



Carbon molecular sieves membranes (CMSM) for gas separation and membrane reactors.

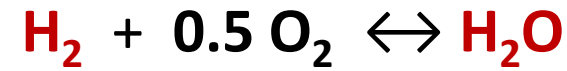
- David A. Pacheco Tanaka, Margot A. Llosa Tanco,
- Arash Rahimalimamaghani , Fausto Gallucci.



Solutions to mitigate global warming



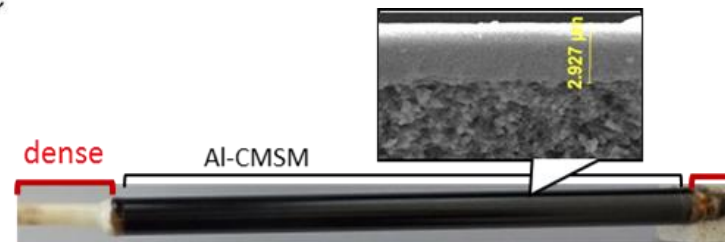
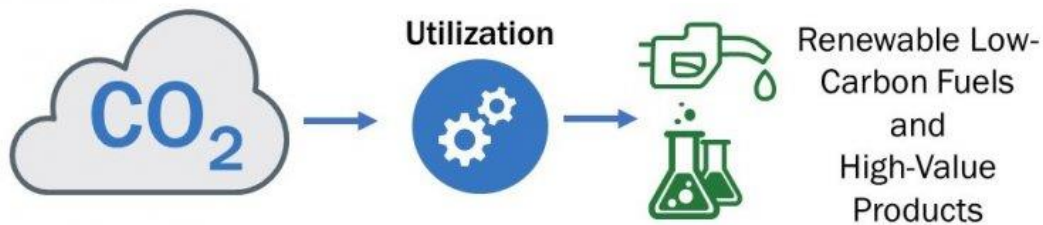
☐ Reduce the emission of greenhouse gases



☐ Use of clean fuels

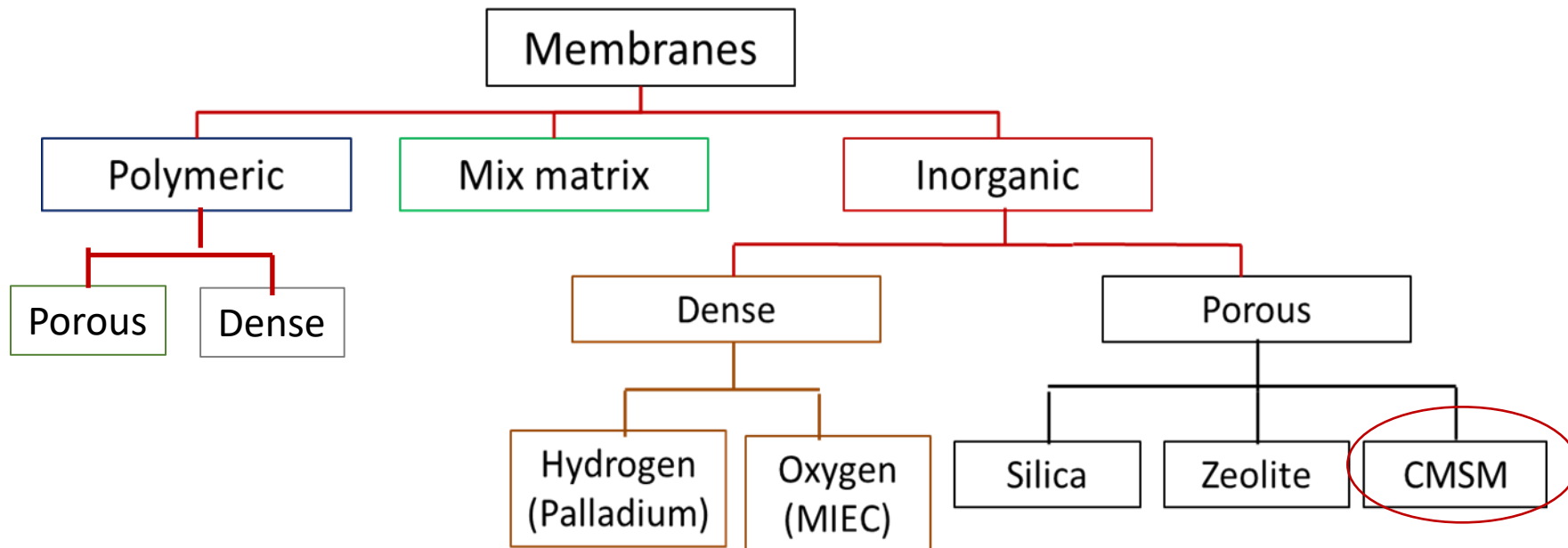
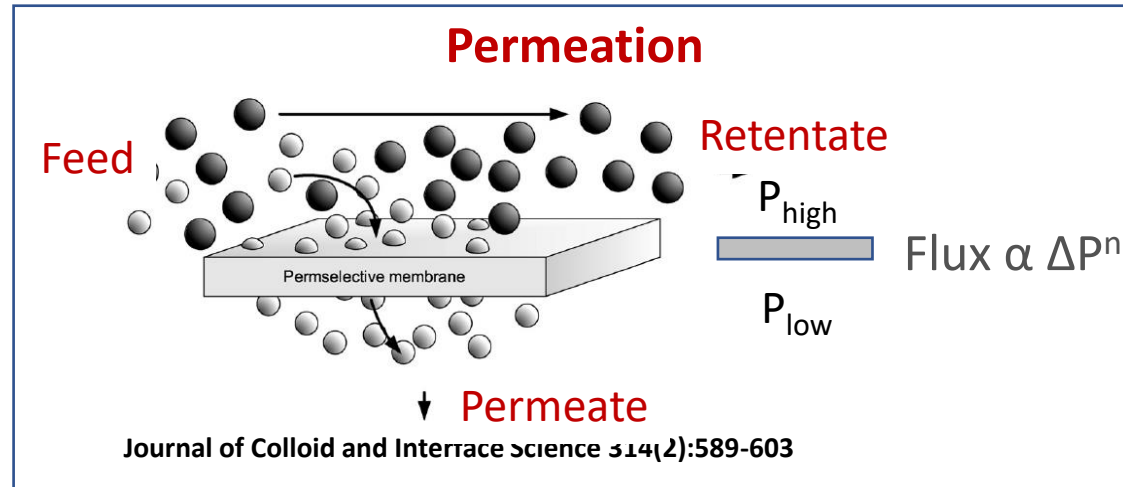


