

Catalysis Engineering lunch meeting
8 November 2018

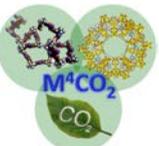
TU Delft

Practical aspects of membrane performance testing and interpretation

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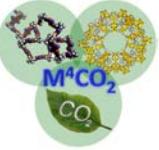
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What you can expect.....

- Goal
- Basics
 - Definitions
 - Membrane types
- Experimental
 - Steady state, transient techniques
 - Data interpretation aspects
- Modelling
- Take home message

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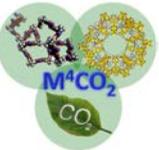


Membrane performance testing

- Characterization membrane in operation
 - Flux through membrane ($\text{mol s}^{-1} \text{m}^{-2}$)
 - of a specific component
 - as single component, in a mixture
 - dependency on operational variables
 - (partial) pressures, temperature
 - Separation of a mixture
 - Comparison with other systems
 - Normalization
 - Applied partial pressure difference - Permeance
 - Membrane thickness - Permeability

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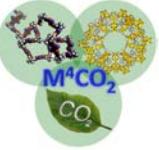


Membrane types

• Zeolite membranes	Well-defined porosity, rigid
• MOF membranes	Well-defined porosity, flexible
• Polymer membranes	Solid, ill defined porosity, flexible
• Mixed matrix membranes	
– MOF in polymer	Solid, porous, flexible
• Metal membranes	Solid, rigid
• Solid oxide membranes	Solid, rigid
• (Supported) Liquid membranes	

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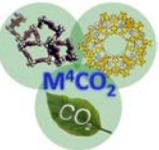


Definitions

		SI units
<ul style="list-style-type: none"> • Flux <ul style="list-style-type: none"> – molar transport rate of a component per unit membrane area 	$J_i = \frac{N_i}{A}$	$\frac{\text{mol}}{\text{s} \cdot \text{m}^2}$
<ul style="list-style-type: none"> • Permeance <ul style="list-style-type: none"> – Flux normalized for partial pressure difference of component over membrane 	$\Pi_i = \frac{J_i}{\Delta p_i}$	$\frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$
<ul style="list-style-type: none"> • Permeability <ul style="list-style-type: none"> – Permeance normalized for thickness separation layer of membrane 	$P_i = \Pi_i \cdot d$	$\frac{\text{mol} \cdot \text{m}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$

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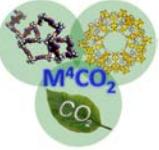


Definitions – other units

		SI units
<ul style="list-style-type: none"> • Flux <ul style="list-style-type: none"> – molar transport expressed in ml_{STP} (1 mmol = 22.4 cm^3 @ 0°C, 1 atm) 	$\frac{\text{cm}^3_{\text{STP}}}{\text{s} \cdot \text{cm}^2}$	$0.446 \frac{\text{mol}}{\text{s} \cdot \text{m}^2}$
<ul style="list-style-type: none"> • Permeance <ul style="list-style-type: none"> – Gas Permeation Unit $\text{GPU} = 10^{-6} \frac{\text{cm}^3_{\text{STP}}}{\text{s} \cdot \text{cm}^2 \cdot \text{cm Hg}}$ 	$3.346 \cdot 10^{-10} \frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$	$3.346 \cdot 10^{-10} \frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$
		$300 \text{ GPU} \approx 10^{-7} \frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$
<ul style="list-style-type: none"> • Permeability <ul style="list-style-type: none"> – Barrer 	$\text{Barrer} = 10^{-10} \frac{\text{cm}^3_{\text{STP}} \cdot \text{cm}}{\text{s} \cdot \text{cm}^2 \cdot \text{cm Hg}}$	$3.346 \cdot 10^{-16} \frac{\text{mol} \cdot \text{m}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$

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Units interconversion - relation

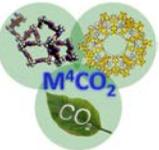
- Relation between GPU (permeance) and Barrer (permeability):
 - Membrane of thickness $1 \mu\text{m}$ (10^{-4} cm) and 1 Barrer has a permeability of 1 GPU:

$$\Pi_i = \frac{P_i}{d}$$

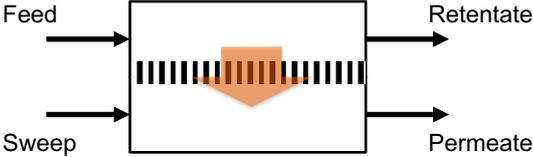
$$\frac{1 \text{ Barrer}}{10^{-4} \text{ cm}} = 10^{-10} \frac{\text{cm}^3_{STP} \cdot \text{cm}}{\text{s} \cdot \text{cm}^2 \cdot \text{cm Hg}} \cdot 10^4 \text{ cm}^{-1} = 10^{-6} \frac{\text{cm}^3_{STP}}{\text{s} \cdot \text{cm}^2 \cdot \text{cm Hg}} = 1 \text{ GPU}$$

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Other nomenclature membranes



- Separation factor
mixed gas selectivity $\alpha_{AB} = \frac{(X_A / X_B)_{permeate}}{(X_A / X_B)_{retentate}}$
- Ideal separation factor $S_F(AB) = \frac{P_A}{P_B}$
ideal selectivity, pure gases

PureApplChem 68(1996)1479-1489 IUPAC-Membranes
W.J. Koros, Y.H. Ma, and T. Shimidzu

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Examples of membrane modules

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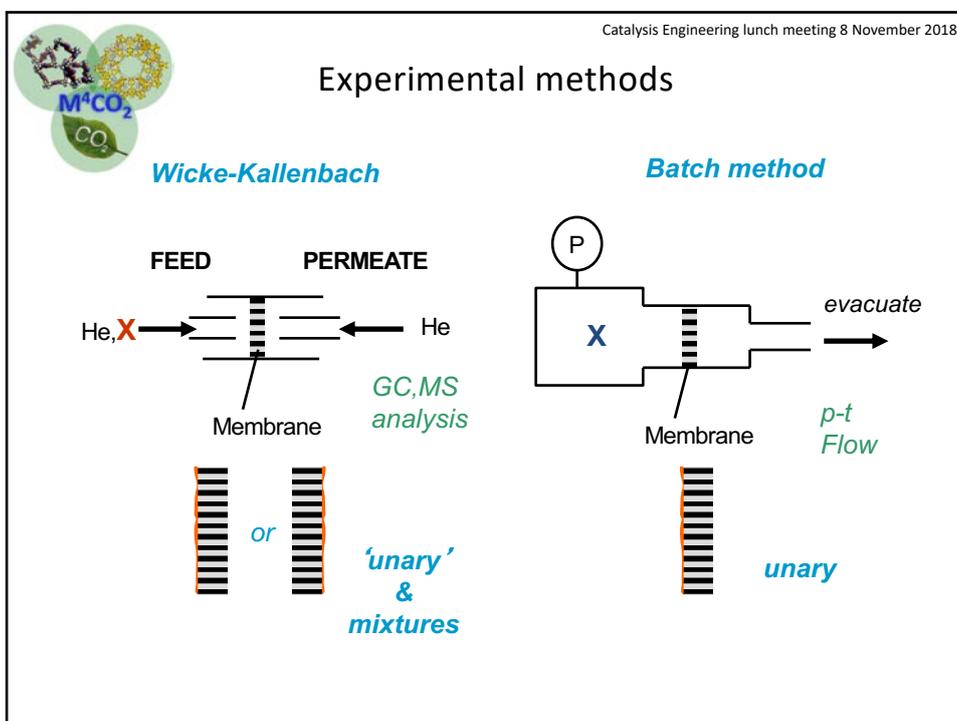
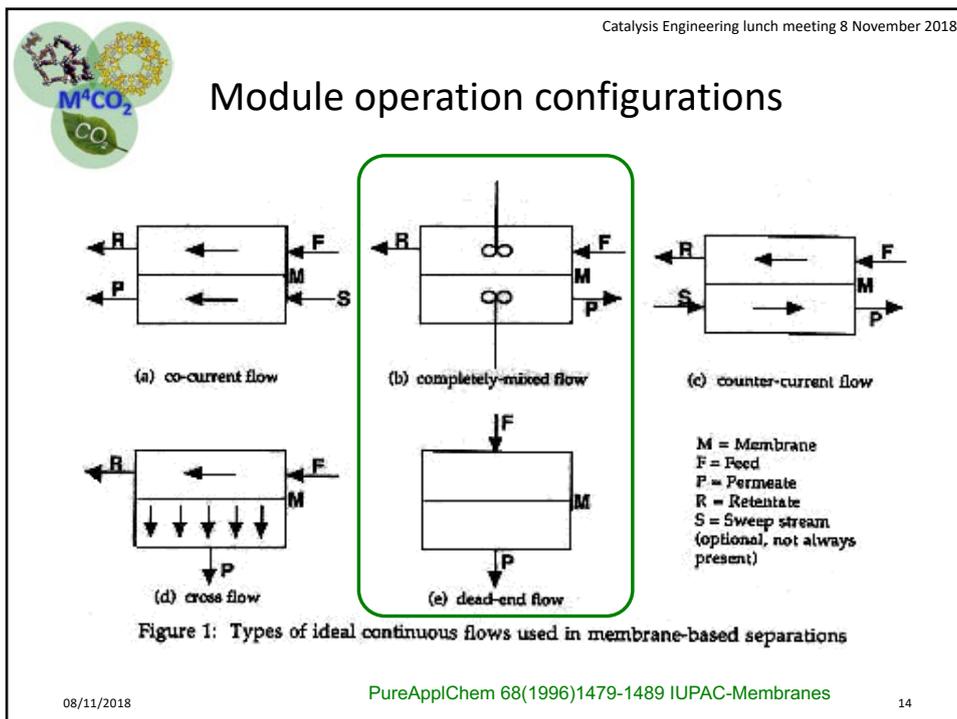
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Modeling aspects - levels

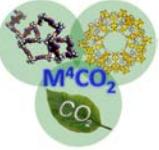
- Levels
 - Module level – transport in system – engineering models
 - Overall performance module – operation mode
 - Local transport, concentration changes, hydrodynamics
 - Membrane level – Support+selective layer
 - Combined through-membrane transport
 - Selective layer – Transport mechanisms
 - Sorption, adsorption - competitive
 - Diffusion types

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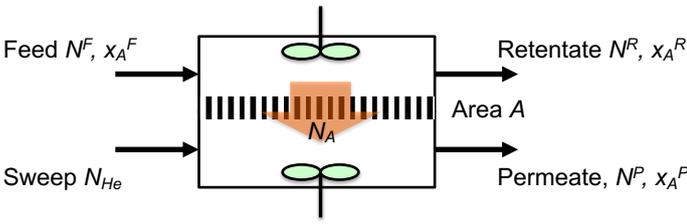


Membrane testing – module assumptions

Single component

Feed N^F, x_A^F

Sweep N_{He}



Retentate N^R, x_A^R

Permeate, N^P, x_A^P

$$N_A = (N^F \cdot x_A^F - N^R \cdot x_A^R) = (N^P \cdot x_A^P) \quad \text{mol/s}$$

