MACBETH
Membranes And Catalysts Beyond Economic and Technological Hurdles

AMBHER H_2

Carbon molecular sieves membranes (CMSM)

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- Arash Rahimalimamaghani , Fausto Gallucci.

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Eindhoven

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

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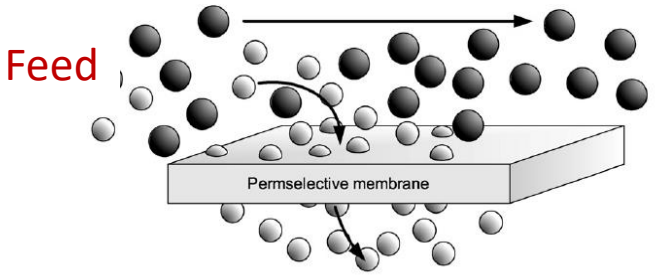
Membranes for gas separation

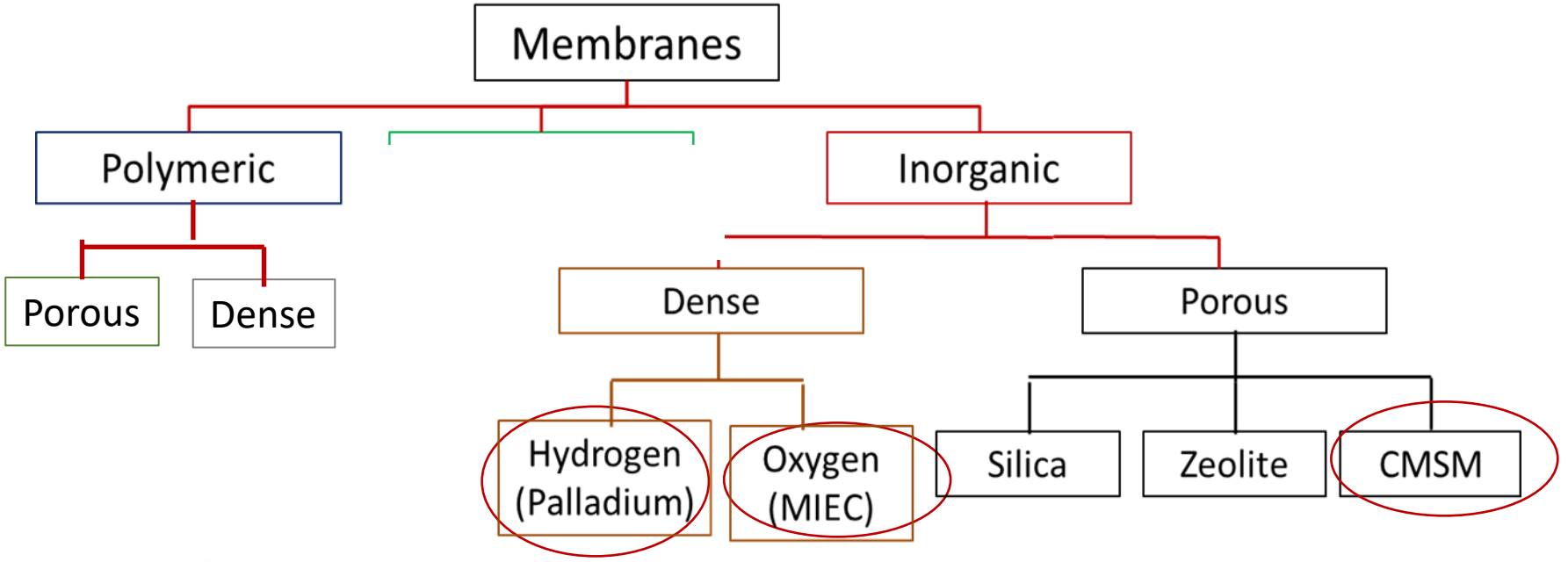
Objective

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

Permeation



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



Microporous
< 2nm

Gas permeation in porous membranes (Pore >2 nm)

Pore
>50 nm

Viscous flow

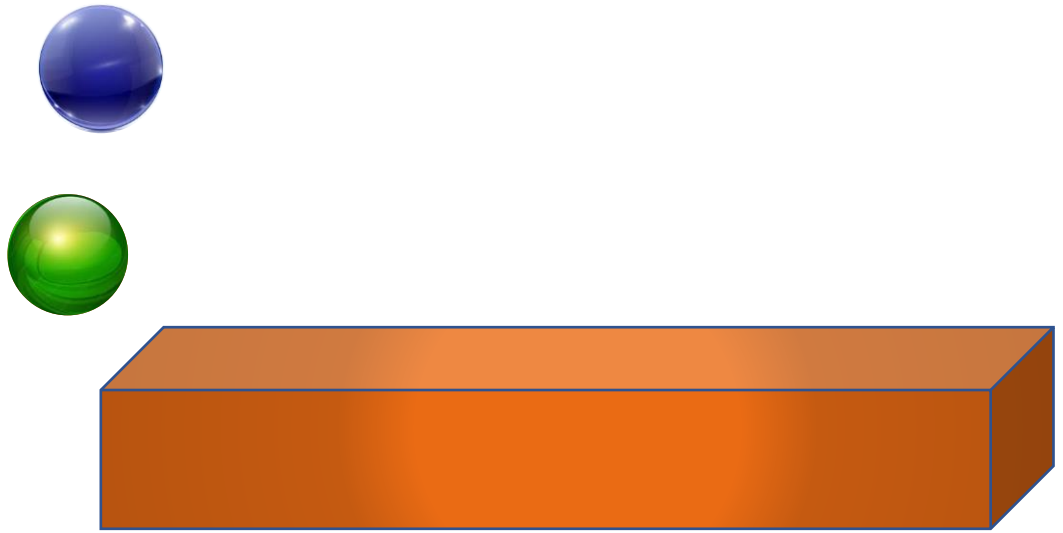
$\alpha_{H2/N2}$=1

Pore
2 - 50 nm

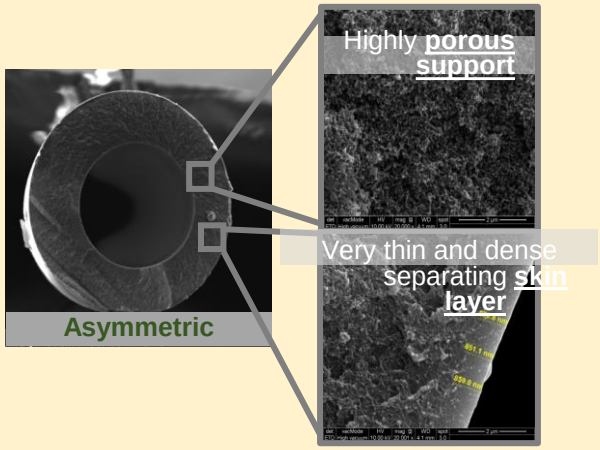
Knudsen

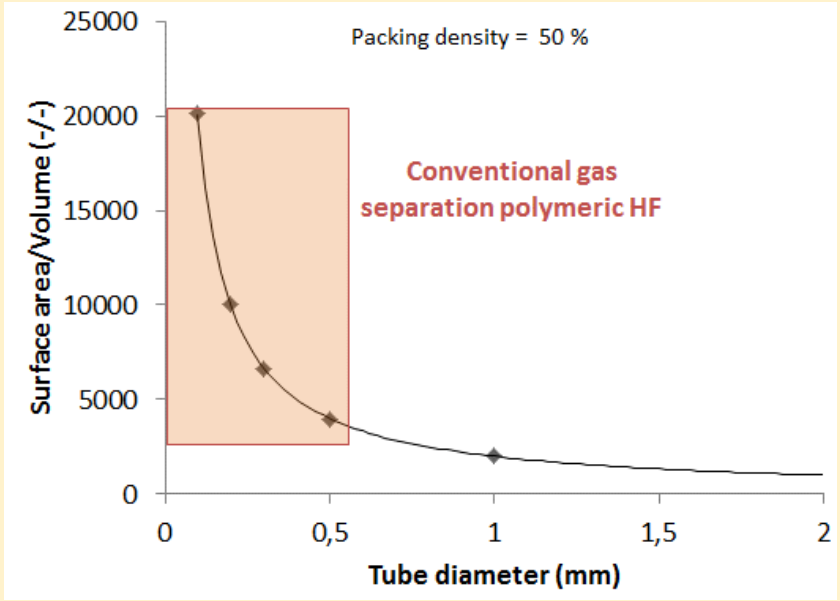
$$\alpha_{H2/N2} = \frac{F_{H2}}{F_{N2}} = \sqrt{\frac{MW_{N2}}{MW_{H2}}} = 3.74$$

Gas permeation in dense membranes

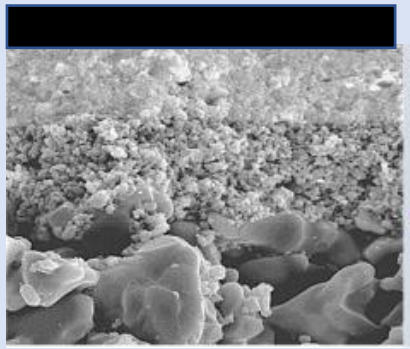


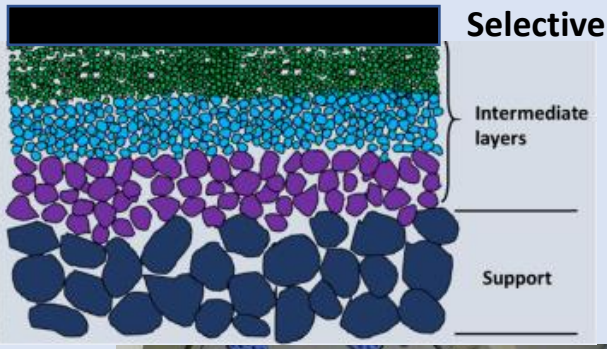
Polymeric hollow fiber membranes

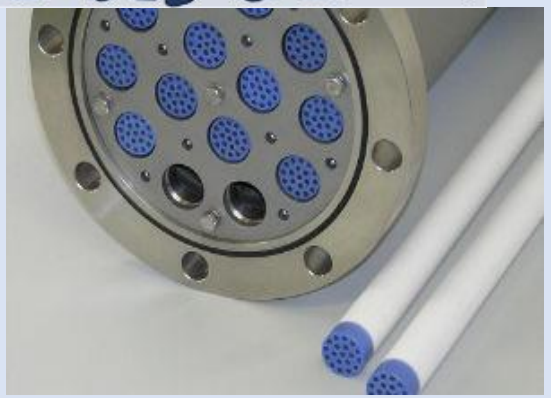




Porous Ceramic supports







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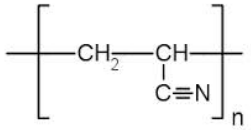
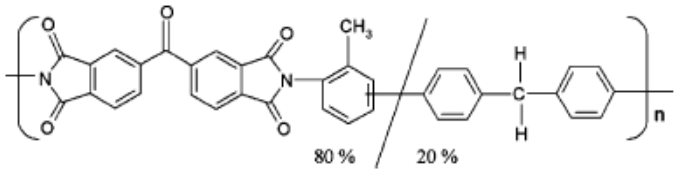
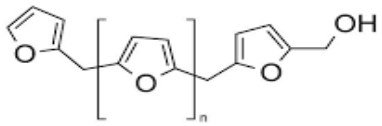
Polymeric precursors for CMSM



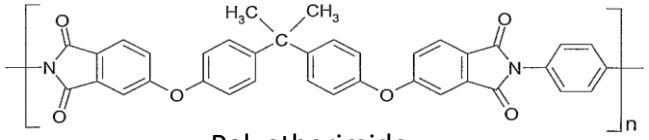
Polyacrylonitrile



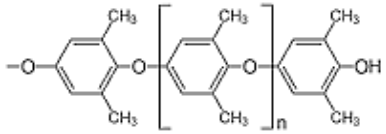
P84 co-polyimide



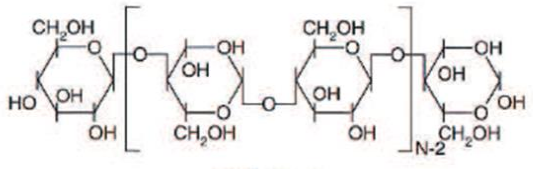
Polyfurfuryl alcohol



Polyetherimide

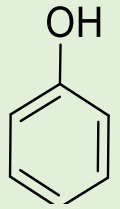


Polyphenylene oxide



Cellulose

Phenolic resins



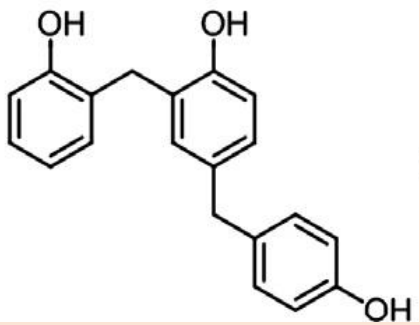
+ $CH_2=O$

Phenol Formaldehyde

Resol : basic media and Formaldehyde /Phenol > 1
the polymerization occurs with the time

Novolac : acidic media and Formaldehyde /Phenol ≈ 0.75-0.85
Stable, can be stored. Need polymerization before use

Novolac phenolic



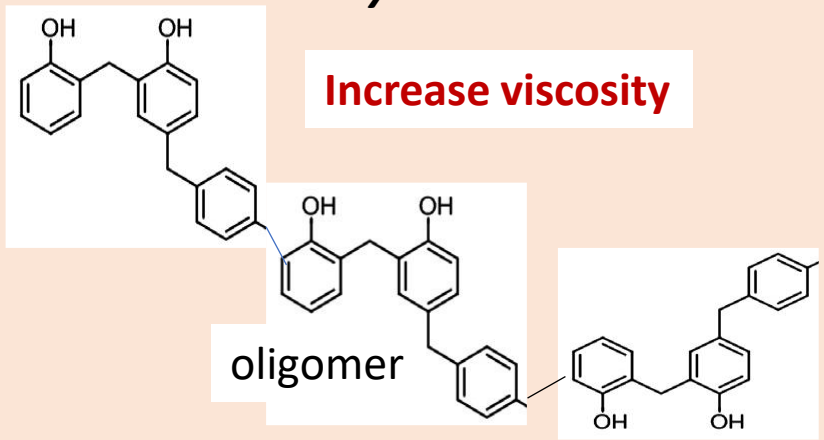
HCHO
(formaldehyde)

Acid: oxalic acid

Basic : KOH

amines

Pre- Polymerization 80 -90 C



oligomer

Increase viscosity

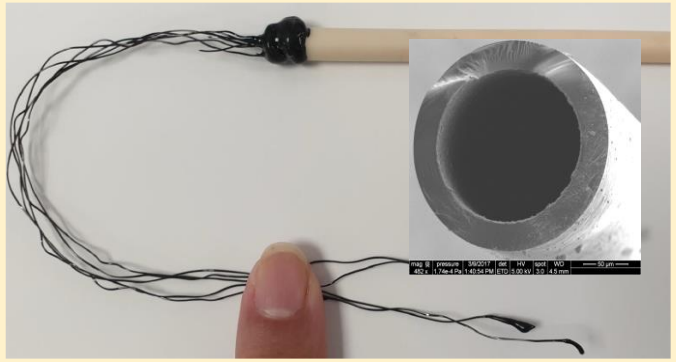
Dip coating

Polymerization on support

Avoid infiltration in support

Preparation of supported Al-CMSM

Carbon membranes

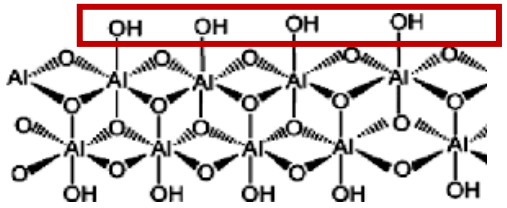


Hollow fibre and Self standing are brittle

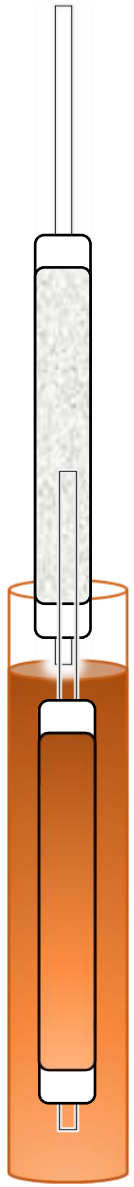
Dipping solution

Boehmite nanoparticles	**0,8 %**
Novolac resin	13,0 %
Formaldehyde	2,0 %
Ethylenediamine	0,6 %
Solvent	NMP