☐ CO2 capture and utilization



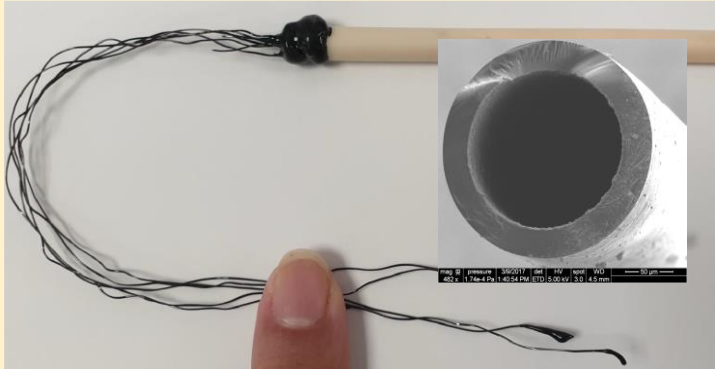
Membranes

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



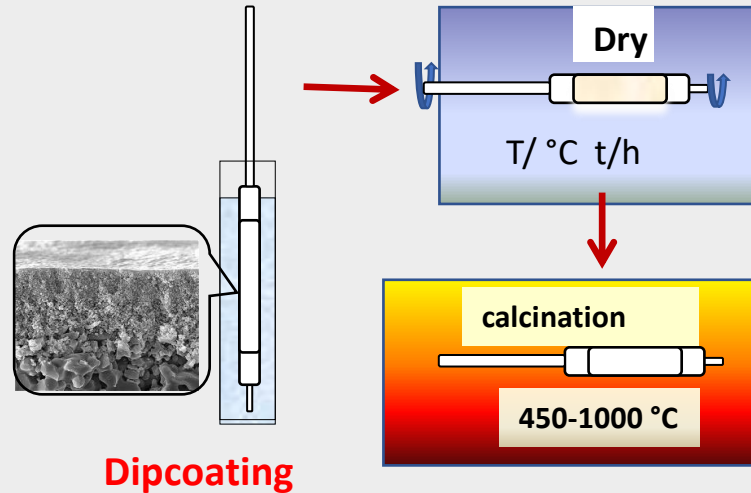
Carbon membranes

-Carbonization thermosetting polymers



Hollow fibre and Self standing are brittle

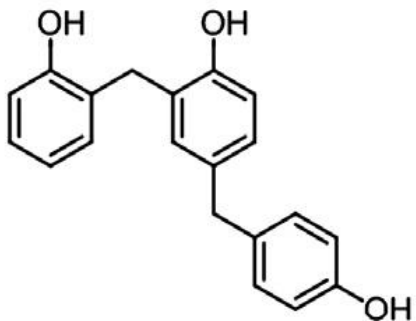
Supported -Alumina-CMSM



Dipping solution

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

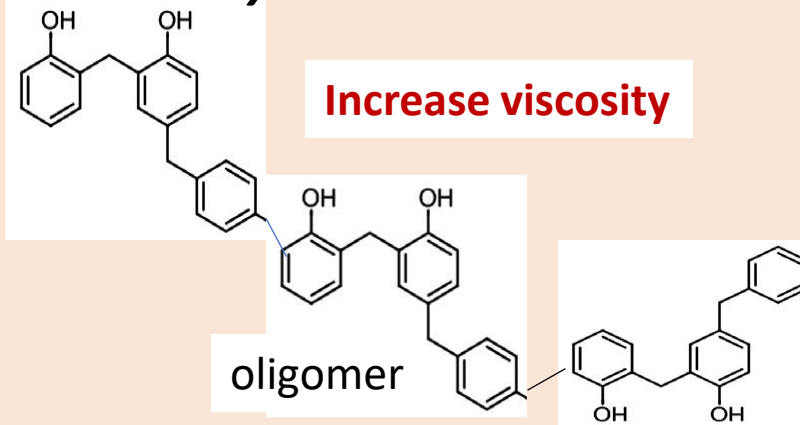
Novolac phenolic



HCHO
(formaldehyde)