- Well mixed volumes
- Local conditions identical
- No sweep permeation

Pure feed:

$$N_A = (N^F - N^R) = (N^P \cdot x_A^P) \approx (N^{sweep} \cdot x_A^P)$$

$$N_A \ll N^{sweep}$$

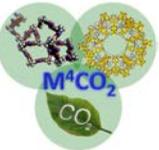
Mixed feed:

$$N_A \approx N^F \cdot (x_A^F - x_A^R) \approx (N^{sweep} \cdot x_A^P)$$

if: $N^R \approx N^F$

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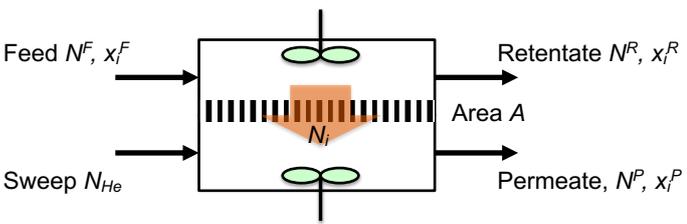


Membrane testing – module assumptions

Mixtures

Feed N^F, x_i^F

Sweep N_{He}



Retentate N^R, x_i^R

Permeate, N^P, x_i^P

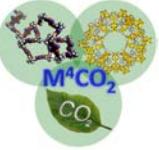
$$N_i \approx (N^{sweep} \cdot x_i^P) \quad N_i \ll N^{sweep}$$

- Well mixed volumes
- Local conditions identical
- No sweep permeation

$$\alpha_{ij} = \frac{(x_i / x_j)_{permeate}}{(x_i / x_j)_{retentate}}$$

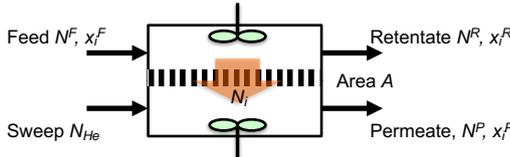
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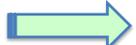


What if sweep gas back-permeates?

- Round Robin experiments
 - Feed gas CO₂/N₂
 - Sweep 3 ml_{STP} /min He



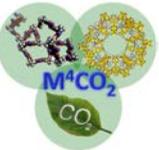
- Pure gas measurement (CO₂-He)
 - Permeation 1 ml_{STP} /min He



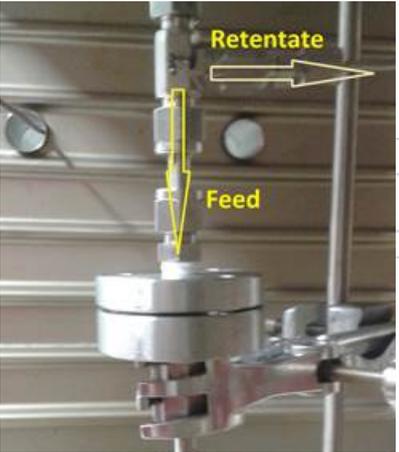
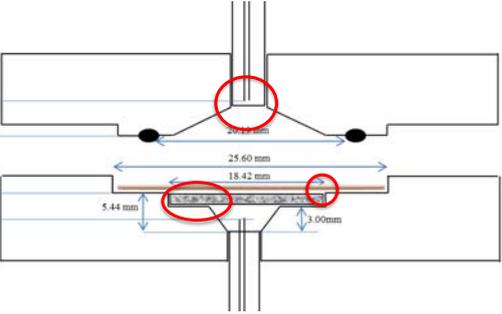
Higher concentration in Permeate
Too high flux calculated?
Hindrance of permeation?

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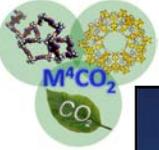


Do assumptions hold?

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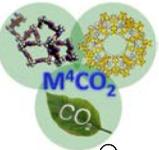
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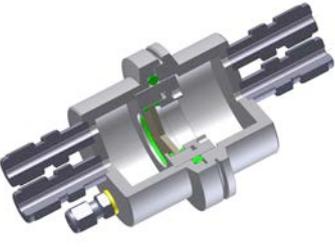


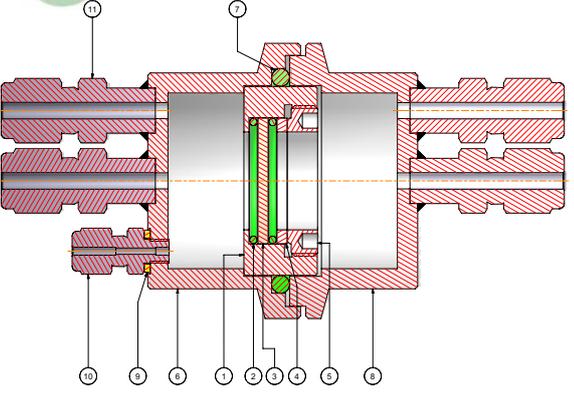
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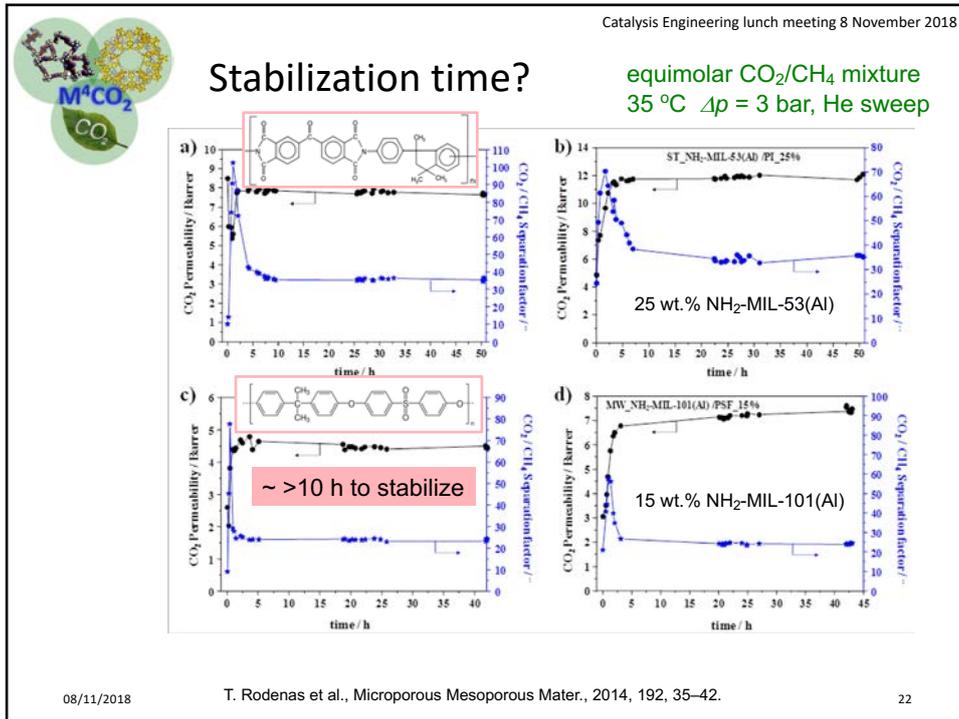
Do assumptions hold?



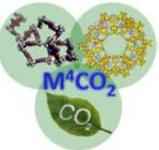


How to test for CSTR behaviour?

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Can we rationalize this time needed?

- Permeability 2 – 8 Barrer
- Thickness 70 μm
- Pressure 4 and 1 bar (abs)
- CO₂ adsorption
 - 200-400 ml_{STP}/g MIL-101 (15 wt%)
 - 50 ml_{STP}/g MIL-53 (25 wt%)

$$J_i = \frac{N_i}{A} \quad \frac{\text{mol}}{\text{s} \cdot \text{m}^2}$$

$$\Pi_i = \frac{J_i}{\Delta p_i} \quad \frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$$

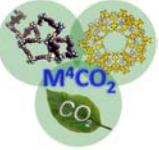
$$P_i = \Pi_i \cdot d \quad \frac{\text{mol} \cdot \text{m}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$$

Estimate time it takes to 'fill' the membrane

$$1 \text{ Barrer} = 3.346 \cdot 10^{-16} \frac{\text{mol} \cdot \text{m}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$$

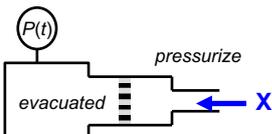
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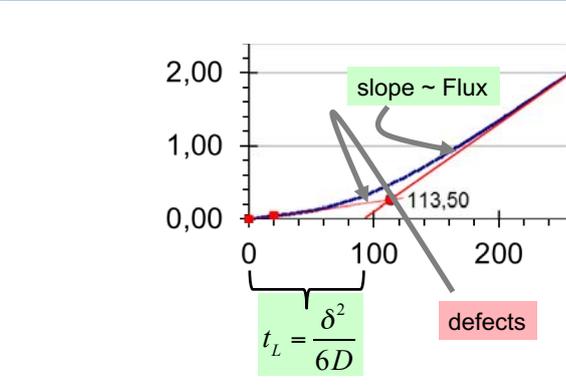
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Transient operation

- How ?
 - Time-lag technique
 - Single component
 - Constant diffusivity

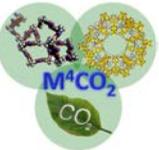




- What information?
 - Permeability $P = flux * \delta / \Delta p$
 - Diffusivity - Wide window
 - Solubility - $S = P/D$

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J.C. Jansen, Polymer (2007)
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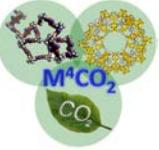
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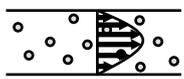
Aspects of transport modeling

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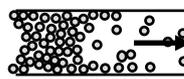
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Transport mechanisms in pores



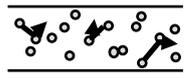
Viscous flow



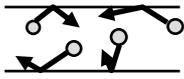
Capillary condensation



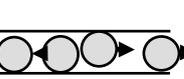
Surface diffusion



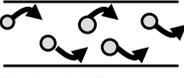
Molecular diffusion



Knudsen diffusion



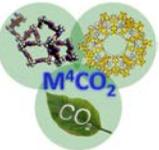
Activated diffusion (zeolites)



Sorbed diffusion (polymers)

How do we know
which type we deal with?

