Zeolitic-nanoblock membranes for gas separation

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SBO Project funded by IWT

Membrane synthesis

- Standard zeolite membranes :

  hydrothermal synthesis

  with in-situ growth, or seeding and secondary growth
- Our method :

  stacking from nano zeolite-precursors

  from clear solution

Nano zeolite-precusors

R&D in different groups :

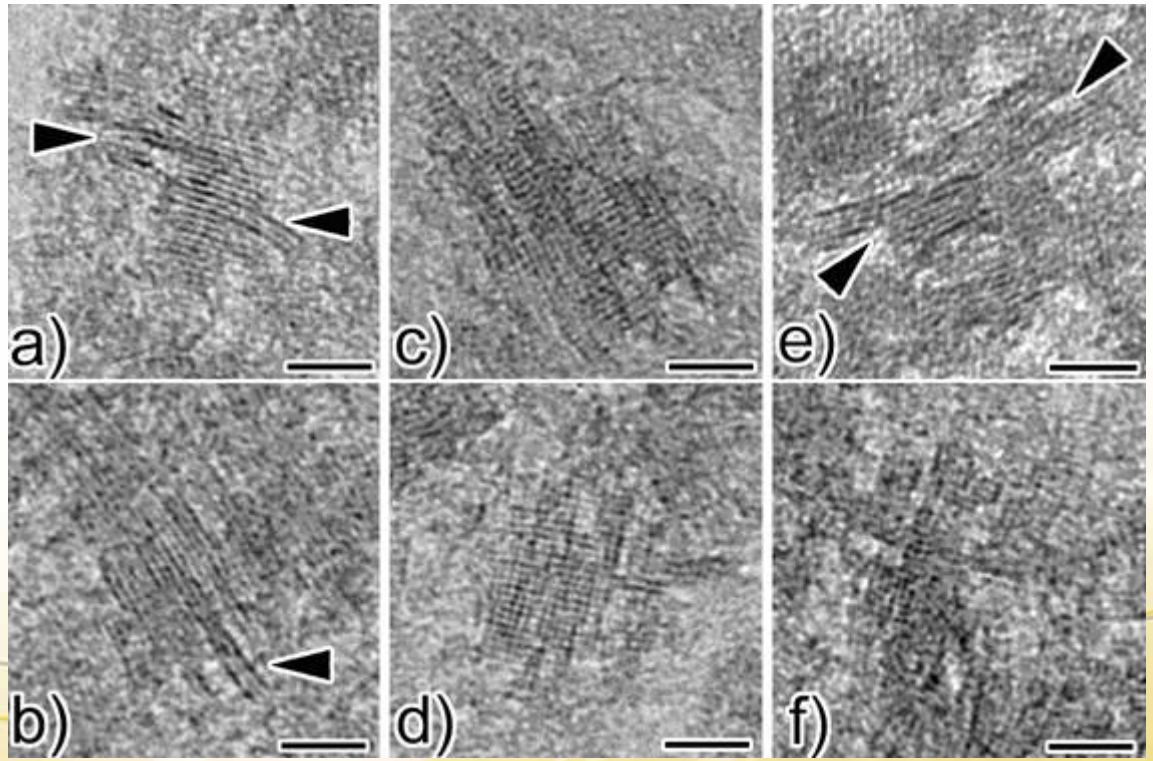
[Tsapatsis], [Schoeman], [Corma], [Martens] :

- In clear solution
- With specific ratio of TPA/SiO_2 in solution
- Existence of precursor nanoparticles of a few nm
  by SAXS, DLS, TEM, HRTEM, AFM
- Contribute to crystal growth by oriented aggregation
- Structure of precursors in debate :
  amorphous or crystalline ?

Nano zeolite-precursors

- TEM on silicalite clear solution, aged at RT (UAntwerpen)