Acid: oxalic acid
Basic : KOH
amines

Pre- Polymerization 80 -90 C



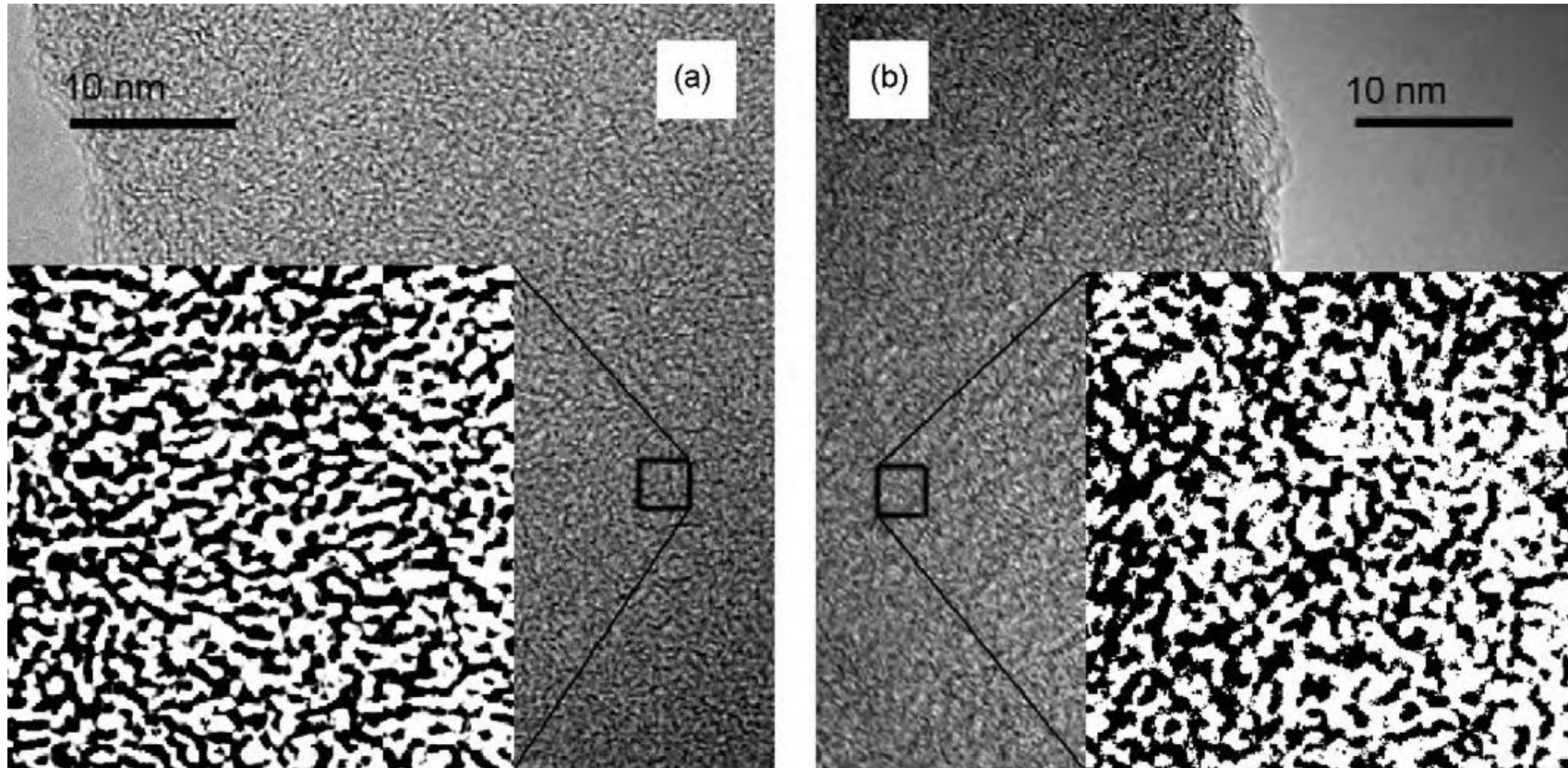
Increase viscosity

Dip coating

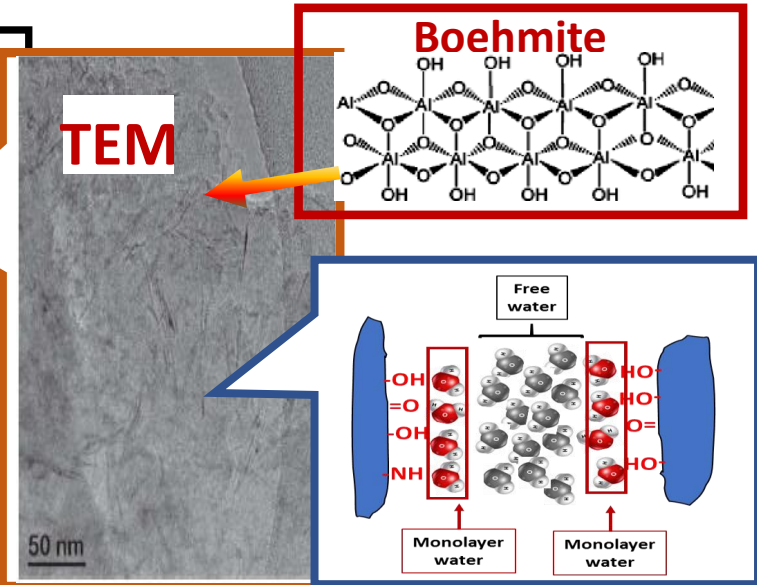
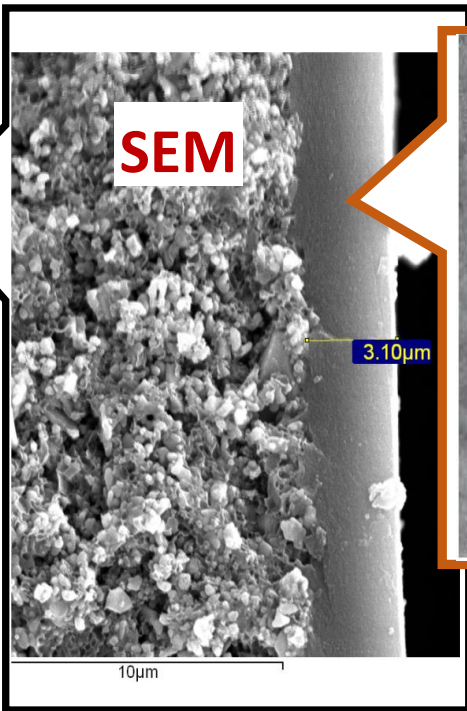
Polymerization on support

Avoid infiltration in support

TEM Carbon Membrane



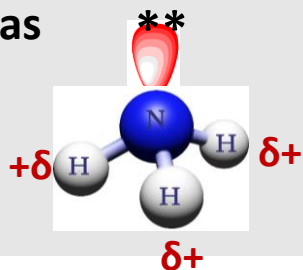
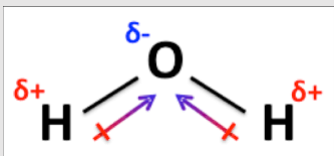
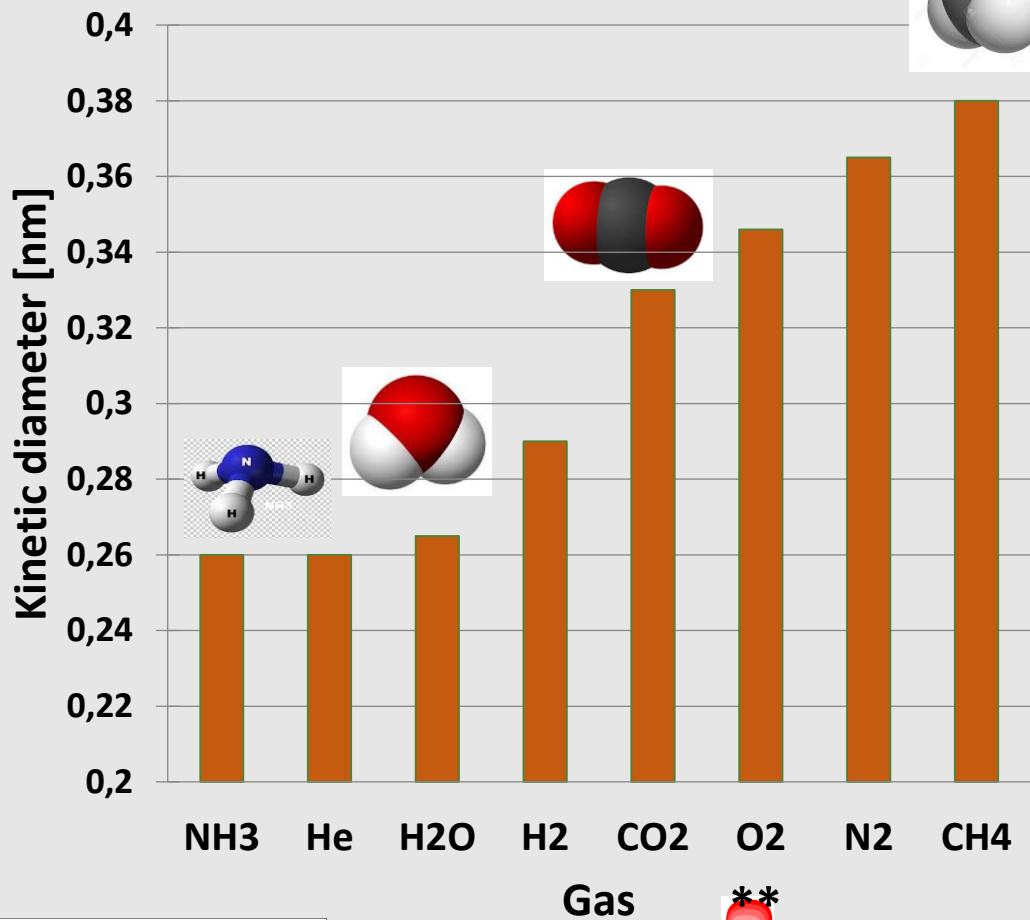
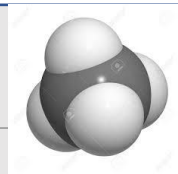
Chengwen S., Tonghua W., Huawei J., Xiuyue W., Yiming C., Jieshan Q., "Gas separation performance of C/CMS membranes derived from poly(furfuryl alcohol) (PFA) with different chemical structure", *J.Membr. Sci.*, 361, 22-27, 2010.