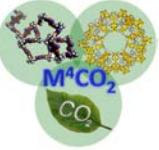
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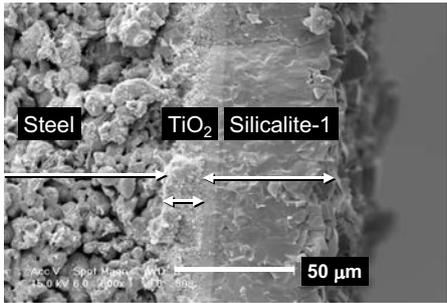
Inorganic membranes – Polymers – Mixed matrix

	Transport regimes	Permselectivity
pores	Viscous flow	~
	Molecular diffusion (>10 nm)	~ (+)
	Knudsen diffusion (1- 10 nm)	$\sqrt{\frac{1}{M}}$
	Surface diffusion	+
solid	Zeolitic diffusion, molecular sieving (< 1 nm)	++
	Hydrogen diffusion	∞
	Mixed conduction transport (O ²⁻ , e)	∞
	Sorbed phase diffusion	+ - ++

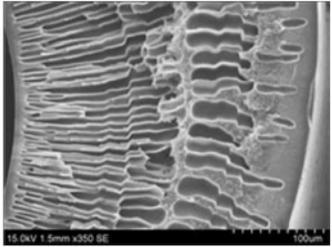
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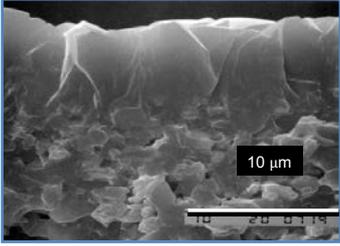
Examples - supported



TRUMEM



HF polymer membrane



DDR membrane

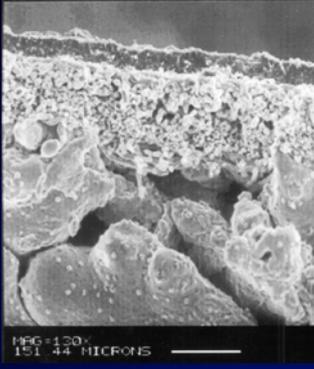
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The silicalite-1 membrane

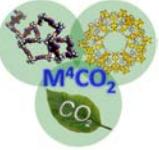
- **Well defined, uniform micro-porous structure**
 - Silicalite-1: ~ 0.55 nm
 - Separation on a molecular level
- **Thermostable**
 - 200 - 700 K
- **Silicalite-1**
(40-60 µm, 3 cm²)
- **Stainless steel support**
(3 mm)



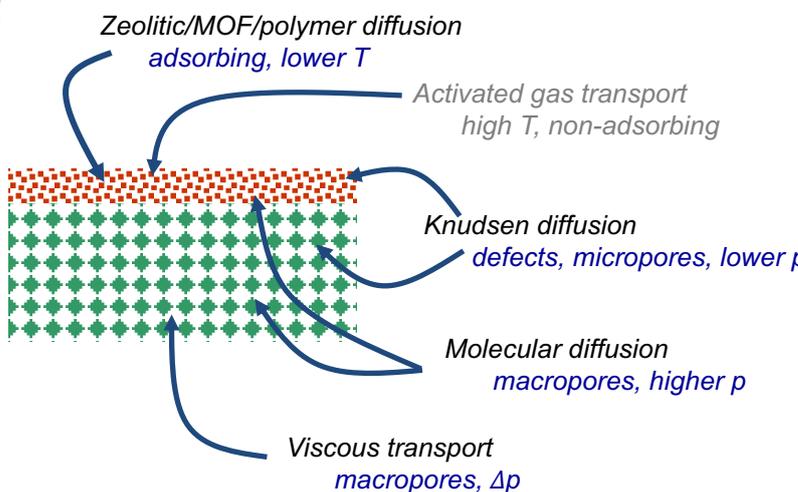


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Transport types – supported membranes



Zeolitic/MOF/polymer diffusion
adsorbing, lower T

Activated gas transport
high T, non-adsorbing

Knudsen diffusion
defects, micropores, lower p

Molecular diffusion
macropores, higher p

Viscous transport
macropores, Δp

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Polymer membranes - supported

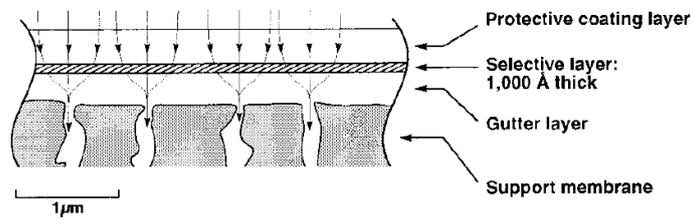


Multilayer composite membrane preparation



- Similar to the above evaporation method
- Polymer solution is cast on top of a suitable porous support

Multilayer Composite Membrane



- Highly permeable top-layer may be added to protect the film.
- Highly permeable intermediate layer may favour transport through the pores of the support.

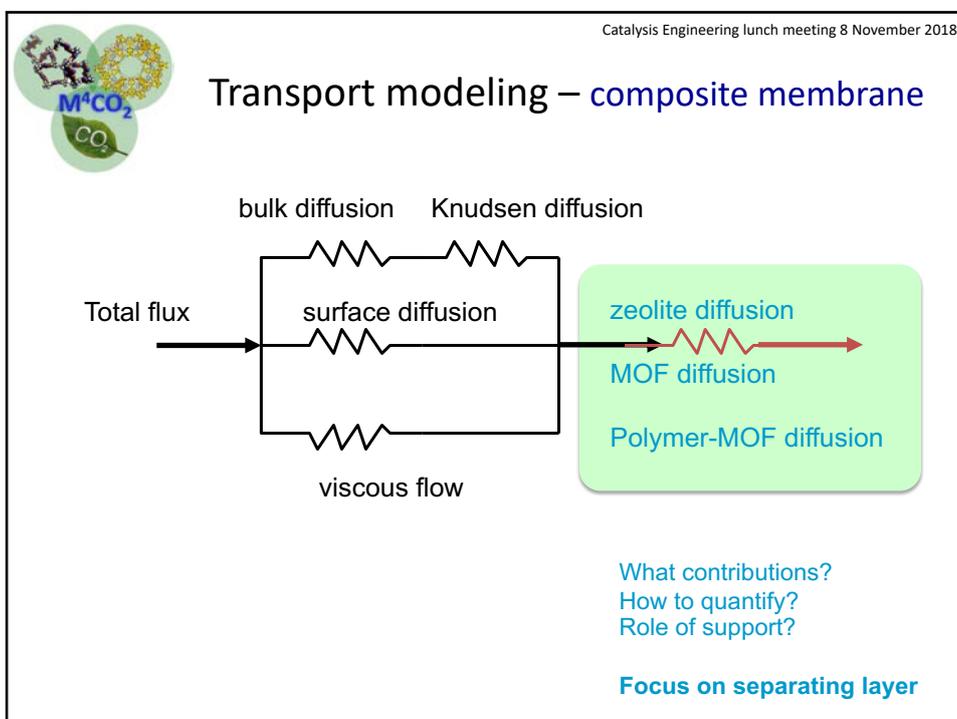
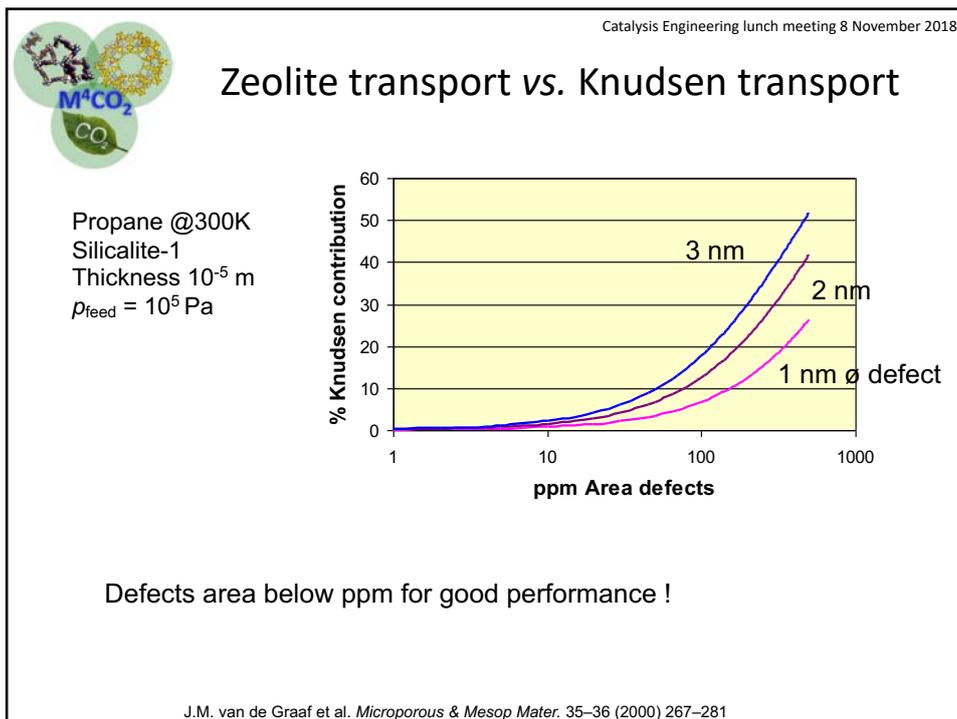
M*CO₂ Workshop 2015

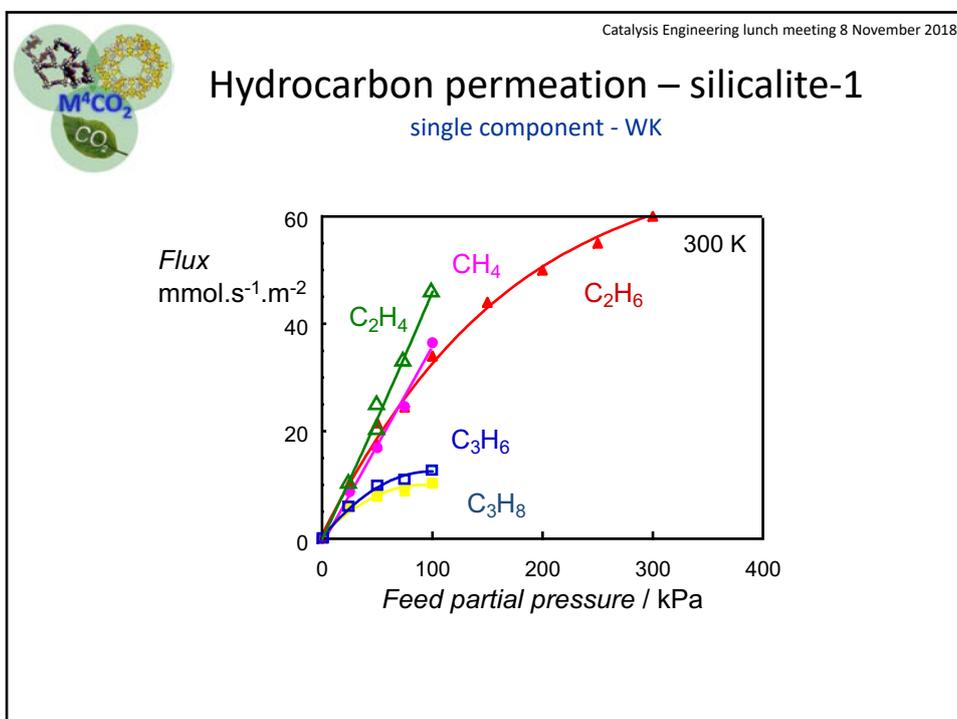
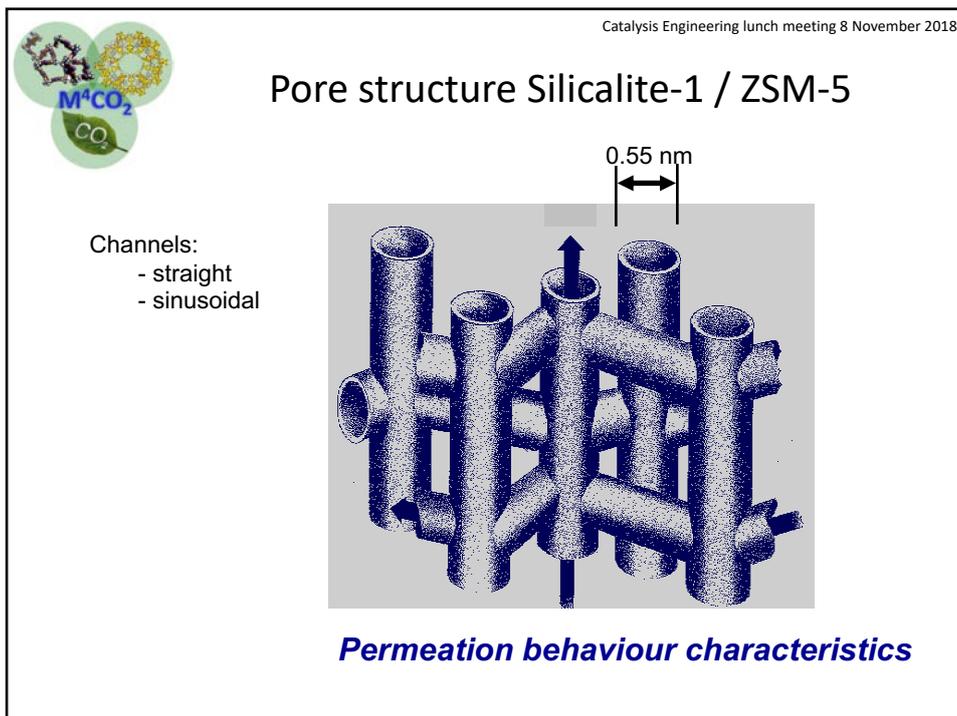
Consiglio Nazionale delle Ricerche