Boehmite

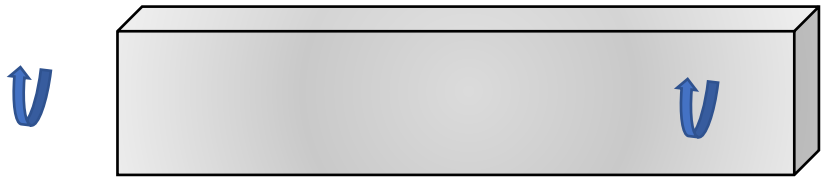


10 x 50 nm

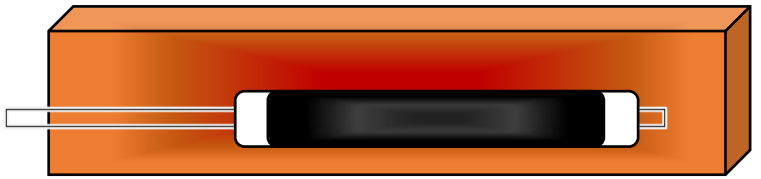


Dipping

Dry under rotation 95 ° C

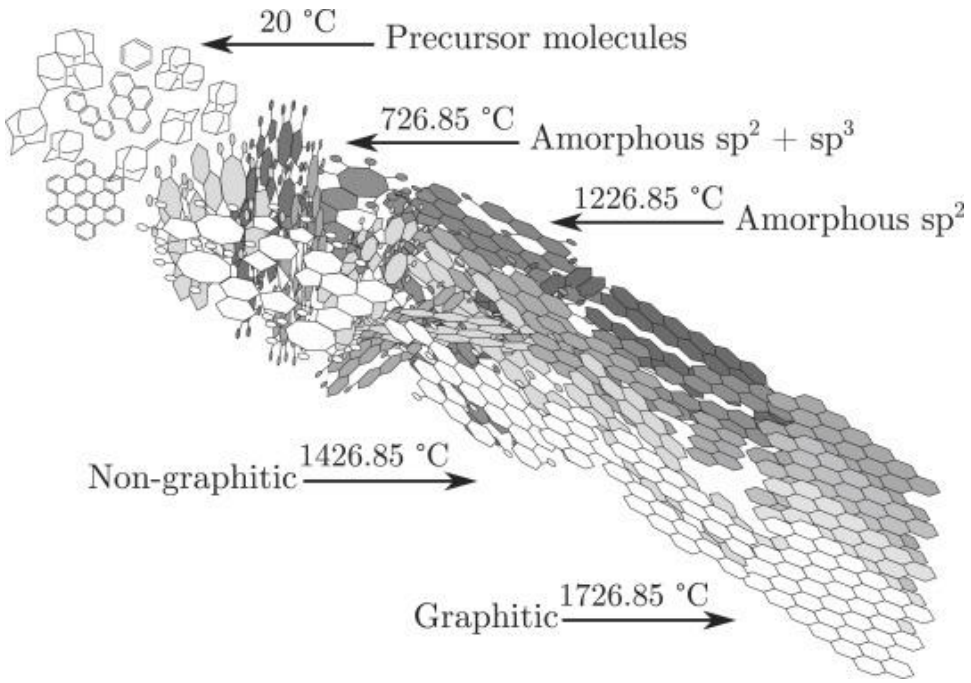


Carbonization >500 °C

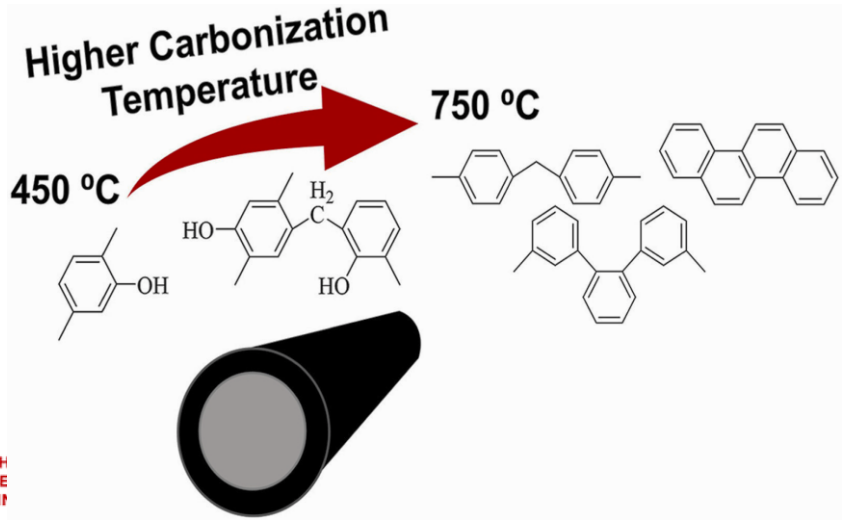


14:49

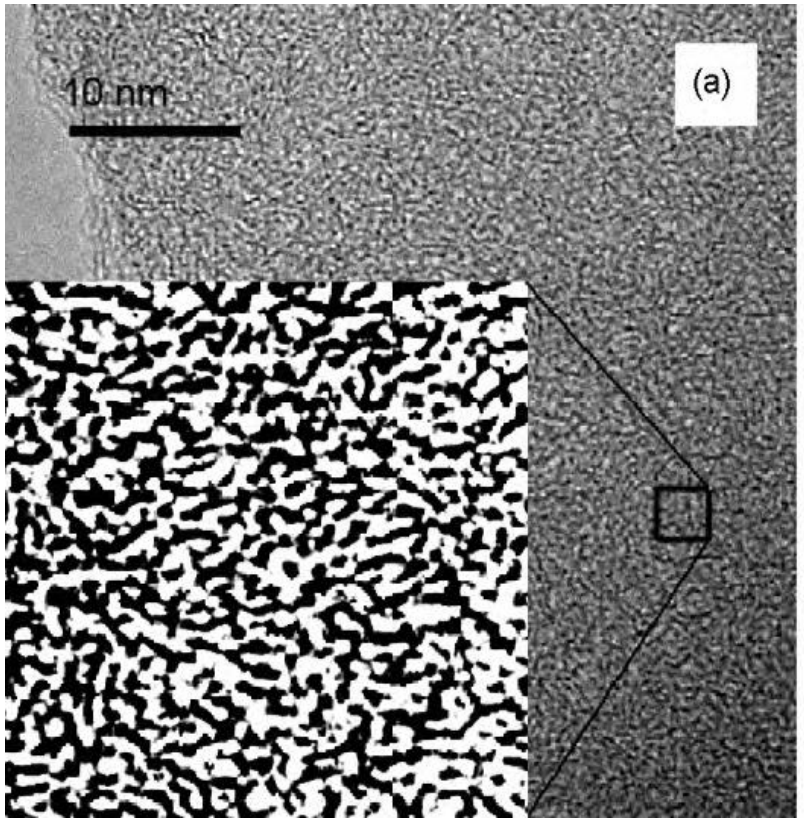
Carbonization



Carbon 161 (2020) 359-372



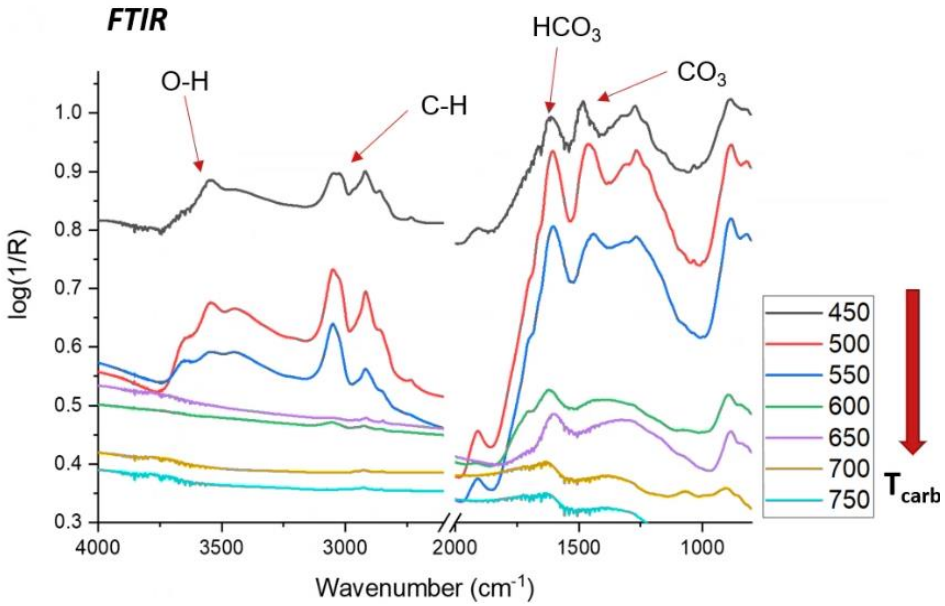
TEM Carbon Membrane

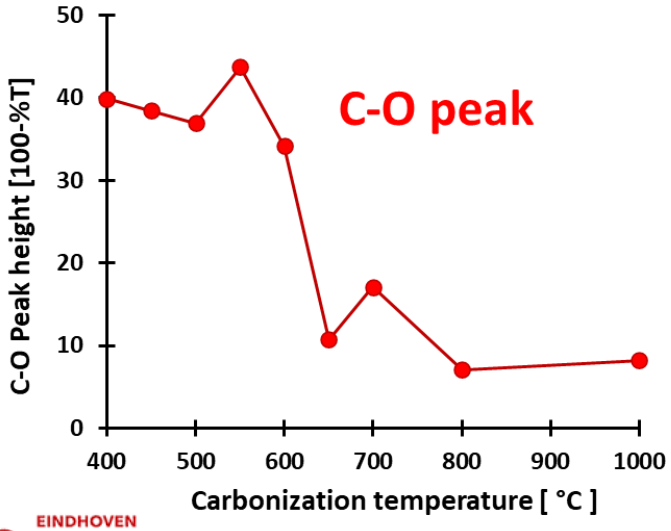


Chengwen S., Tonghua W., Huawei J., Xiuyue W., Yiming C., Jieshan Q., *J.Membr. Sci.*, *361*, 22-27, **2010**.

Effect of the temperature of carbonization

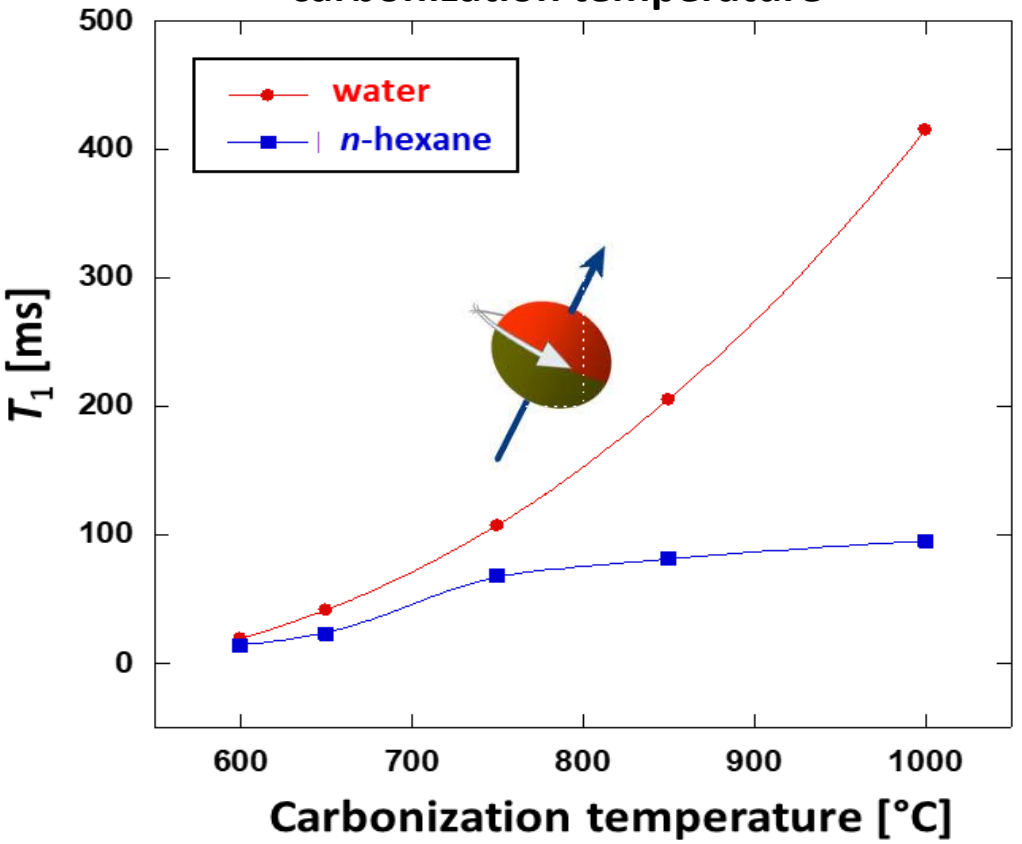
FTIR





Proton -NMR

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



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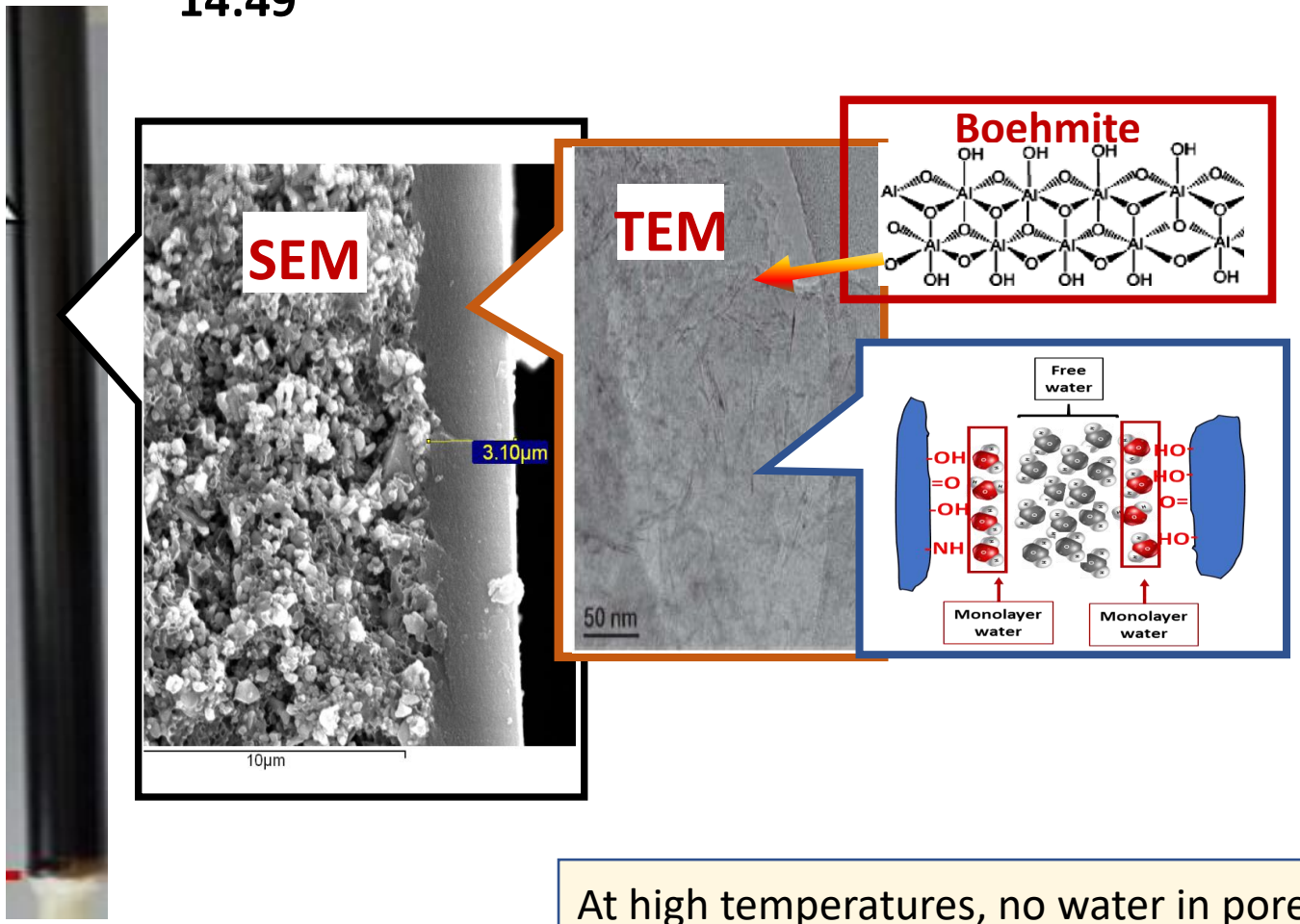
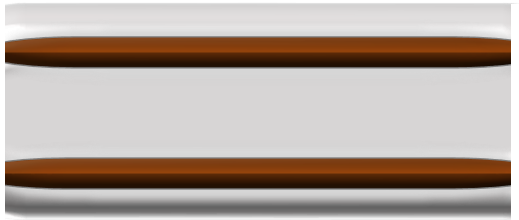