  D. Liang, Van Tendeloo et al, submitted J. Phys. Chem. C.



Black bar = 10 nm

Nano zeolite-precursors

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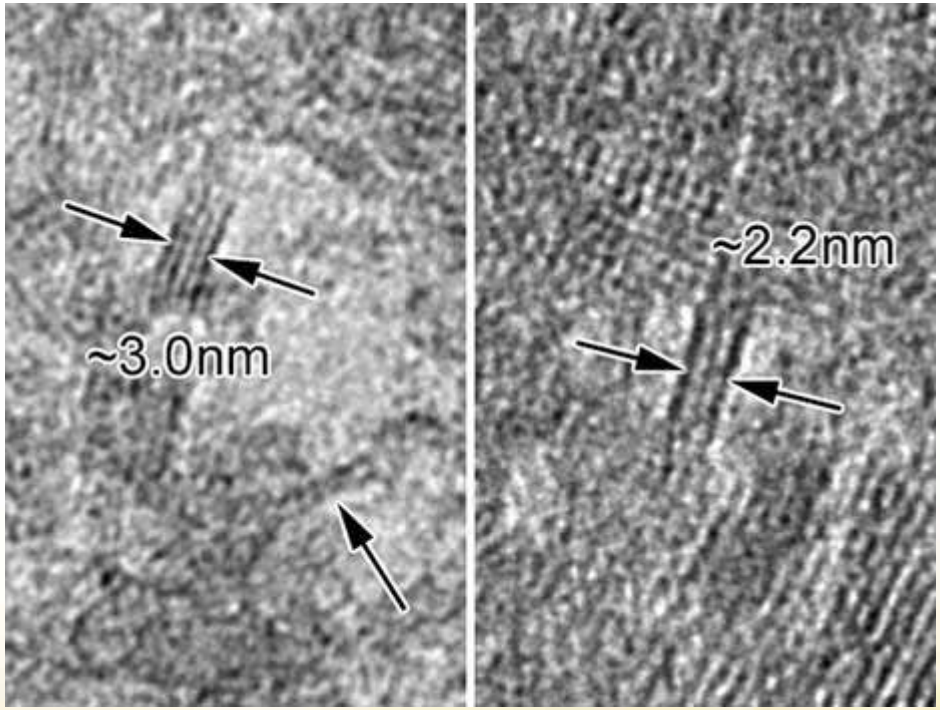
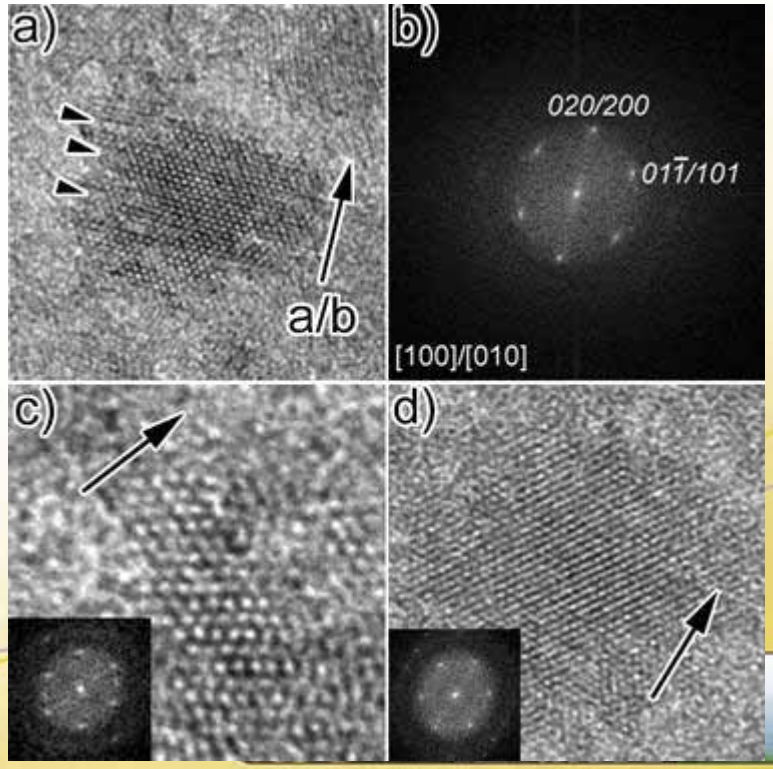




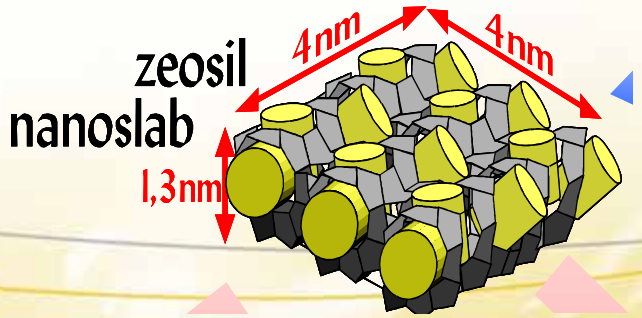
Crystalline nanoblocks !

Zeolitic nanoblocks

View of K.U.Leuven

Kirschock et al., Angewandte Chemie, 40, 2637; 2001

- Basic unit = rectangular nanoblock
- Nanoblocks have zeolite-like properties = zeolitic
- Nanoblocks are 4x4x1.3 nm^3
- Can be used as building units



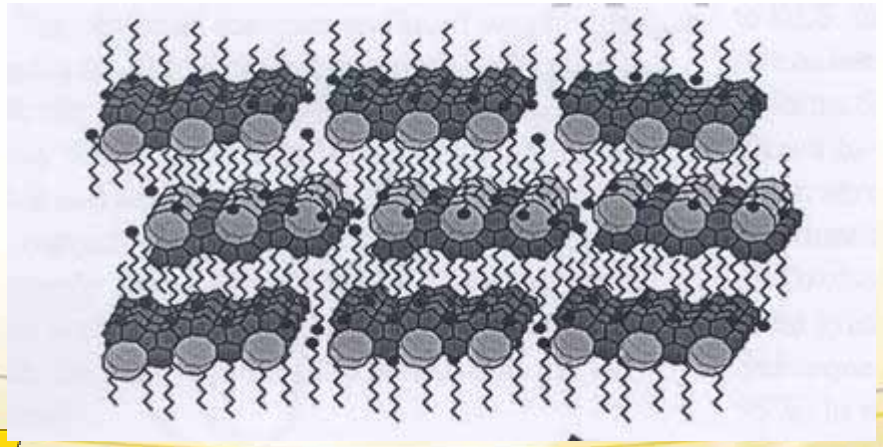
- 9 short zig/zag channels along a-axis
- 3 long,straigth channels along b-axis
- channels 0.5 nm wide

