$ = mole fractions i and j in the permeate (y) and feed (x)

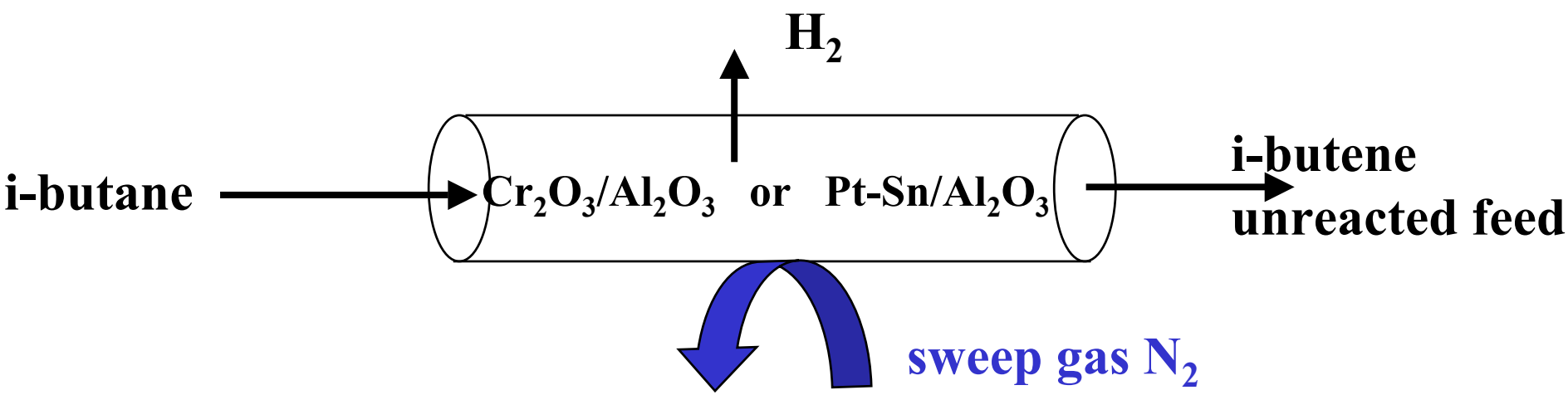


- **At low T**: permeation is adsorption controlled: butane-selectivity
- **At highT**: permeation is diffusion controlled: hydrogen-selectivity
- **After one week** of operation (5 regenerations) no ageing