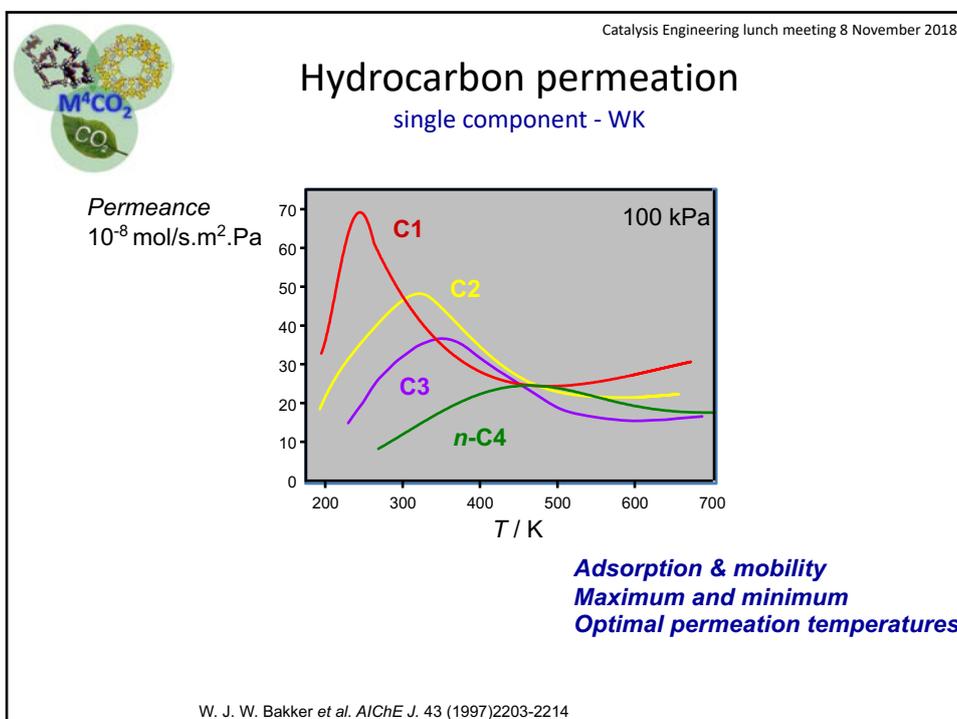
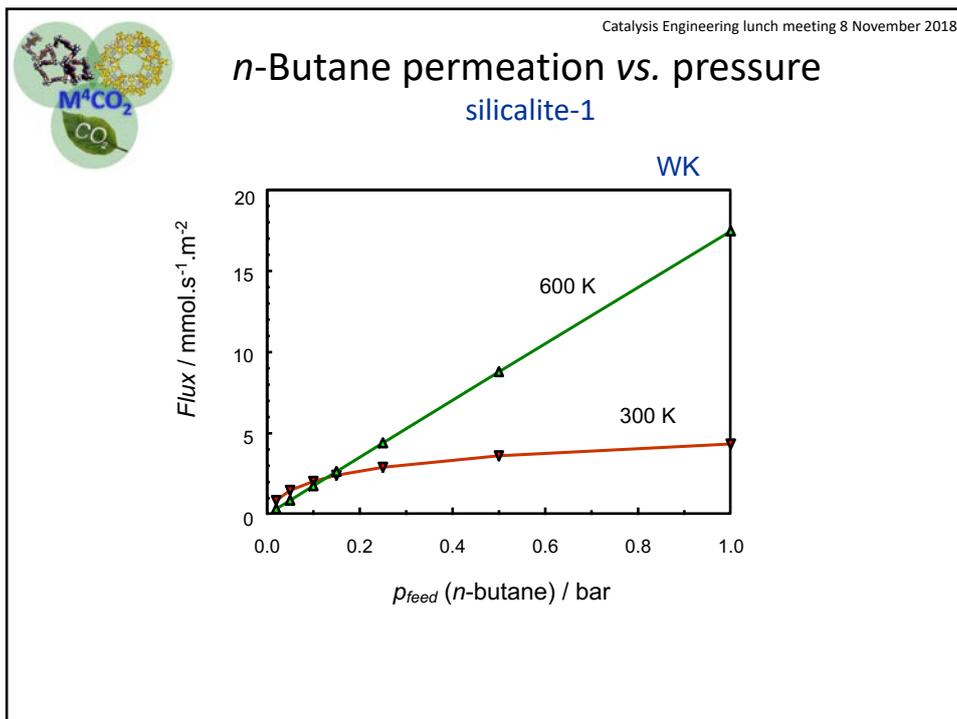


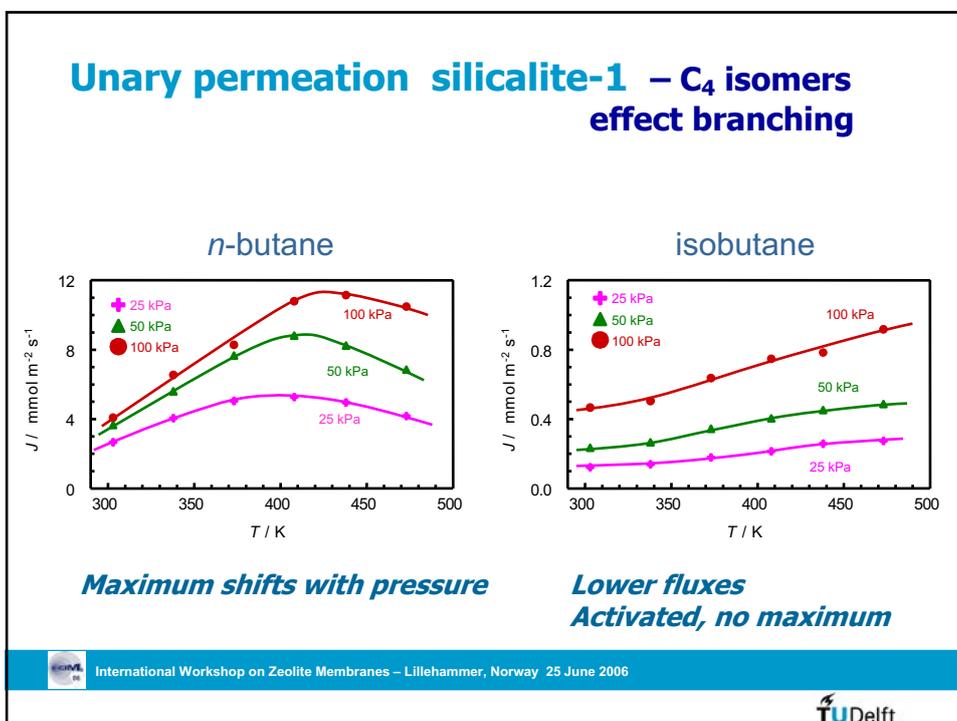
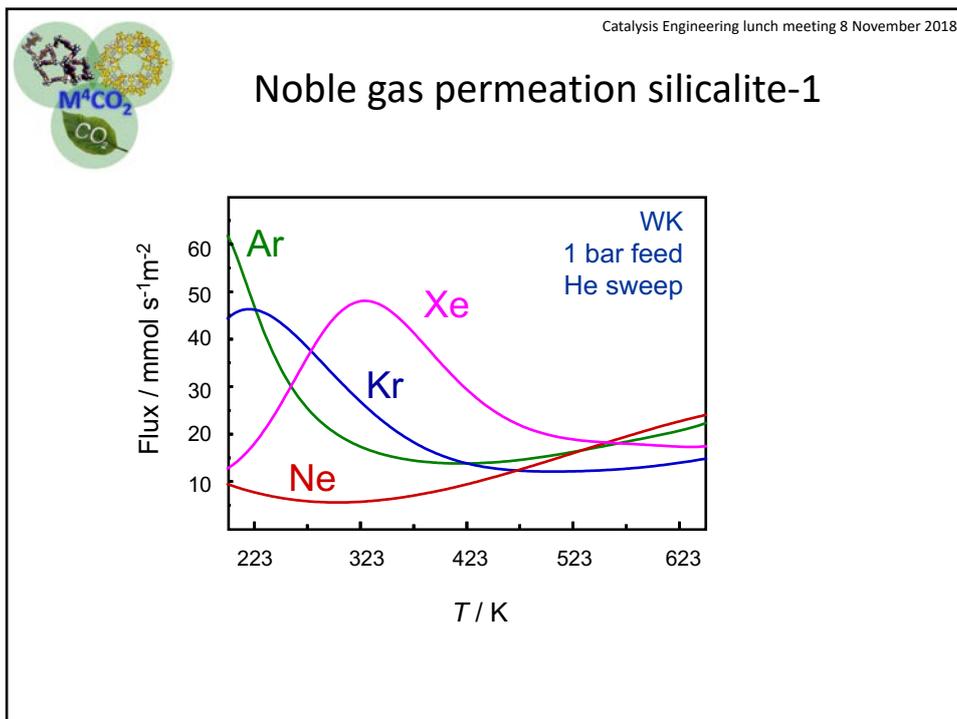
John C Jansen, CNR

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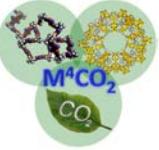








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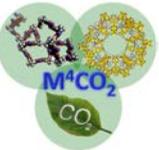


Unary permeation – some observations

- Flux linear and non-linear with feed pressure
- Temperature dependency depends on component:
 - Exhibits maximum and minimum
 - Activated behaviour
 - Hardly any dependence
- Behaviour strongly dependent on
 - Adsorption plays important role – local conditions
 - Molecular size and shape important
 - Similar behaviour different zeolites

How to catch this in a model?

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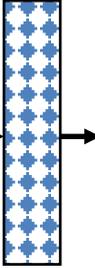
Zeolite permeation modeling

Single component

Driving force transport ~ chemical potential gradient

$$-\nabla \mu_i = RT \frac{u_i}{D_i}$$

$$\mu_i = \mu_i^0 + RT \ln p_i$$

$$N_i \equiv \rho q_i u_i$$


$$\frac{\nabla \mu_i}{RT} = \nabla \ln p_i = \frac{\partial \ln p_i}{\partial q_i} \nabla q_i = \frac{\Gamma_{ii}}{q_i} \nabla q_i$$

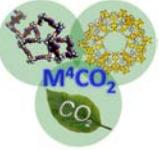
$$\Gamma_{ii} = \frac{q_i}{p_i} \frac{\partial p_i}{\partial q_i}$$

Adorption isotherm needed
Thermodynamic correction factor

Which?