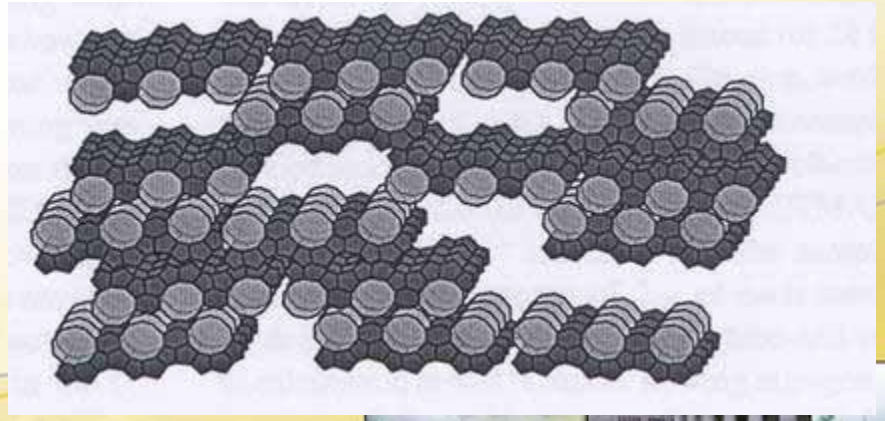
[X]

Zeogrid powder

Kremer at al., Adv. Funct. Mater., 12, 286, 2002 (KULeuven)

- Nanoblocks can be stacked in an layered way
  with the use of appropriate surfactants
- Leads to micrometer large grains called zeogrid
- Zeogrid calcined has dual porosity : micropores + interblock voids

