D. Alfredo Pacheco Tanaka

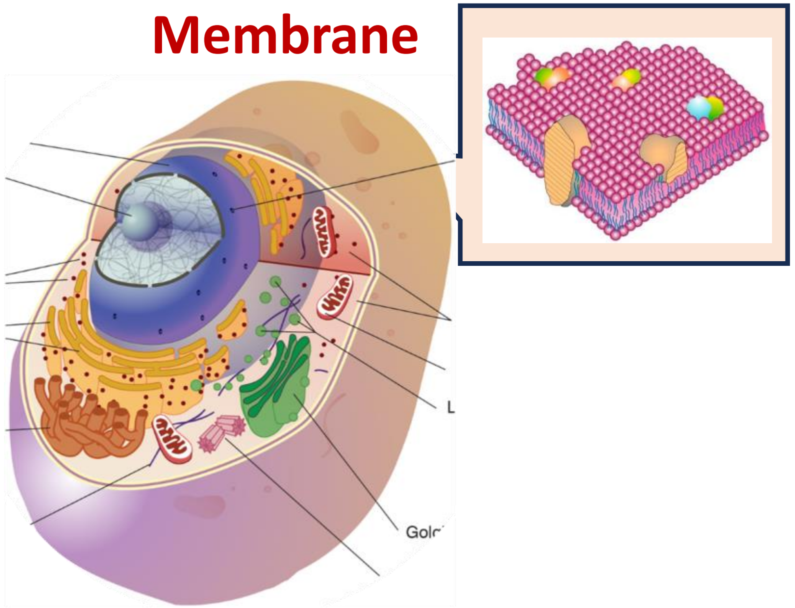
Pd and Carbon membranes for hydrogen separation

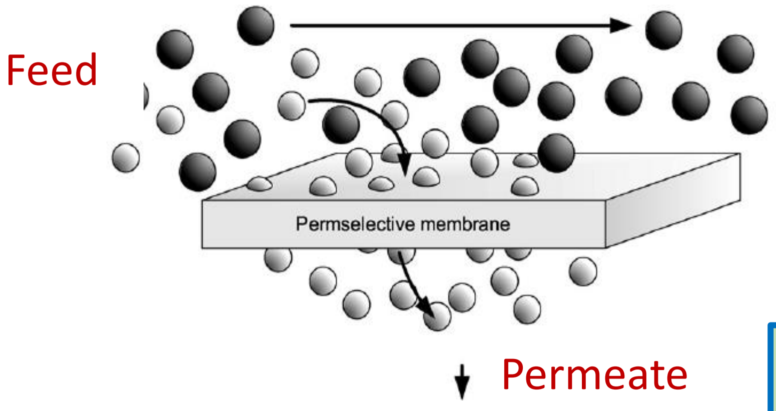
This work has received funding by the European Commission under Agreement 101112118.

Views and opinions expressed are however those of the author only and do not necessarily reflect those of the European Union nor the granting authority can be held resposable for them

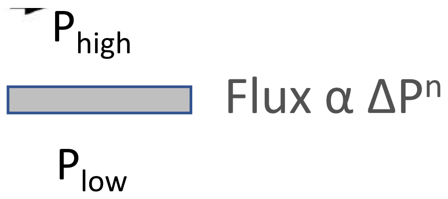
Synthetic membranes

Biological Membrane





Journal of Colloid and Interface Science 314(2):589-603



Objective

- ✓ **High selectivity**
- ✓ **High permeation**
- ✓ **Stable at operation conditions**
- ✓ **Cheap**

- Membranes
  - Polymeric
    - Porous
    - Dense
  - Mix matrix
  - Inorganic
    - Dense
      - Hydrogen (Palladium)
      - Oxygen (MIEC)
    - Porous
      - Silica
      - Zeolite
      - CMSM

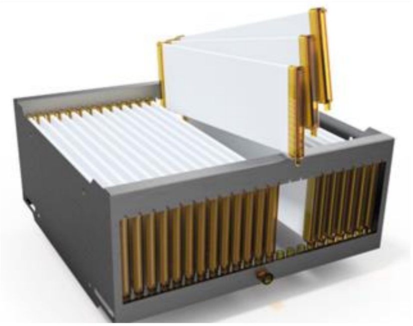
Microporous < 2nm

Polymeric membranes

Flat sheets

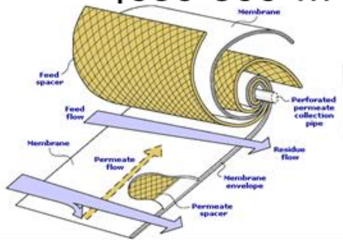
Plate and frame

[330-500 m^2/m^3]

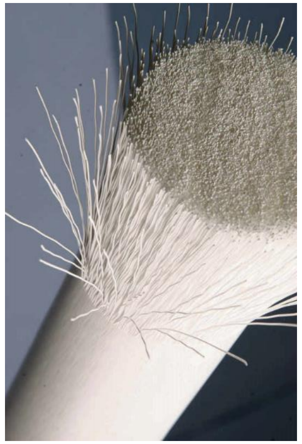


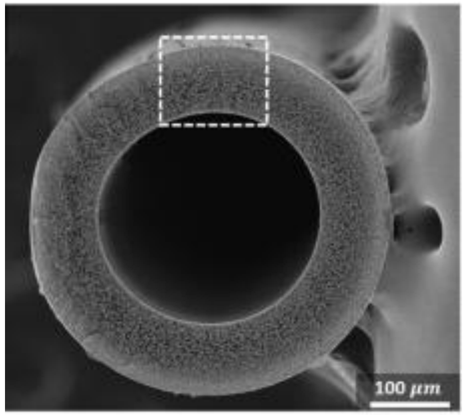
Spiral wound

[650-800 m^2/m^3]

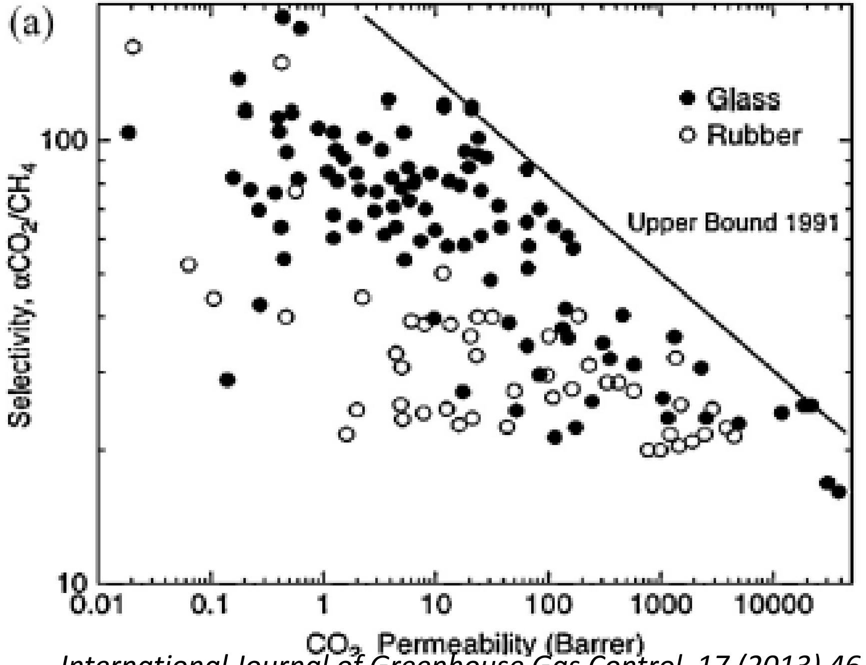


Hollow fiber
(< 0.5mm)





Robeson upper bond limit

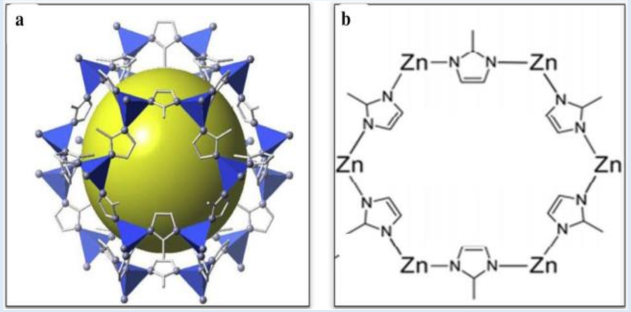


International Journal of Greenhouse Gas Control 17 (2013) 46–65

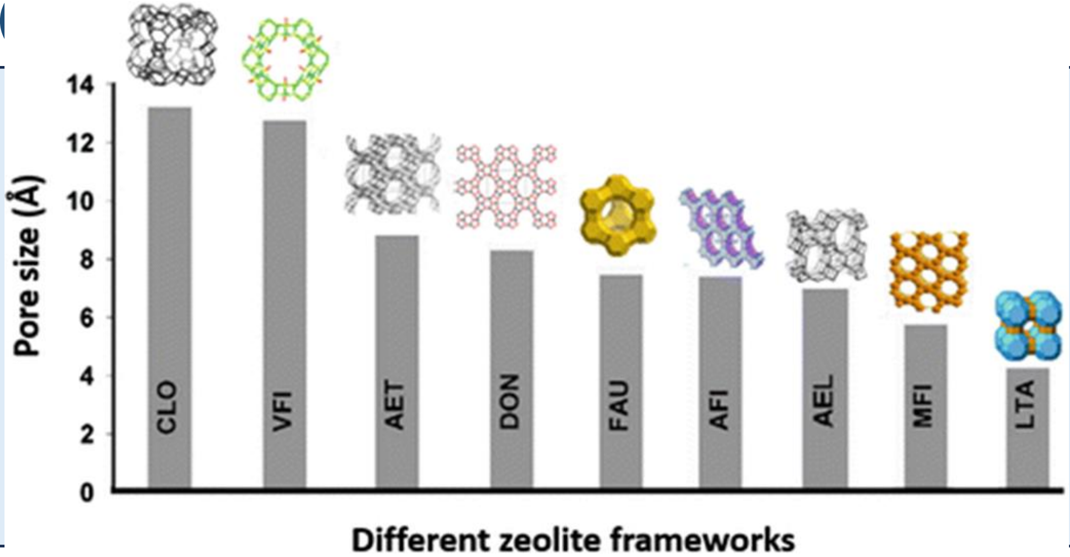
Mechanically and thermally not stable

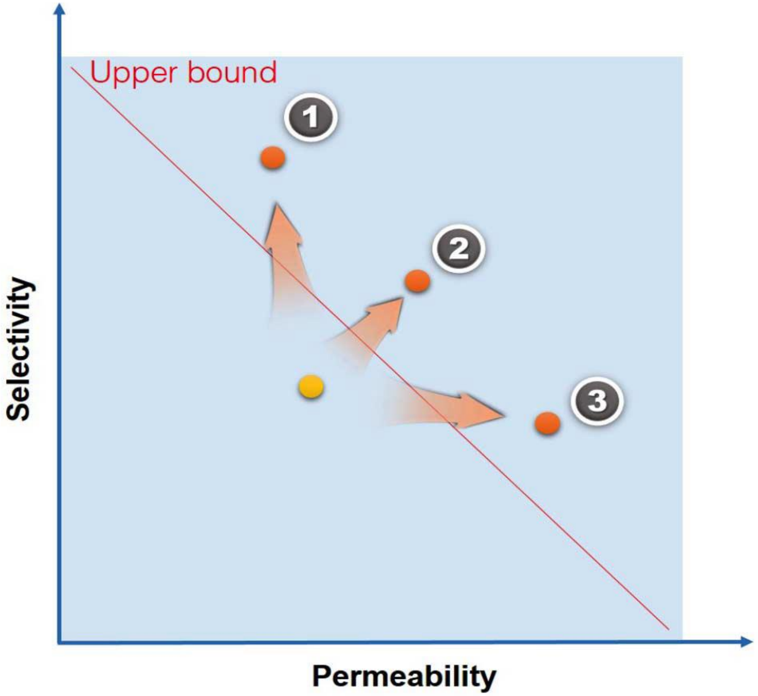
Mix Matric Membranes (

1



MOF Metal organic framework

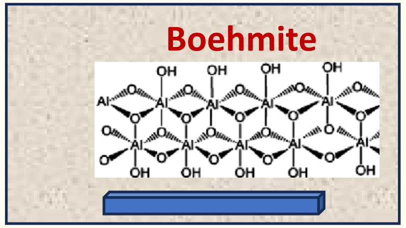




Park *et al.*, *Science* **356**, eaab0530 (2017)