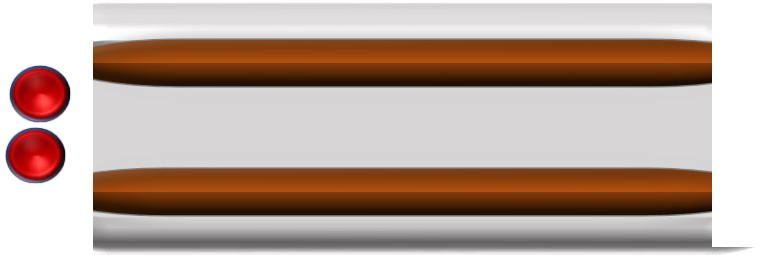
Gas permeation in CMSM

Monolayer water in the pores

Molecular sieving



Adsorption diffusion



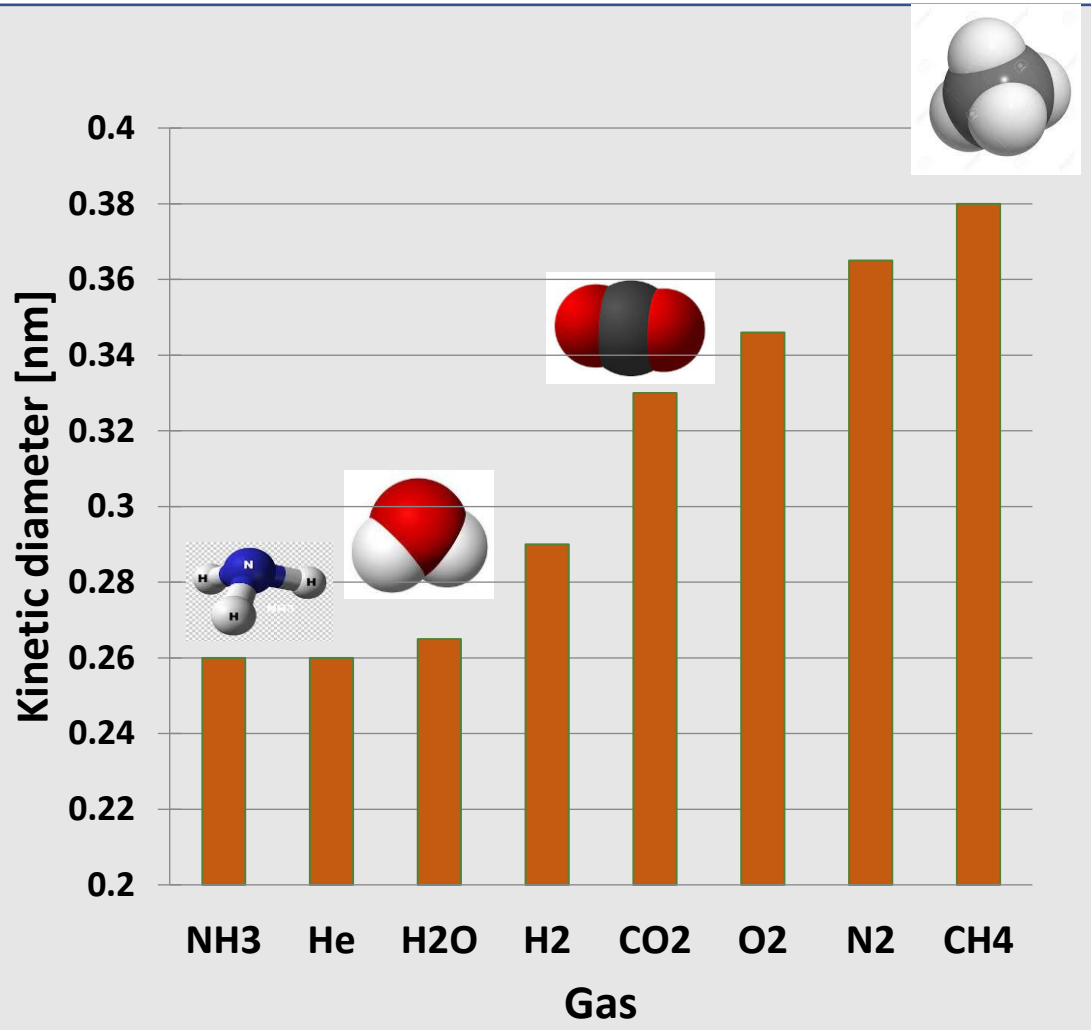
At high temperatures, no water in pores

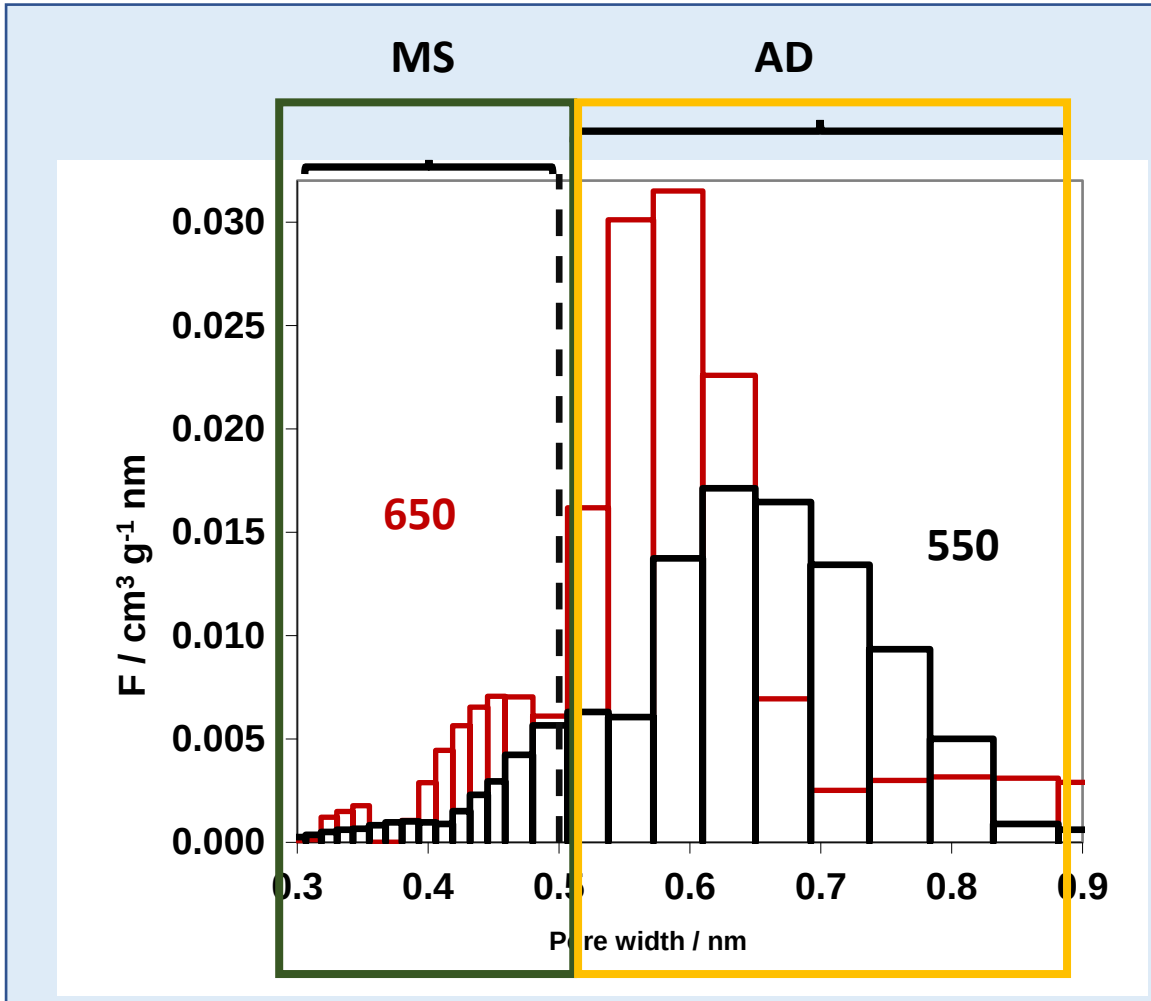
Knudsen permeation

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

flux	H_2 >	NH_3
MW	2	17

Microporous Knudsen (MK) no water in pores



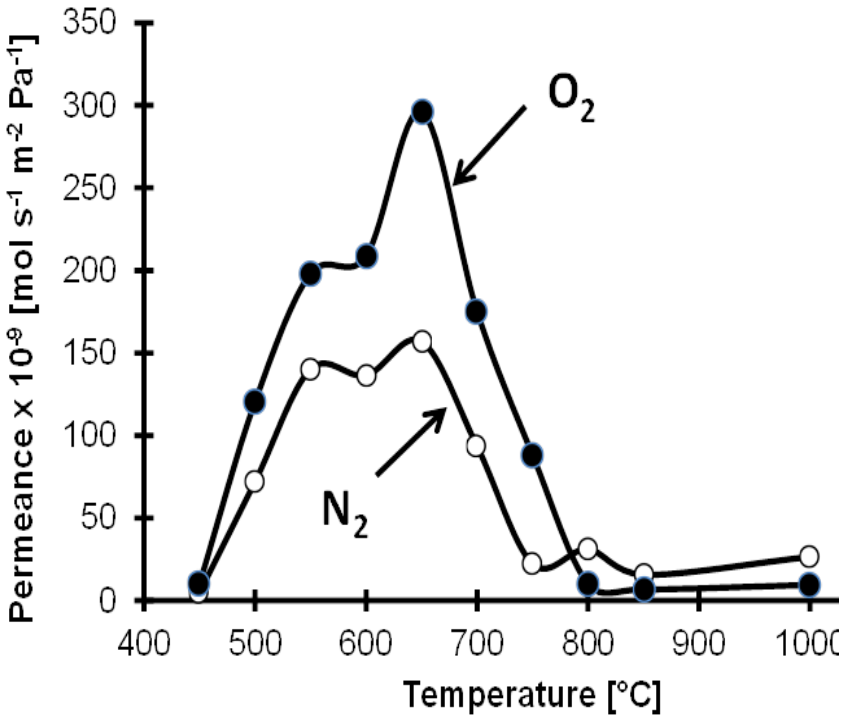


MS
Size separation

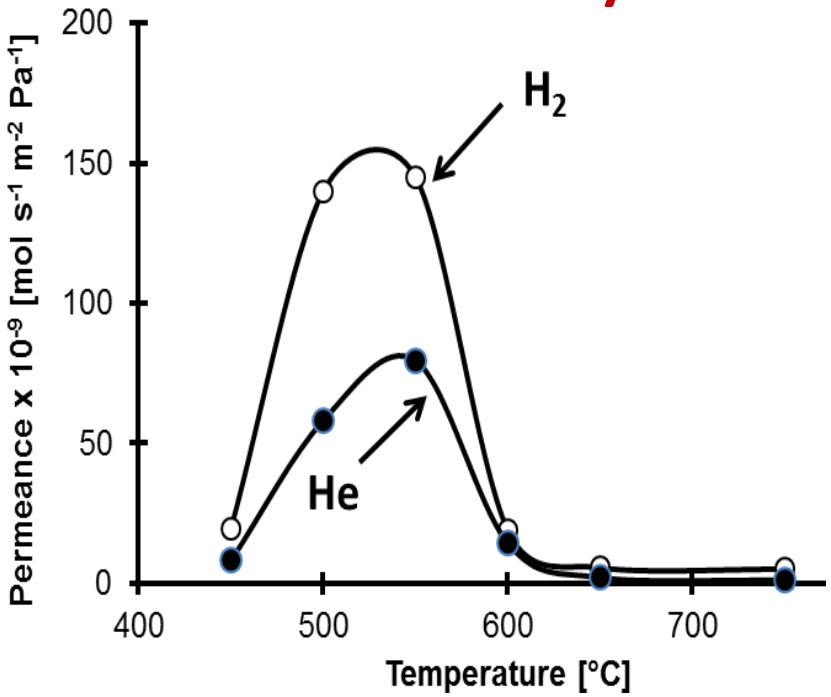
Adsorption
Difussion

Al-CMSM Effect of carbonization temperature

Fresh membrane



After one day



O_2 and N_2 very low flux

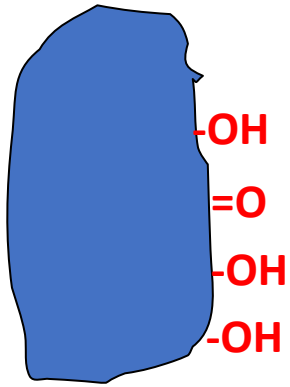
Llosa , Pacheco et.al Int J.hydrogen energy 40 (2015) 5653 40 (2015) 3485

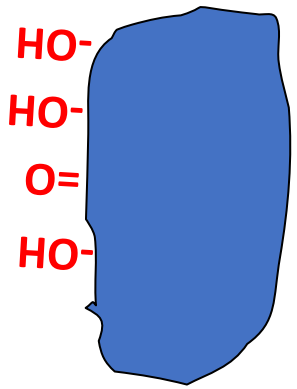
Modification on the porous

Just after carbonization

N_2 66 ml/min

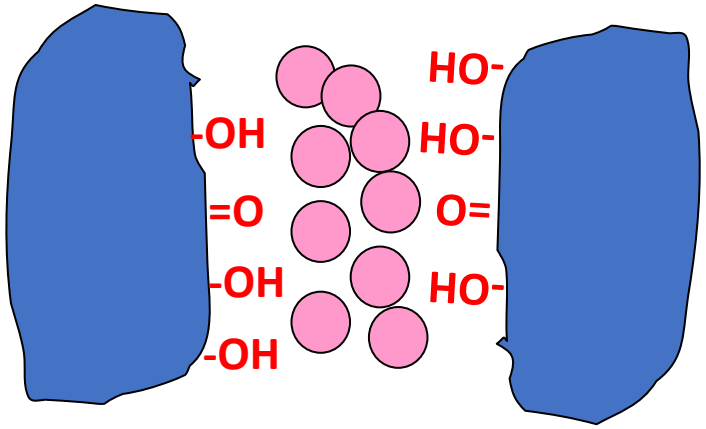
Active places react with water (water chemisorption)





N_2 20 ml/min

Water physisorption



water

Solutions to mitigate global warming

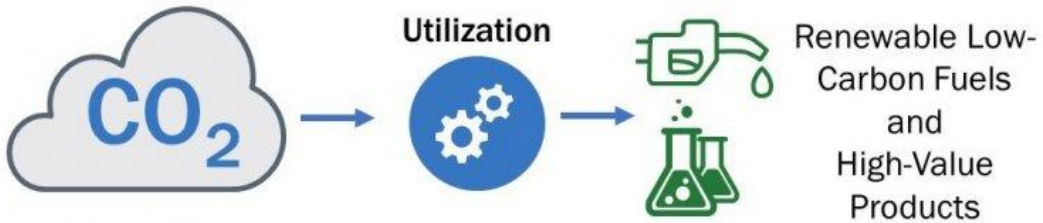
credit : gloly67

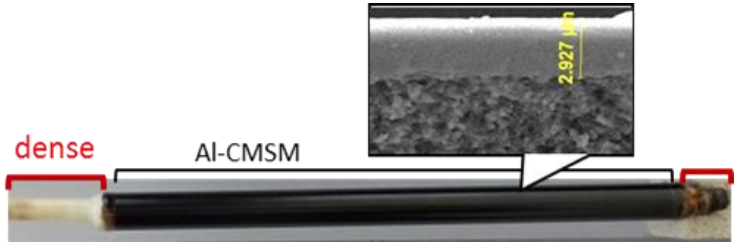
- Reduce the emission of greenhouse gases
- Use of clean fuels

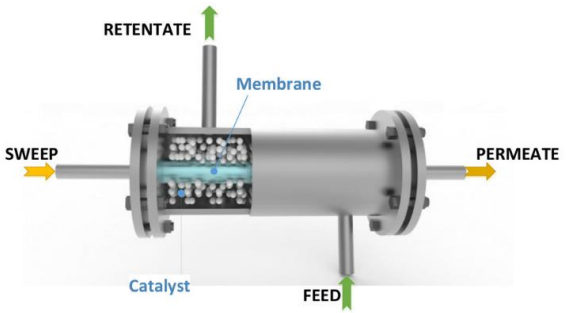
$$H_2 + 0.5\,O_2 \leftrightarrow H_2O$$

$$3\,H_2 + N_2 \leftrightarrow 2\,NH_3$$

- CO2 capture and utilization

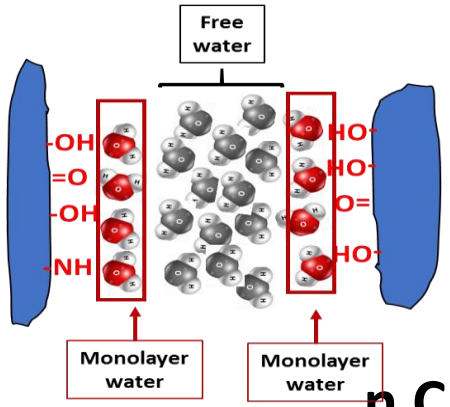






AI-CMSM

Valorization of CO_2 e-Fuels



$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2H_2O$

MEASURED

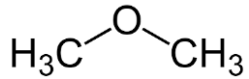
$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O$

CiCO2 Gasification Integrated with CO2 capture and conversion

$n\,CH_3OH + H_2 \leftrightarrow CH_3(CH_2)_{n-2}CH_3 + nH_2O$ Gasoline

$n\,CH_3OH + H_2 \leftrightarrow CH_2{=}CH(CH_2)_{n-2}CH_3 + nH_2O$ Light olefines

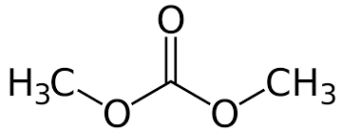
$2CO_2 + 6\,H_2 \leftrightarrow CH_3\text{-}O\text{-}CH_3 + 3H_2O$



Dimethyl ether

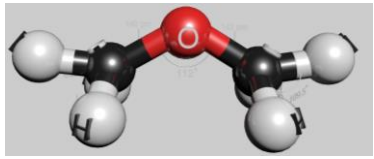
C2FUEL

$2CO_2 + 6\,H_2 \leftrightarrow CH_3\text{–}O\text{-}CO\text{-}O\,CH_3 + 3H_2O$



Dimethyl carbonate DMC

Synthesis of dimethyl ether using membrane reactors



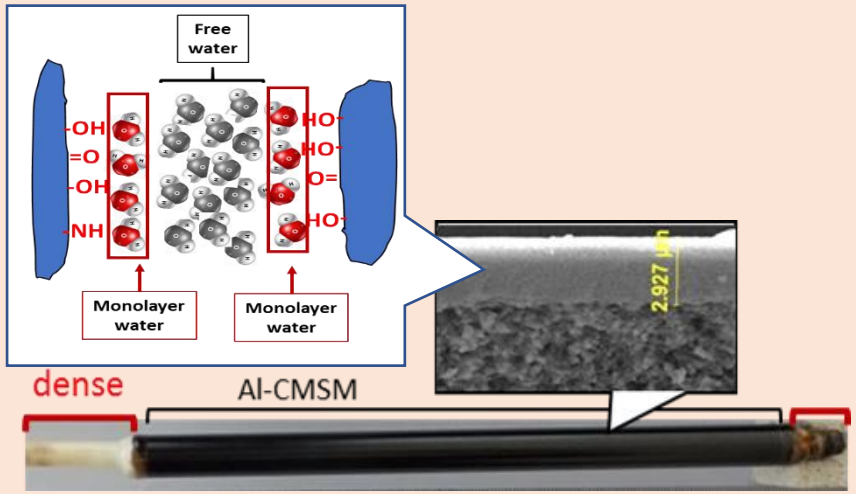
$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O$ MeOH synthesis

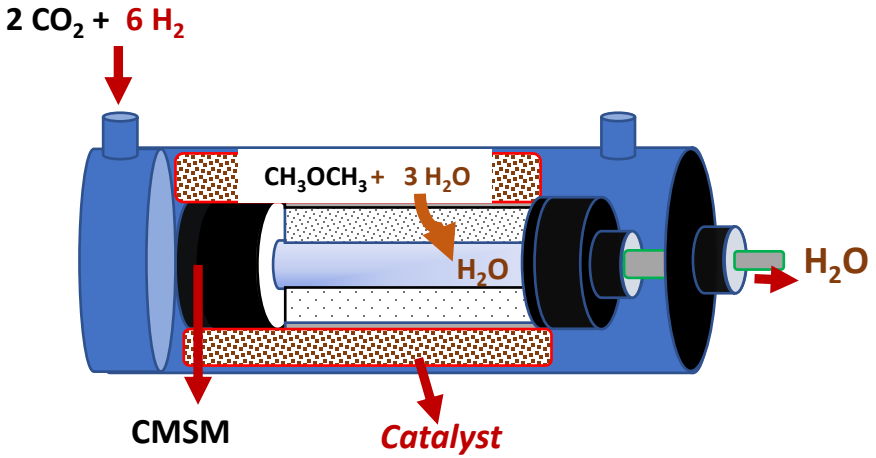
$2\,CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$ MeOH dehydration