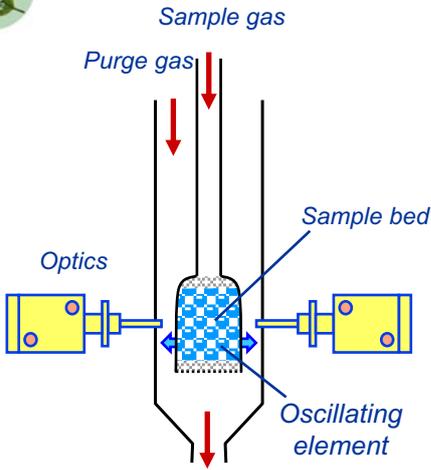
F. Kapteijn et al. In *Structured catalysts and reactors*, Taylor & Francis (2005) 700-746

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Tapered element oscillating microbalance

TEOM



Operating principle

$$\Delta M = K_0 \cdot \left[\frac{1}{f_2^2} - \frac{1}{f_1^2} \right]$$

Operating conditions

T: 300-823 K

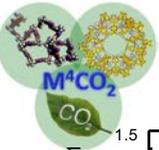
p: 0-10 bar

sensitivity 1 μg

- Conditions relevant practice
- Deactivation
- Adsorption/Diffusion

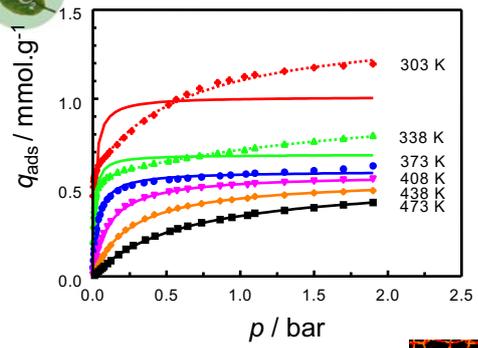
Quartz Crystal Microbalance similar principle

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Iso-butane adsorption in silicalite-1

(TEOM)



Langmuir adsorption

$$q_i = \frac{q_i^{sat} K_i p_i}{1 + K_i p_i}$$

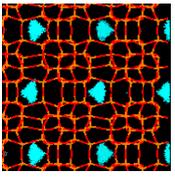
Dual site Langmuir adsorption

$$q_i = q_i^{satA} \frac{K_i^A p_i}{1 + K_i^A p_i} + q_i^{satB} \frac{K_i^B p_i}{1 + K_i^B p_i}$$

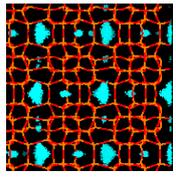
Intersections

Channels

303 K & 0.1 kPa

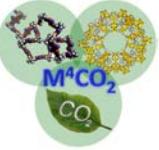


303 K & 100 kPa



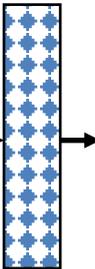
Vlugt *et al.* J.Am.Chem.Soc 120(1998)5599-5600

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Zeolite permeation modeling

Single component



Driving force transport ~ chemical potential gradient

$$-\nabla\mu_i = RT \frac{u_i}{D_i}$$

$$\mu_i = \mu_i^0 + RT \ln p_i$$

$$N_i \equiv \rho q_i u_i$$

$$\frac{\nabla\mu_i}{RT} = \nabla \ln p_i = \frac{\partial \ln p_i}{\partial q_i} \nabla q_i = \frac{\Gamma_{ii}}{q_i} \nabla q_i$$

$$\Gamma_{ii} = \frac{q_i}{p_i} \frac{\partial p_i}{\partial q_i}$$

$$q_i = \frac{q_i^{sat} K_i p_i}{1 + K_i p_i} = q_i^{sat} \theta_i$$

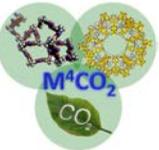
$$\Gamma_{ii} = \frac{q_i^{sat}}{q_i^{sat} - q_i} = \frac{1}{1 - \theta_i}$$

$$N_i = -q_i^{sat} \rho \cdot \frac{D_i}{1 - \theta_i} \cdot \nabla \theta_i = q_i^{sat} \rho D_i \cdot \nabla \ln(1 - \theta_i)$$

Langmuir

F. Kapteijn et al. In *Structured catalysts and reactors*, Taylor & Francis (2005) 700-746

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Limiting cases

$$N_i = -q_i^{sat} \rho \cdot \frac{D_i}{1 - \theta_i} \cdot \nabla \theta_i = q_i^{sat} \rho D_i \cdot \nabla \ln(1 - \theta_i)$$

Low loading (high T , low p)

$$N_i = -q_i^{sat} \rho D_i K_i \cdot \frac{\Delta p_i}{\delta}$$

Henry range Linear adsorption range

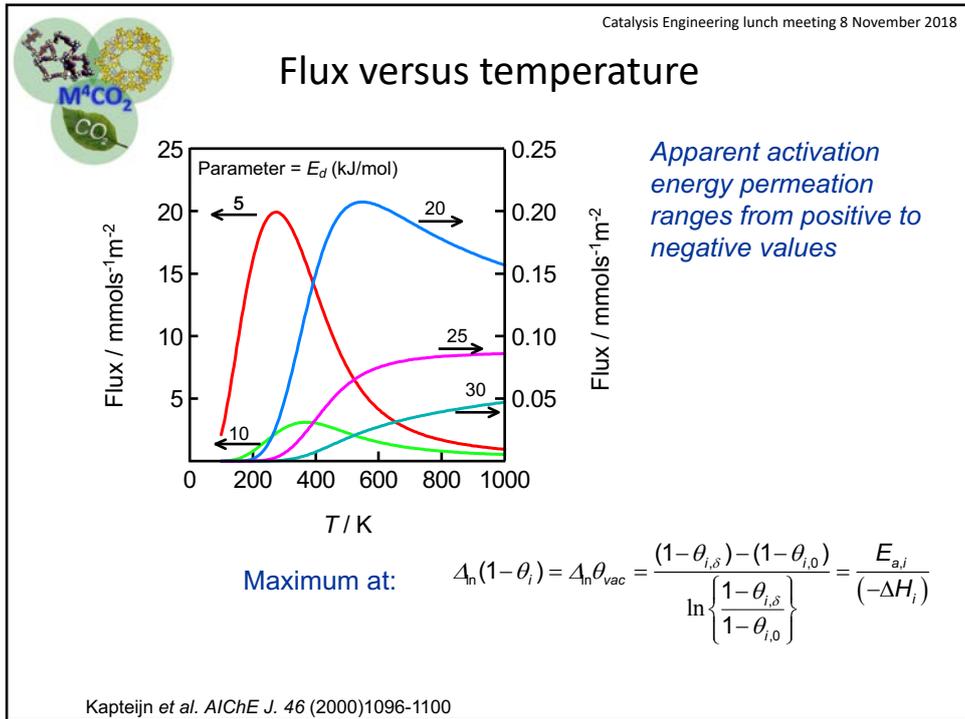
$K_1 \cdot D_1 = K_{10} \cdot D_{01} \exp\left(-\frac{\Delta H_1 + E_{D,1}}{RT}\right)$

High loading (low T , high p)

$$N_i = -q_i^{sat} \rho D_i \cdot \frac{\Delta \ln p_i}{\delta}$$

$D = D_0 \exp\left\{\frac{-E_a}{RT}\right\}$

Apparent activation energy permeation changes



Assumptions

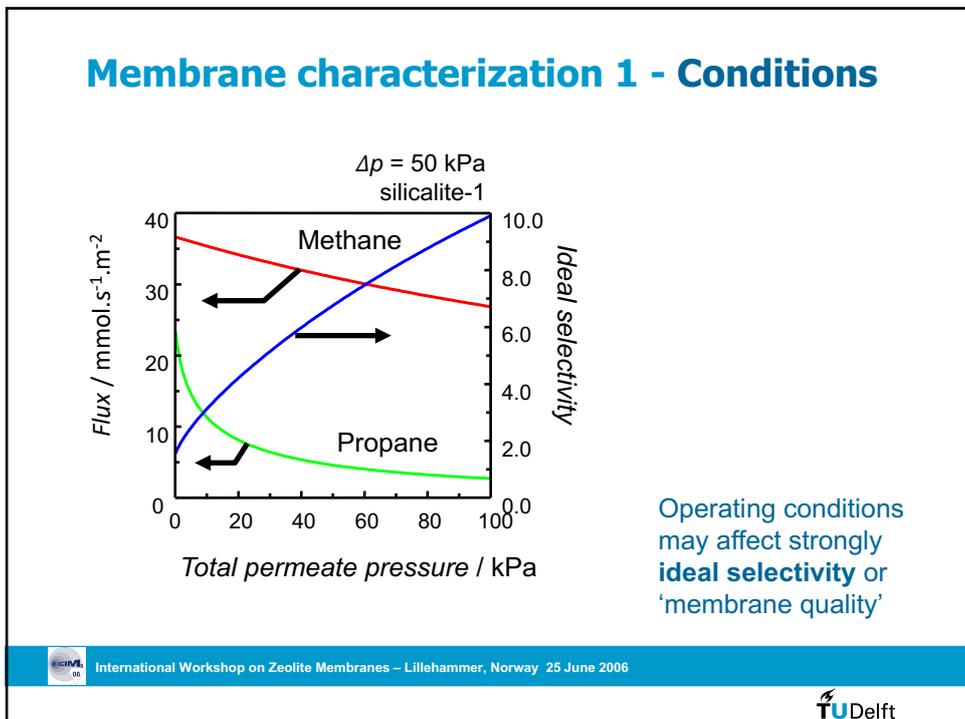
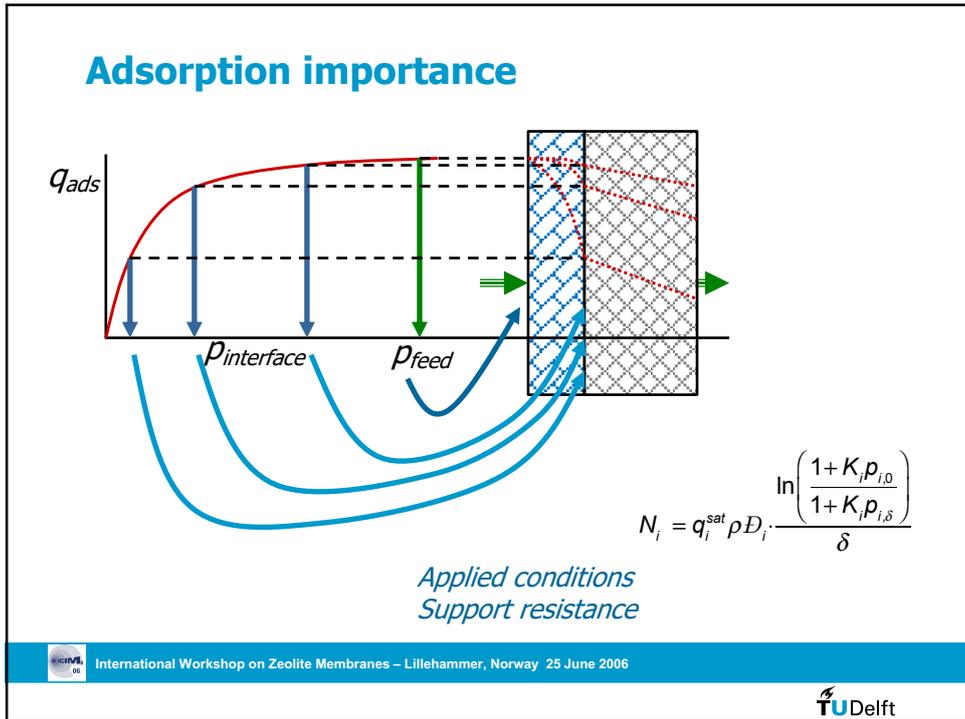
$$N_i = -q_i^{sat} \rho \cdot \frac{D_i}{1-\theta_i} \cdot \nabla \theta_i = q_i^{sat} \rho D_i \cdot \nabla \ln(1-\theta_i)$$