2

Nano size or nanosheet shapes



3

- ✓ Interaction of nanoparticles (metals) with polymer

Increase stability,reduce polymer chain mobility

Improve permeation properties

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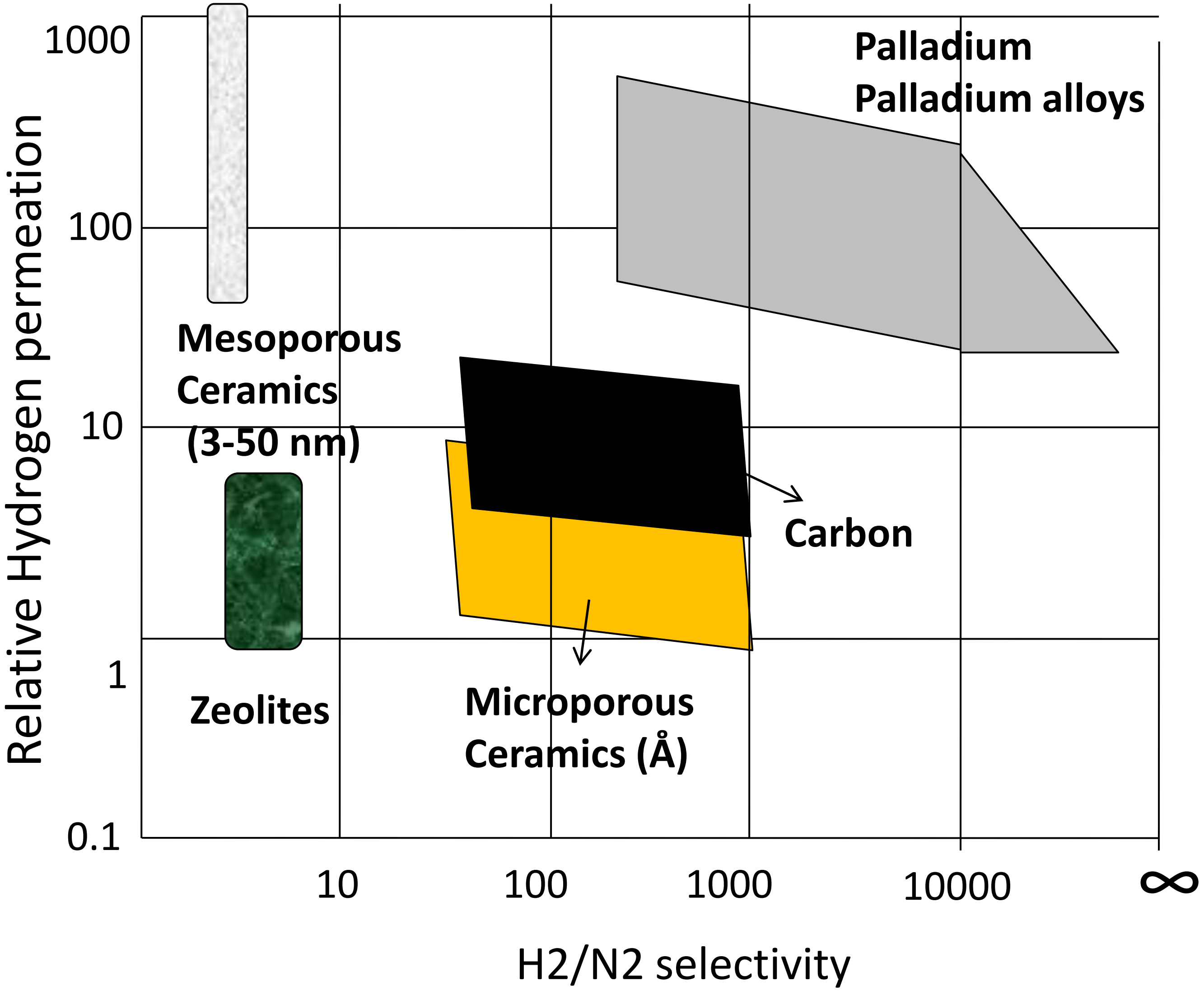
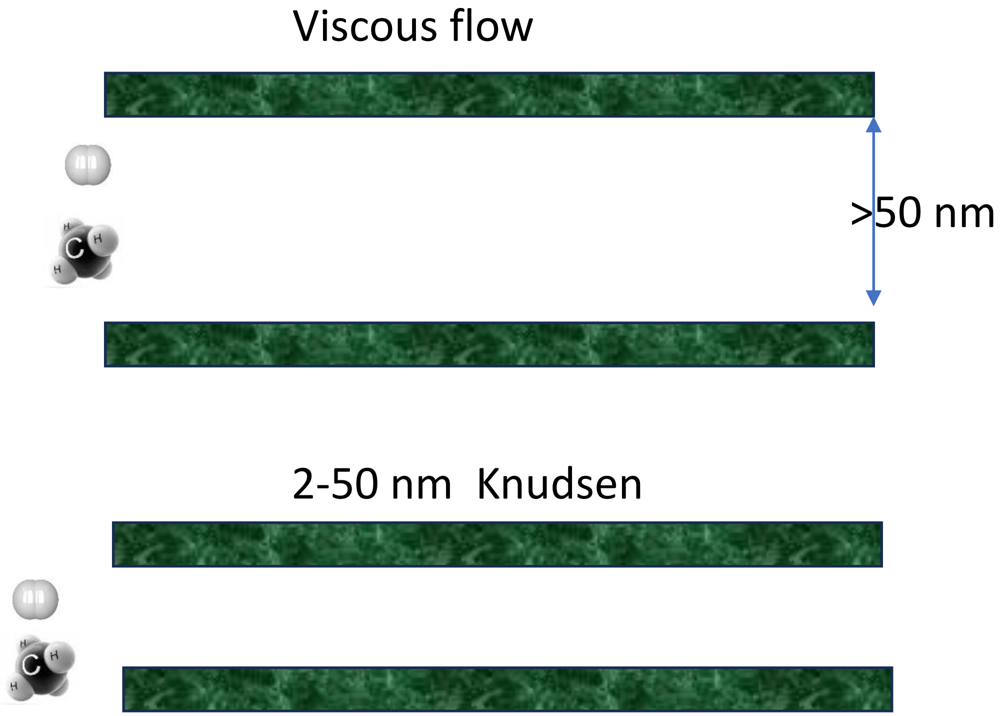
Permation of H2 against H2/N2 selectivity



Gas permeation on porous membranes



< 50 nm Knudsen separation $\frac{H_2}{N_2}$ $\sqrt{\frac{M_{N2}}{M_{H2}}}$ $\sqrt{\frac{28}{2}}$ **3.7**

$$Flux \alpha \frac{1}{\sqrt{T}}$$

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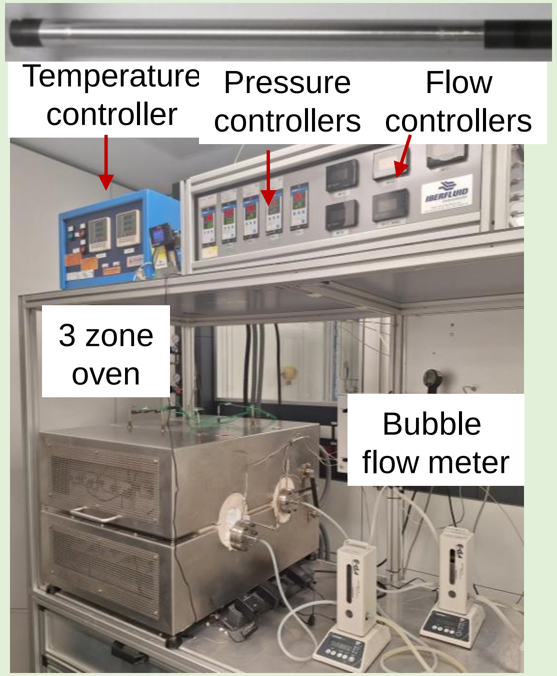
Gas permeation test for detection of defects



-Flow ml min^{-1}

- **Atmospheric pressure (P)**
- **Temperature (T)**

PV= nRT **mol/s**

A=membrane area

Flow/Area = Flux [mol m^{-2}s^{-1}]

Permeance = Flux/ΔP

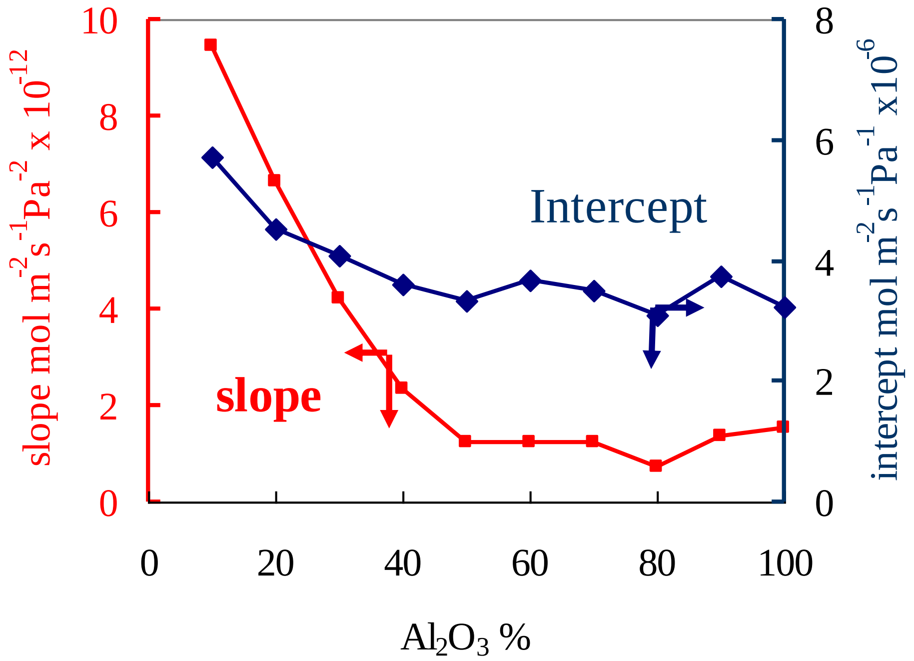
[mol m^{-2}s^{-1}Pa^{-1}]