$2\,CO_2 + 6\,H_2 \leftrightarrow CH_3OCH_3 + 3\,H_2O$ Direct DME synthesis

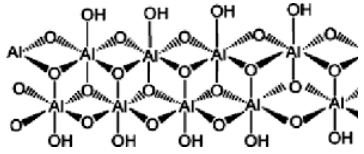
C2FUEL

Carbon molecular sieve Water gas membrane



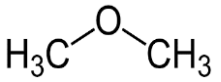


Boehmite



Gas permeation of Al-CMSM containing 0.8 % of boehmite

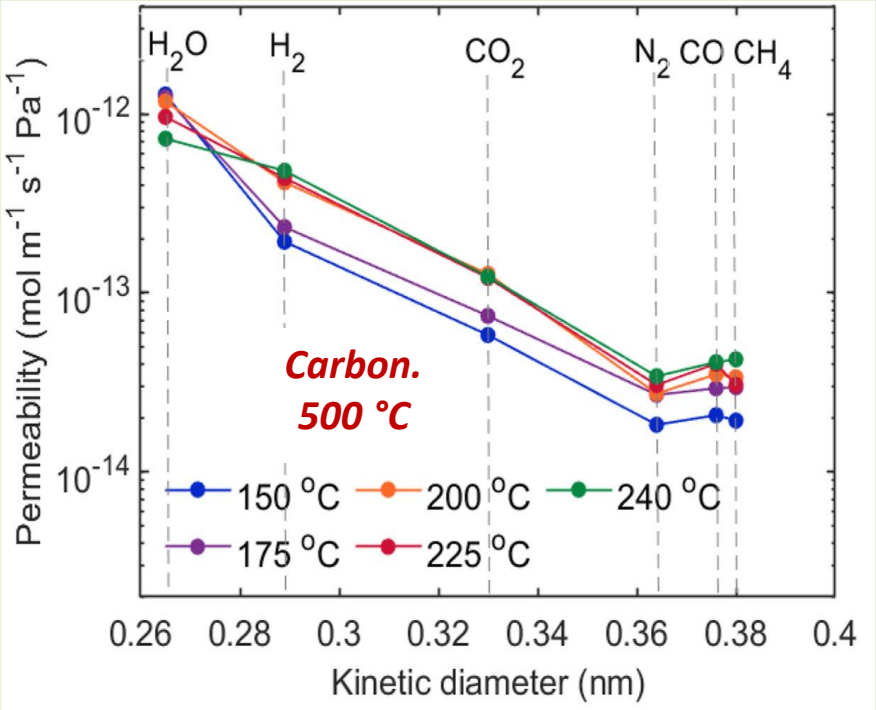
$2CO_2 + 6H_2 \leftrightarrow CH_3\text{-}O\text{-}CH_3 + 3H_2O$



Dimethyl ether

Effect of permeation temperature

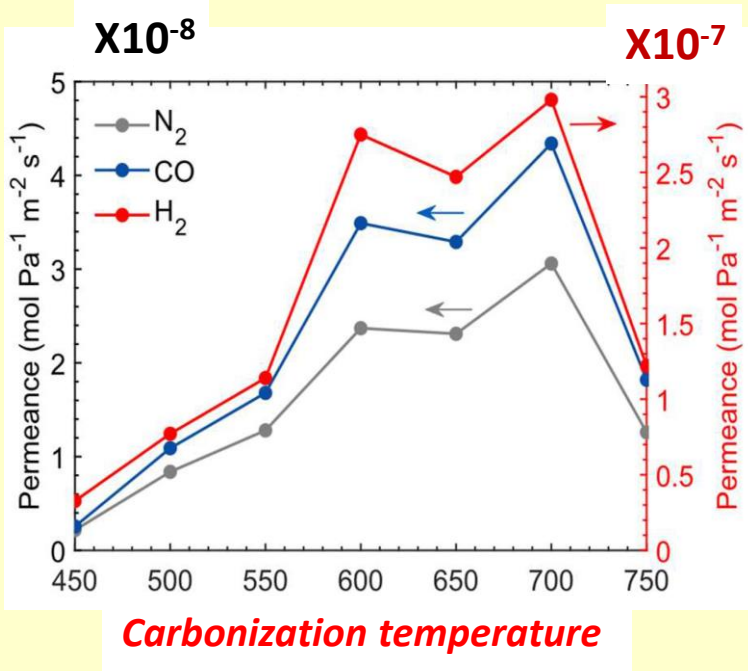
Al-CMSM carbonization 500 °C

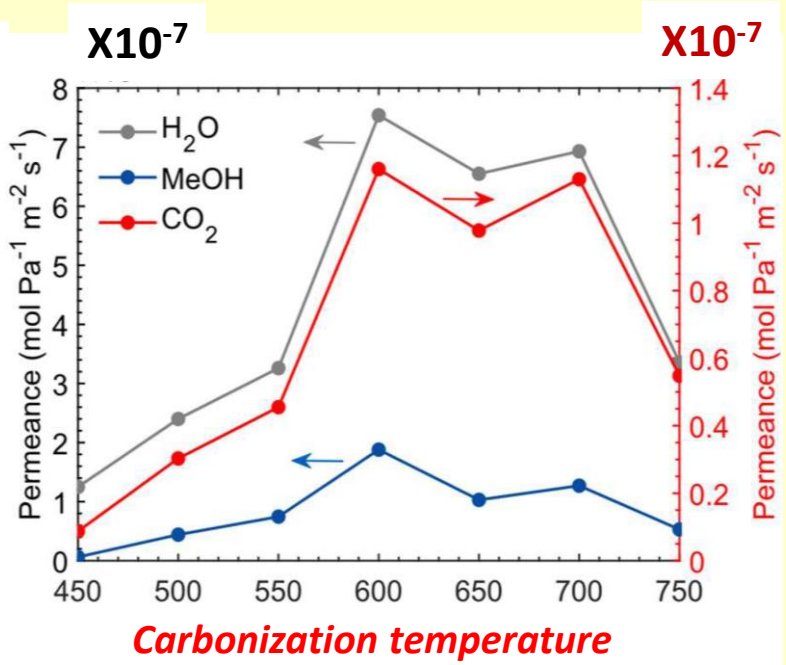


S. Poto et.al. *Int. J. hydrogen energy* 47(2022)11385

Effect of carbonization temperature

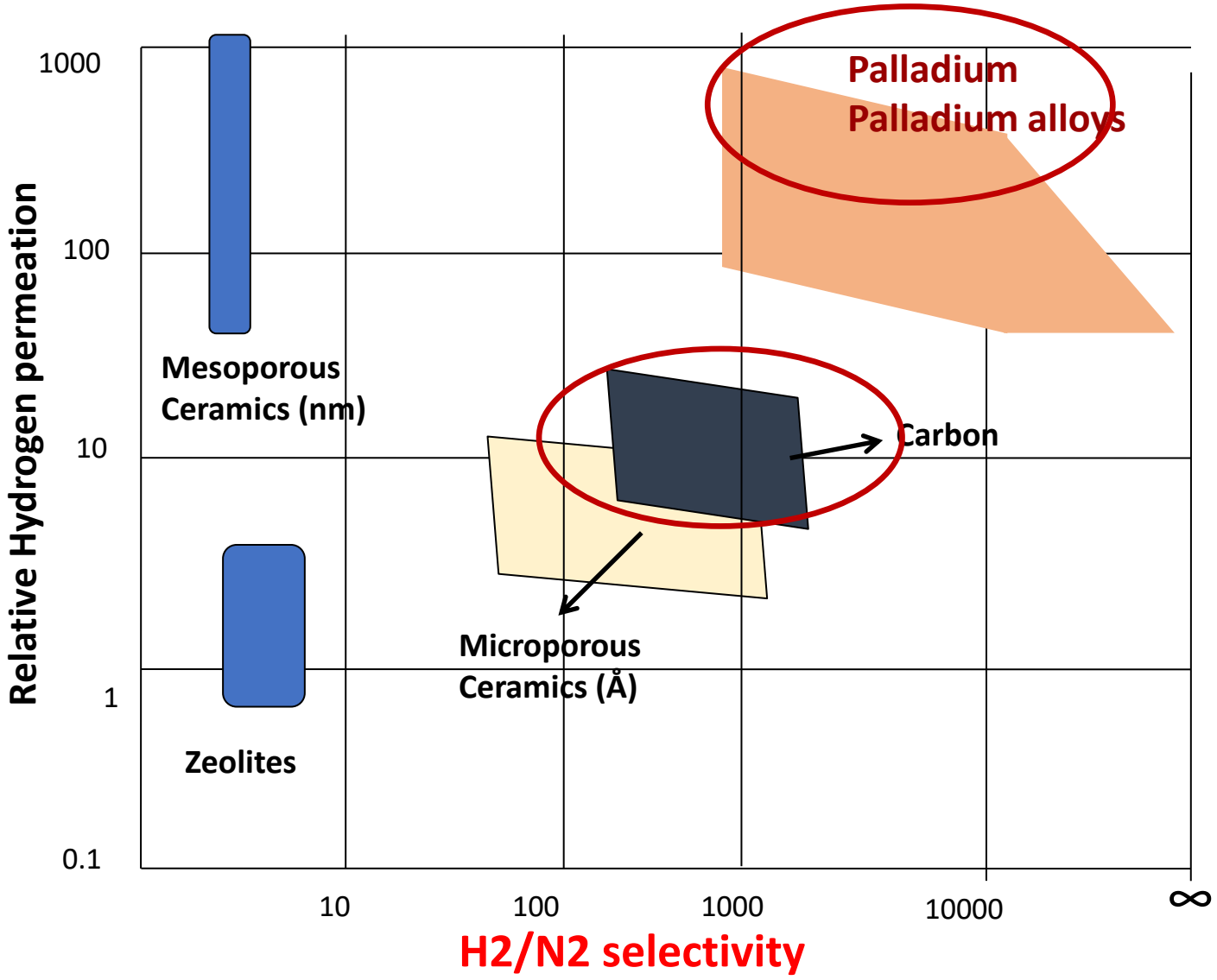
(permeation 200 °C)





S. Poto et.al. *J. Membr. Sci. 677*(2023)21613

H_2 selective membranes

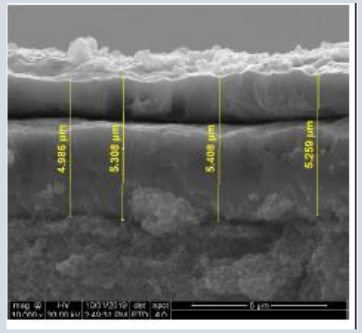


HyGrid

Blend hydrogen (10 % with NG)

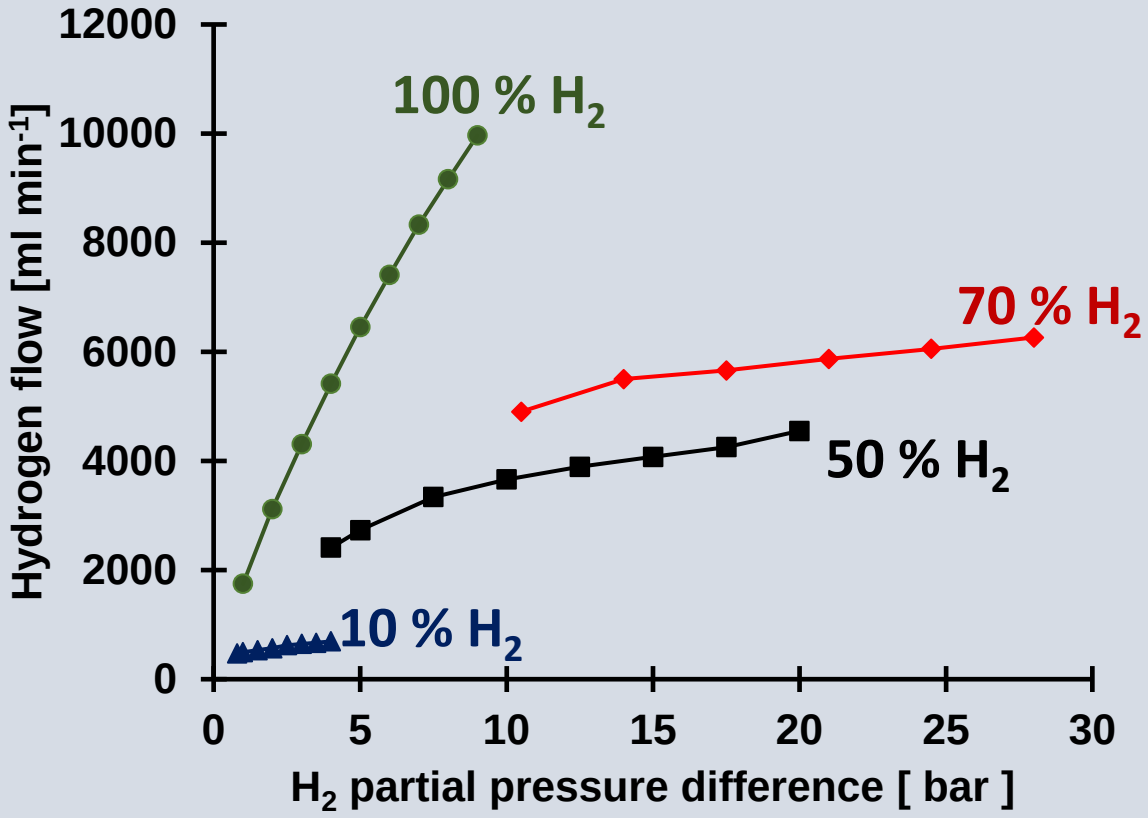
H_2 CH_4

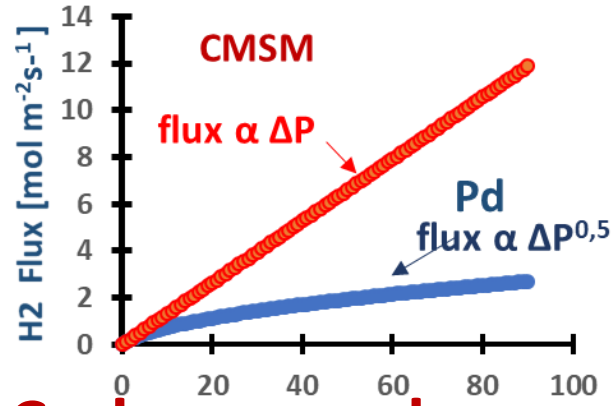
H_2 flow from H_2/CH_4 mixtures



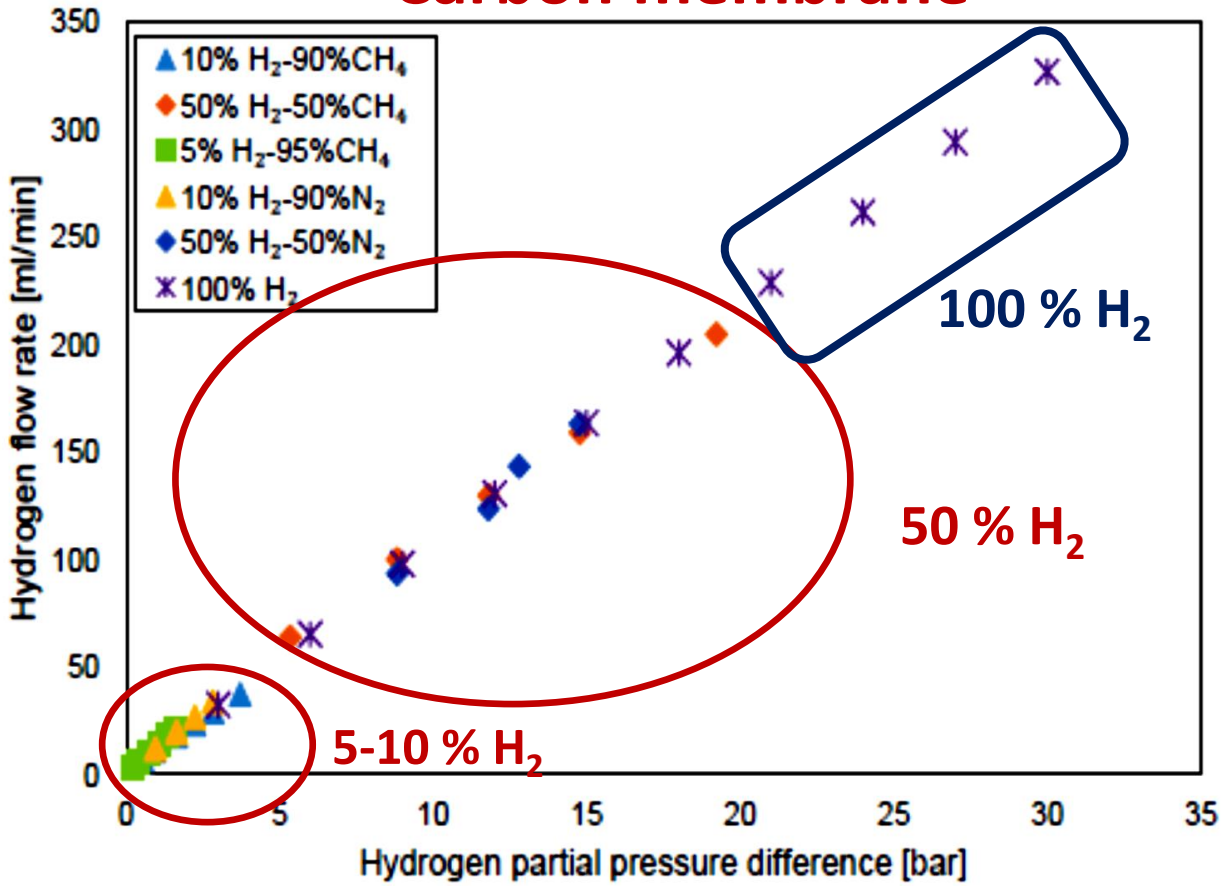
Pd-Ag double skin

400 °C



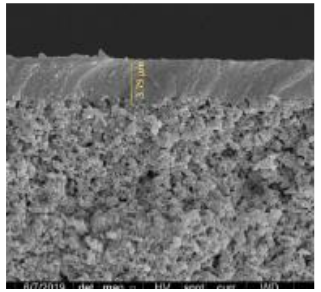


Carbon membrane

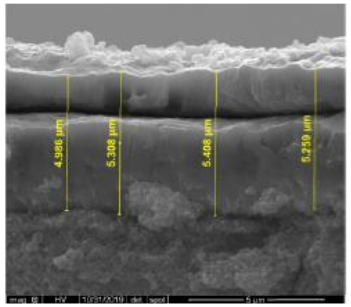


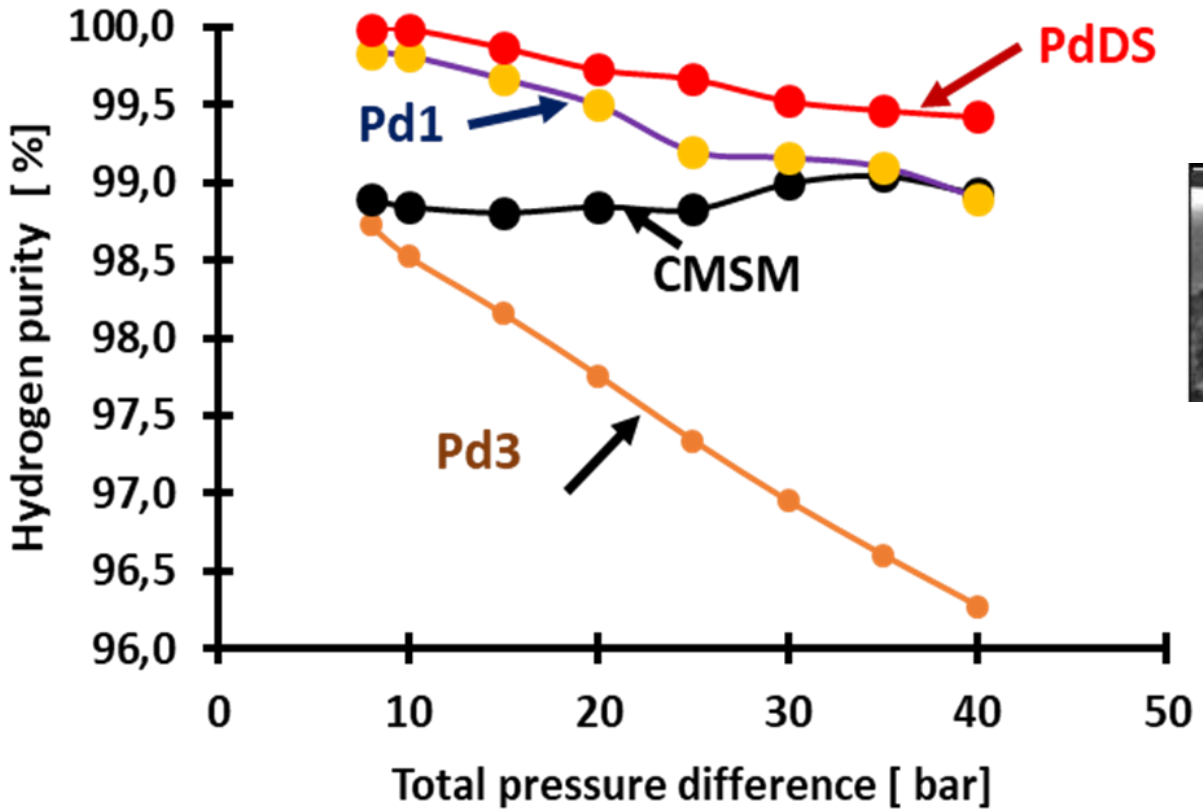
Gas grids for storage and distribution of CH_4 10% H_2 /90 % CH_4