U. Illgen, M. Noack, J. Caro et al., Catal. Commun. 49 (2001) 25

3. Dehydrogenation of i-butane in a membrane reactor with MFI membrane





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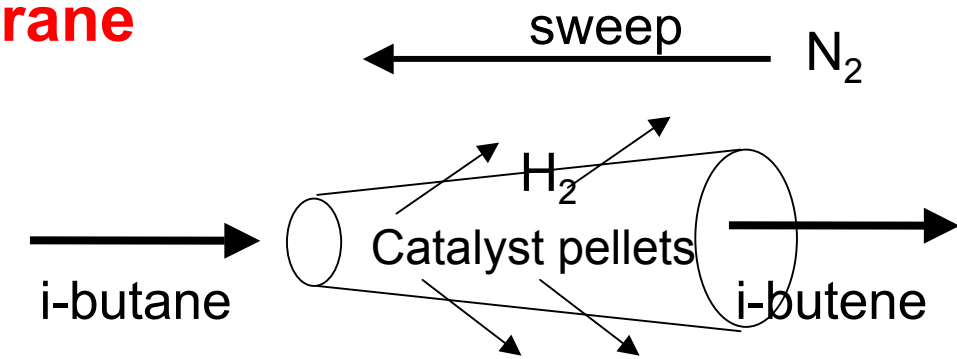
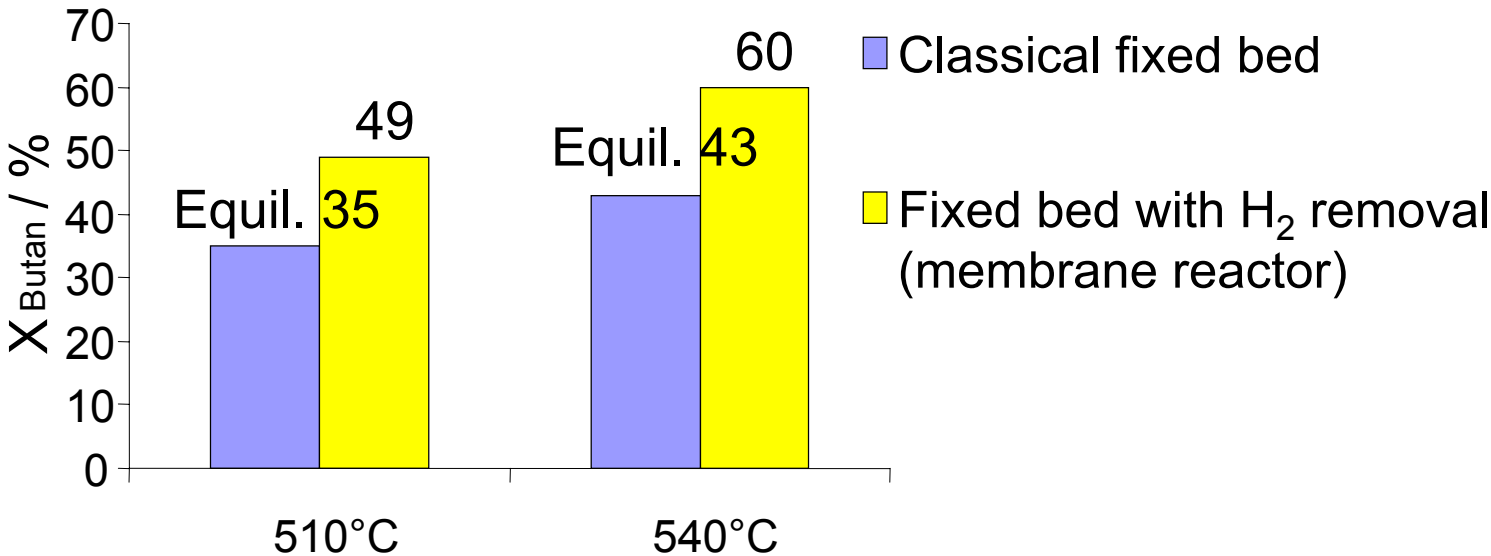


i-butane conversion



Illgen, Caro et al., Catal. Commun. 2 (2001) 339
Conversion of i-butane can be increased by about 15 % at a WHSV of 1,0 h^{-1} (data after 20 min time on stream)

3. Dehydrogenation of i-butane in a membrane reactor with MFI membrane

☺

→ Conversion of i-butane increases by 15%

→ Selectivity of i-butene formation increases from 92 to 97% (side reaction hydrogenolysis is reduced because of the H_2 removal)

} i-butene yield is increased

→ Membrane properties unchanged after 1 week at 500°C (5 oxidative regenerations)

☹

→ Due to coking, the i-butene yield of the membrane reactor drops after 120 min under the classical fixed bed