2- 50 nm Knudsen flow **> 50 nm viscous flow defects**

Total permeance= Knudsen + Viscous

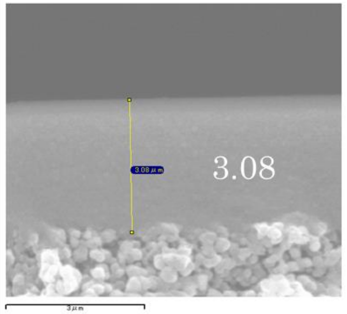
$$Permeance = \alpha + \beta . P_{av}$$

β=0 Kundsen permeance **β> 0** Kundsen + Viscous

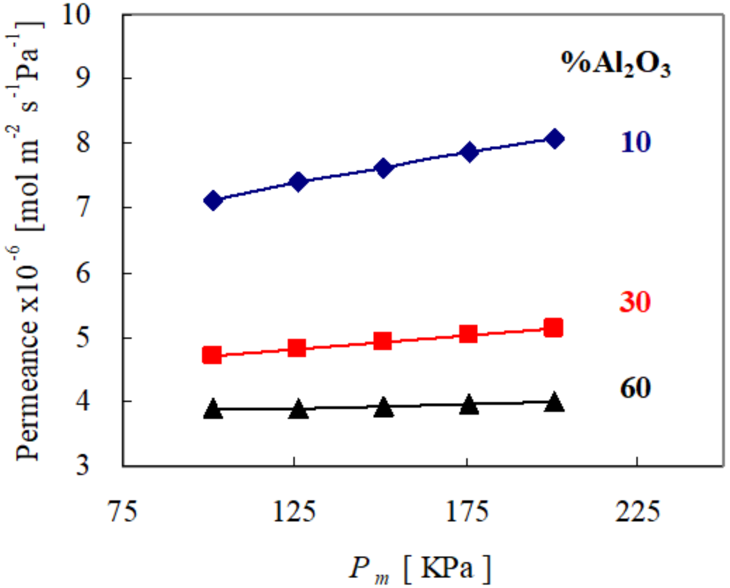


YSZ + Al_2O_3 3.7%
PVA 1.4%
PEG 0.4%

Al_2O_3 40%



N_2 permeance



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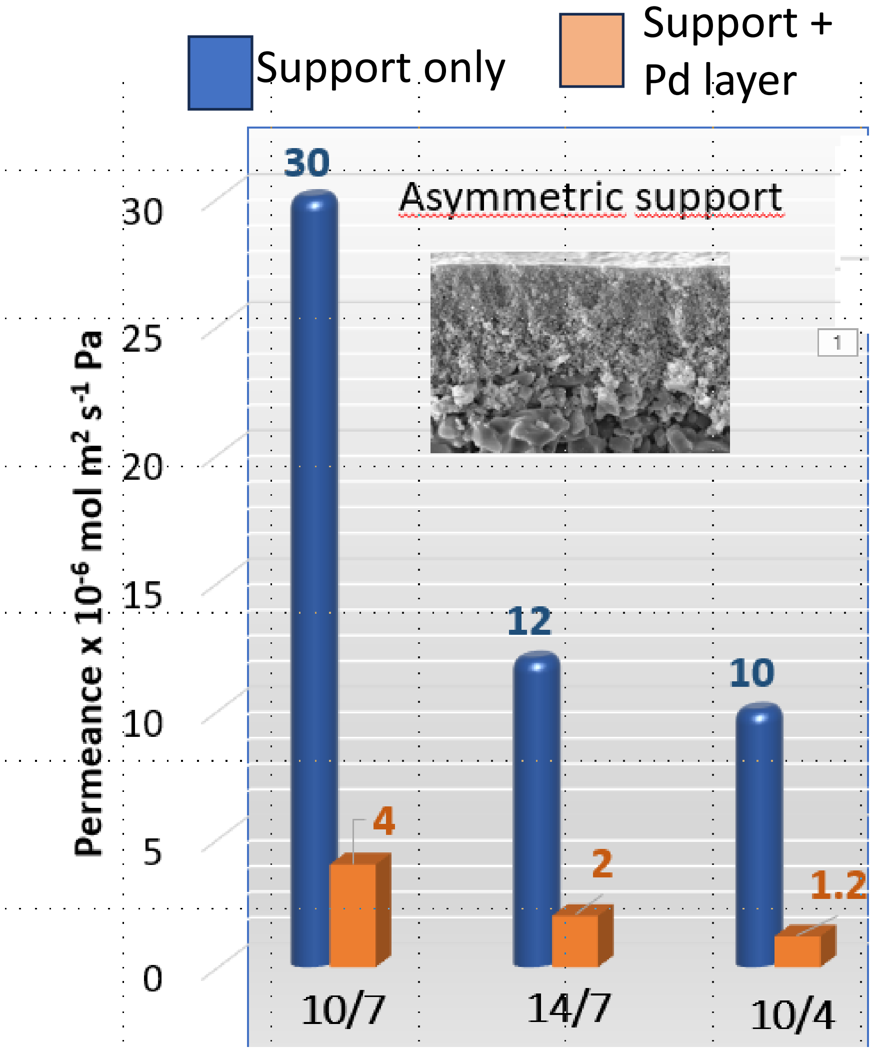
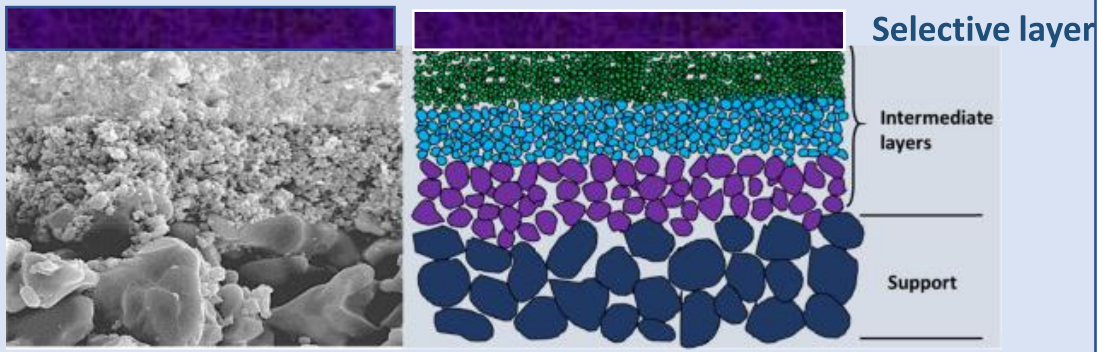


1.5 3.5

Inner / Outer diameter (mm)

Wall thickness (mm)

Porous Ceramic supports

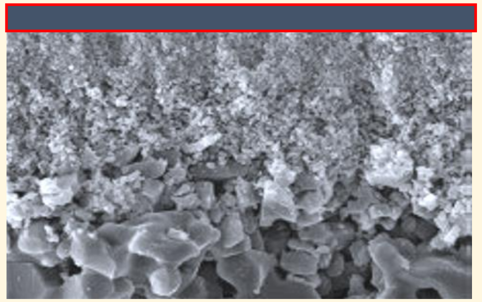


https://doi.org/10.1016/j.desal.2018.04.015

Thin supported Membranes < 5 μm

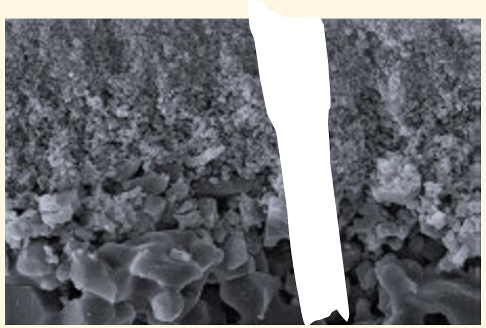
Ceramic support

Low resistance to gas permeation

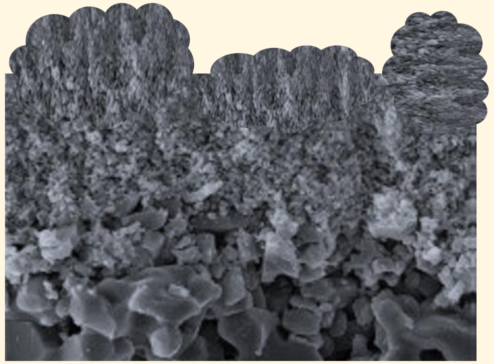


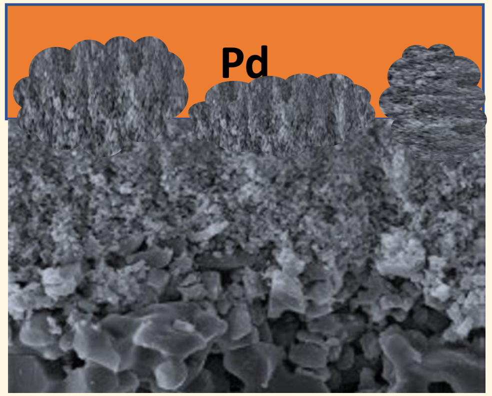
- ✓ Asymmetric
- ✓ High porosity

✓ Small pore size



✓ Smooth surface





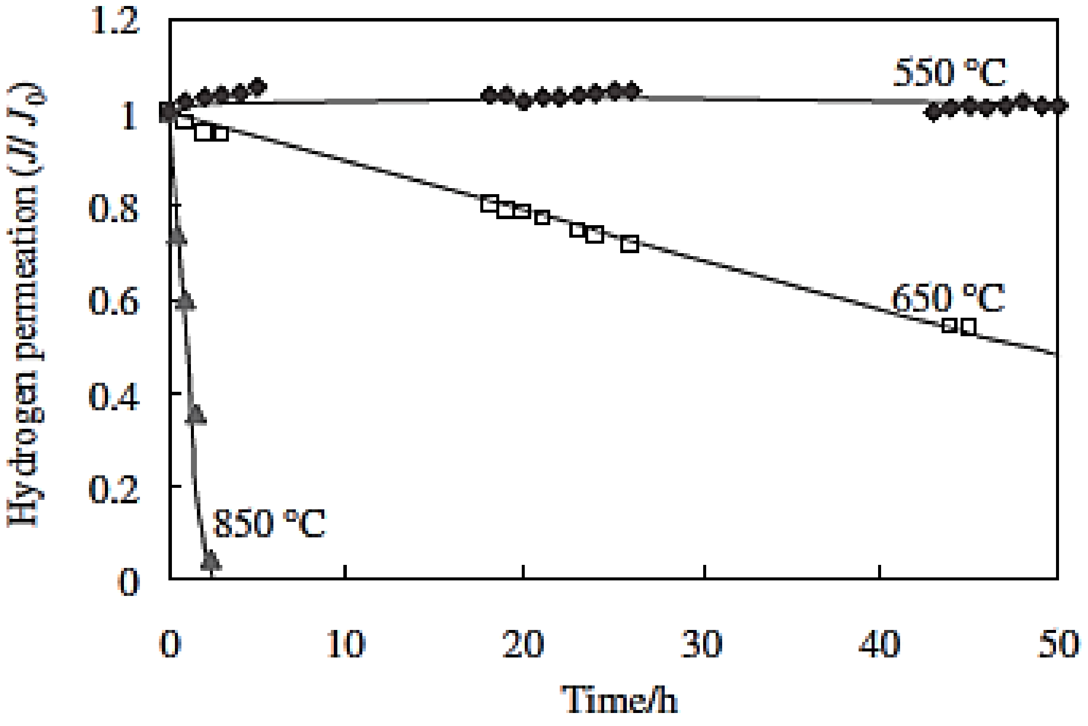
3 times the biggest pore

Pd- Support strong interaction

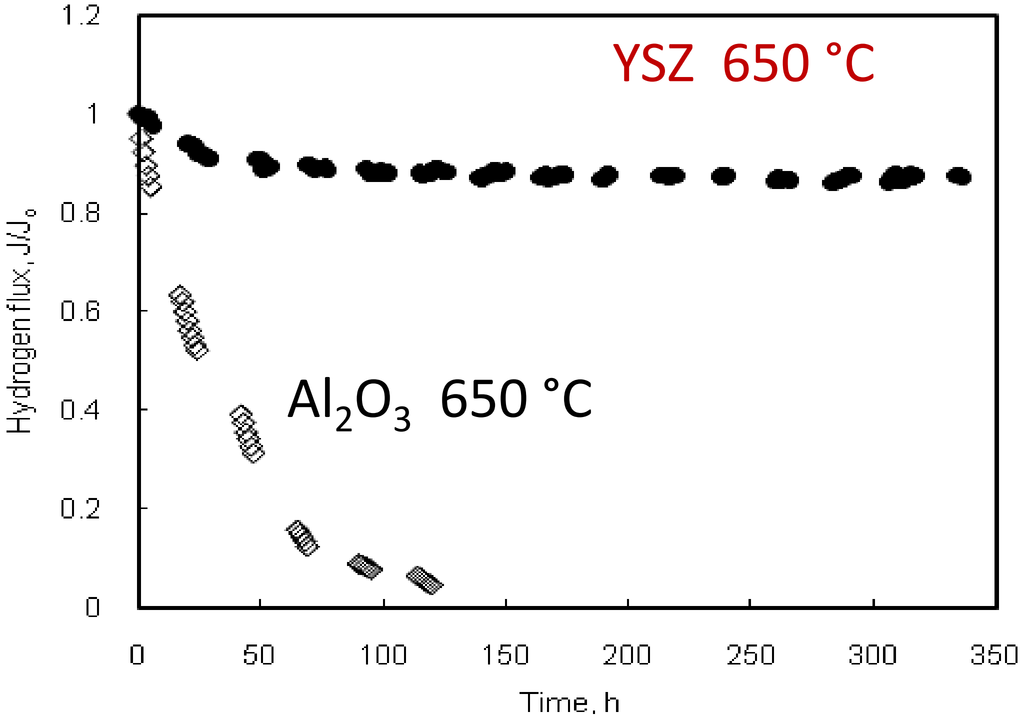
$$Al_2O_3 + 3H_2 \overset{Pd}{\leftrightarrow} 2Al + 3\,H_2O$$

$$Al + Pd \leftrightarrow AlPd_{alloy}$$

α-alumina support



Okasaki, Pacheco Tanaka…,
Chemistry Letters Vol.37, No.9 (2008)