Pd 1 and Pd3

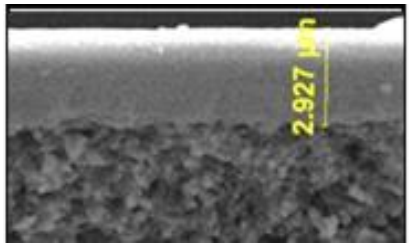


Pd 2 DS





CMSM



Techno-economic evaluation on a hybrid technology for low hydrogen concentration separation and purification from natural gas grid

Maria Nordio [a], *Solomon Assefa Wassie* [a], *Martin Van Sint Annaland* [c], *D. Alfredo Pacheco Tanaka* [b], *José Luis Viviente Sole* [b], *Fausto Gallucci* [a,*]

Int. J. hydrogen energy 46(2021)23417

Comparison between carbon molecular sieve and Pd-Ag membranes in H_2-CH_4 separation at high pressure

Maria Nordio [a], *Jon Melendez* [b], *Martin van Sint Annaland* [c], *D. Alfredo Pacheco Tanaka* [b], *Margot Llosa Tanco* [b], *Fausto Gallucci* [a,*]

Int. J. hydrogen energy 45(2020)28876

14:49

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 47 (2022) 14570–14579

Effect of aluminium acetyl acetonate on the hydrogen and nitrogen permeation of carbon molecular sieves membranes

A. Rahimalimamaghani [a], D.A. Pacheco Tanaka [a,b], M.A. Llosa Tanco [a,b], F. Neira D'Angelo [a], F. Gallucci [a,c,*]

Al-CMSM

Boehmite nanoparticles

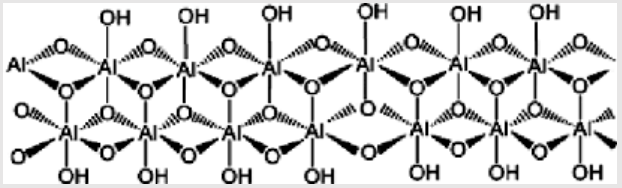
Novolac resin

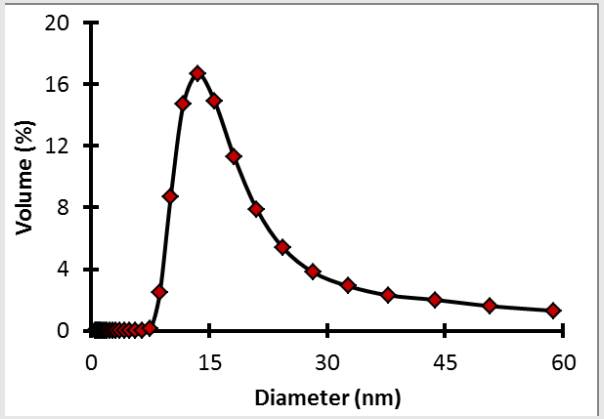
Ethylenediamine

HCHO

NMP

Boehmite γ-Al(O)OH





Atomic Al-CMSM

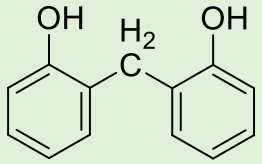
$Al(acac)_3$

Novolac resin

Oxalic acid

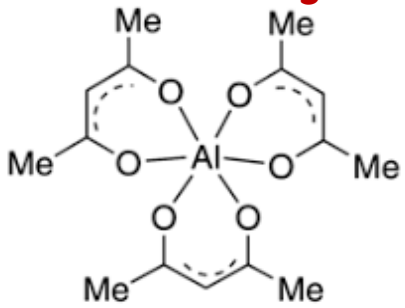
HCHO

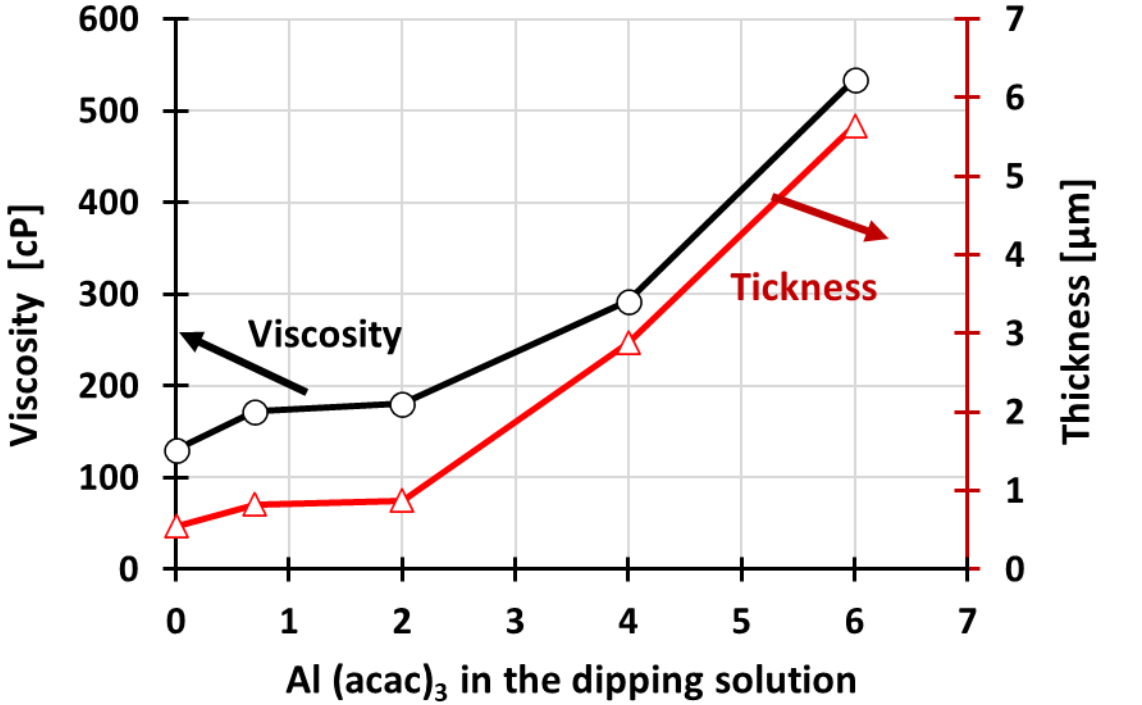
NMP



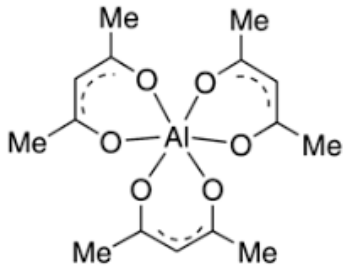
Novolac

$Al(acac)_3$

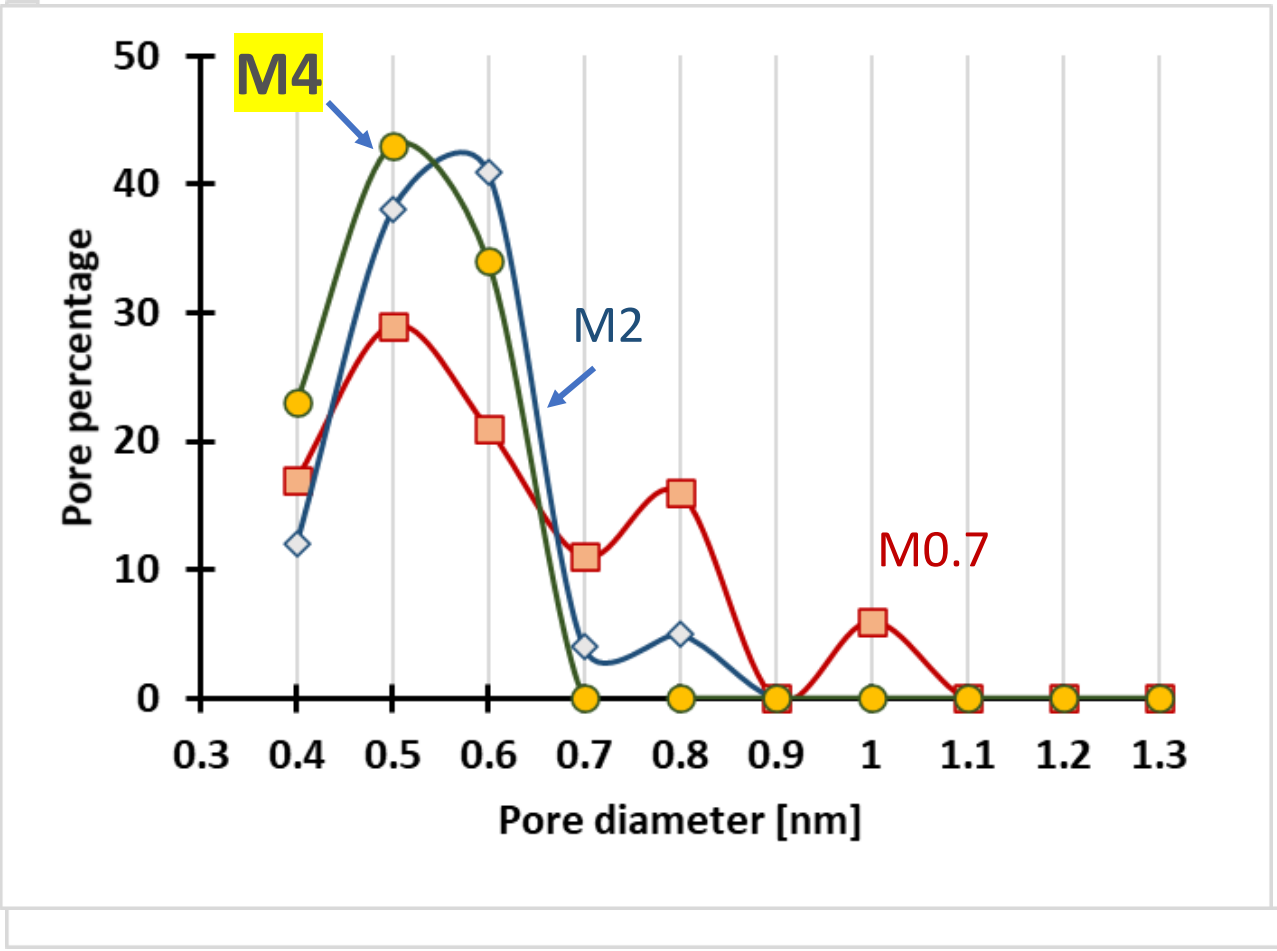


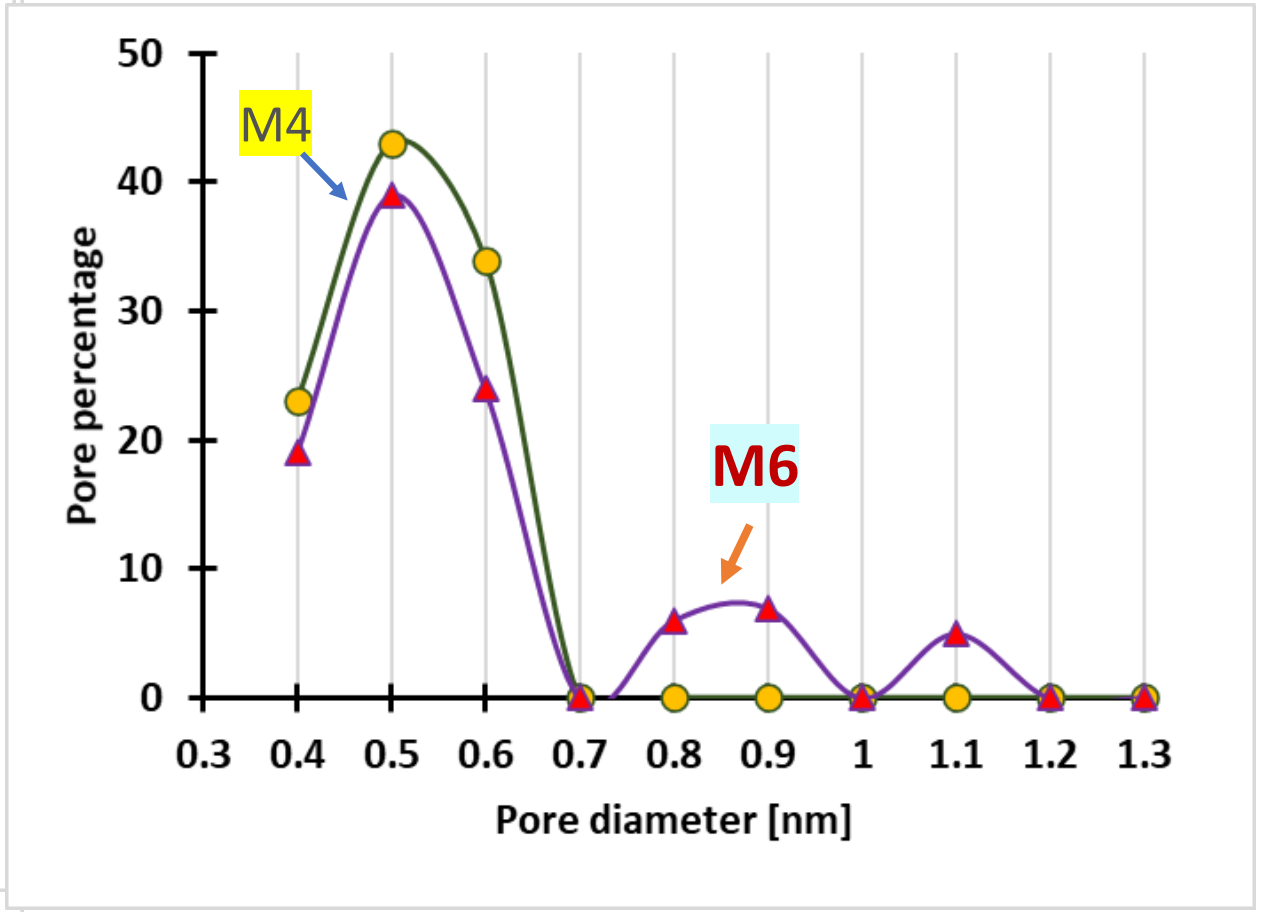


14:49

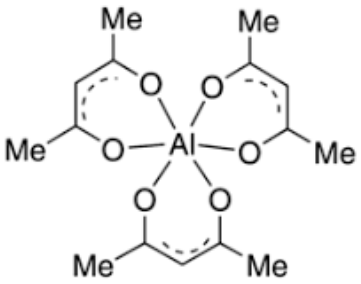


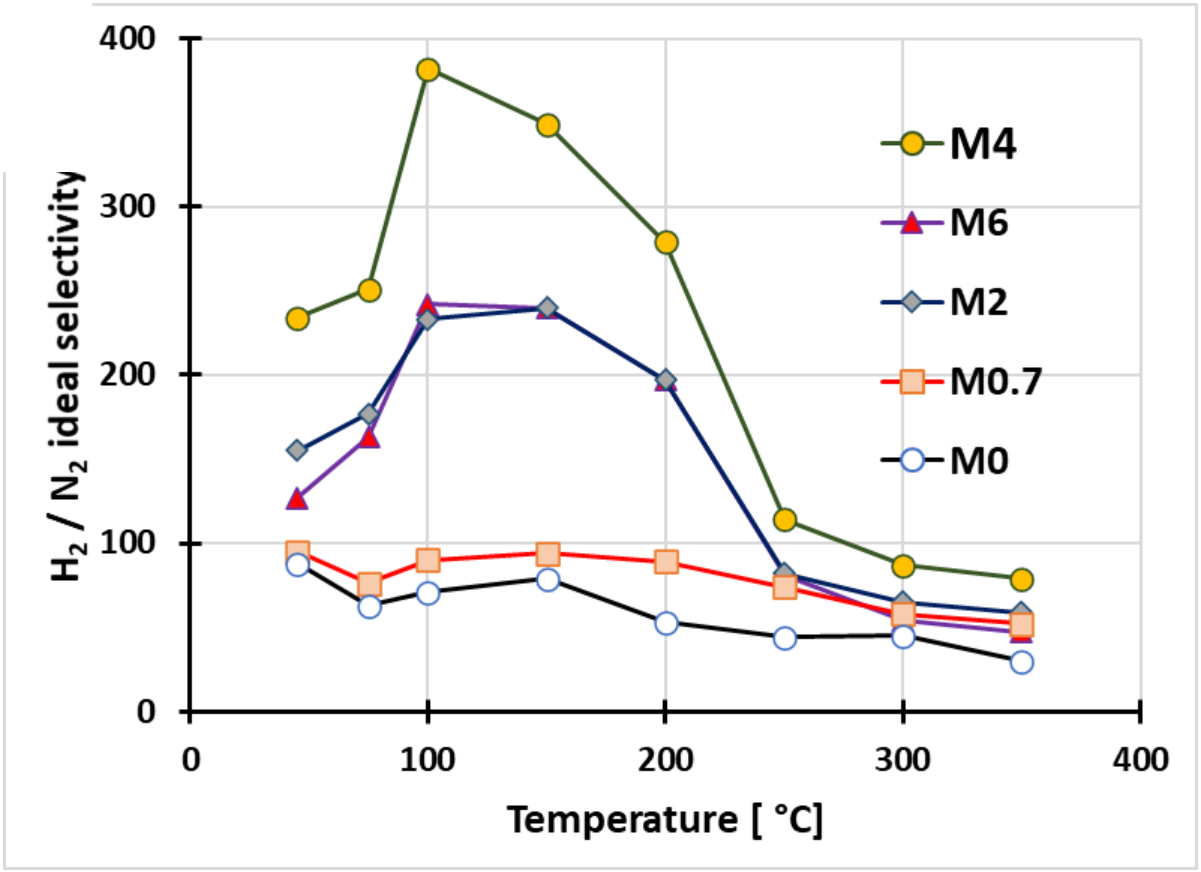
Pore size distribution by perm-porosimetry