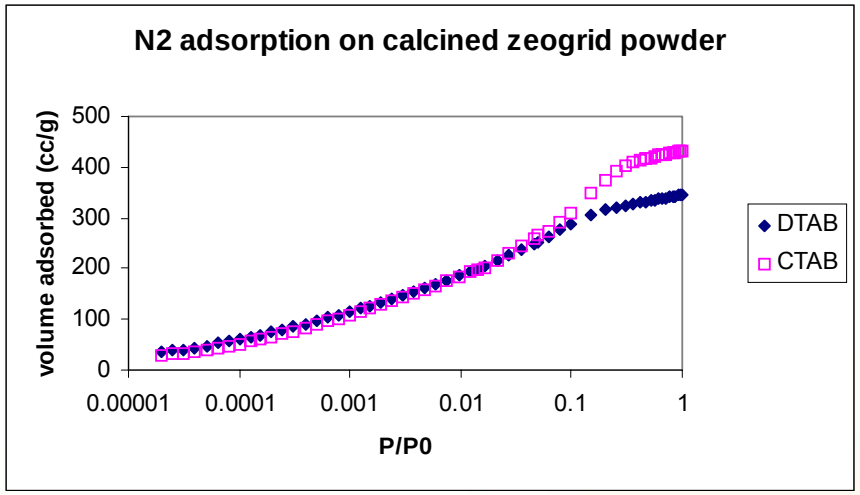




Zeogrid powder

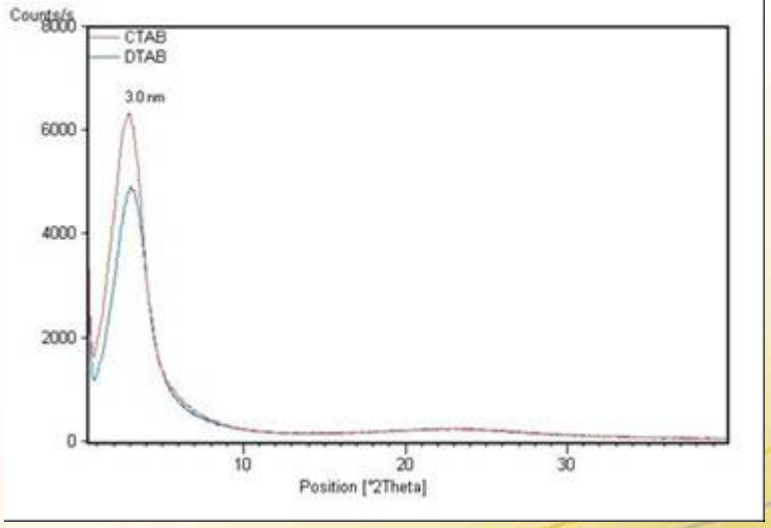
N_2 adsorption : **bi-porosity**

micropores + supermicropores



Low-angle XRD : **no zeolite**

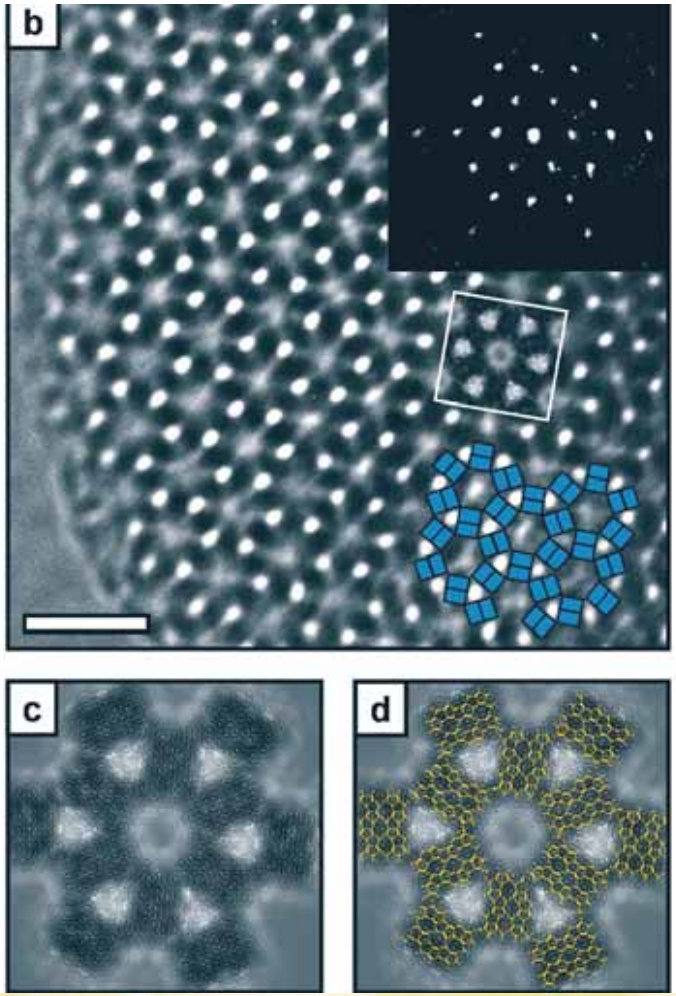
layering with repetition of 3 nm



sample	V(micro) cc/g	V(big micro) cc/g	S(tot) m^2/g
CTAB	0.14	0.53	1243
DTAB	0.14	0.40	948

Zeotile powder

Kremer at al., Adv. Mater., 20, 1705, 2003 (KULeuven)



Different way of stacking
with the aid of surfactants :

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Hexagonal stacking
of double nanoslab units

↓

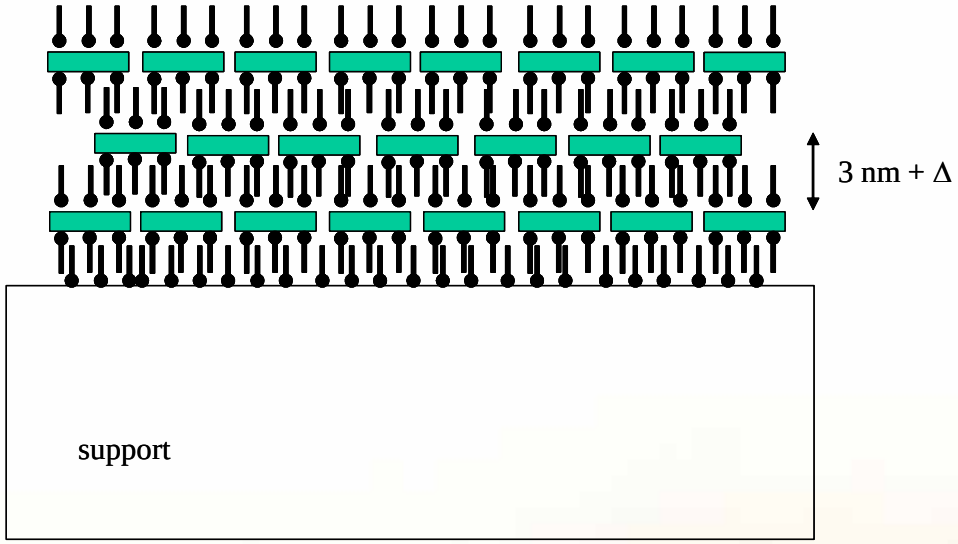
One dimensional channels
of ~3.5 nm

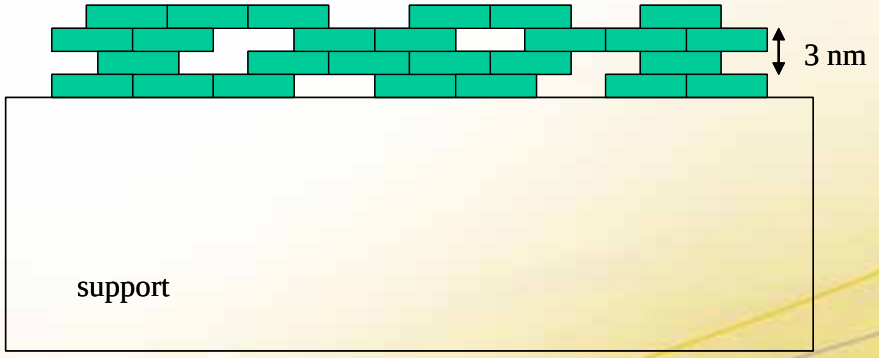
White bar = 10 nm
Images: UAntwerpen

Zeolitic-nanoblock membranes

- Zeogrid on porous support :