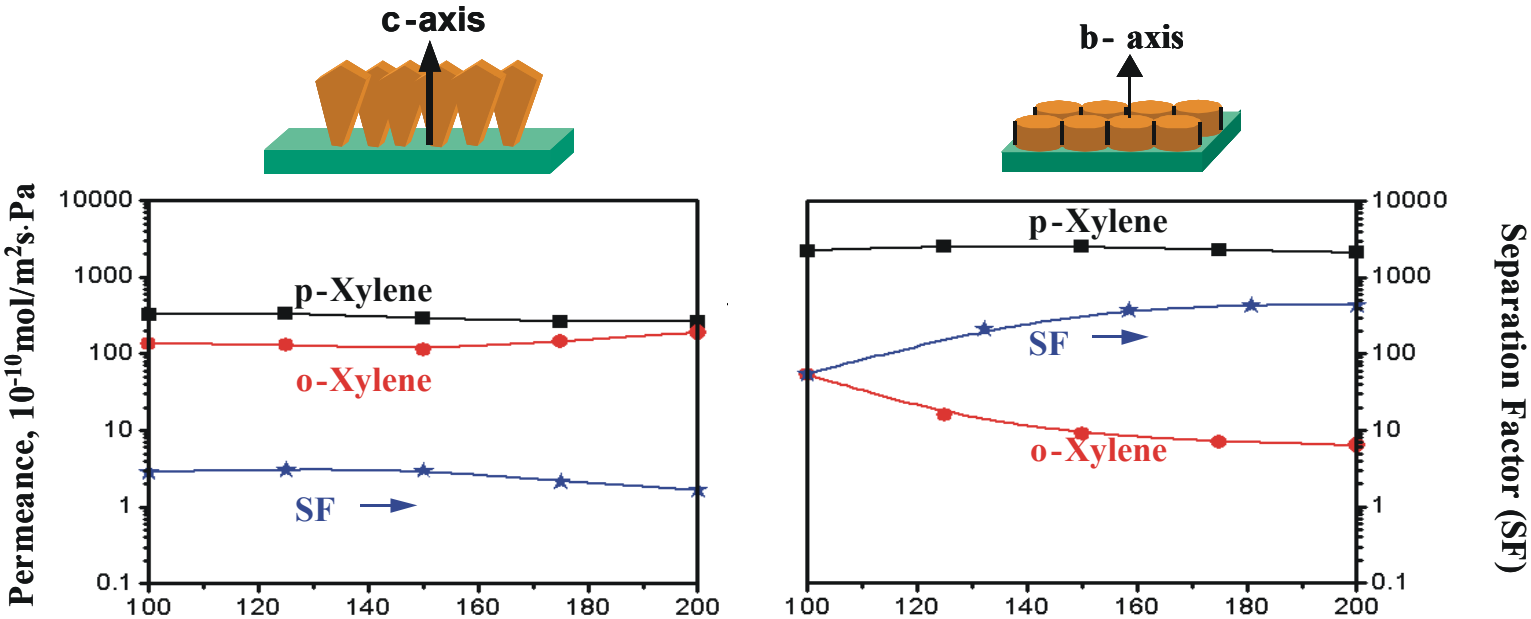
Evaluation of the concept

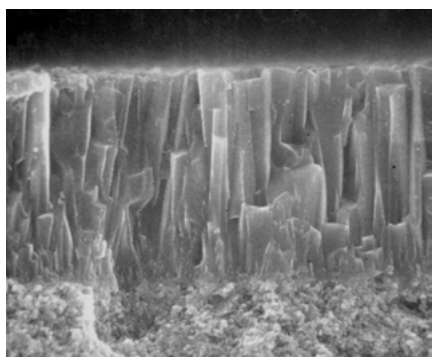
Stability and selectivity problems with SiO_2 sol-gel (not stable, provides no fuel cell grade H_2, Pd membranes (not stable, expensive)

For an economic solution:

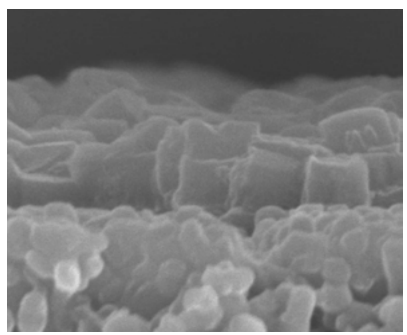
We need diffusion-controlled narrow pore membranes