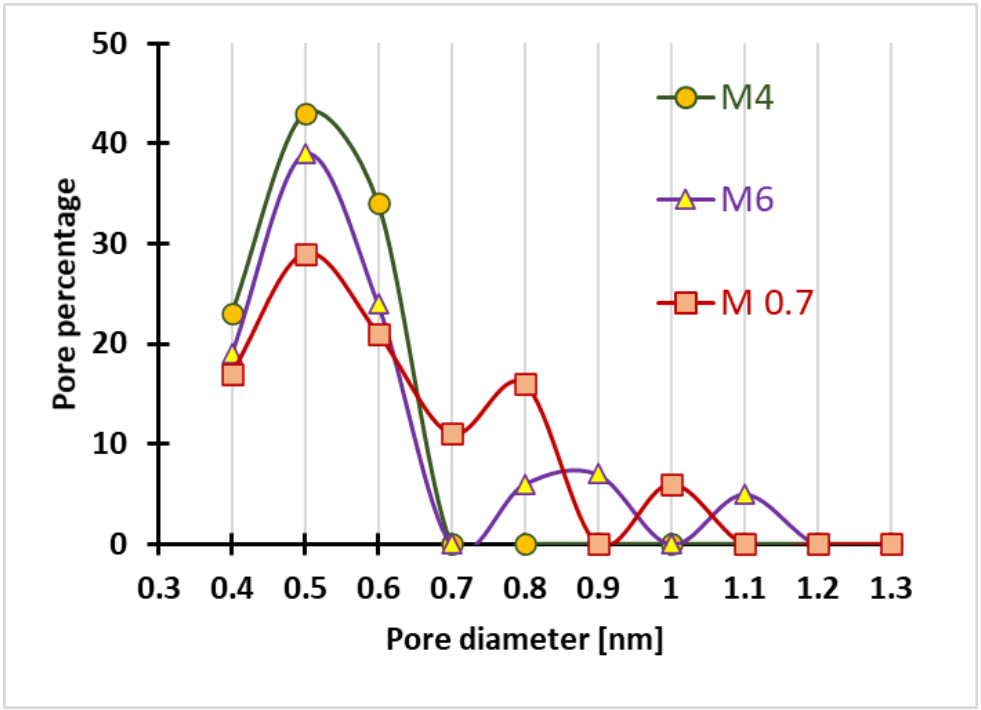




H_2 / N_2 ideal selectivity at various temperatures of permeation in function of the content of $Al(acac)_3$ in the dipping solution







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CMSM for Selective CO_2–Separation at Elevated Temperatures and Pressures

Journal of CO2 Utilization 68 (2023) 102378

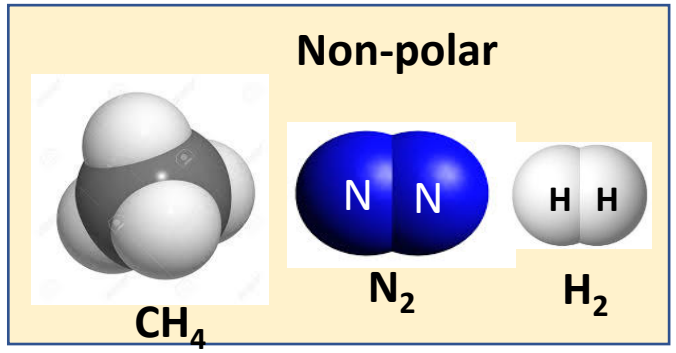
Contents lists available at ScienceDirect

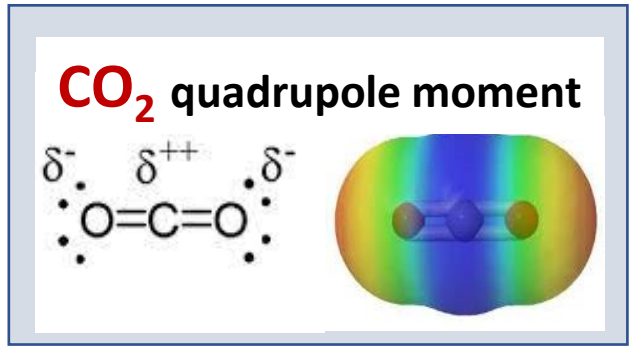
Journal of CO2 Utilization

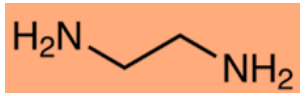
journal homepage: www.elsevier.com/locate/jcou

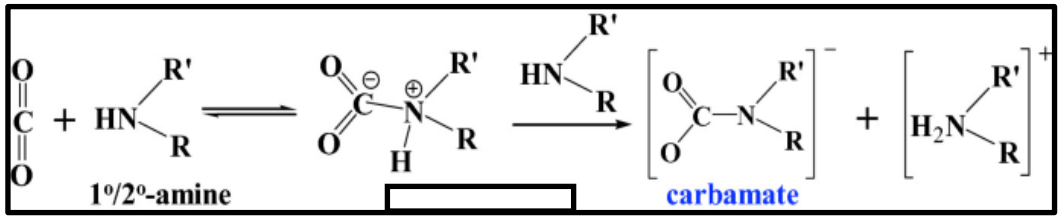
Carbon molecular sieve membranes for selective CO_2 separation at elevated temperatures and pressures

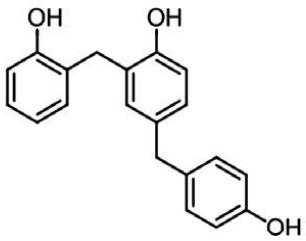
A. Rahimalimamaghani [a], H.R. Godini [a,*], M. Mboussi [a], A. Pacheco Tanaka [a,b], M. Llosa Tenco [a,b], F. Gallucci [a,c,**]





Addition of ethylenediamine  in olygomerization

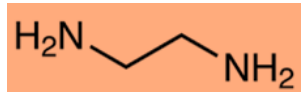


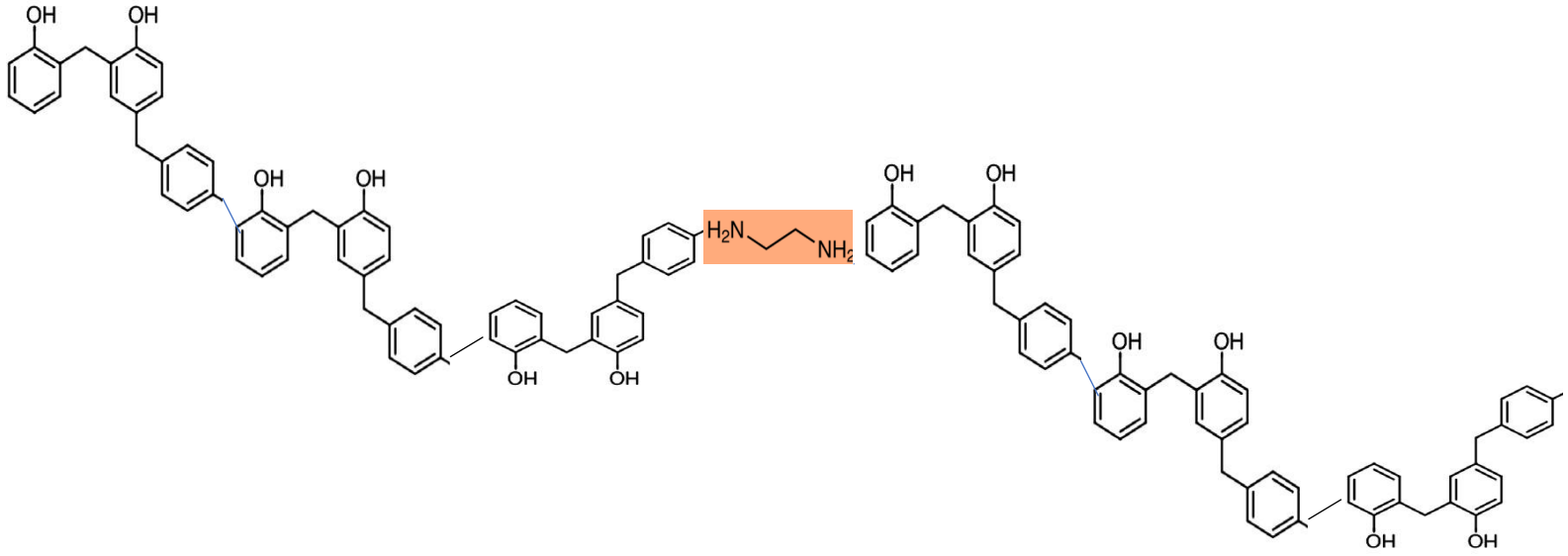


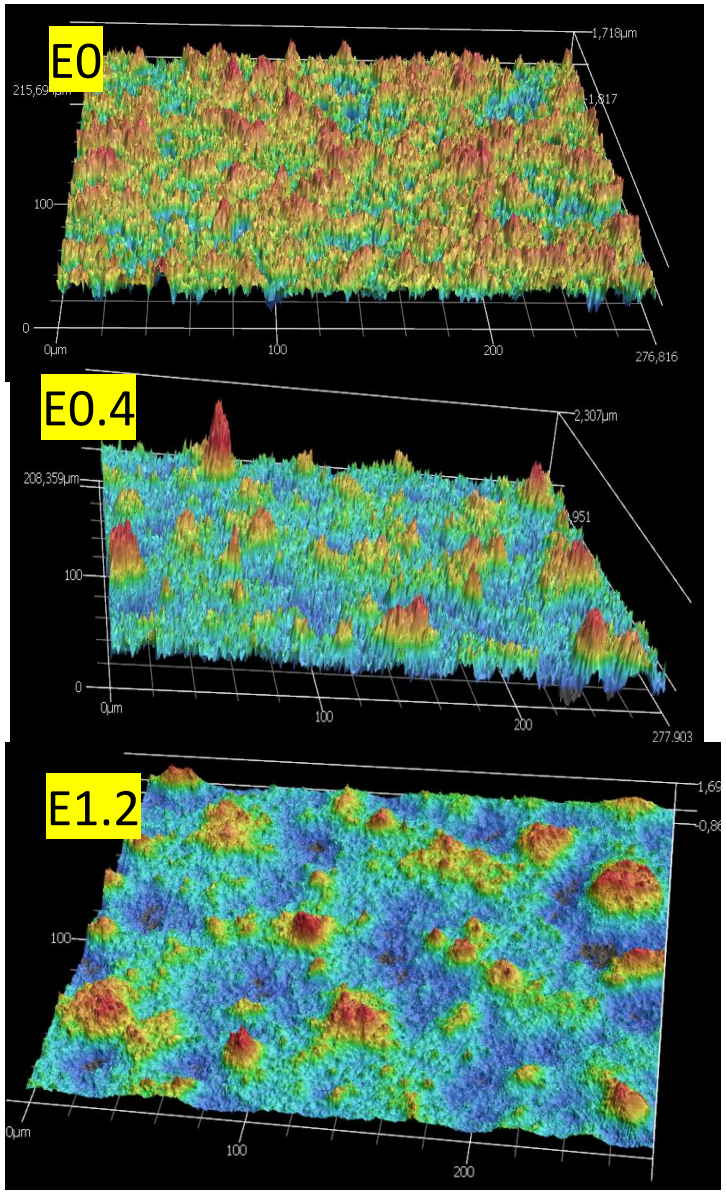
HCHO
formaldehyde

Novolak

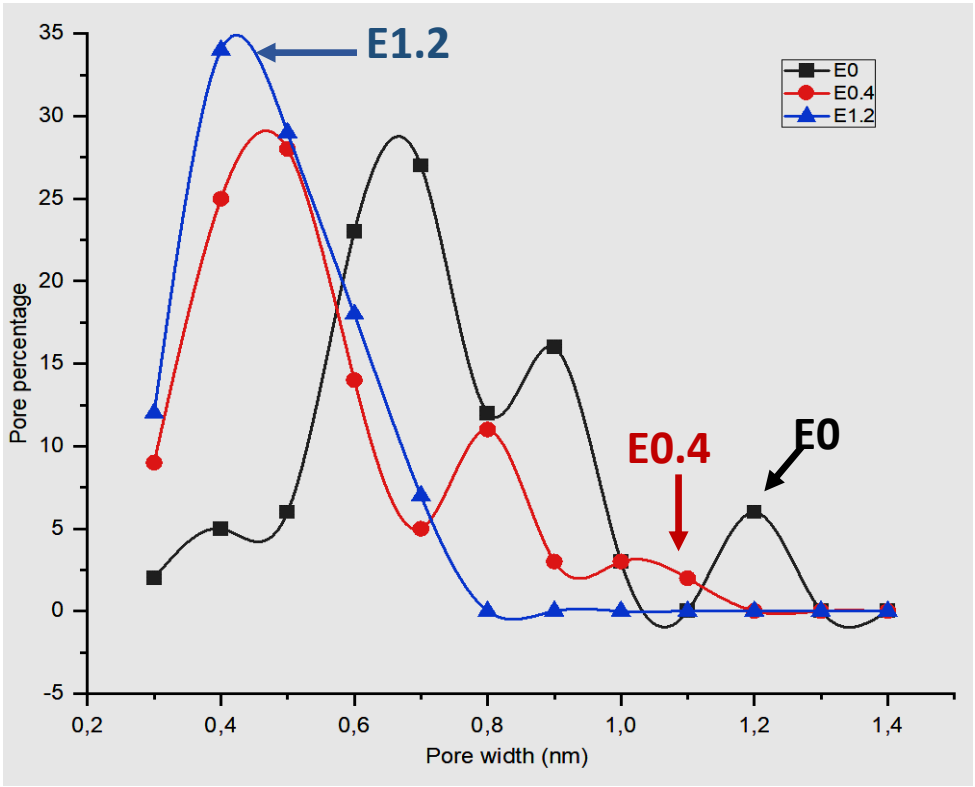
Acid: oxalic acid

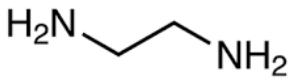






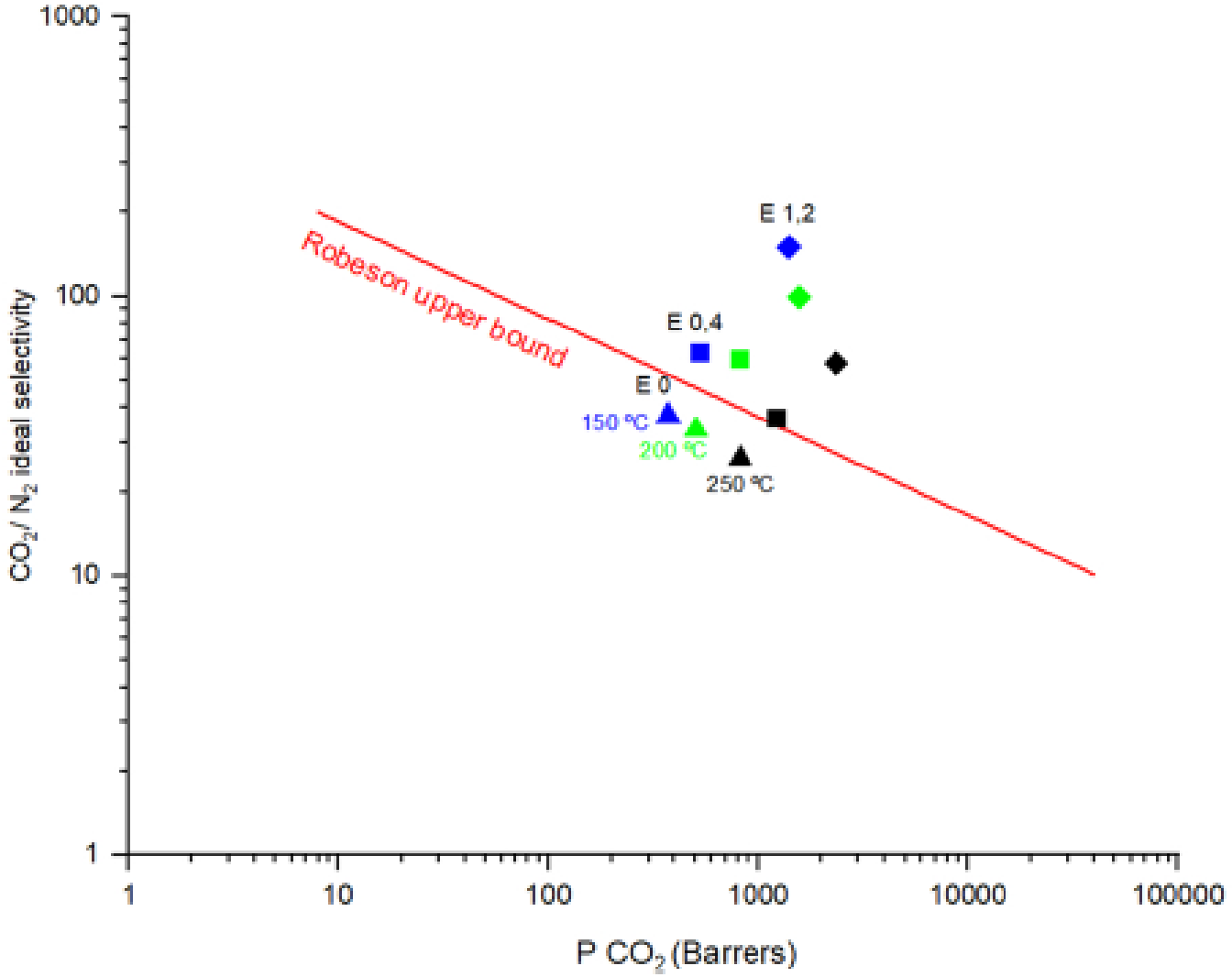
H_2N–⟋⟍–NH_2	C		H		O		N		MW
	% *	# atoms	% *	# atom	% *	# atom	% *	# atom	
Novolac	76.97	19	6.79	20.0	16.24	3	--	--	296
E 0	94.12	31	1.53	6.00	4.35	1.07	--	--	395
E 0.4	92.09	122	1.90	30.0	5.05	5.02	0.96	1.1	1590
E 1.2	89.08	187	2.36	59.0	5.74	5.07	2.82	9.04	2519