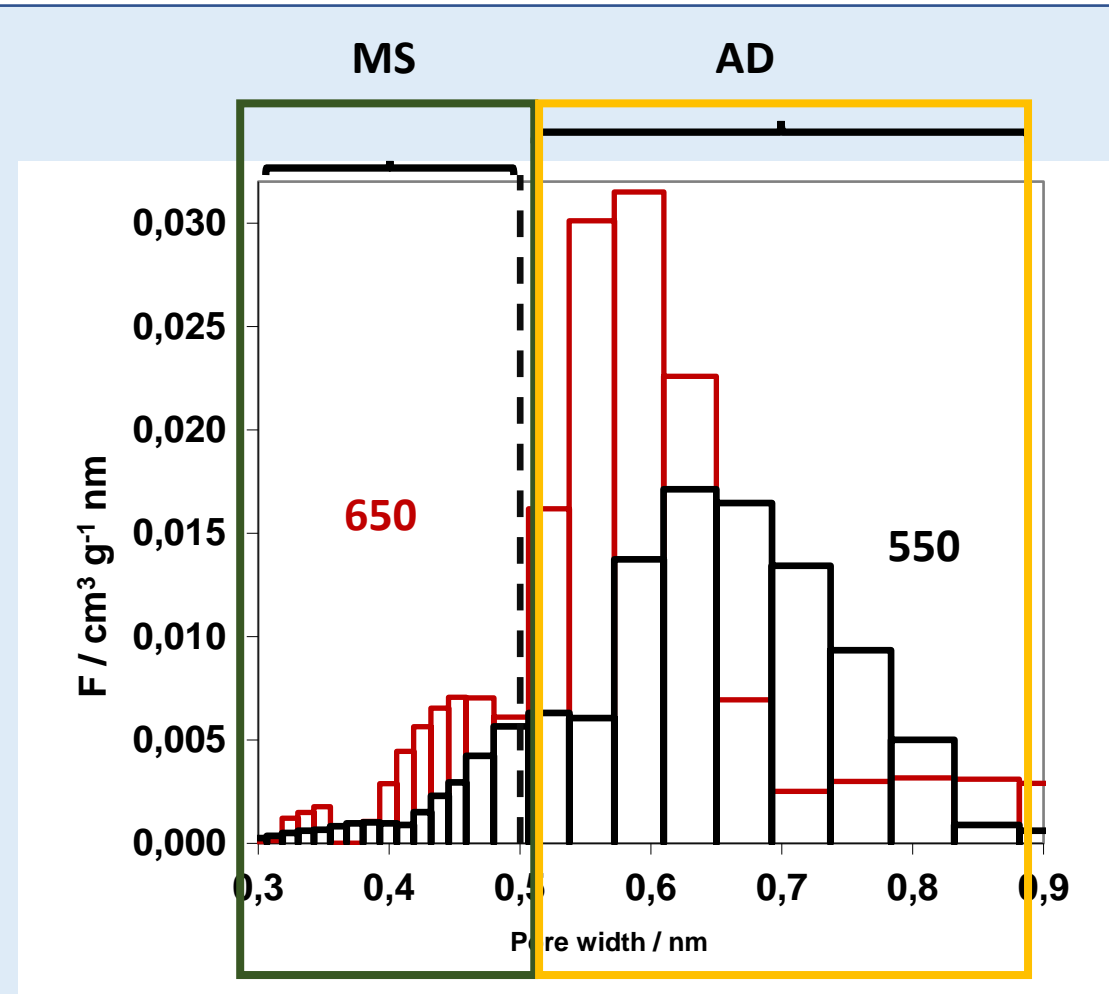
At high temperatures, no water in pores
 Knudsen permeation

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

<i>flux</i>	H ₂	>	NH ₃
MW	2		17



NH₃ Dipole, pair electrons (H-bonding)