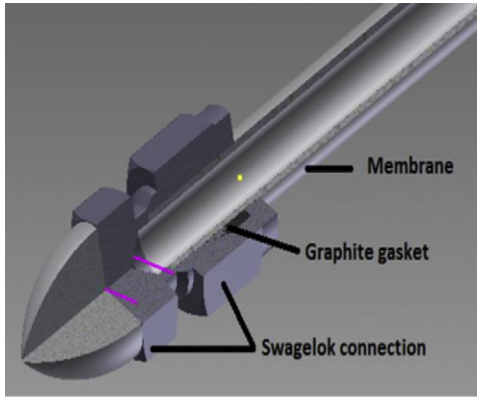


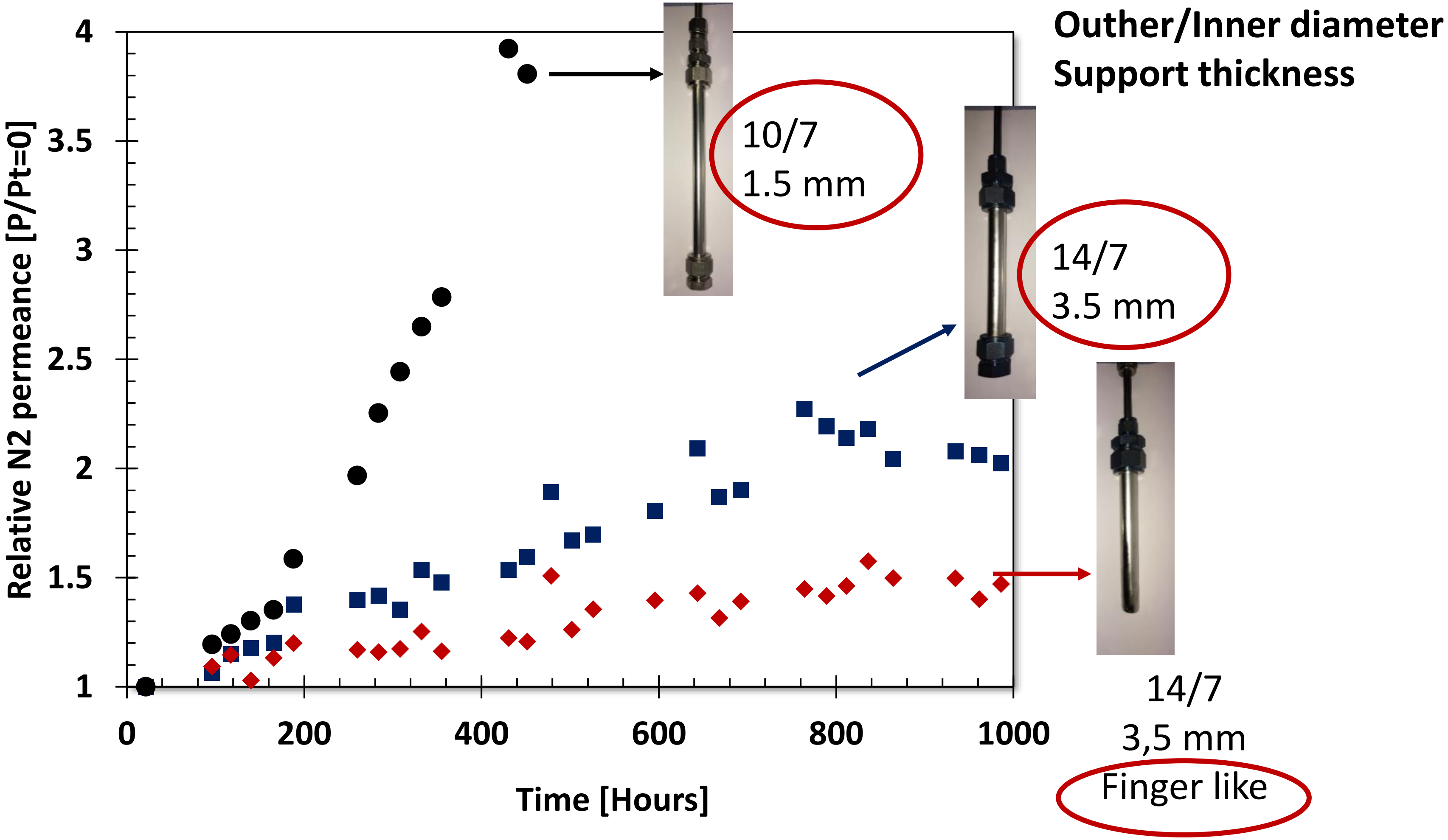
Okasaki-. Pacheco Tanaka…
Phys. Chem. Chem. Phys., 11,8632-8638 (2009)

Effect of the alumina support type on the long time H_2 permeation test at 500°C

Niek de Nooijer Process 7 (2019) 106

Leak zone





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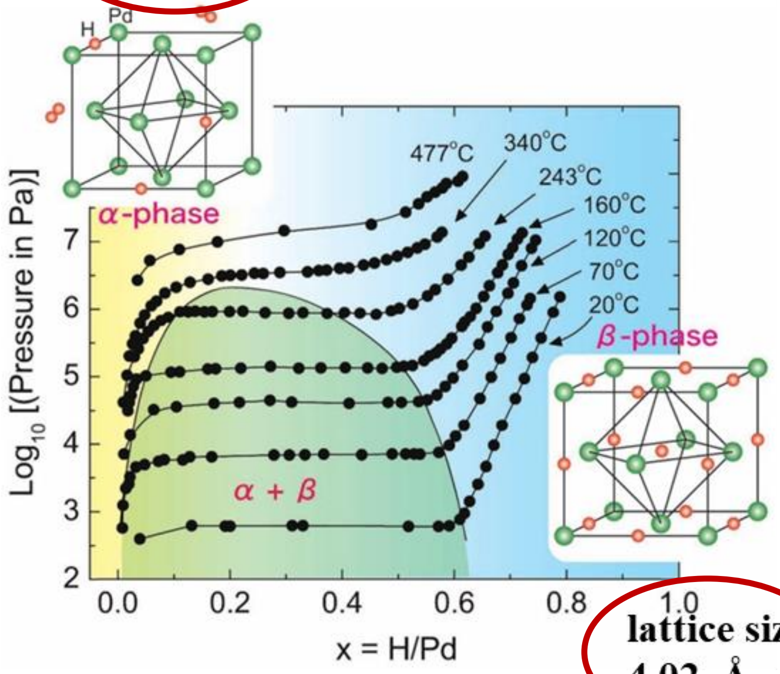
PdH embrittlement α-β transition

lattice size 3.89 Å

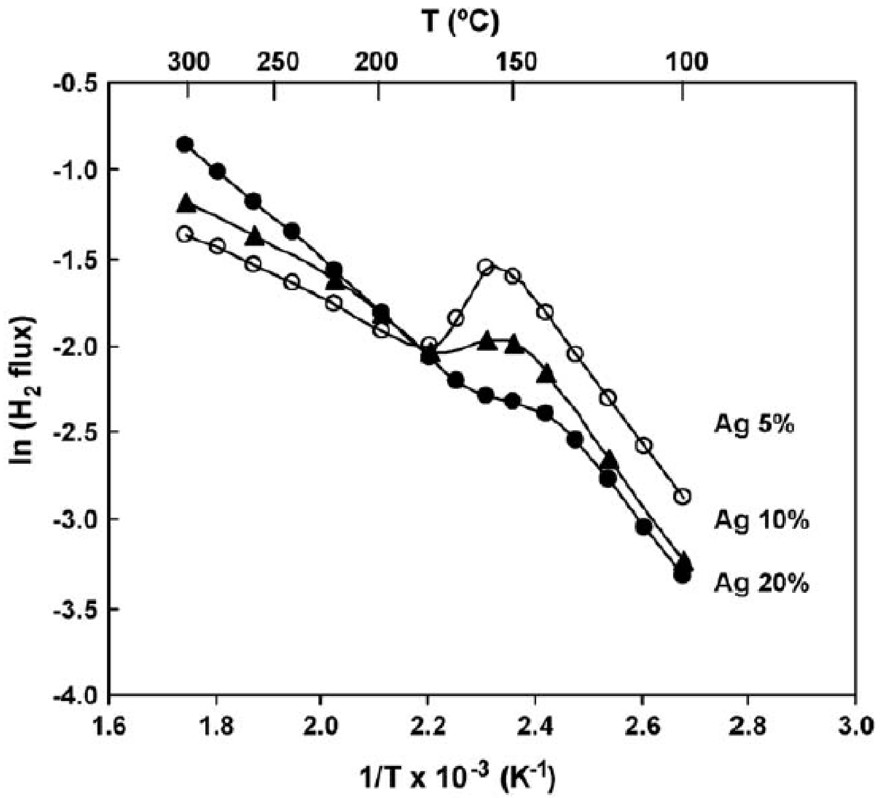


lattice size 4,02 Å

•DOI: 10.1002/cphc.201900109

Change in lattice size (Å) of the α- and β-phase in Pd-Ag alloy

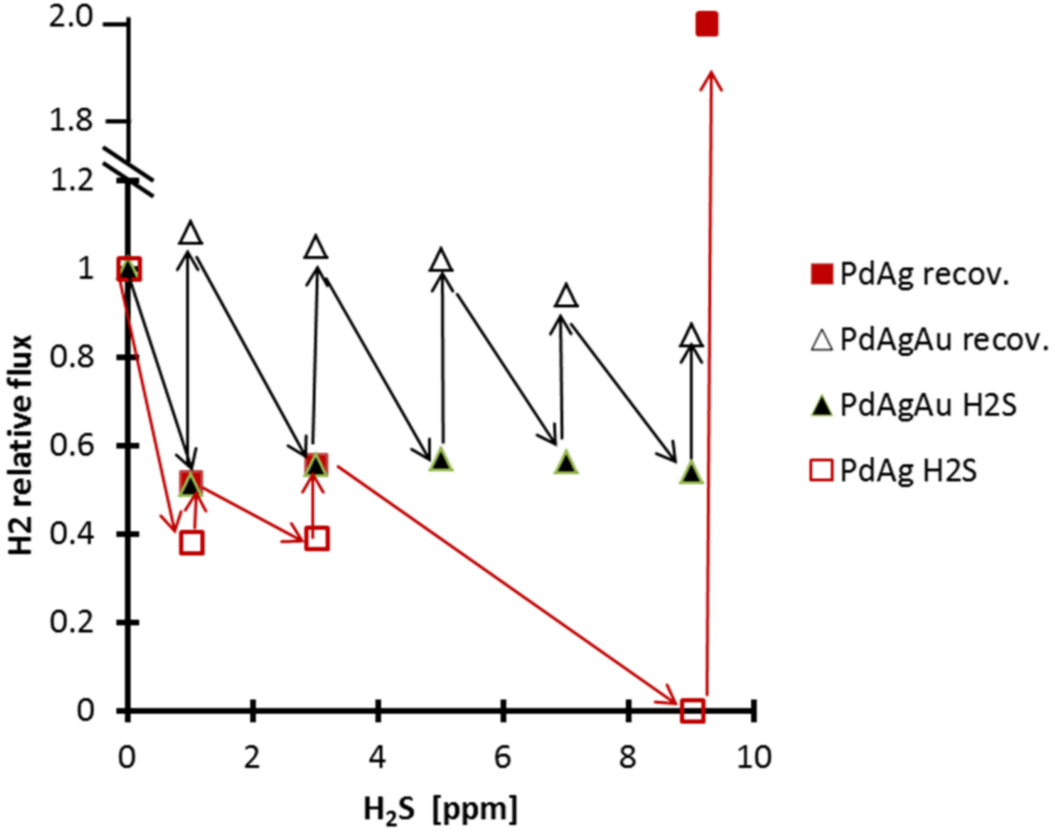
Atom % Ag	α- phase	β-phase	Increase %
0	3.89	4.02	3.3
10	3.92	4.00	2.0
20	3.94	3.99	1.3
24	3.99	4.00	0.3
30	3.94		