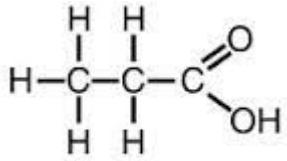


crosslink

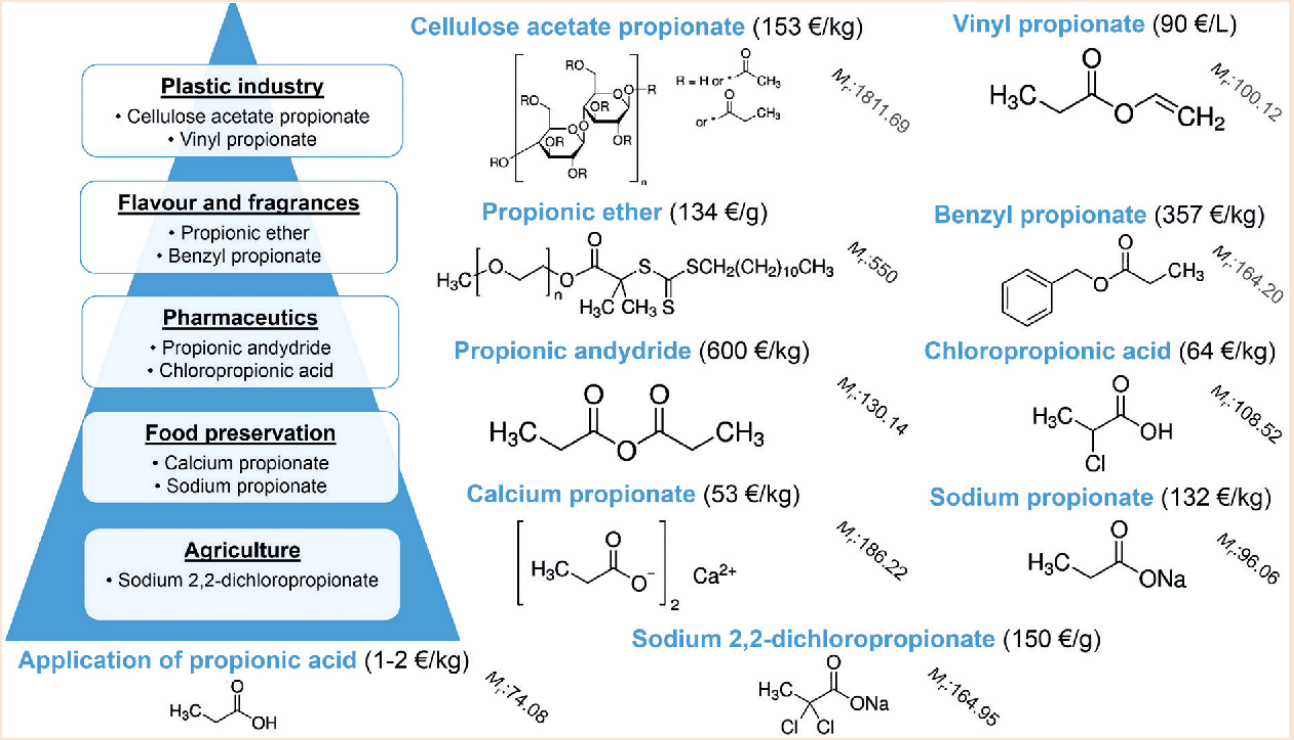
14:49


1000
100
10
1
CO_2/ N_2 ideal selectivity
Robeson upper bound
E 1,2
E 0,4
E 0
150 ºC
200 ºC
250 ºC
1
10
100
1000
10000
100000
P CO_2 (Barrers)

Propionic acid production by membrane bio-reactors



Applications of propionic acid (PA)

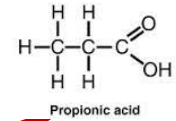


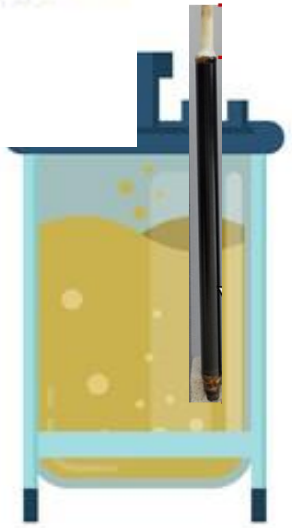
https://doi.org/10.17113/ftb.58.02.20.6356

M. Ciani, ... I. Mannazzu, in
Encyclopedia of Ecology (Second Edition), 2013

Inhibition by product (PA)

Pervaporation

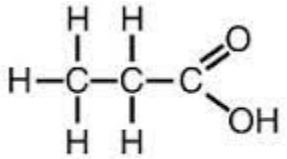




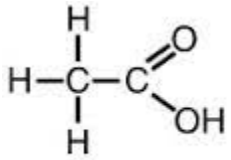
shutterstock.com · 1996305308

Bio-reactor

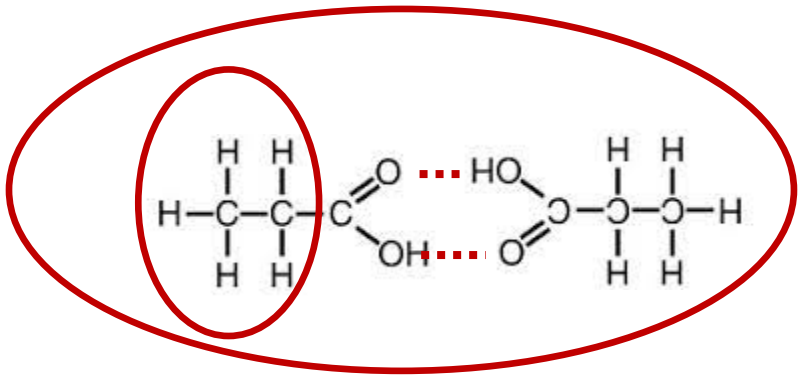
Physico-chemical properties



Propionic acid



Acetic acid



hydrophobic

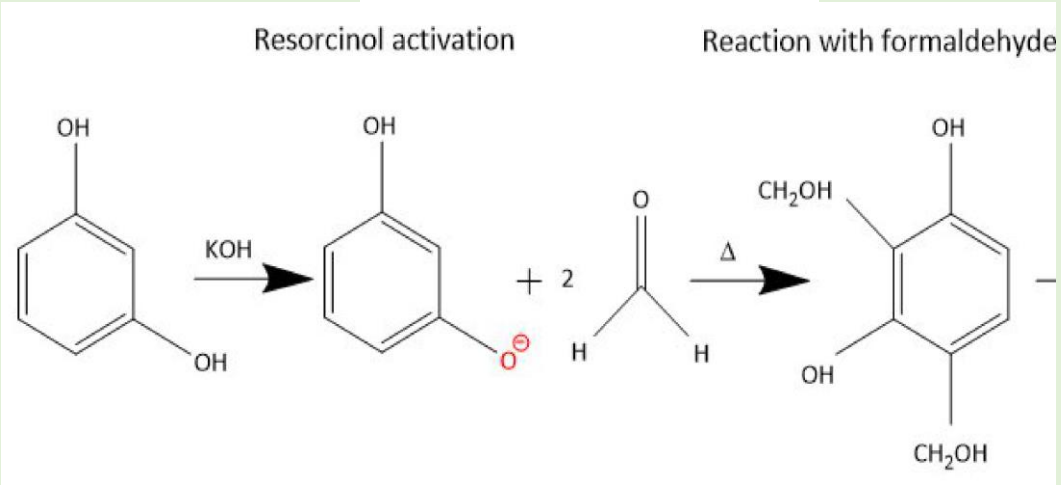
	MW g mol^{-1}	Kin Dia [a] nm	BP [b] °C	MP [c] °C	Dipole moment D
H_2O	18	0.265	100	0	1.85
CH_3-COOH	60	0.436	118-119	16-17	1.74
CH_3-CH_2-COOH	74	0.480 *	141	-20.5	0.63

Tailoring carbon membrane

Hydrophobic (Water will not pass)

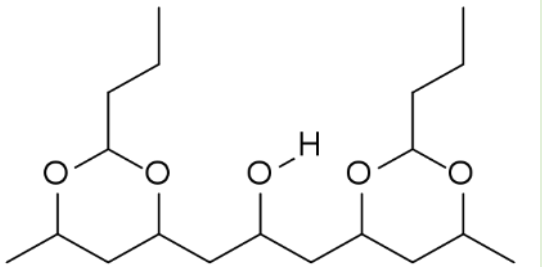
Pores 0.5 – 0.6 nm

Resol phenolic resin

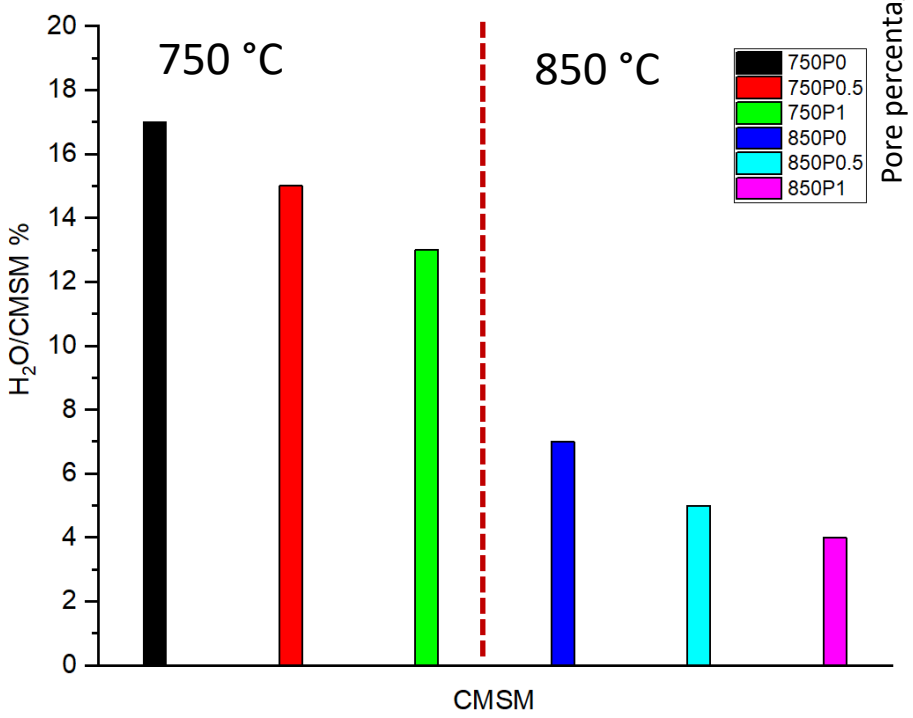


Pore-forming agent

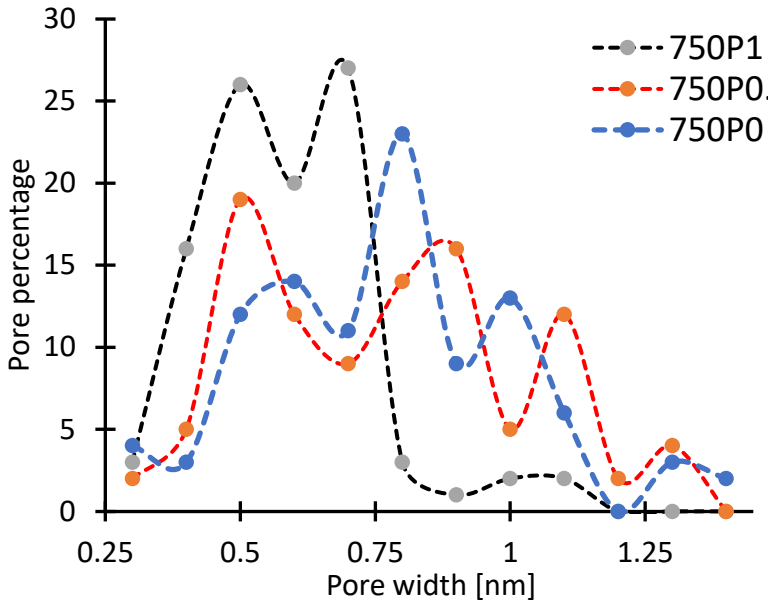
Polyvinyl butiral (PVB)

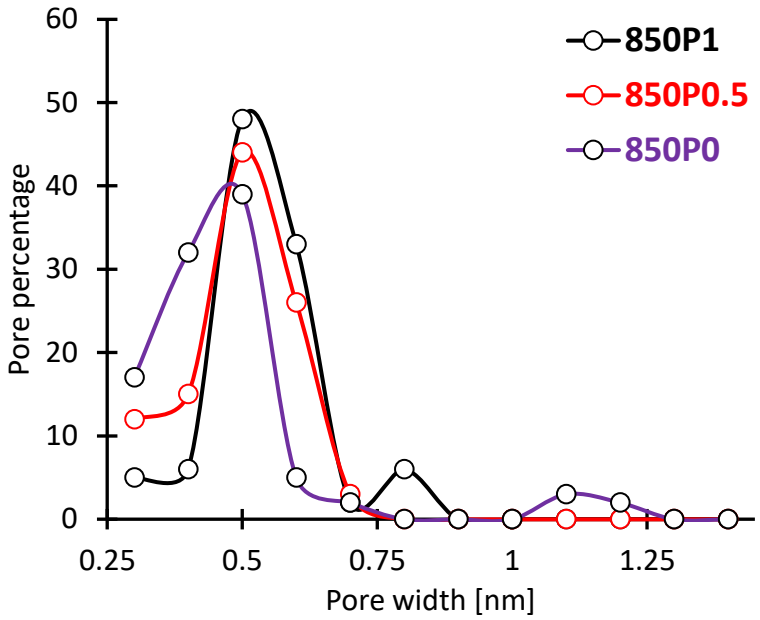


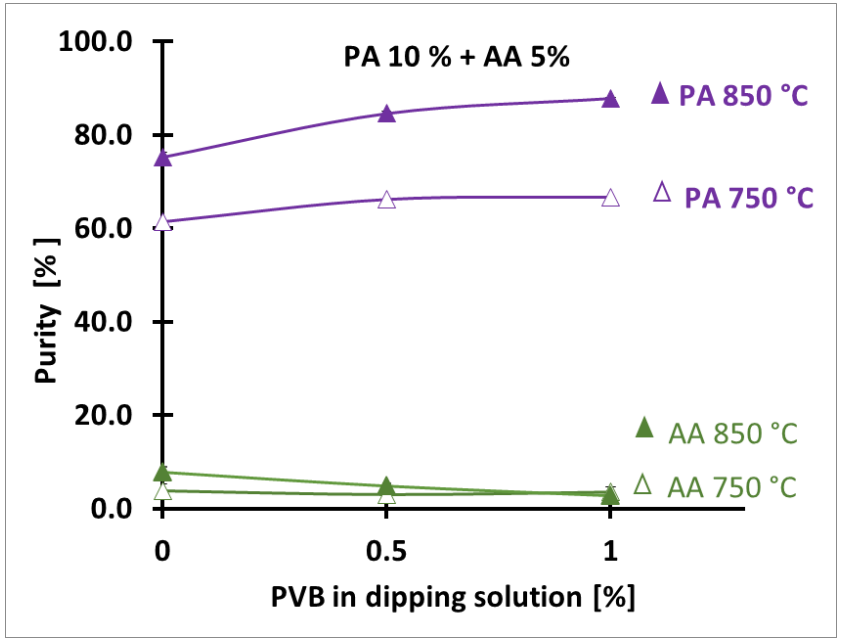
Hydrophilicity (water adsorption)