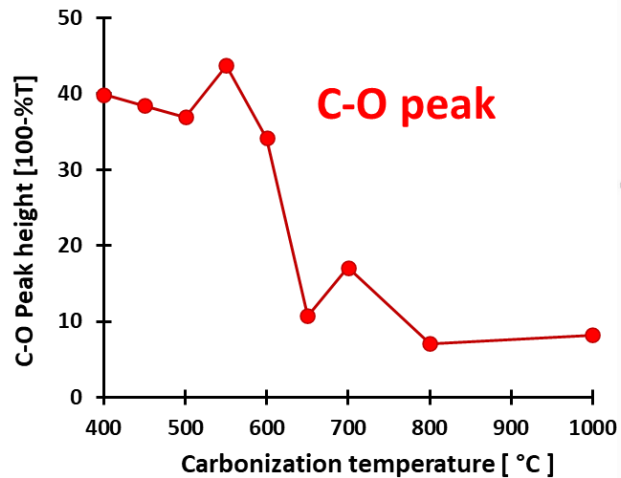
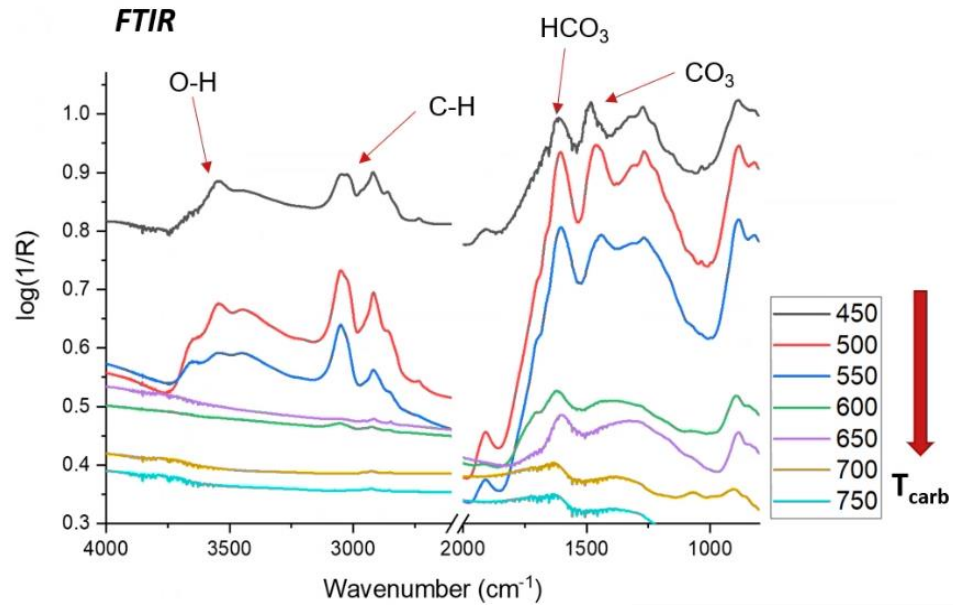


MS
Size separation

Adsorption
Difussion

Effect of the temperature of carbonization

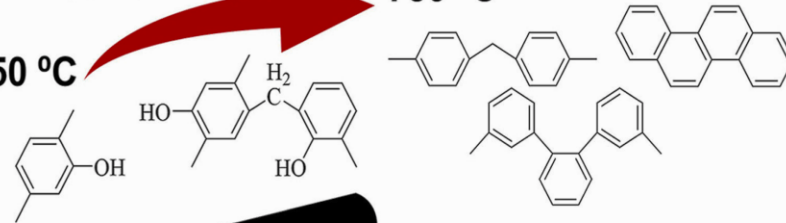
FTIR



Higher Carbonization Temperature

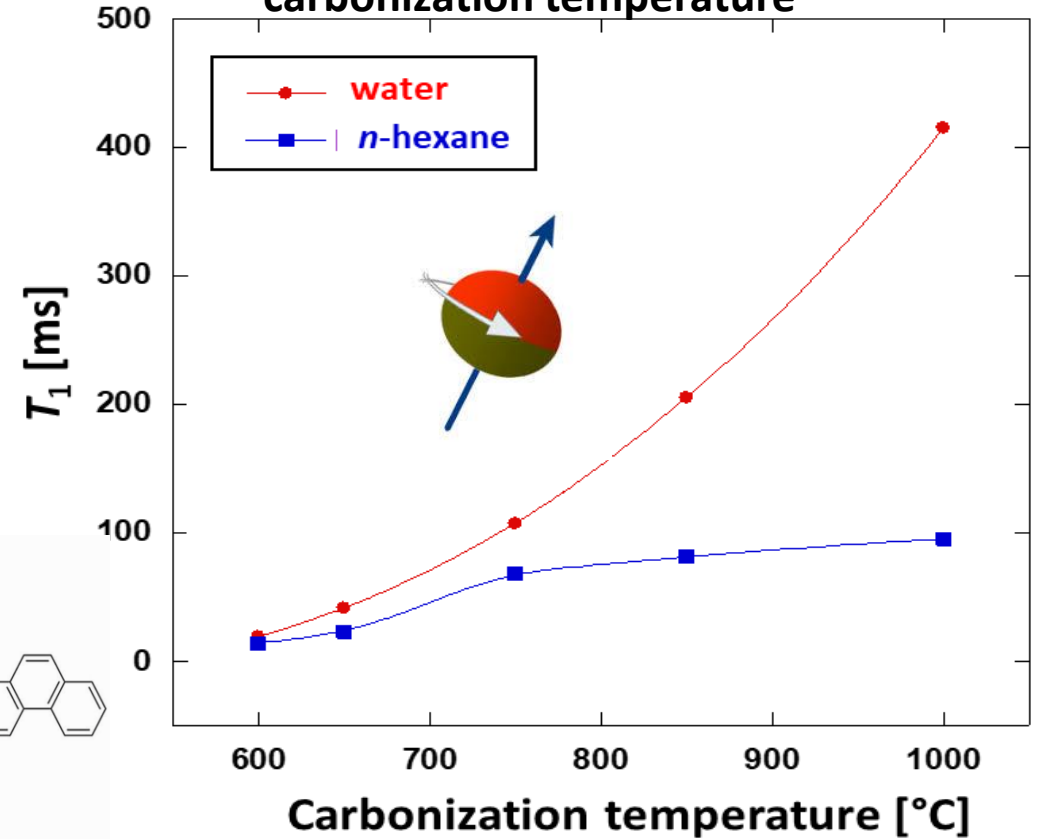
450 °C

750 °C



Proton -NMR

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

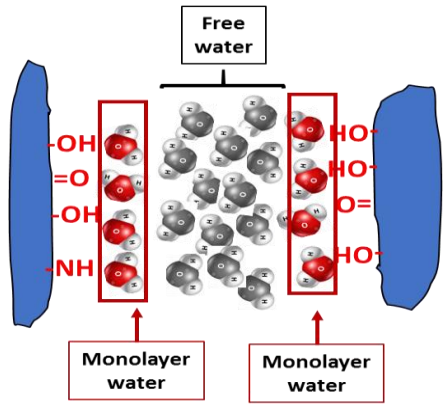


Chemical Engineering Journal 424 (2021) 129313

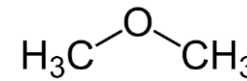
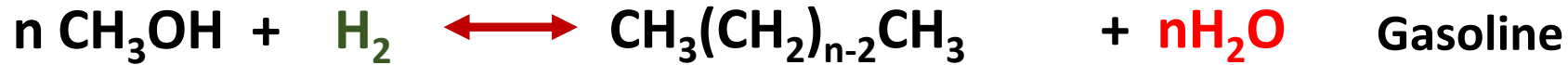
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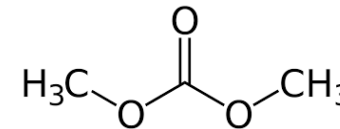
journal homepage: www.elsevier.com/locate/cej