  dipping in solution of nanoblocks + surfactants



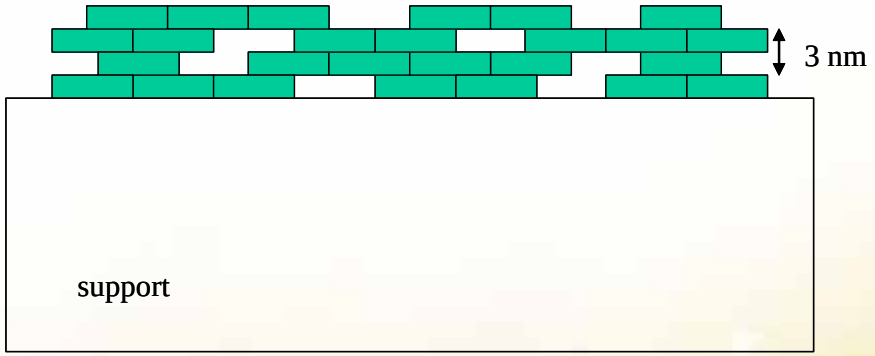


Calcination = removal of surfactant/TPA, no crystal growth

Zeolitic-nanoblock membranes

Possible advantages :

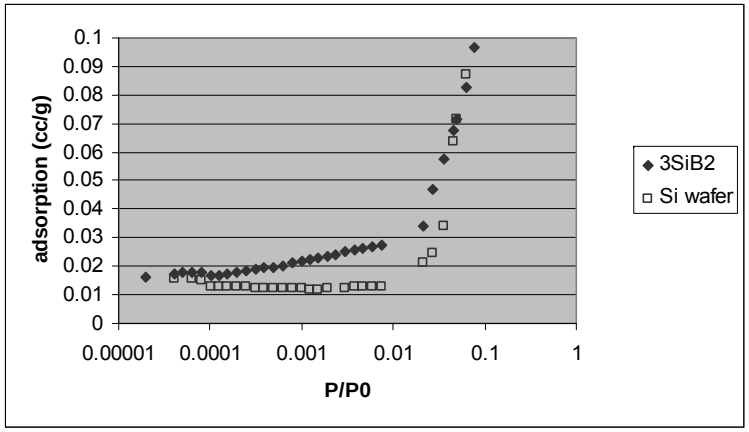
- thin membranes < 100 nm : high flux, crack free
- bi-porosity : extra high flux
- defect-free + entrance via nanoblock : high selectivity

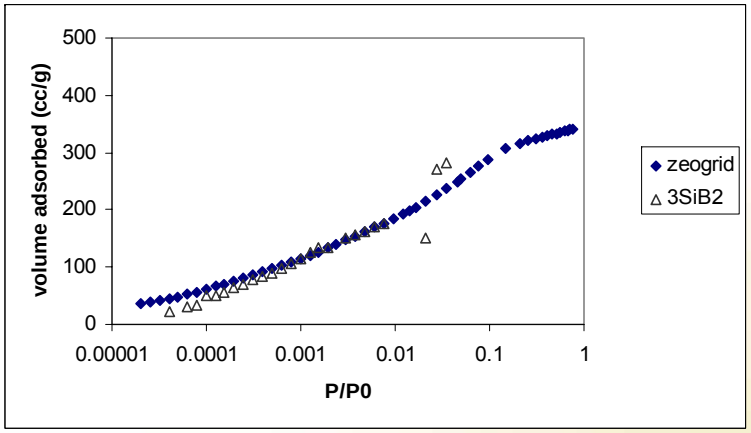


Goal : Potential of these membranes ?

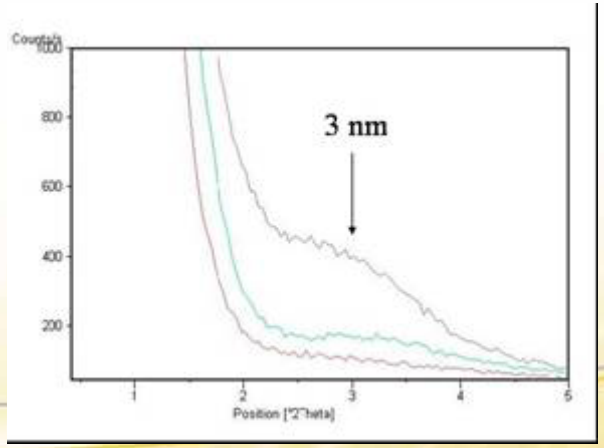
Preliminary tests : Zeolitic-nanoblock film on Si wafer

N_2 adsorption :





Low angle XRD :



Zeolitic film

~

zeogrid powder

Zeolitic-nanoblock membranes

Zeogrid layer on porous support :

- flat and tubular
- α-Al2O3/TiO2 (50-100 nm) + TiO2 (3 nm)

Quality test :