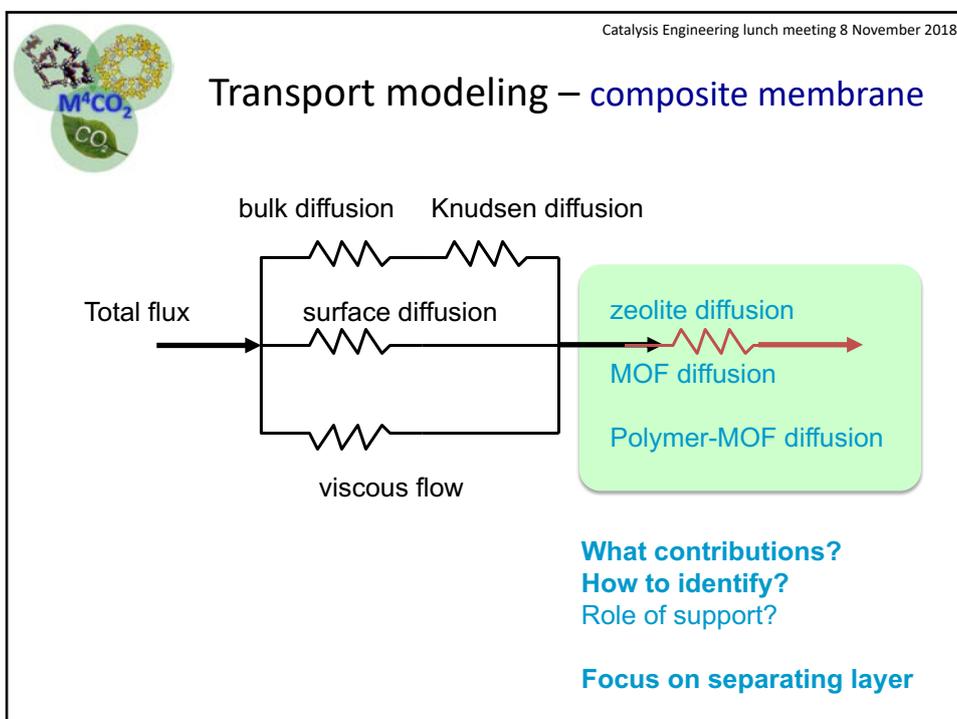
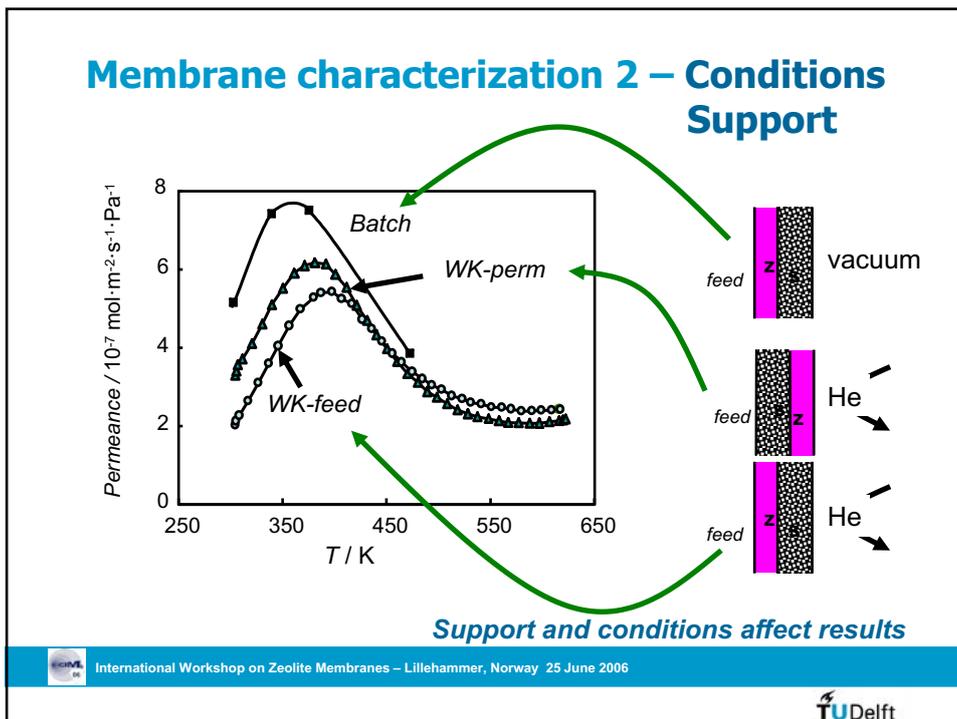
- Continuum description, no topology included
- Adsorption equilibrium both sides
- Diffusional transport rate determining
- This case:
 - D_i loading independent
 - Langmuir adsorption

Essential:
Adsorption data
Partial pressures at both sides

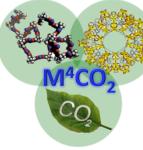
$$N_i = q_i^{sat} \rho D_i \cdot \frac{\ln\left(\frac{1+K_i p_{i,0}}{1+K_i p_{i,\delta}}\right)}{\delta}$$

International Workshop on Zeolite Membranes – Lillehammer, Norway 25 June 2006





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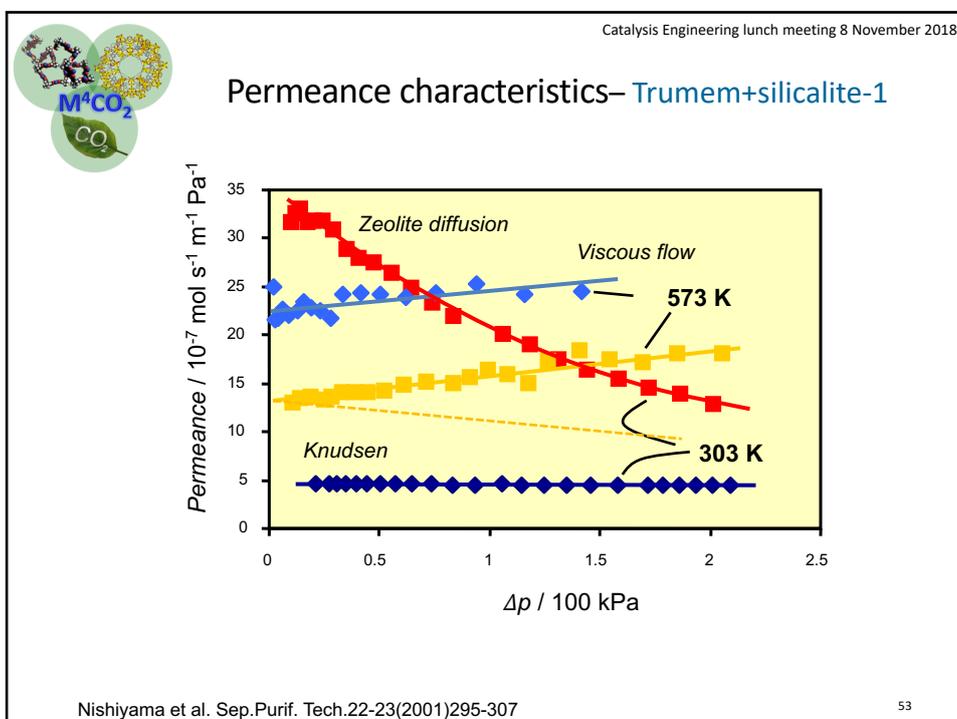
Transport mechanisms - Permeance Π_i

- Viscous flow
support, large defects
- Molecular diffusion
support, large defects
- Knudsen diffusion
small pores, low p
- Activated Knudsen
zeolite, micropores
- Zeolitic diffusion
zeolite

$$\Pi_i = \frac{N_i}{\Delta p_i}$$

	p, T dependency gas
$\Pi_i = -\frac{1}{RT} \cdot \frac{g}{\delta} \cdot \frac{r_0^2}{\eta_i} \cdot \bar{p}_i$	$\propto T^{-2}, p_i$
$\Pi_i = -\frac{1}{RT} \cdot \frac{g}{\delta} \cdot D_{ij}$	$\propto T^{0.75}, p_i^{-1}$
$\Pi_i = -\frac{1}{RT} \cdot \frac{g}{\delta} \cdot D_i^{Kn}$	$\propto T^{-0.5}, p_i^0$
$\Pi_i = -\frac{1}{RT} \cdot \frac{g}{\delta} \cdot D_i^g$	$\propto T^{-0.5} \exp(T^{-1}), p_i^0$
$\Pi_i = \frac{\rho \cdot c_i^{sat} \cdot g \cdot D_i^s \cdot \nabla \ln(1-\theta_i)}{\Delta p_i}$	$\propto f(T, p_i)$

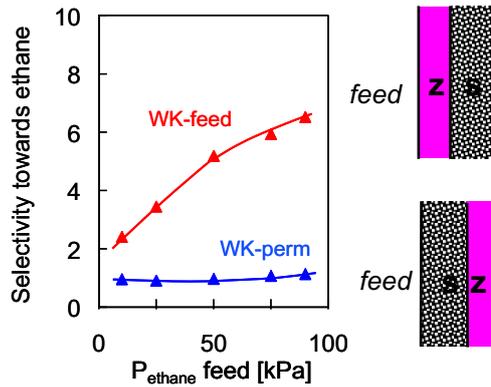
Fingerprint transport mechanism



Effect of support layer: separation

- Separation of ethane/methane mixtures
- Different experimental configurations
(303 K, $P_{tot}=101$ kPa)

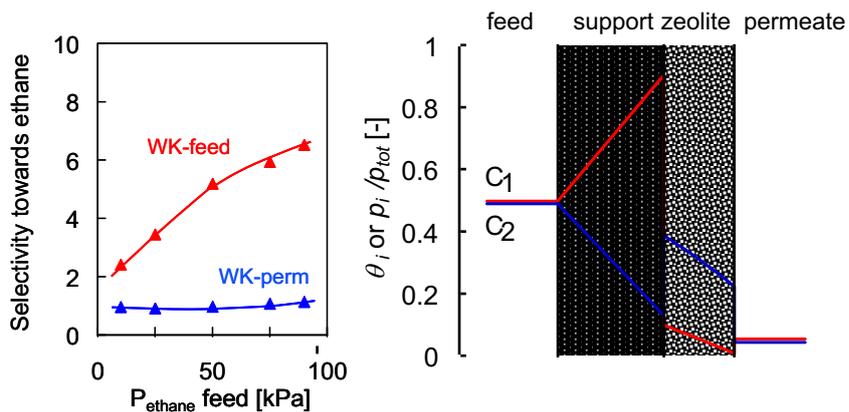
- Selectivity is lost when membrane is reversed