Valorización de CO₂ e-Fuels



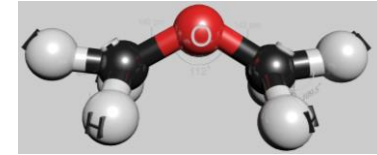
Dimethyl ether



Dimethyl carbonate DMC



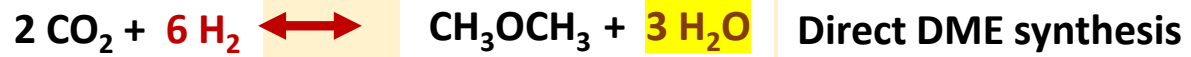
Synthesis of dimethyl ether using membrane reactors



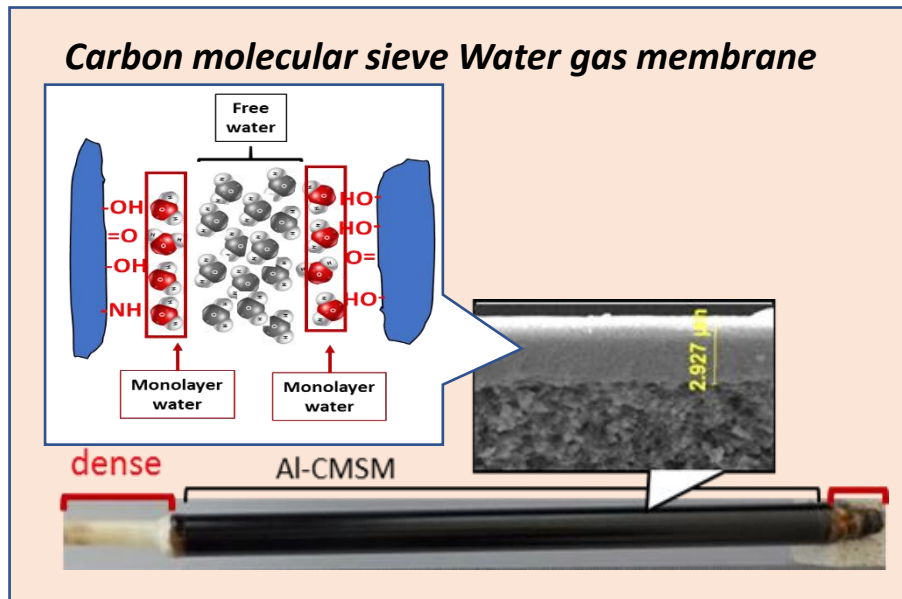
MeOH synthesis

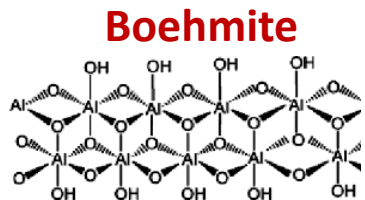


MeOH dehydration



Direct DME synthesis



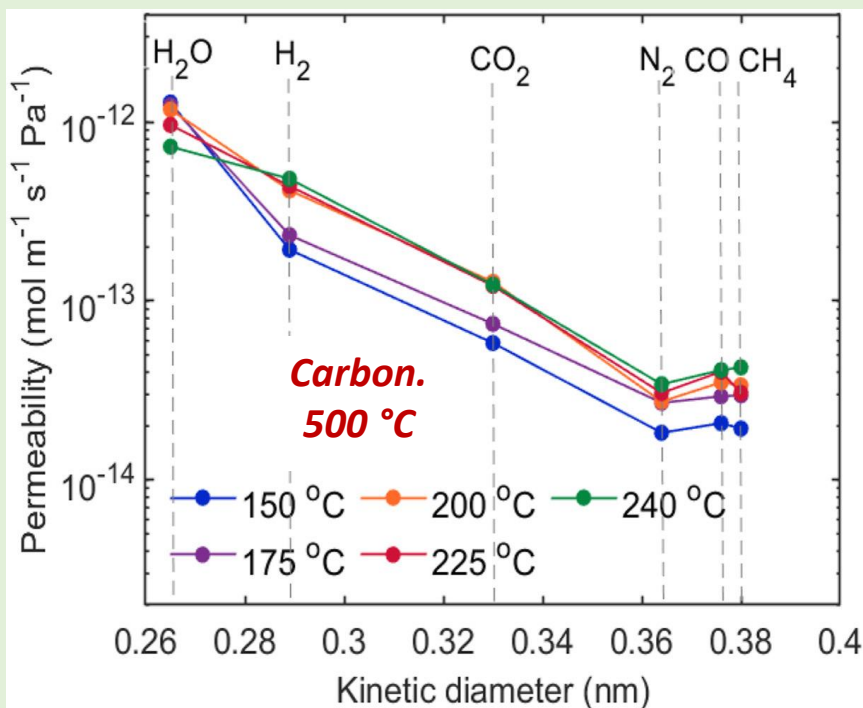