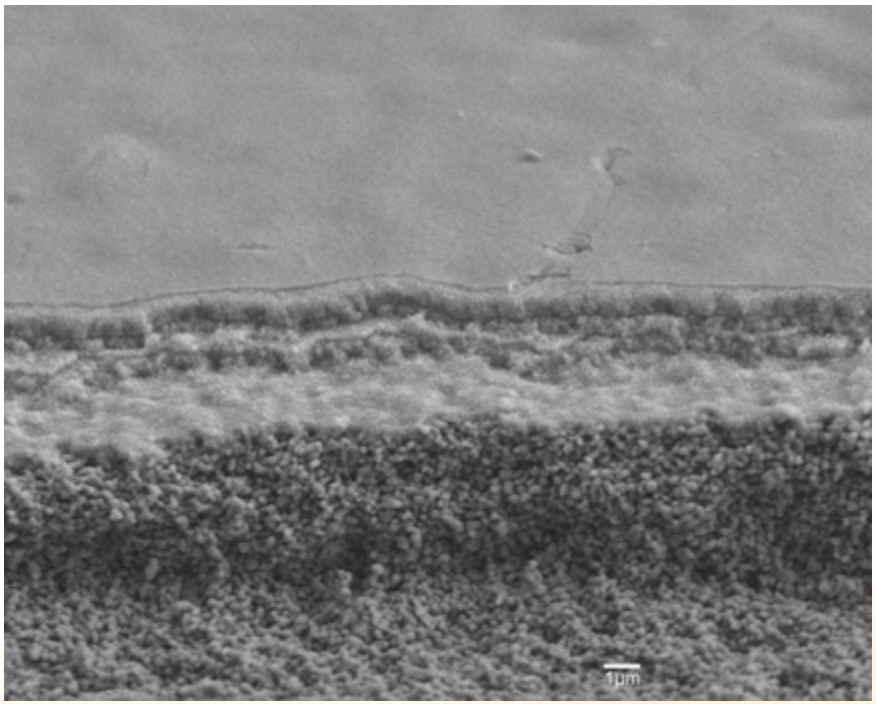
- NF with small PEG's in water (200, 600, 1500 Dalton)
- defect-free membrane has MWCO < 200 D + low flux
- R(1500D) measures defects and supermicropores > 1.5 nm

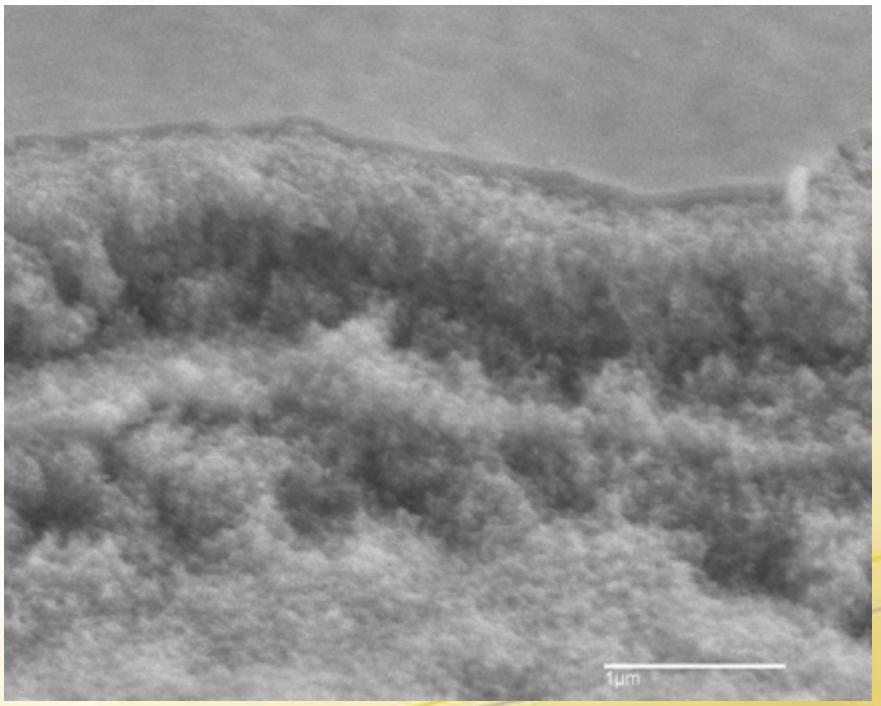
Current quality on tubes :