International Workshop on Zeolite Membranes – Lillehammer, Norway 25 June 2006



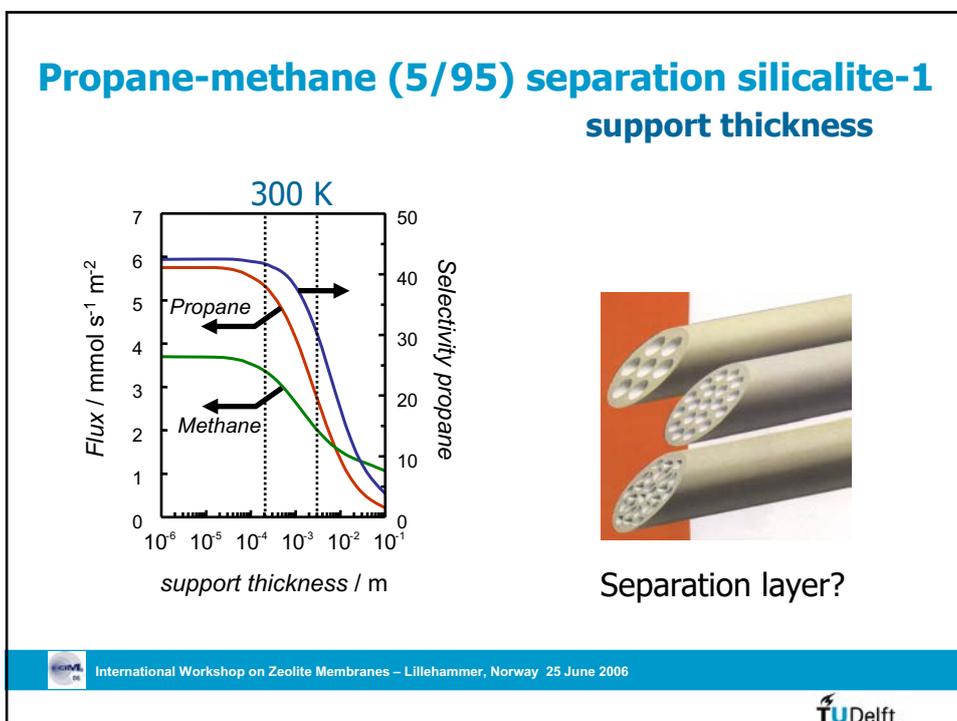
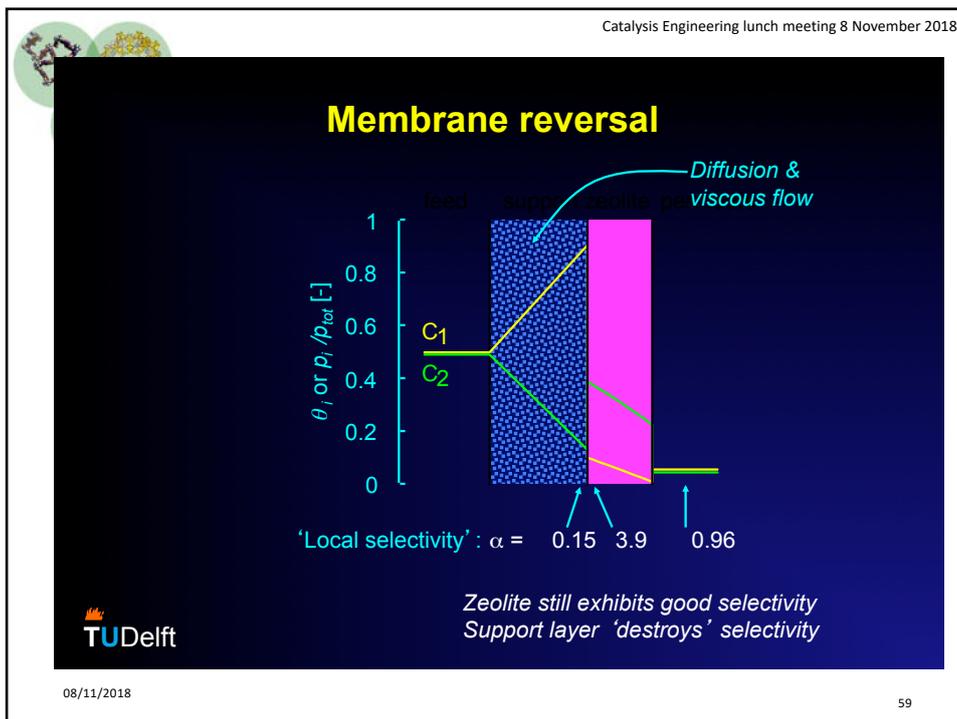
Effect of membrane orientation on separation

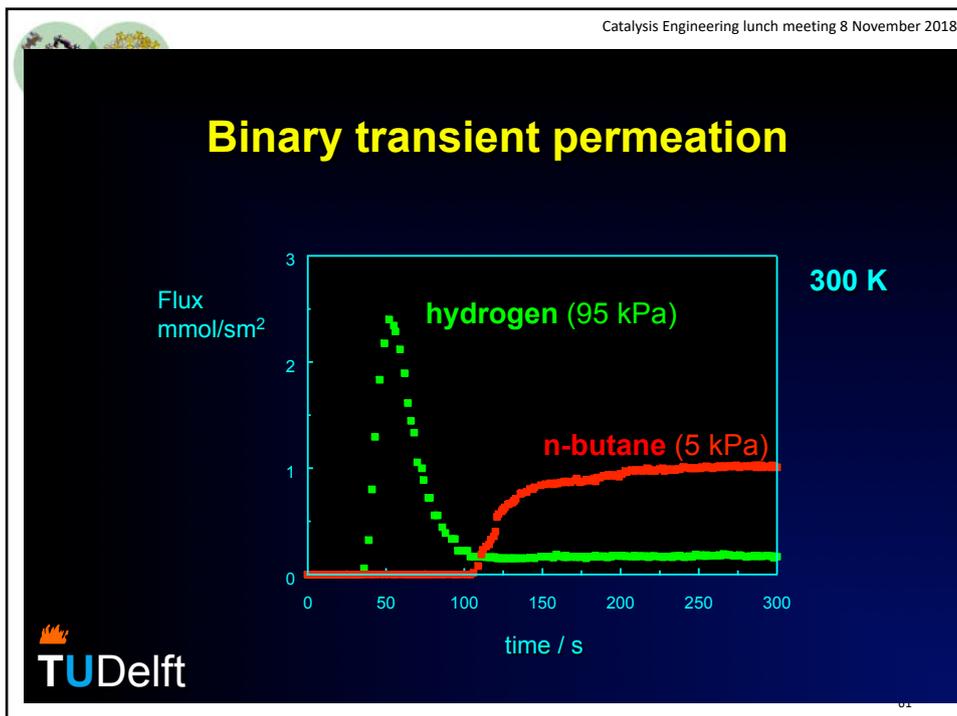


- Zeolite layer facing permeate side: Support becomes limiting factor
- Zeolite layer performs well: concentration polarization

International Workshop on Zeolite Membranes – Lillehammer, Norway 25 June 2006







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Modeling mixture separation

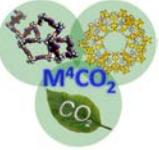
- Next time

Adsorption control Diffusion control Molecular sieving

Kapteijn, F.; Zhu, W.; Moulijn, J. A.; Gardner, T. Q., Zeolite membranes: modeling and application. In *Structured catalysts and reactors, second edition*, Cybulski, A.; Moulijn, J. A., Eds. CRC Taylor & Francis: Boca Raton, USA, 2006; pp 700-746.

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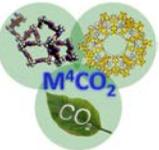


What about (pure) MOF membranes?

- Available literature
 - Like zeolite membranes: hard to make
 - Gas permeation data shows similarity with zeolites
 - Separation more fuzzy than zeolites
 - (local) Flexibility of structure, hardly any sieving example
 - Less clear distinction between molecular size
 - Adsorption effects sometimes visible

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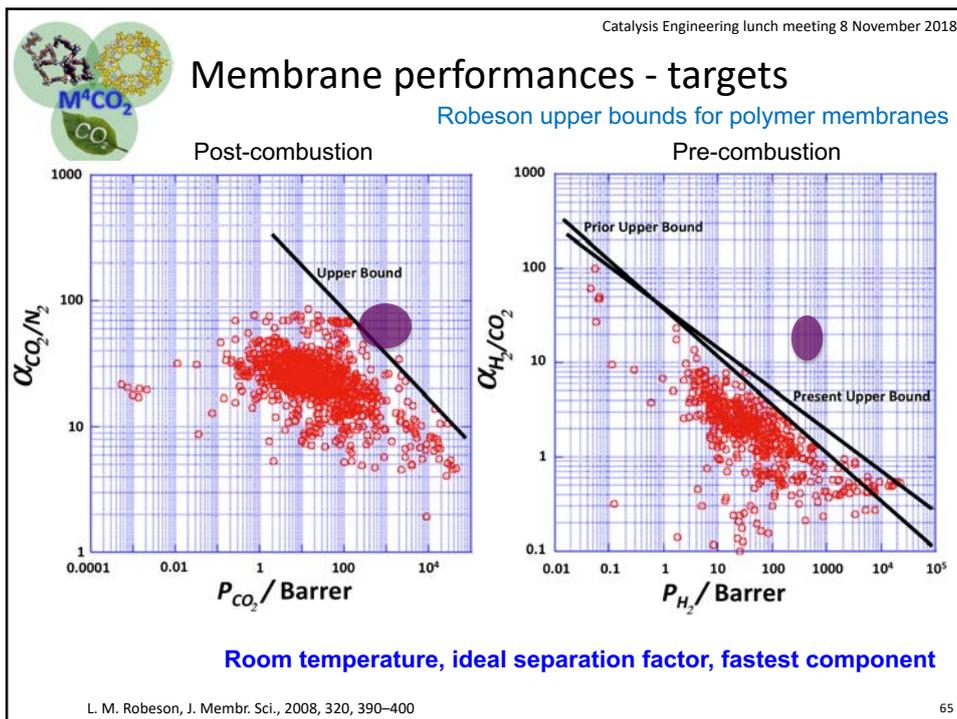
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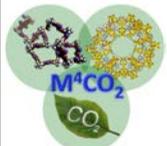
What about Polymer membranes?