Pore size distribution







H_2 vs NH_3

H_2

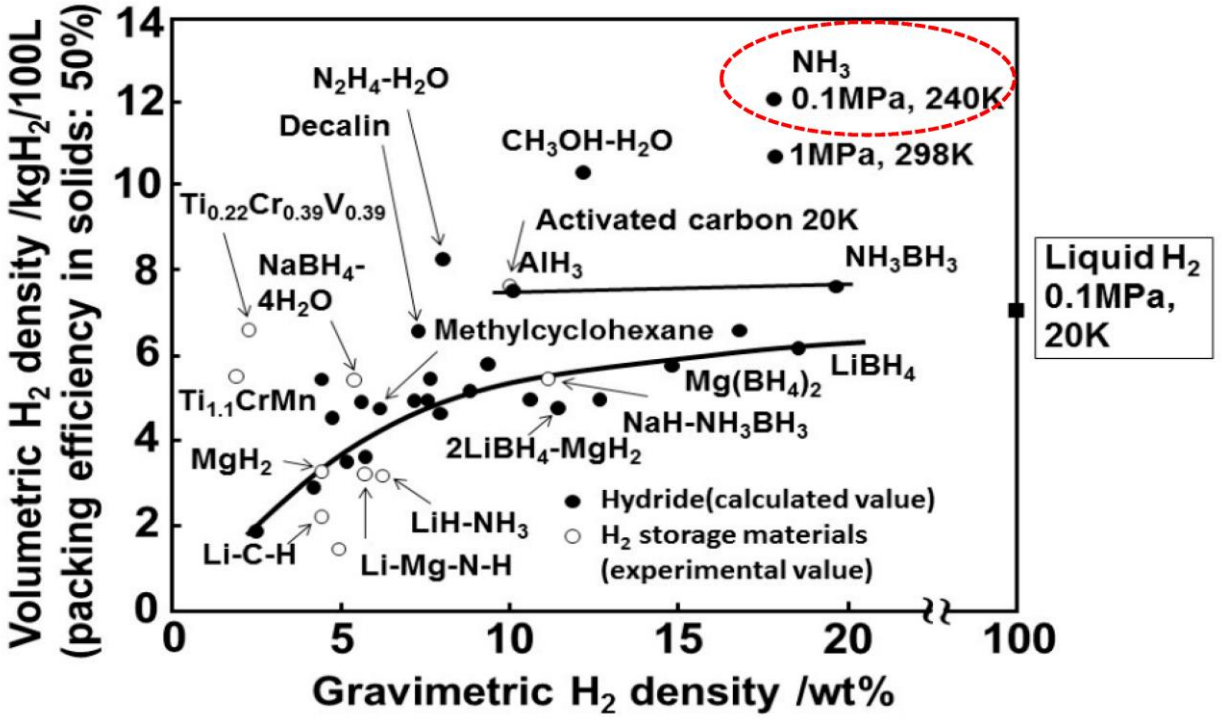
Liquid H2 is at least 10 times more expensive to produce and store than NH_3 because it requires high pressure and low temperature

NH_3

Liquid at 10 bar or -33 °C
Ammonia has a supply chain and storage well established

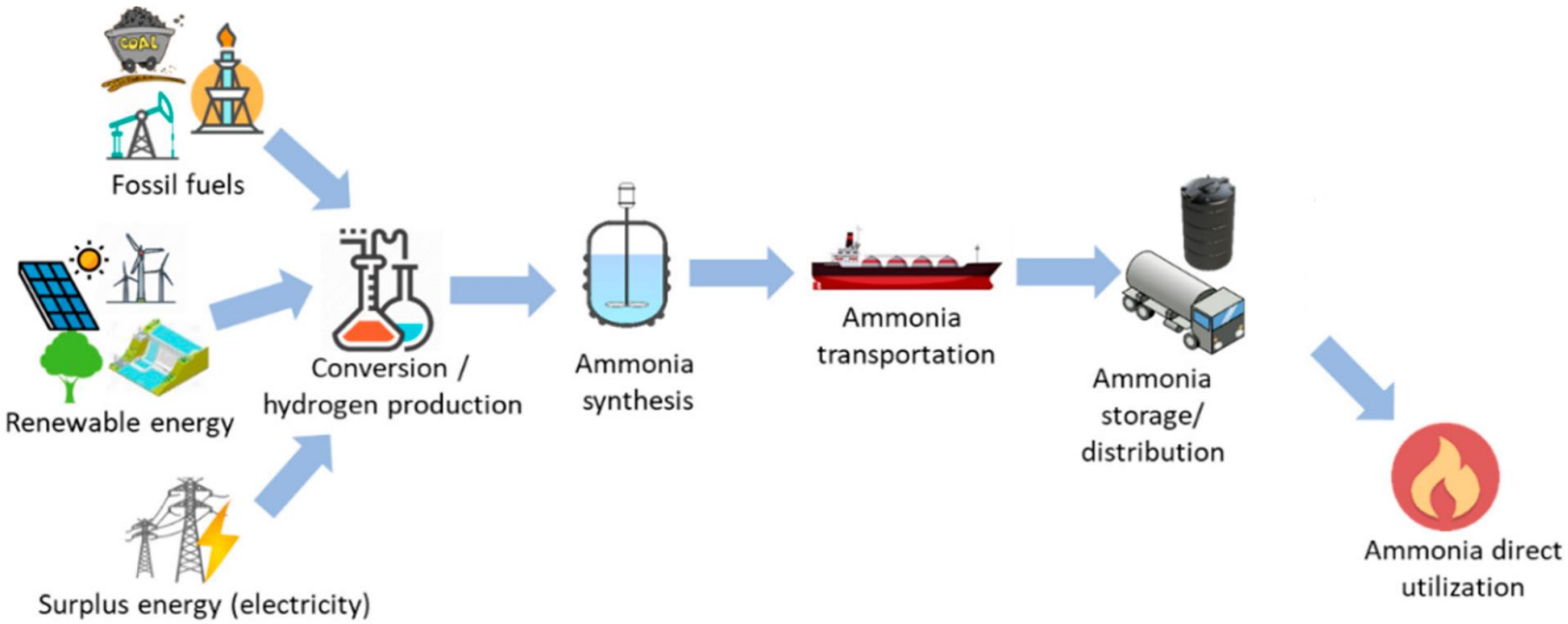
NH_3 was used in internal combustion engines since 1800

The density of hydrogen in hydrogen carriers



Energies **2021**, *14*(13), 3732

NH_3 as transport and storage of H_2



Descomposition of ammonia

$$2\ NH_3 \rightarrow 3H_2 + N_2$$

areNH3a

NH_3 Synthesis

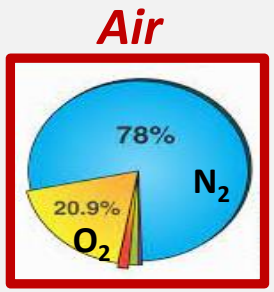
Haber-Bosch (H-B) process (1913)

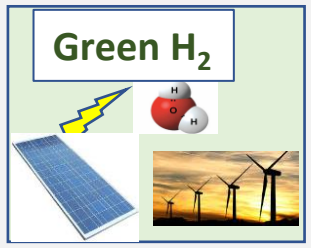
$6H_2O + 3CH_4 + 4N_2 \rightarrow 3CO_2 + 8\ NH_3$

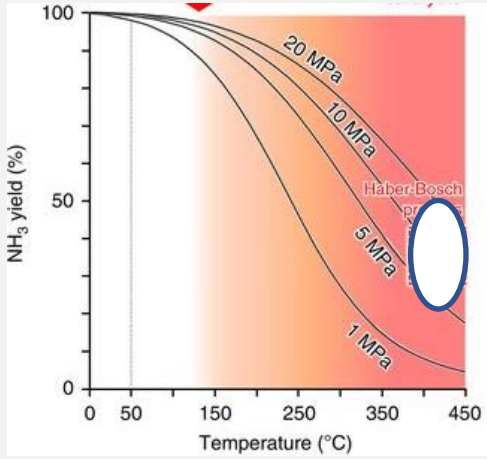
1.8% energy consumed **1.8% CO_2** produced **in the world**

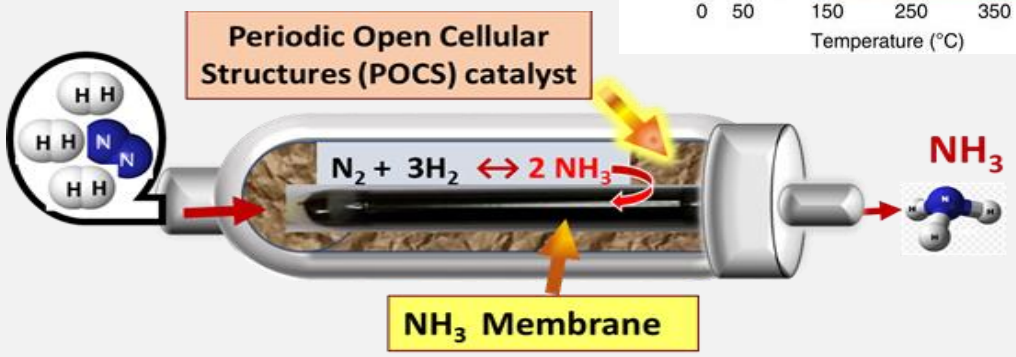
Catalytic Membrane Reactor (CMR)

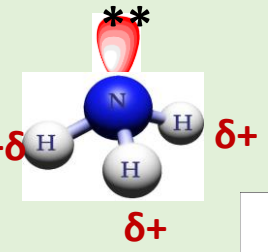
$N_2 + 3H_2 \rightarrow 2NH_3$ **ΔH - 46 kJ/mol**

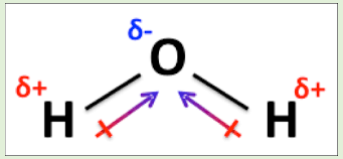




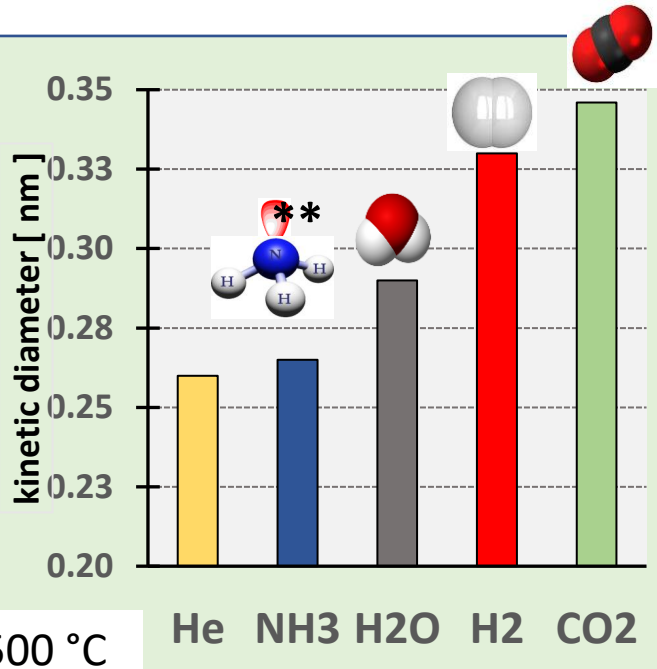




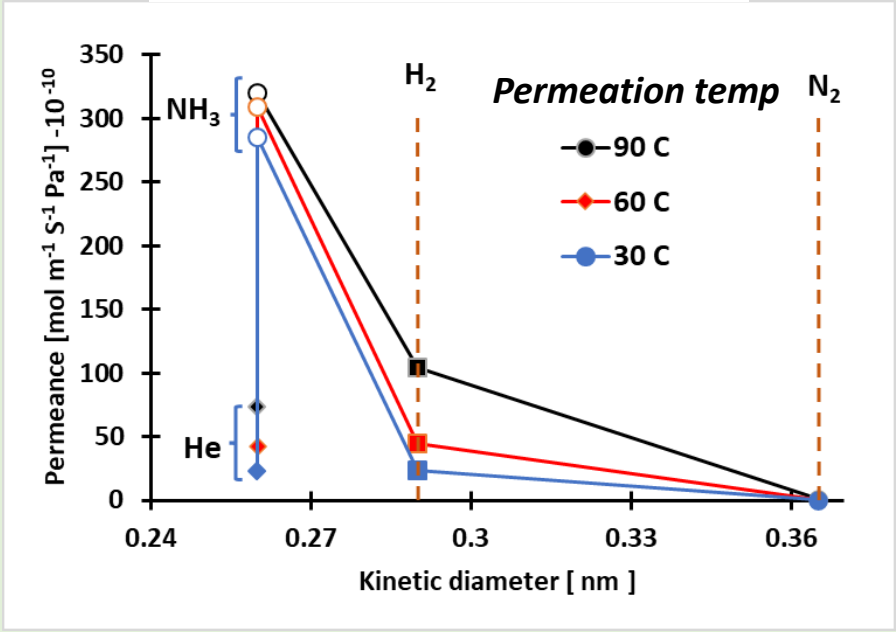




NH_3 Dipole, pair electrons (H-bonding)



Al-CMSM carbonized 500 °C



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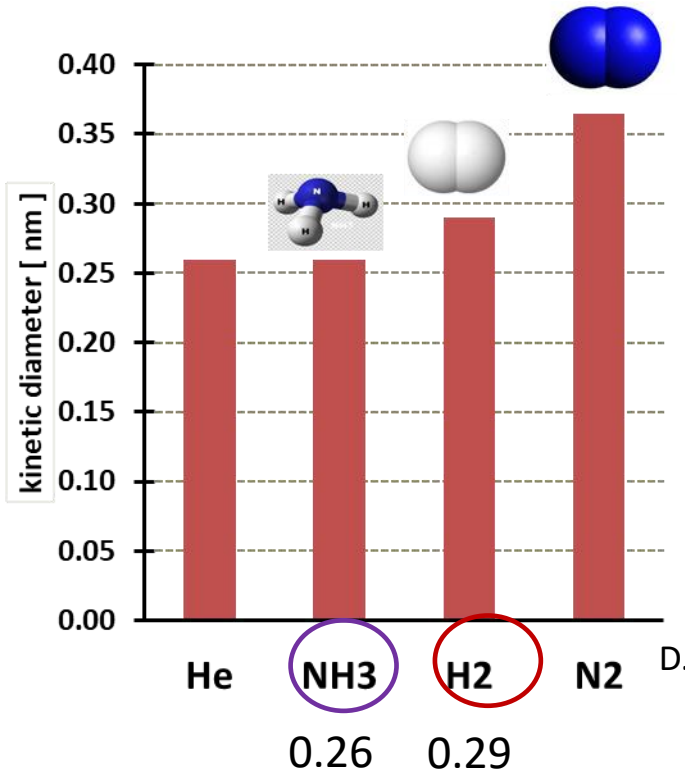
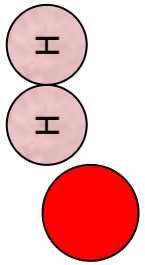
14:49

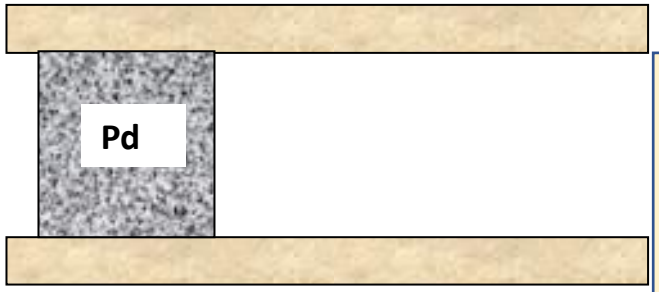
Separation of H_2 from NH_3 cracking

Kinetic diameter

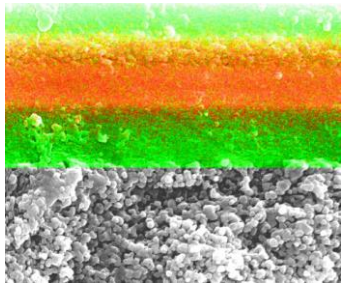


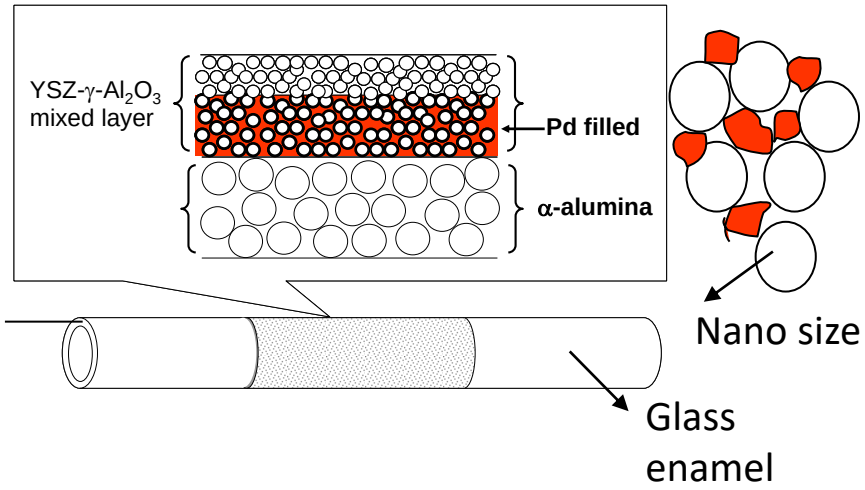
$$2NH_3 \leftrightarrow N_2 + 3H_2$$



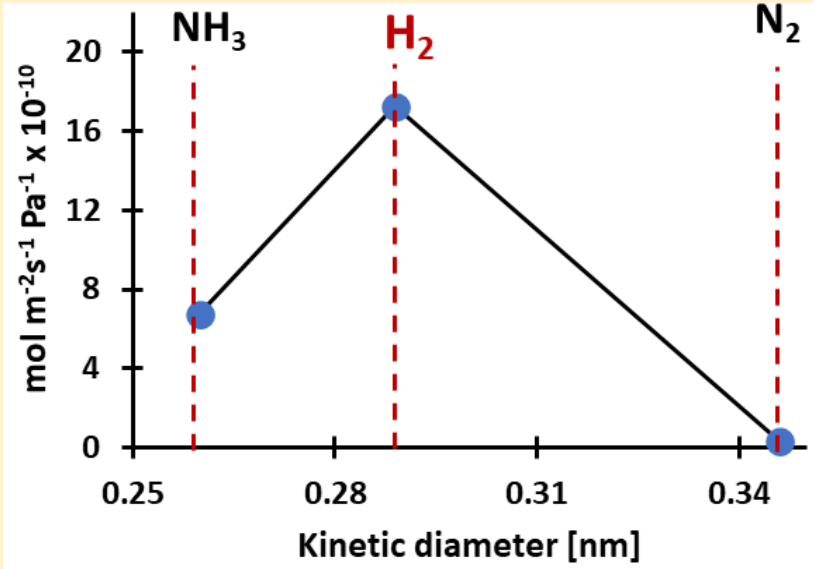


D.A. Pacheco Tanaka…, Advanced Materials 18, 2006, 630-632





CMSM filled with Pd



Pd particles are confined in the nano-space of YSZ-γ-Al_2O_3

Conclusions CMSM

- The pore size, pore size distribution and interaction of the pores with gases can be tunned by modifying :
  - Polymer.
  - Carbonization temperature.
  - Addition of fillers.

- Comparing with polymeric membranes CMSM
  - For gas separation, they have better permeation properties
  - Thermal and mechanical more stable
  - More expensive

- CMSM have great potential in Membrane reactors

acknowledgements

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Many thanks