Improving sulphur poisoning resistance

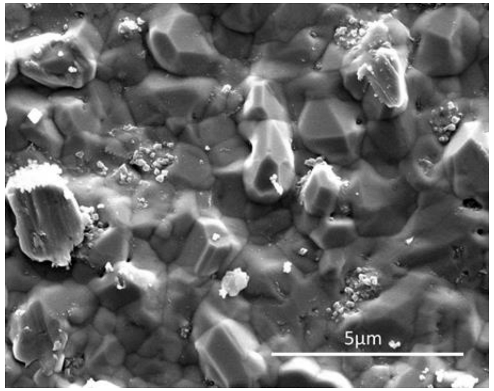
Effect of H_2S on the PdAg and PaAgAu membranes H_2 permeation

Pd96.1Ag3.9/ Pd91.5 Ag4.7 Au3.8

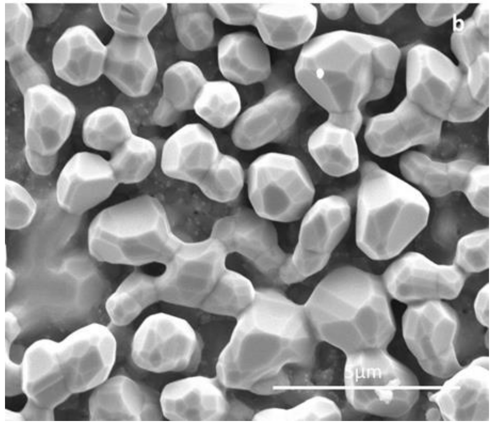


SEM after H_2S test

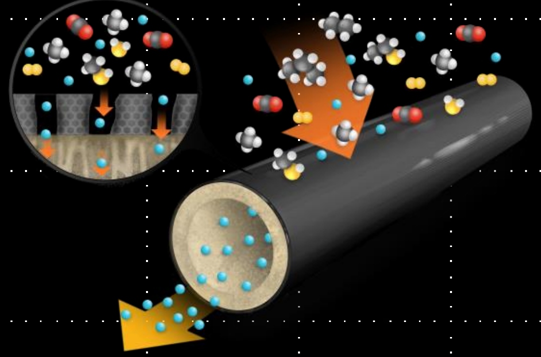
Pd91.5 Ag4.7 Au3.8



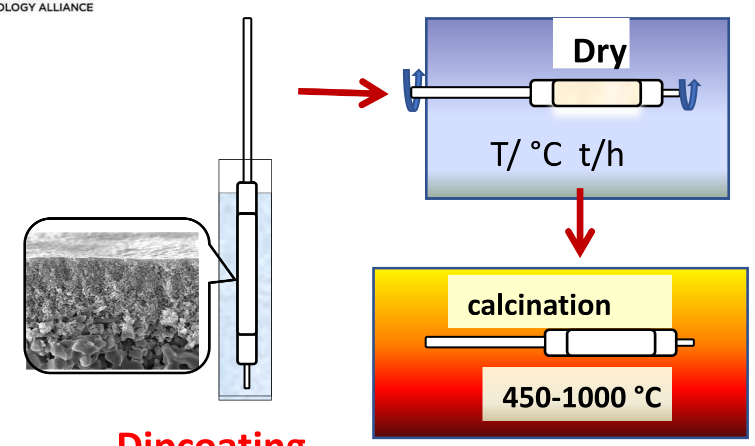
Pd96.1Ag3.9



CARBON MOLECULAR SIEVES MEMBRANES (CMSM)

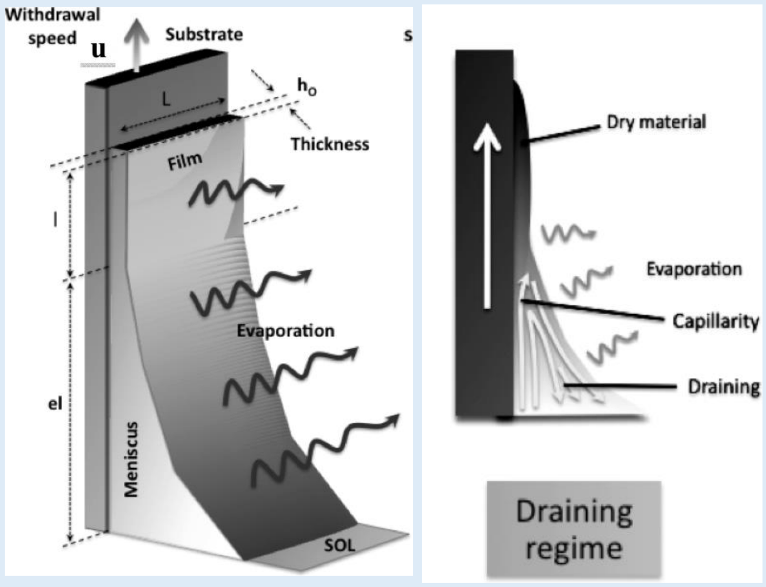


For a non evaporating Newtonian fluid



Dipcoating

Dipping on a porous substrate



J. Phys. Chem. C **2010,** *114,* 7637–7645

h_s = thickness

$$h_s = \frac{0.94\eta_s^{2/3}}{\gamma_s^{1/6}(\rho_s g)^{1/2}}u^{2/3}$$

Dipping Solution

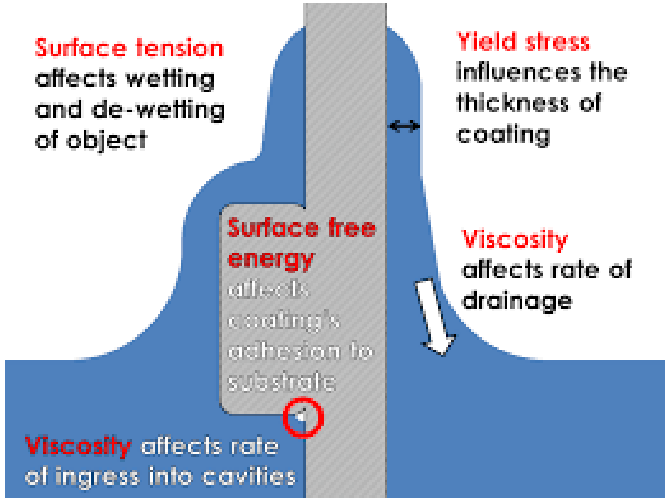
η_s = viscosity

γ_s = surface tension

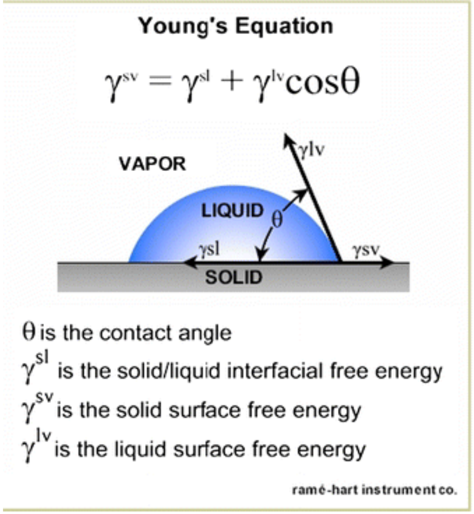
δ_s = density

g = gravity

µ =withdrawing speed



Surface tension



Porous substrate

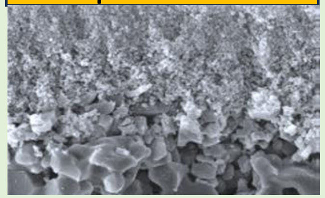
Nature

Pore size

Pore size distribution

Viscosity

Dip solution



Viscosity depends on

- Polymer Molecular weight and concentration
- Degree of branching polymer
- Addition of rheological modifiers
- Temperature

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POLYMER

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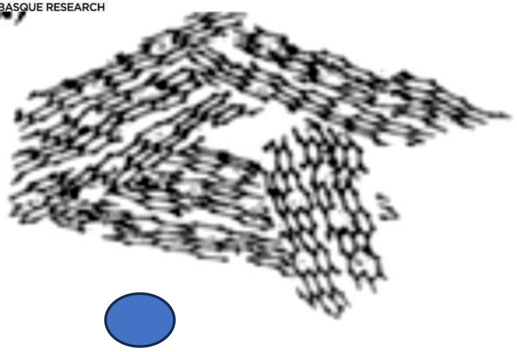
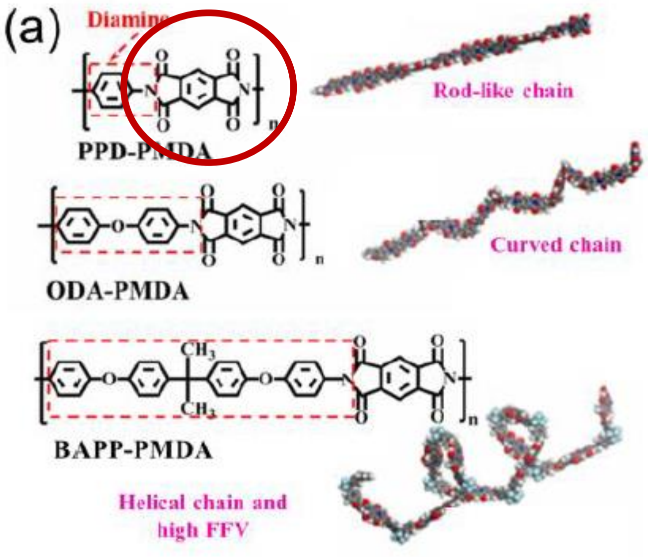
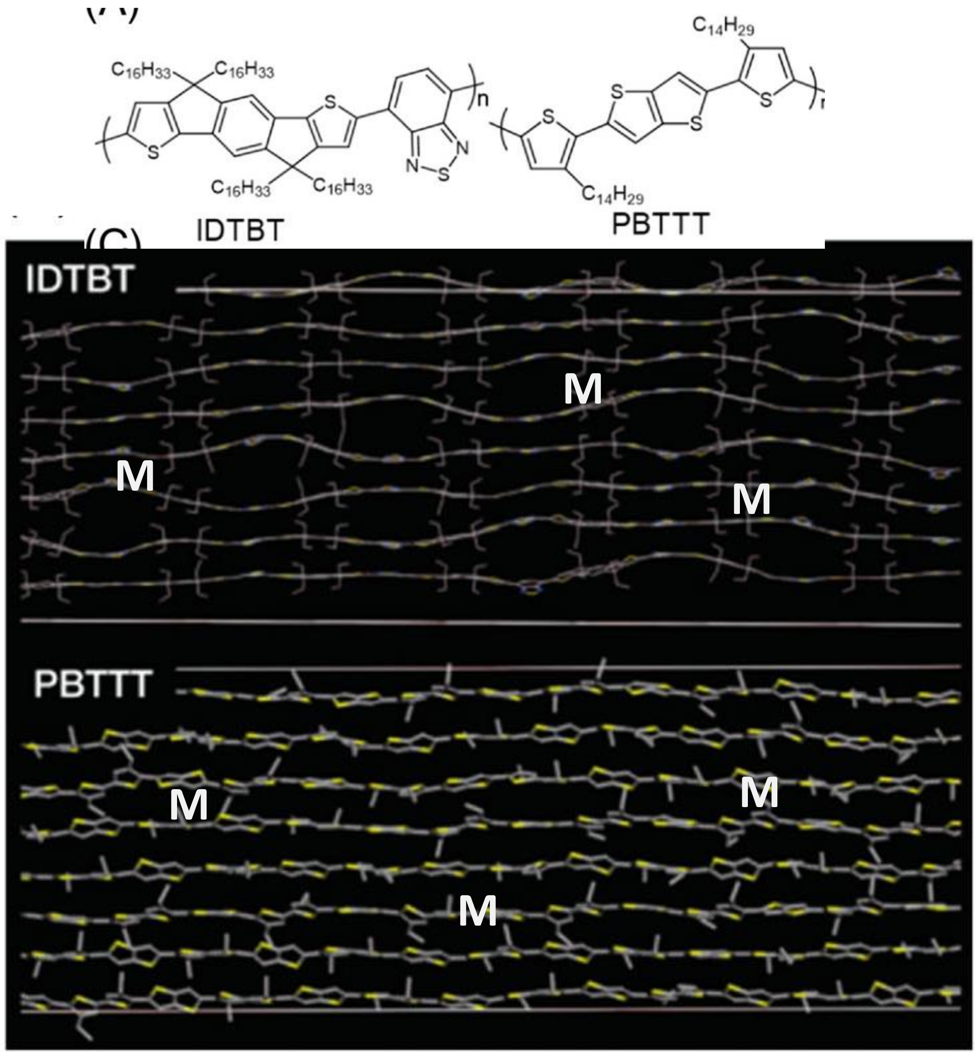