4. Separation of xylene isomers by zeolite MFI membrane





Tsapatsis et al. Science, 300 (2003) 456

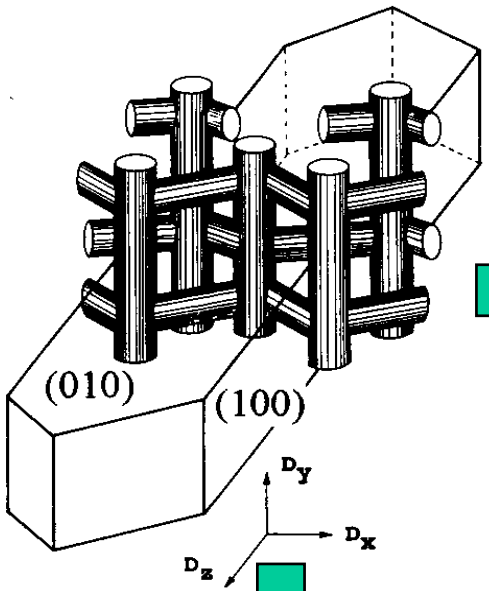


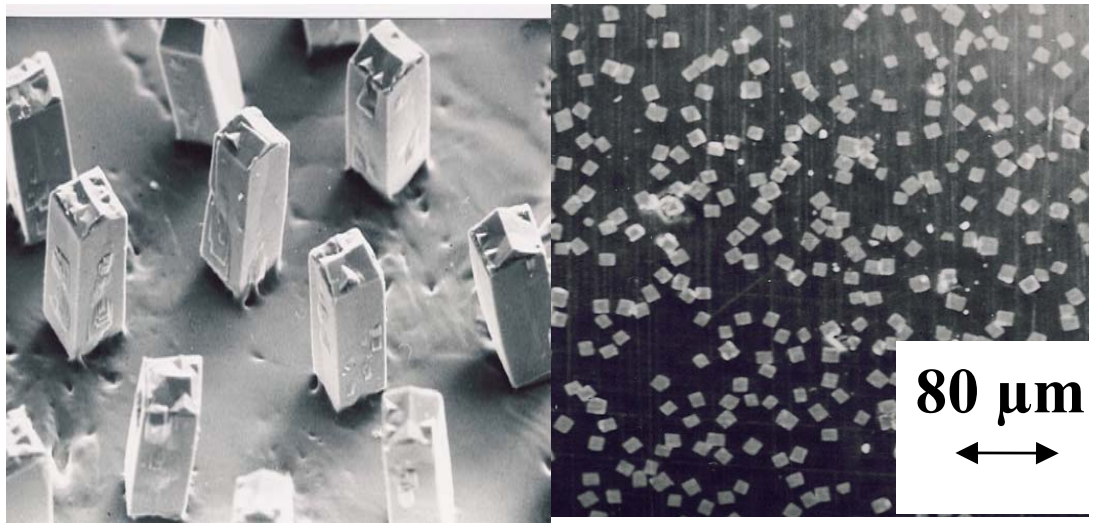
b-orientation: high separation, high p- and low o-xylene fluxes

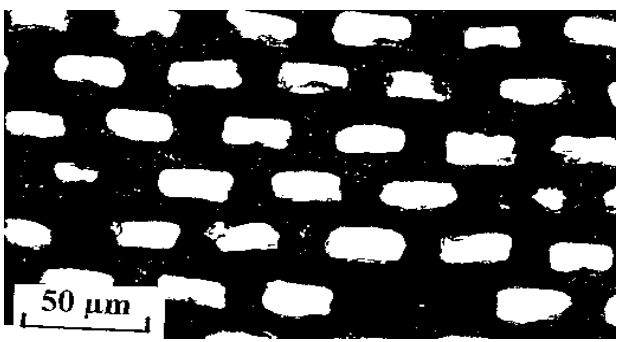
c-orientation: medium fluxes for both o- and p-xylene

Puzzle: The different T-dependencies of o- and p-xylene fluxes

4. Separation of xylene isomers by zeolite MFI membrane







Determination of direction dependent diffusion coefficients (tensor components)
by permeation studies on model membranes with oriented MFI crystals in a metal matrix