Gas permeation of Al-CMSM containing 0.8 % of boehmite



Effect of permeation temperature

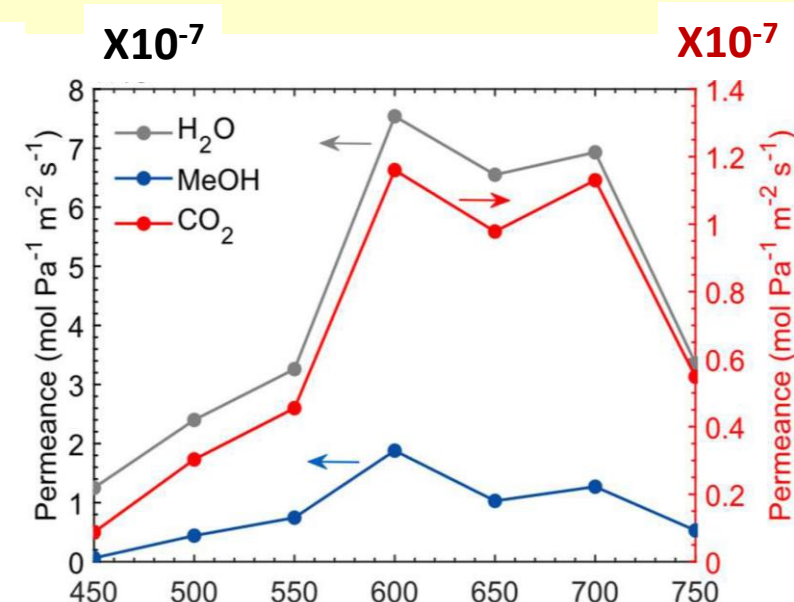
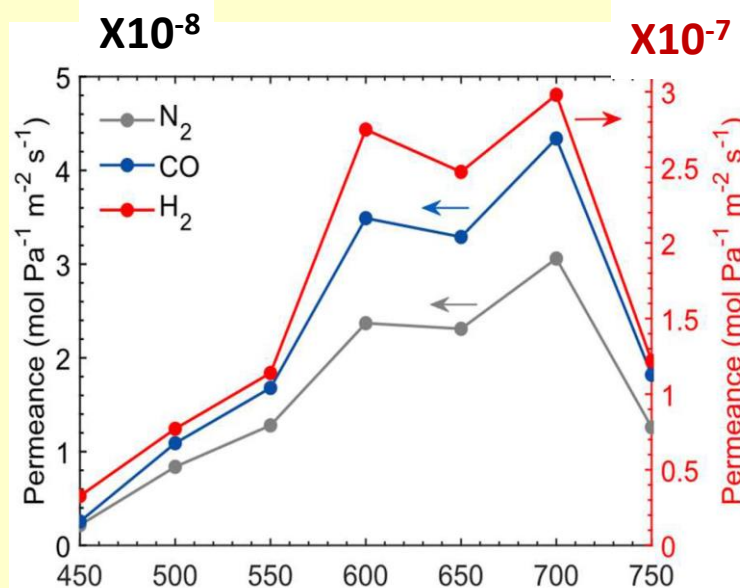
Al-CMSM carbonization 500 °C



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

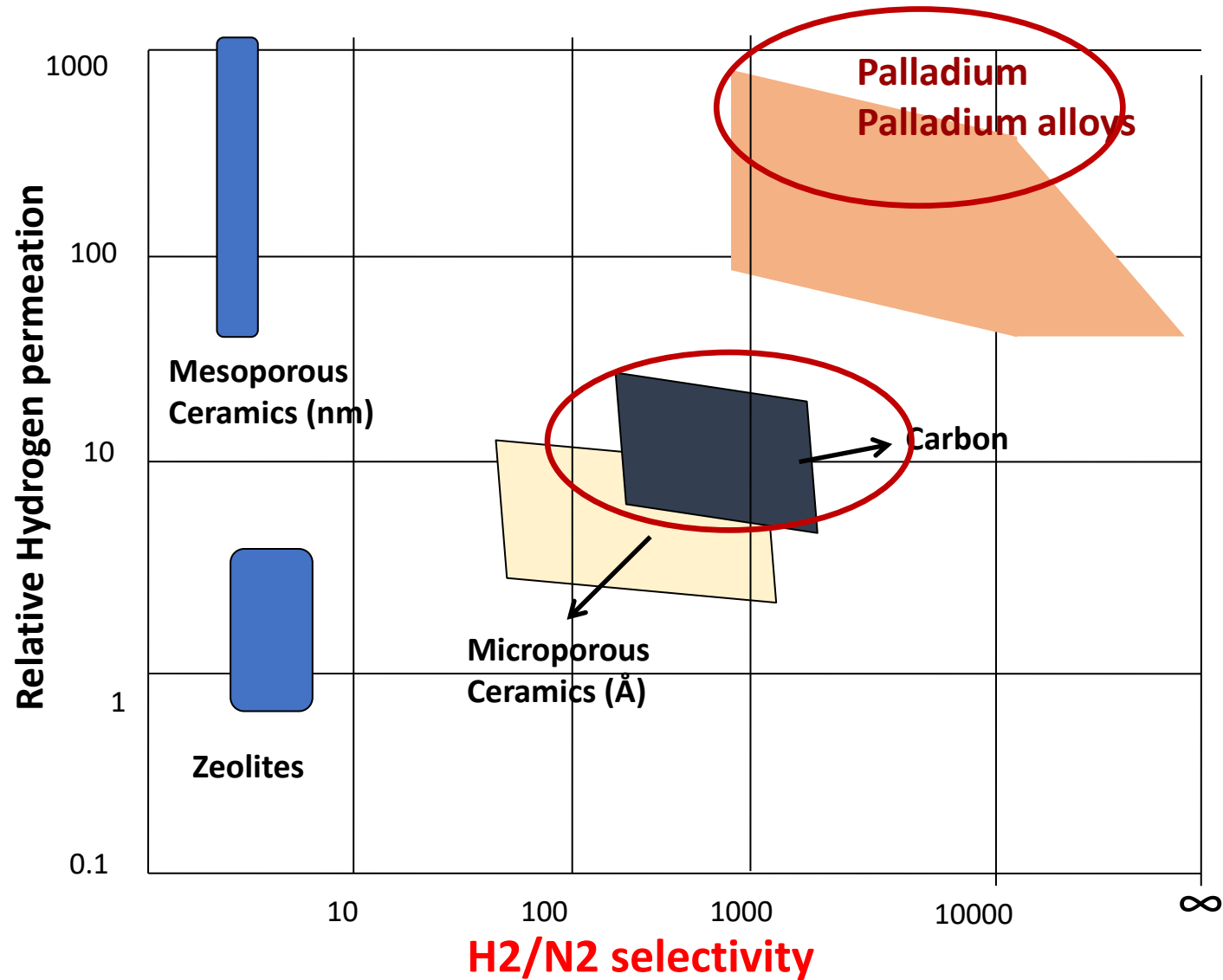
Effect of carbonization temperature

(permeation 200 °C)