Long aligned chains

In general, a transition from sp3 hybridization to sp2 or sp for the main chain atoms can greatly enhance the rigidity of macromolecules

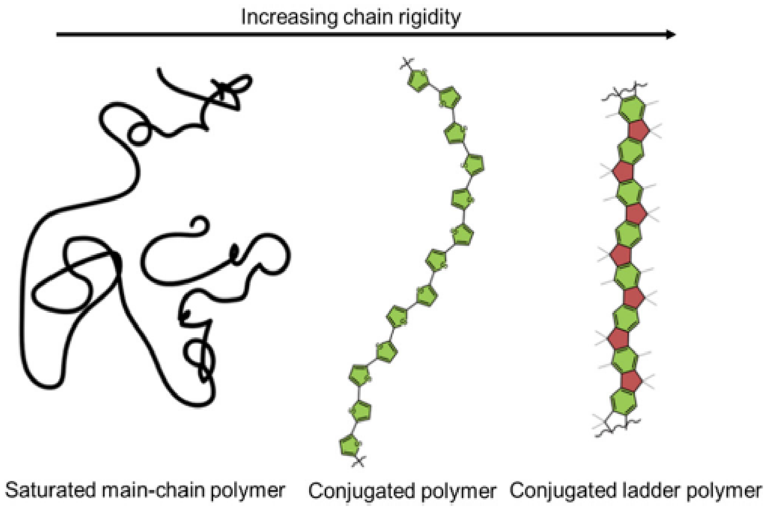
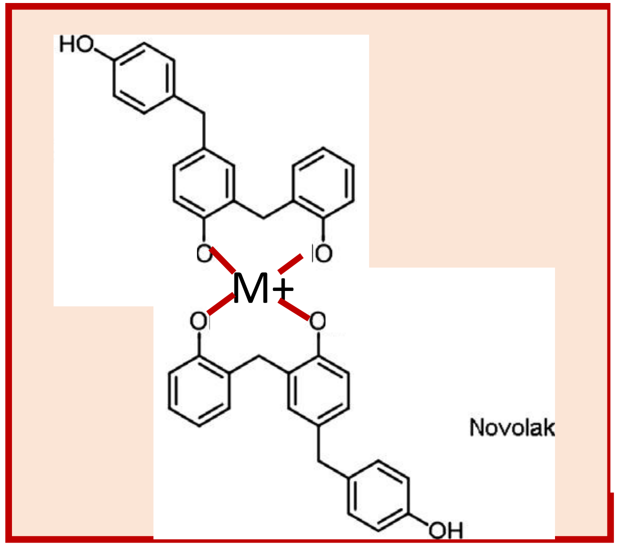


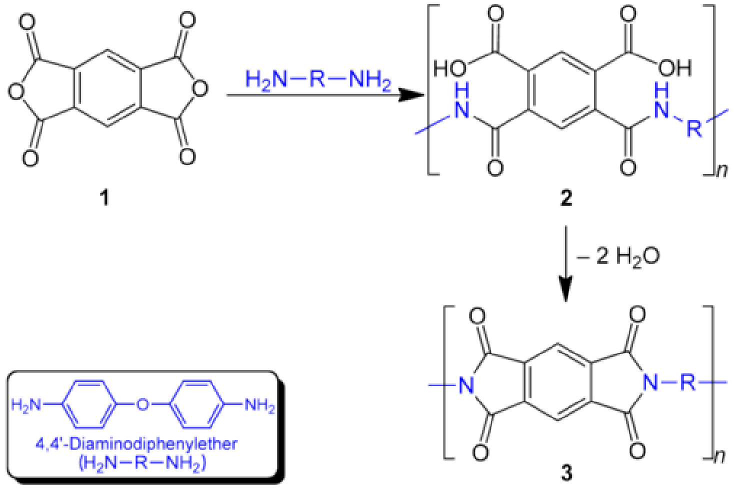
FIGURE 1 Schematic representation of the escalating rigidity from saturated sp^3 polymer to conjugated polymer, and to conjugated ladder polymer

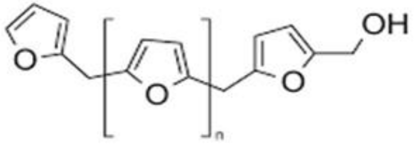
DOI: 10.1002/pol.20210550



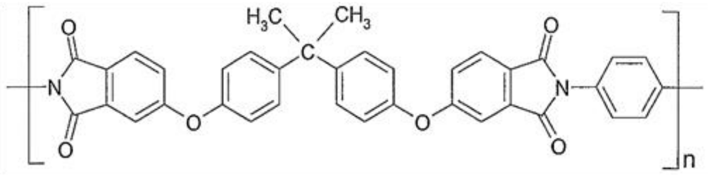
Polymers for carbon membranes

Polyimide

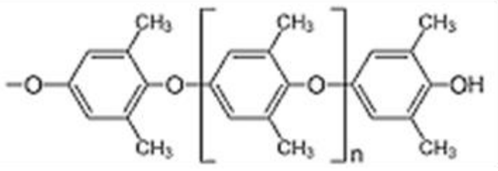




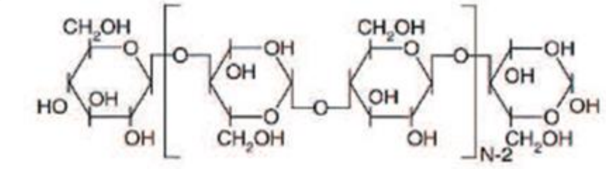
Polyfurfuryl alcohol



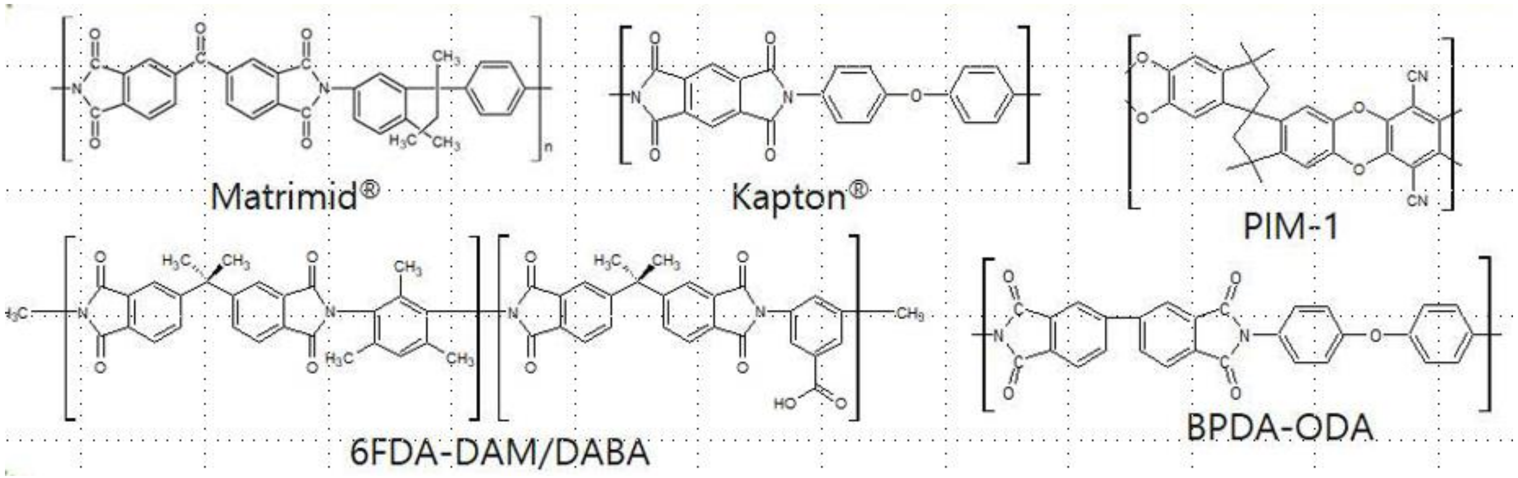
Polyetherimide

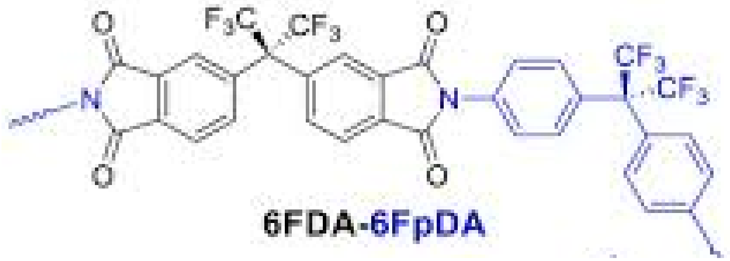


Polyphenylene oxide



Cellulose





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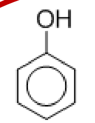
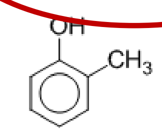
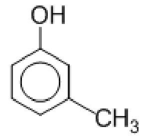
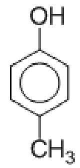
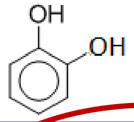
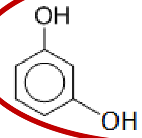
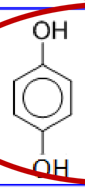
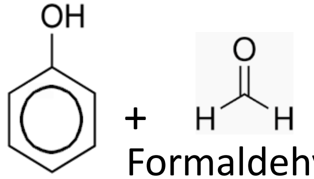
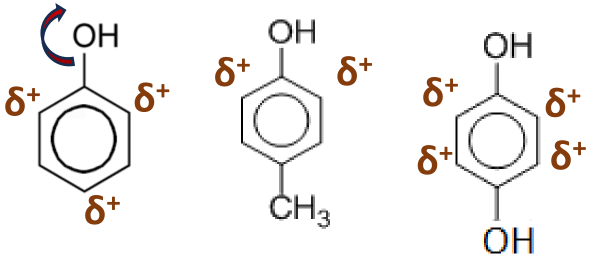
Phenolic resins

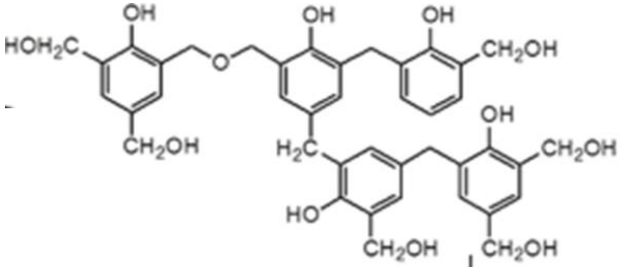
Structure	Common name
	Phenol
	o-cresol
	m-cresol
	p-cresol
	Catechol
	Resorcinol
	Quinol