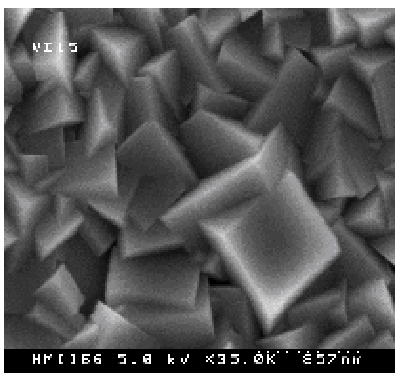
The gas-tight Ni or Ag film can be prepared by galvanic techiques or sputtering (European Kärger Project)

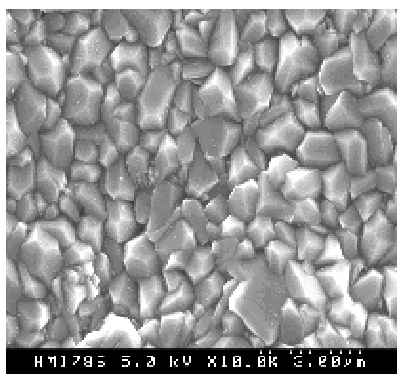
5. Semi-technical application of zeolite LTA membranes in water/alcohol pervaporation pilote plants

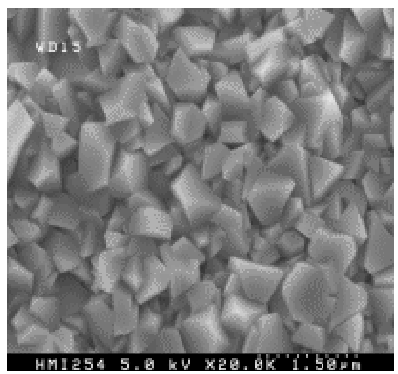
Despite semi-industrial application
→ There is no information on molecular mass transport:
interplay of mixture adsorption and diffusion is not understood

From the relationship betweeen pore diameter of LTA (4.2 Å) and the kinetic diameters of water (2.9 Å) and ethanol (4.5 Å) it could be a shape selective separation…

But n- and i-paraffines are separated only by the Knudsen ratio







crystal size of 1 μm^3
10^8 zeolite crystals per cm^2
$\Rightarrow$ 200 m crystal boundary per cm^2

6. Outlook

There are shape-selective separations using MFI membranes in pilote scale:

- xylene separation
- n/i hydrocarbon separation

However, before a wide industrial application, we have to solve 4 problems:

a) The cost problem

b) The membrane problem

c) The module problem

d) Forecast of flux and seperation

6. Outlook

a) The cost problem (Part I)

The profit in application must justify the high manufacturing costs.

What are the unique properties of a zeolite membrane (compared to other organic or inorganic membranes)?

Main property: (i) Shape-selective separation
(ii) at elevated temperatures

Second order properties: Catalytic function, selective adsorption, oxidative regeneration, sterilization…

Focus the application on the unique property: shape-selectivity

→ n-/i-alkanes → H_2 from other gases → xylenes

More difficult to realize: Separation based on mixture adsorption

→ aromatics from aliphatics → permeation + reaction

6. Outlook

d) Forecast of flux and separation

So far no established methods exist

2 challenges:

Experiments:

One or a few selected well-characterized zeolite crystals in a gas-tight matrix

Theory:

Development of reliable models to forcast the multi-component permeation on the basis of mixture adsorption equilibria and mixture diffusion coefficients

Both topics will be dealt within the European Kärger Project

DIFFUSION IN ZEOLITES

Confusion on FAU-Membr.

Morooka (ICIM, Vol. 5, 1998, 29)

$\alpha_{CO2-CH4}$ = 15

α_{CO2-N2} = 20 -100

Noack (MMM, 54, 2002, 27)

$\alpha_{CO2-CH4}$ = 0.3

α_{CO2-N2} = 0.1

Acknowledgement

I thank Dr. Manfred Noack and his colleagues of the Research Group „Membrane catalysis“ at the ACA for 12 years of fruitful co-operation in the field of zeolite membranes.