- MWCO : 500 à 1000 D, R(1500D) > 95%

FESEM characterisation

on a fracture plane, 30° tilt





TEM characterisation

100nm

- disordered pore structure of few nm
- no ED = no regular stacking

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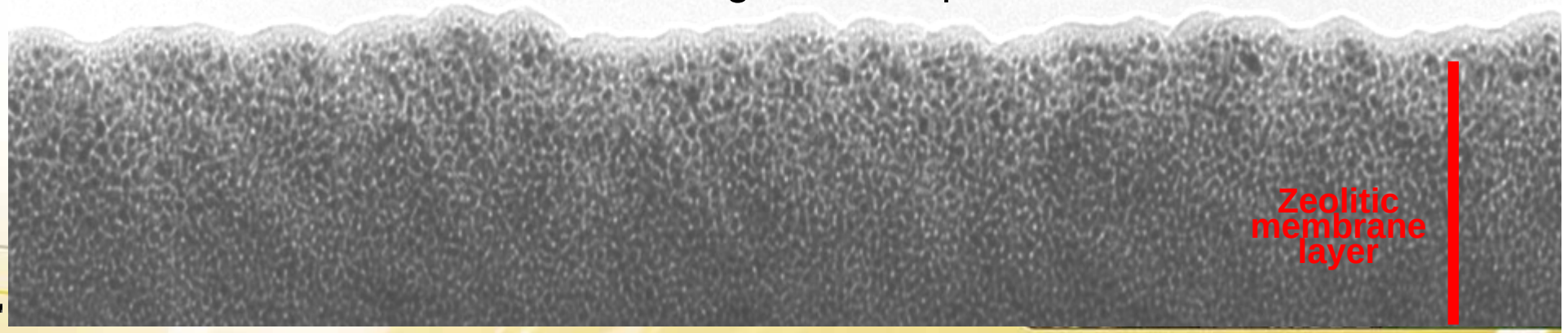
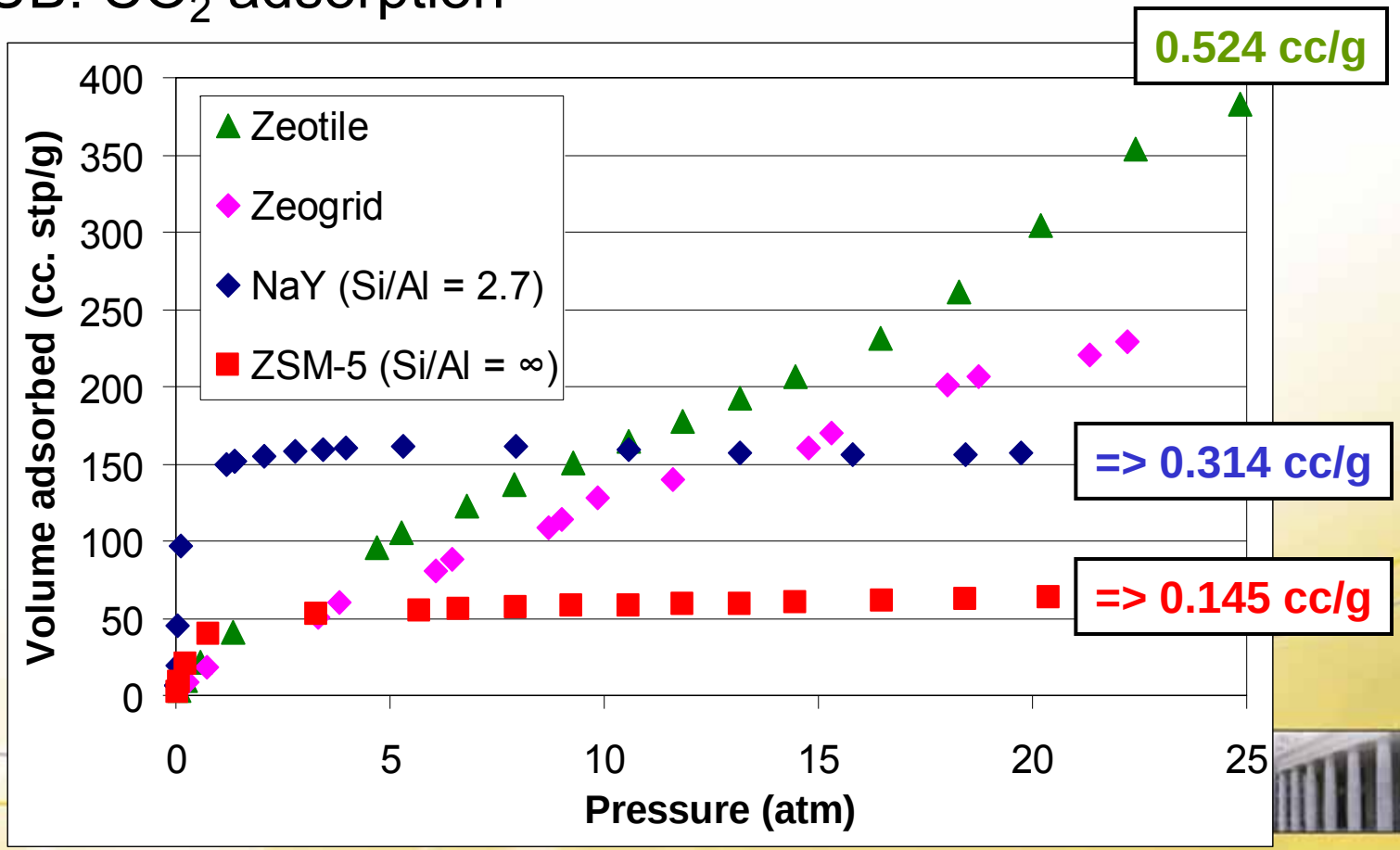
entrance through supermicropores