Formaldehyde

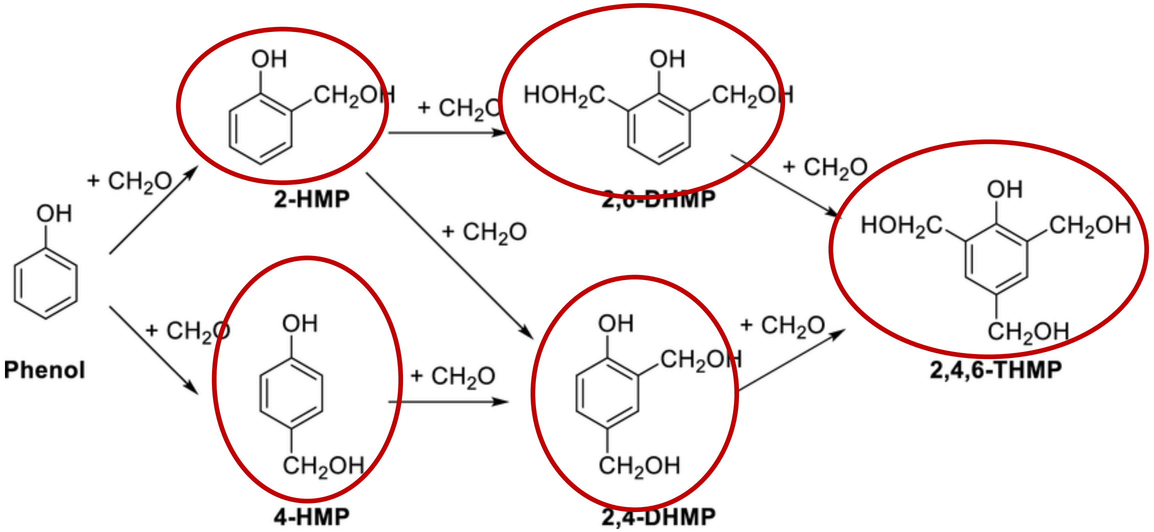
	Formaldehyde/Phenol	Media
Novolac	0.75-0.85	acid
Resol	<1	basic

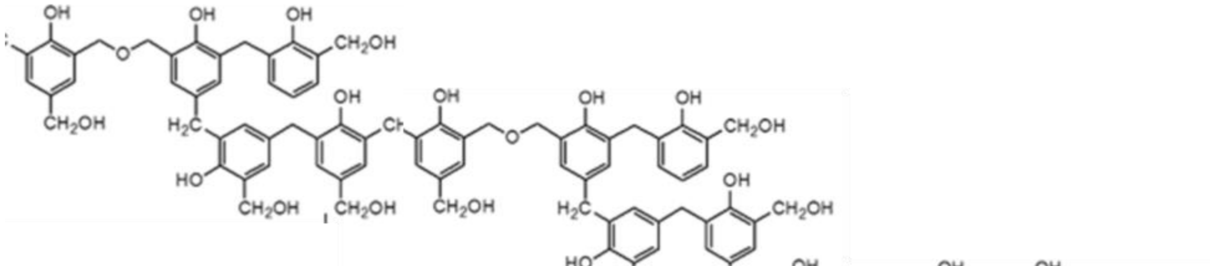
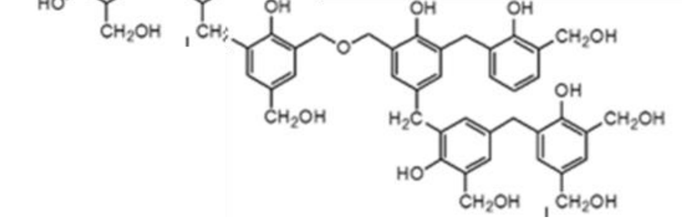




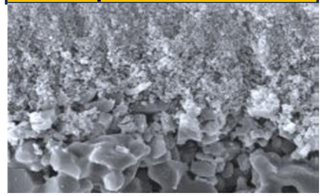
Novolac (oligomer) Low MW

HCHO
Acid
base
amine



Dip solution



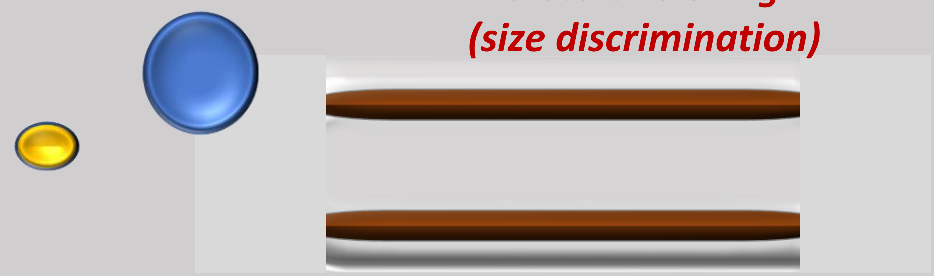
Work under progress

Control linear or no linear polymer

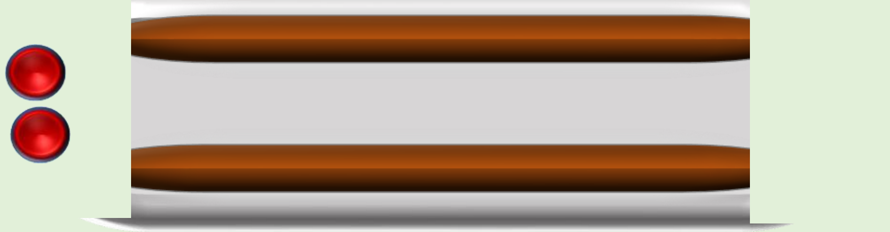
Gas permeation in CMSM

Combination of molecular sieving and adsorption

Molecular sieving (size discrimination)



Adsorption diffusion (selective gas adsoption)