- Available literature
 - Single phase mode – sorption-diffusion
 - Dual mode permeation – free volume transport also
 - Separation more fuzzy
 - (local) Flexibility of structure
 - Plasticization due to sorption (higher pressures)
 - Robeson trade-off

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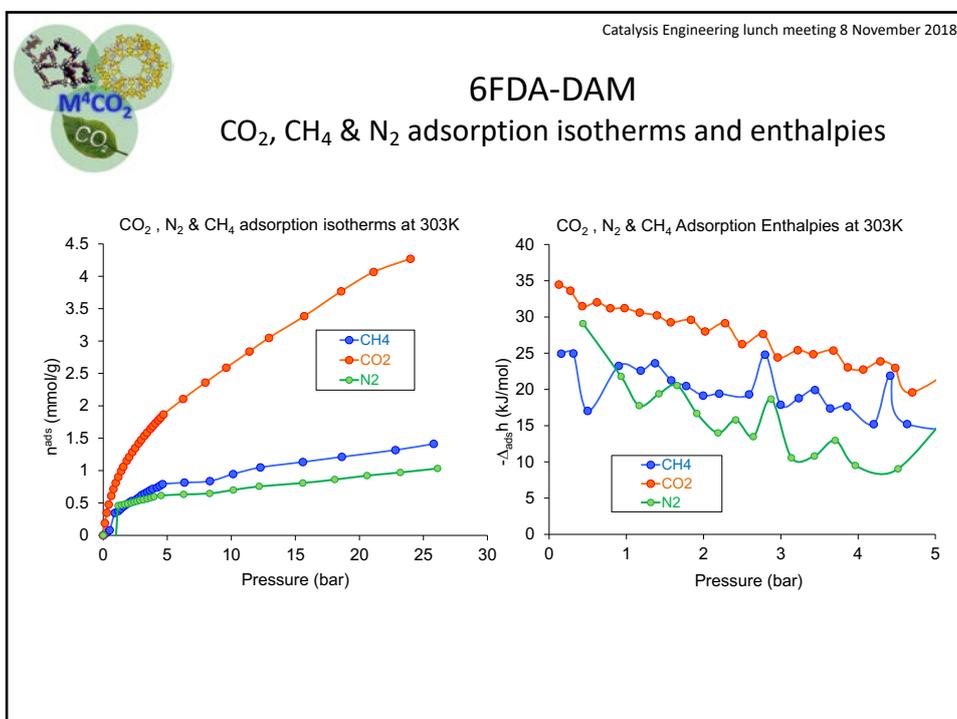
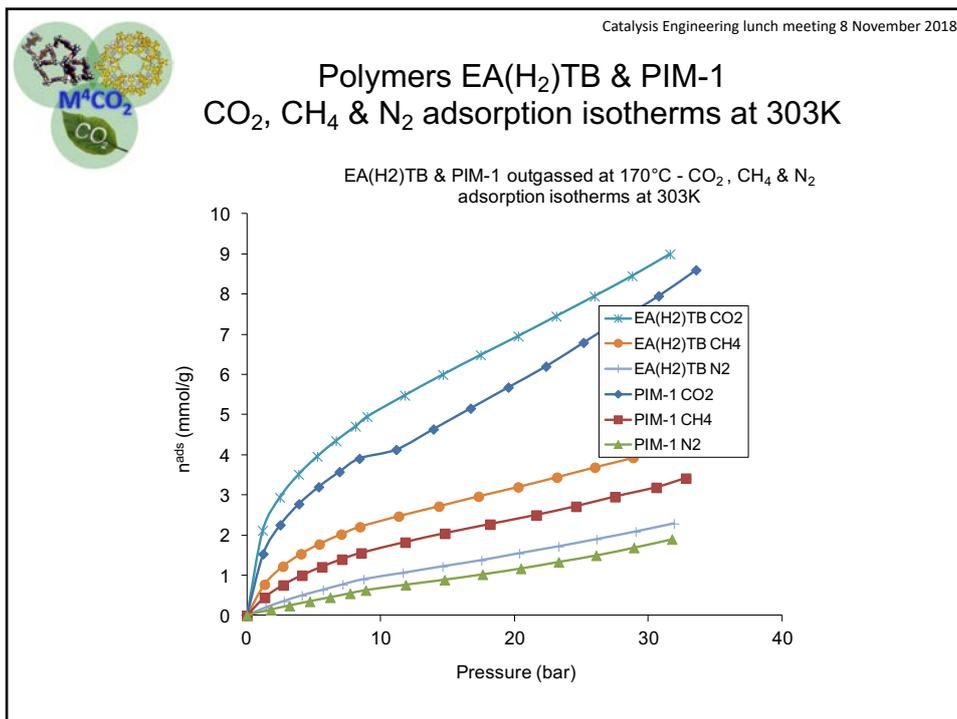
Adsorption isotherm polymers

- Solid polymers
 - Dissolution of permeants Sorption-diffusion
- Porous polymers
 - Adsorption in pores ('free volume') Adsorption-diffusion
 - Dissolution Sorption-diffusion

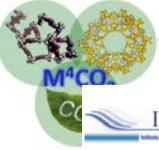
Connectivity?

Dual transport mode

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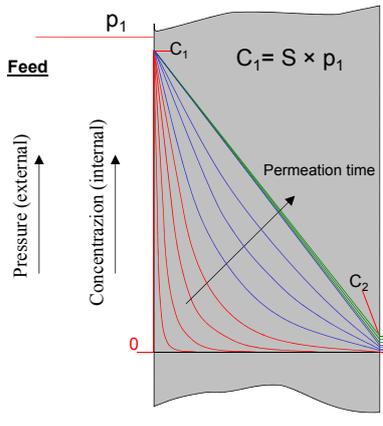
Polymer membranes – time lag method





Non-stationary permeation





Feed
Pressure (external) ↑
Concentration (internal) ↑

$C_1 = S \times p_1$

Permeation time

Permeate
Pressure (external) ↓
Concentration (internal) ↓

0

p_1 C_1 C_2 p_2

Immediately after exposure of the membrane to the gas or to the vapour, an equilibrium concentration is reached at the interface of the membrane and the gas phase at the feed side.

Subsequently, the permeant starts diffusing into the membrane and if $p_1 \gg p_2$ a linear concentration profile will be reached in the membrane after some time.

The speed with which the stationary state is reached depends on the diffusion coefficient.

3 stages of permeation:
 1) Penetration
 2) Transient
 3) Stationary

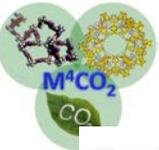
MFCO₂ Workshop 2015

Consiglio Nazionale delle Ricerche

John C Jansen, CNR

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Polymer membranes – time lag method





Permeation curve : expansion of series



$$p_i = p_0 + \left(\frac{dp}{dt}\right)_0 \cdot t + \frac{RT \cdot A \cdot l}{V_p \cdot V_m} \cdot p_f \cdot S \left(\frac{D \cdot t}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D \cdot n^2 \cdot \pi^2 \cdot t}{l^2}\right) \right)$$

Baseline slope (leaks)

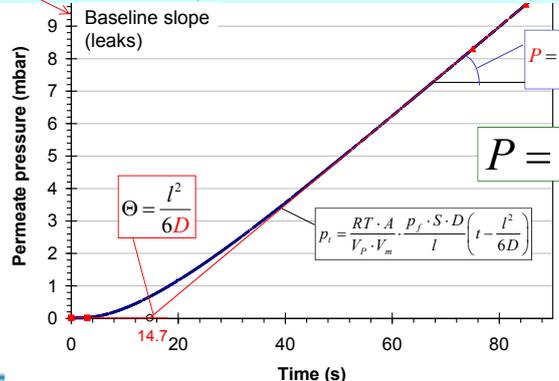
Offset (starting pressure)

$\Theta = \frac{l^2}{6D}$

$P = \frac{V_p \cdot V_m \cdot l}{RT \cdot A \cdot p_f} \cdot \frac{dp}{dt}$

$P = D \cdot S$

$p_i = \frac{RT \cdot A \cdot p_f \cdot S \cdot D}{V_p \cdot V_m \cdot l} \left(t - \frac{l^2}{6D} \right)$



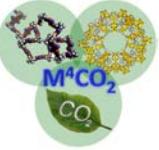
MFCO₂ Workshop 2015

Ricerca

John C Jansen, CNR

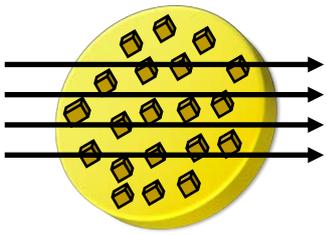
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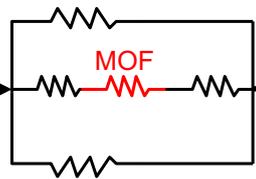


MOF-based mixed matrix membranes

- Polymer continuous phase
- MOF filler, below percolation

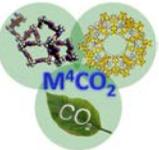


Flux →



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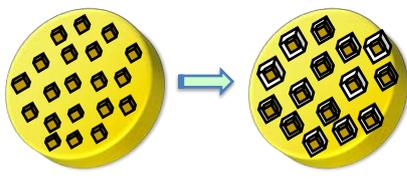
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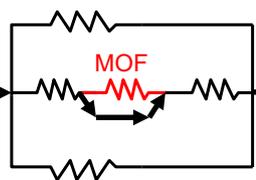
MOF-based mixed matrix membranes

What if?

- Polymer continuous phase
- MOF filler surrounded by gaps



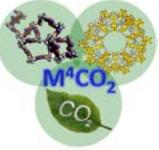
Knudsen diffusion ?



- Bypassing
 - higher flux
 - same selectivity

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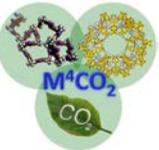
What M⁴ configuration do we want? What properties of materials?

- Models don't capture performance
 - Volume fraction filler important parameter - **loading**
 - Control transport pathways
- Highly dispersed MOF, nanoparticles
 - Large pore – polymer penetration?
 - Large aspect ratio filler (3rd gen.)
 - Hollow spheres, core shell (3rd gen.)

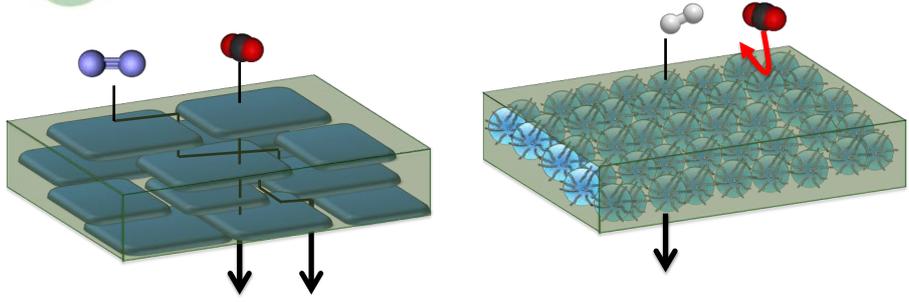
<ul style="list-style-type: none"> • Molecular sieving (H₂) • Adsorption-diffusion (CO₂) 	<ul style="list-style-type: none"> - MOF, polymer - high polymer permeability selective adsorption
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Flux - Selectivity improvements



High flux polymers:

- Selective fillers
- Increased path-lengths
- tuned aspect ratio

Selective polymers:

- Flux improvements
- Shorter effective path-lengths

M4CO274



Take home messages

- Experimentation
 - Check assumptions – are these obeyed?
 - Module design important
 - Beware of sweep gas backpermeation – Ar as sweep better?
 - Estimate uncertainty in selectivity
 - Verify mass balances
- Important characteristics materials (MOF and polymer)
 - (Ad)sorption isotherms, temperature dependency
 - Diffusivities – different transport mechanisms, not constant
 - Swelling, aging, dual mode,...
- Modelling
 - Predictive models M^4 do not exist, simulations important