Measurement : G. Van Tendeloo, D. Liang, UAntwerpen

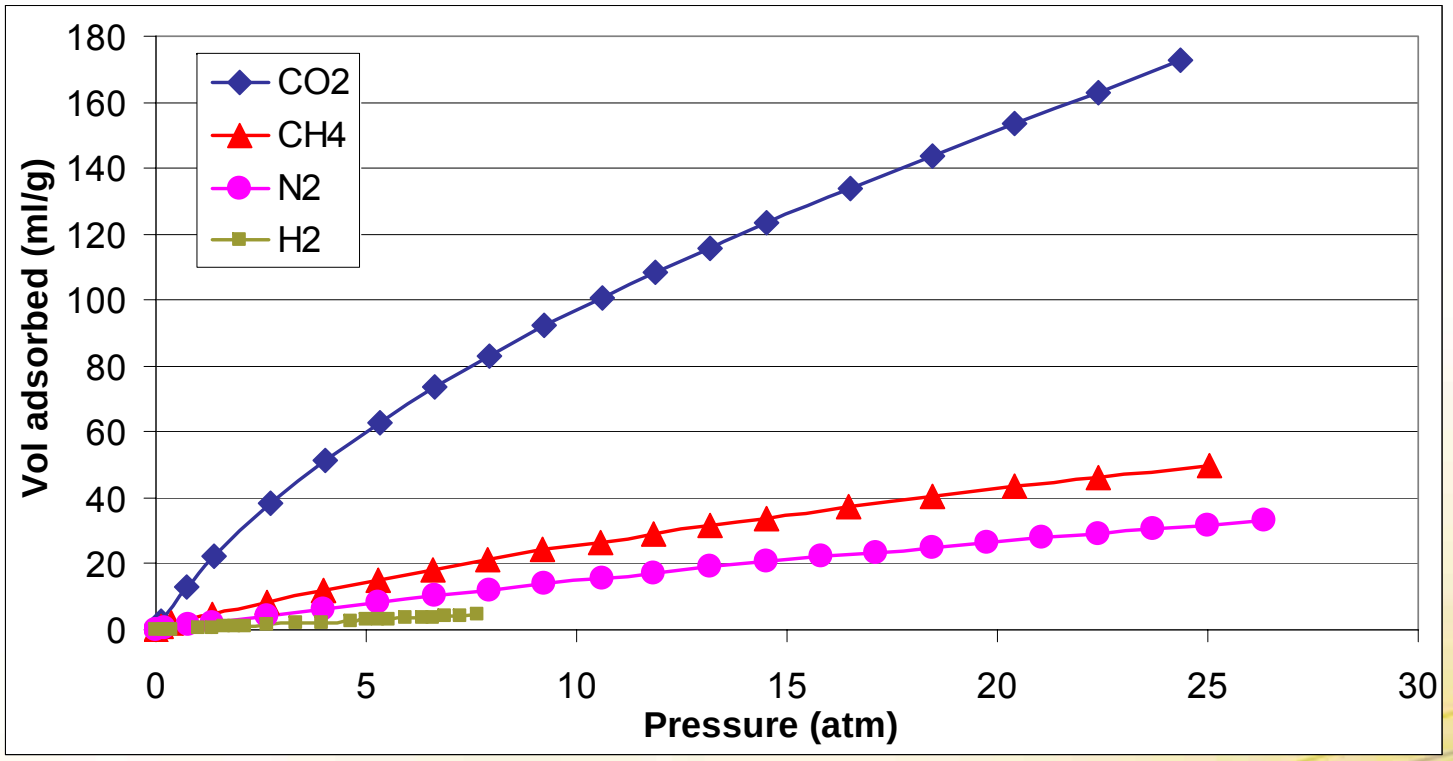


Adsorption measurements on zeotile/zeogrid powder at RT

VUB: CO_2 adsorption



Adsorption measurements on zeogrid powder at RT



Measurements: VUB

powder interesting as CO_2 adsorbent

membranes interesting for CO_2 gas separation

Single gas separation measurements

gas	Permeability at RT (l/hm^2.bar)	Permeability at 200°C (l/hm^2.bar)
N_2	M1 : 1290 M2 : 4500	M1 : 1800 M2 : - -
SF_6	M1 : 960 M2 : 1950	M1 : - - M2 : - -
H_2	M1 : 4200 M2 : 11700	M1 : 5850 M2 : - -
CO_2	M1 : 1500 M2 : 3300	M1 : 2100 M2 : - -

1000 l/hm^{2}bar = 1,24 10^{-7} mol/m^{2}sPa

- permeabilities independant of TMP
- ~ Knudsen permselectivities
- permeabilities increase with T

Double gas separation measurements

gas	Selectivity	Permeability at RT (l/hm^2.bar)
N_2/CO_2 88/12	0.6 (1.25)	3000
H_2/CO_2 40/60	1.7 (4.7)	9000

Permeate side : P = 1 atm

TMP = 1 or 2 bar

↓

CO_2 adsorption
High fluxes
Low selectivities

Conclusions for zeolitic membranes

- SEM/TEM show nice membranes with clear bi-porosity
- Current quality : 500 à 1000 D, R(1500D) > 95%
- Adsorption on powder shows extra high CO_2 capacity at high pressures : clear potential
- First gas separation results :
  - Single gas separation shows
    ~ Knudsen behavior, high fluxes increasing with T
  - Double gas separation at low pressure shows
    CO_2 adsorption, high fluxes
- Gas separation measurements at high pressure planned