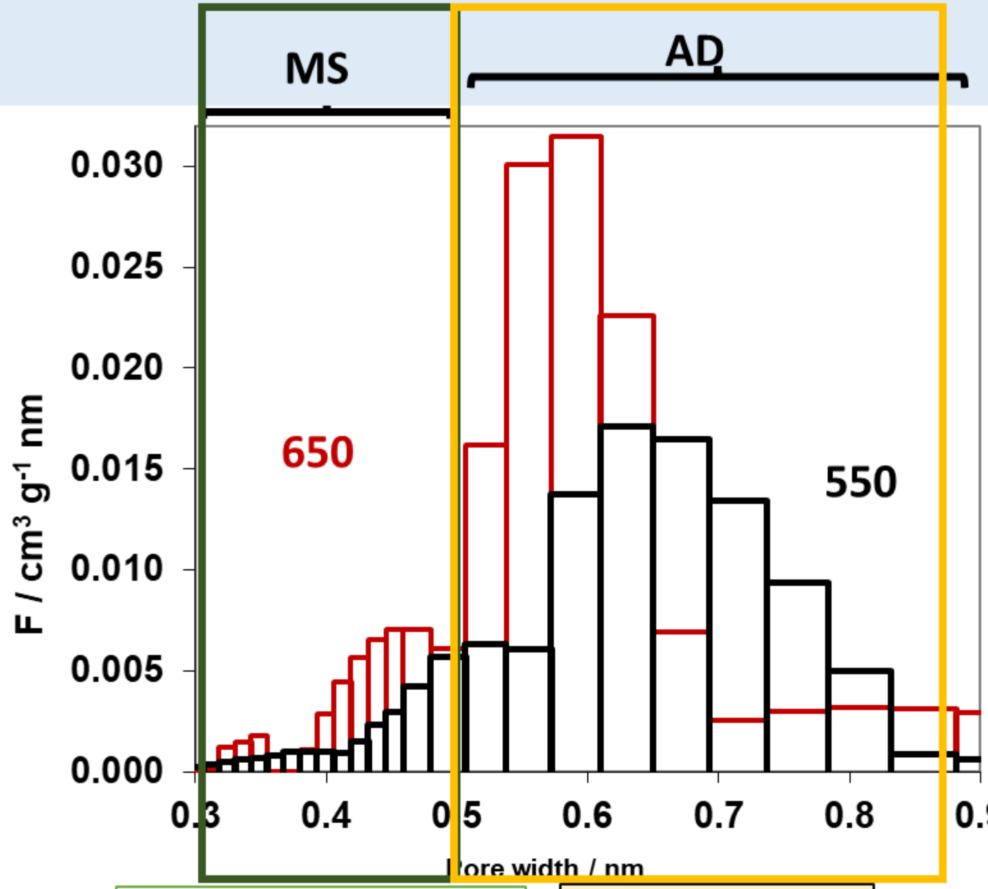


Microporous Knudsen (MK) no adsorption

$$flux = 1/\sqrt{MW}$$

flux	H_2 >	NH_3
MW	2	17

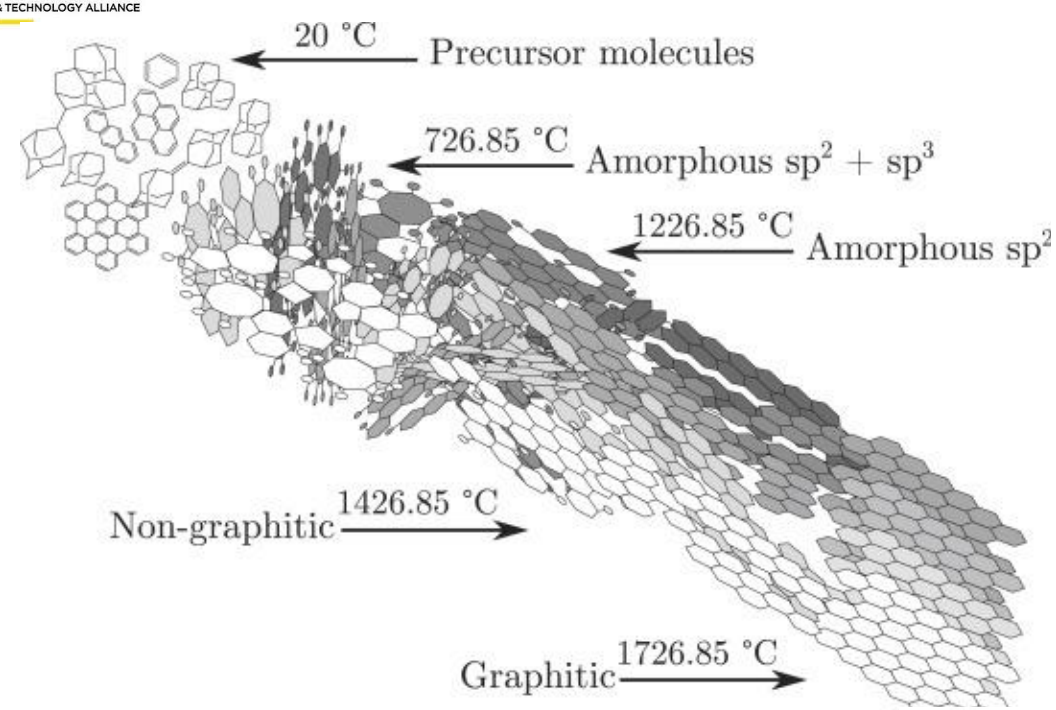
Al-CMSM pore size distribution

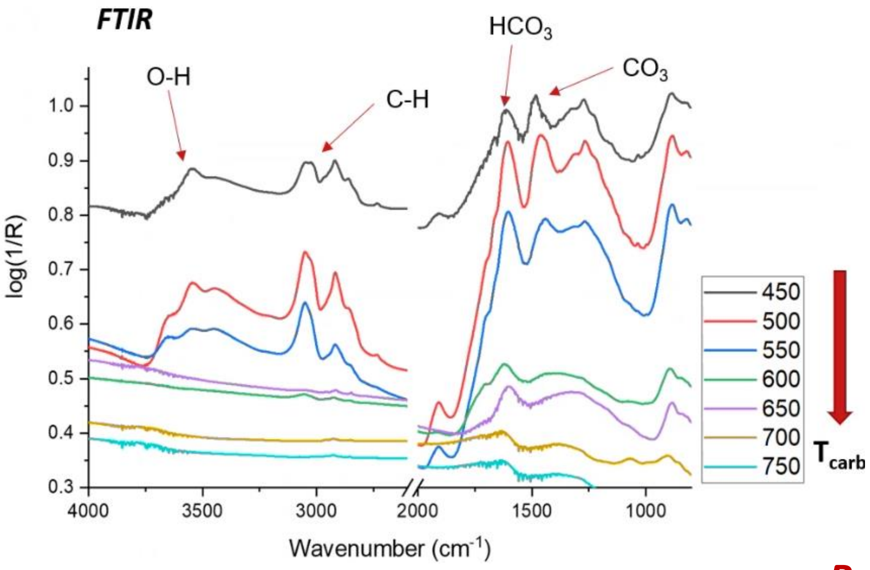


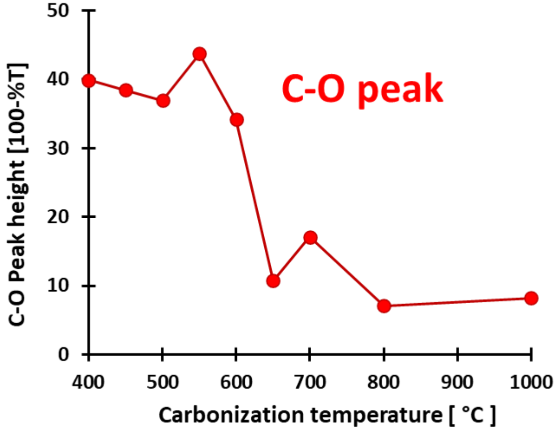
MS
Size separation

Adsorption
Diffusion

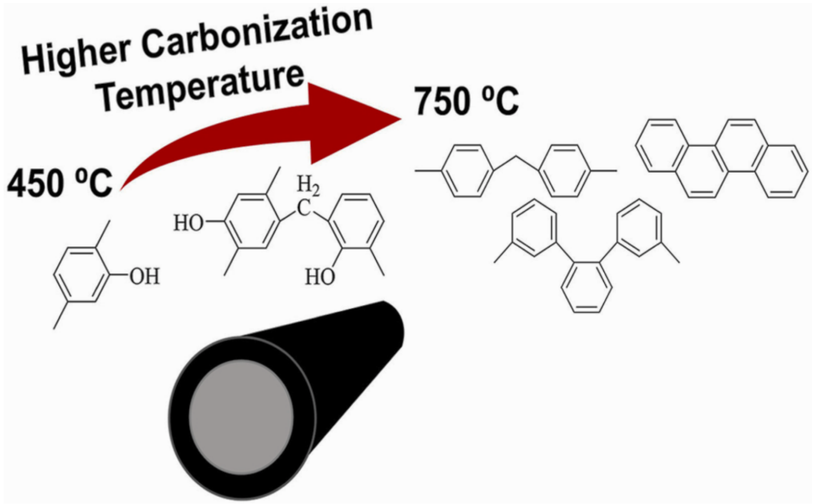
Carbonization

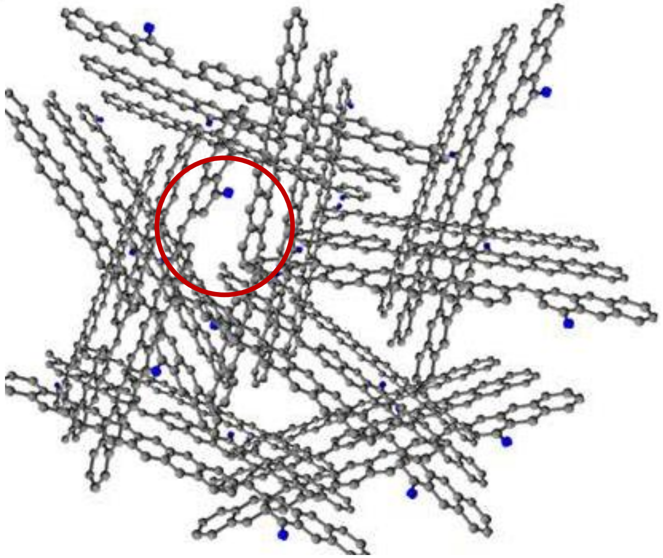






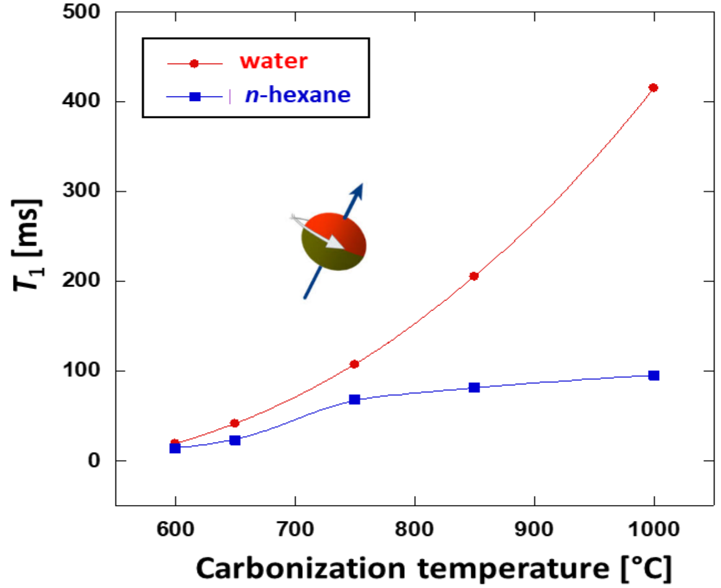
Carbon 161 (2020) 359-372



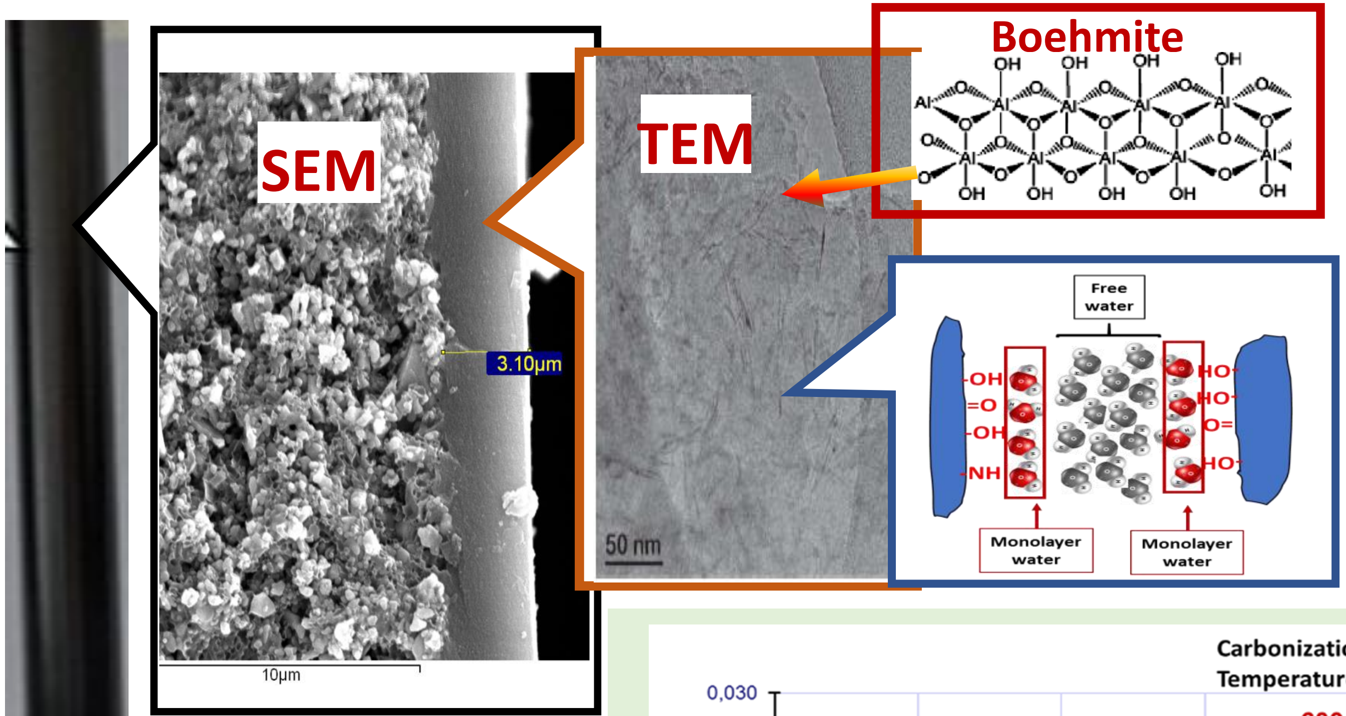


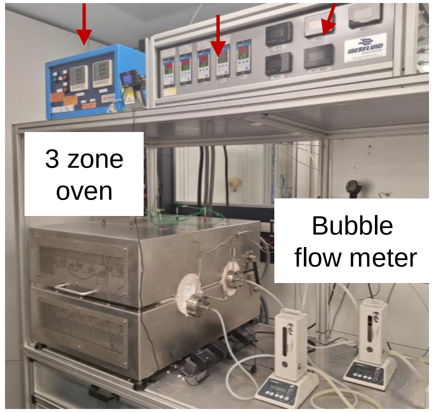
Proton -NMR

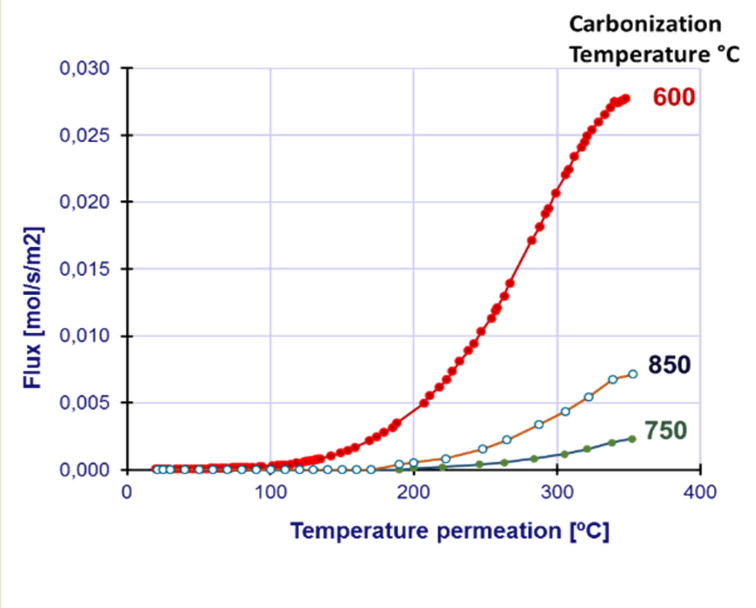
T_1 values of n-hexane and water confined as function of carbonization temperature



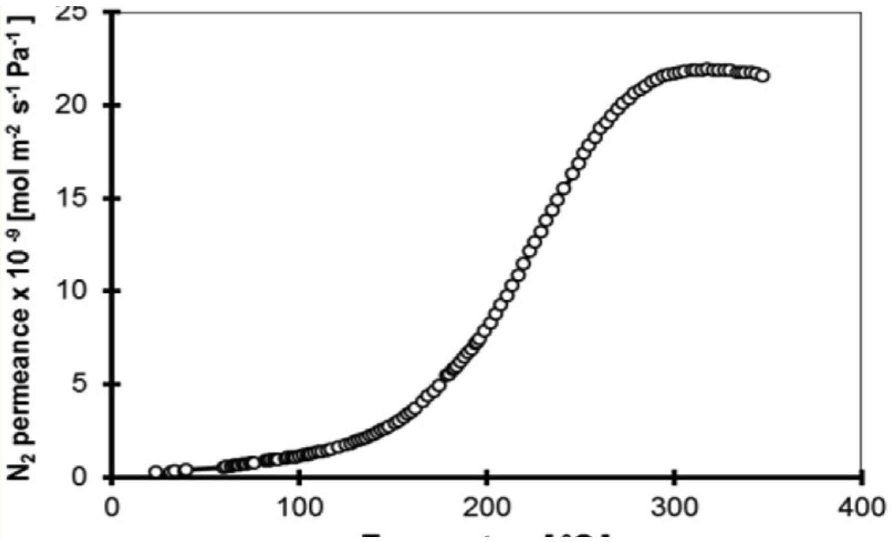
Al-CMSM







N2 permeance at 400 kPa pressure difference in function of temperature (heating rate 0.7 C/ min



cooled down to room temperature, immediately, a boat containing water was introduced to the reactor.