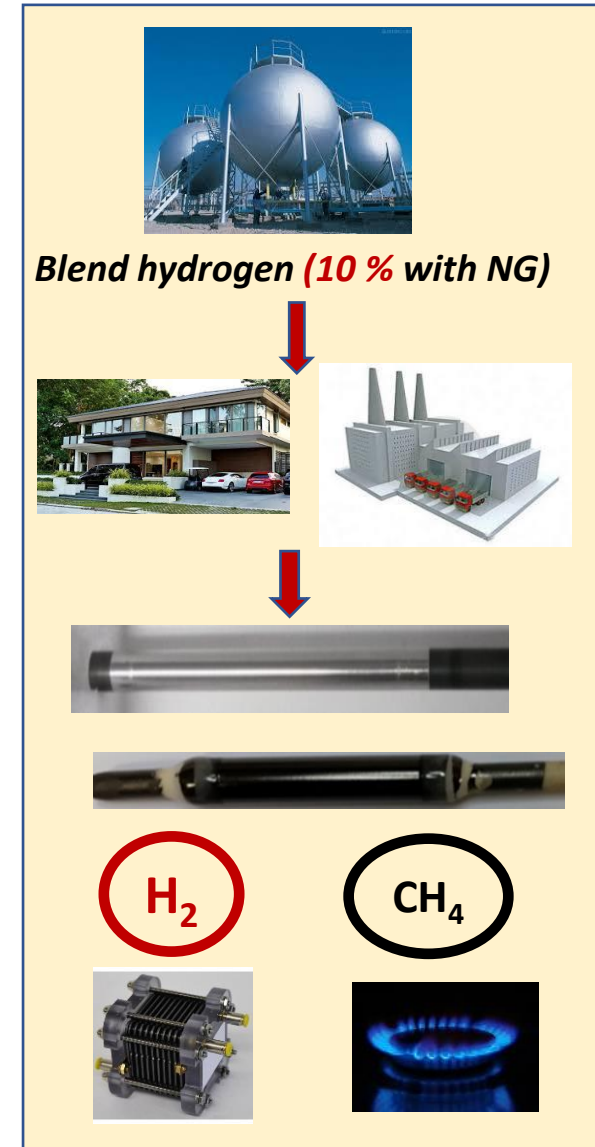


S. Poto et.al. *J. Membr. Sci.* 677(2023)21613

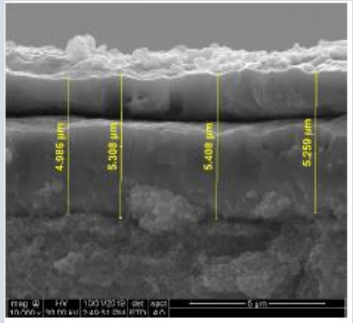
H₂ selective membranes



HyGrid

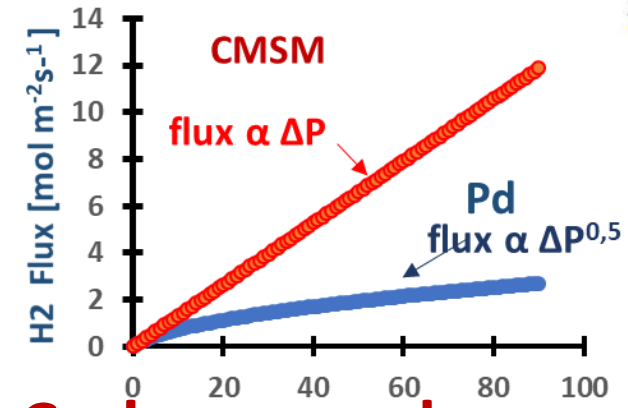
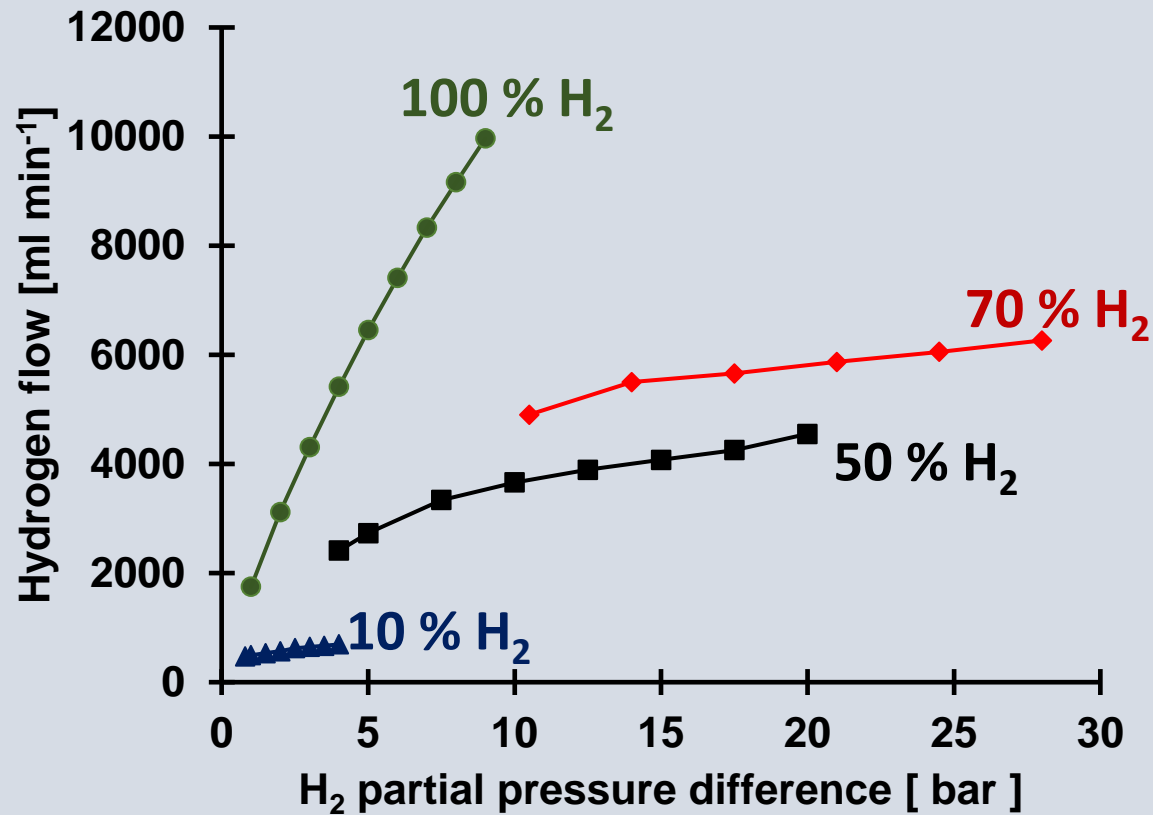


H₂ flow from H₂/CH₄ mixtures

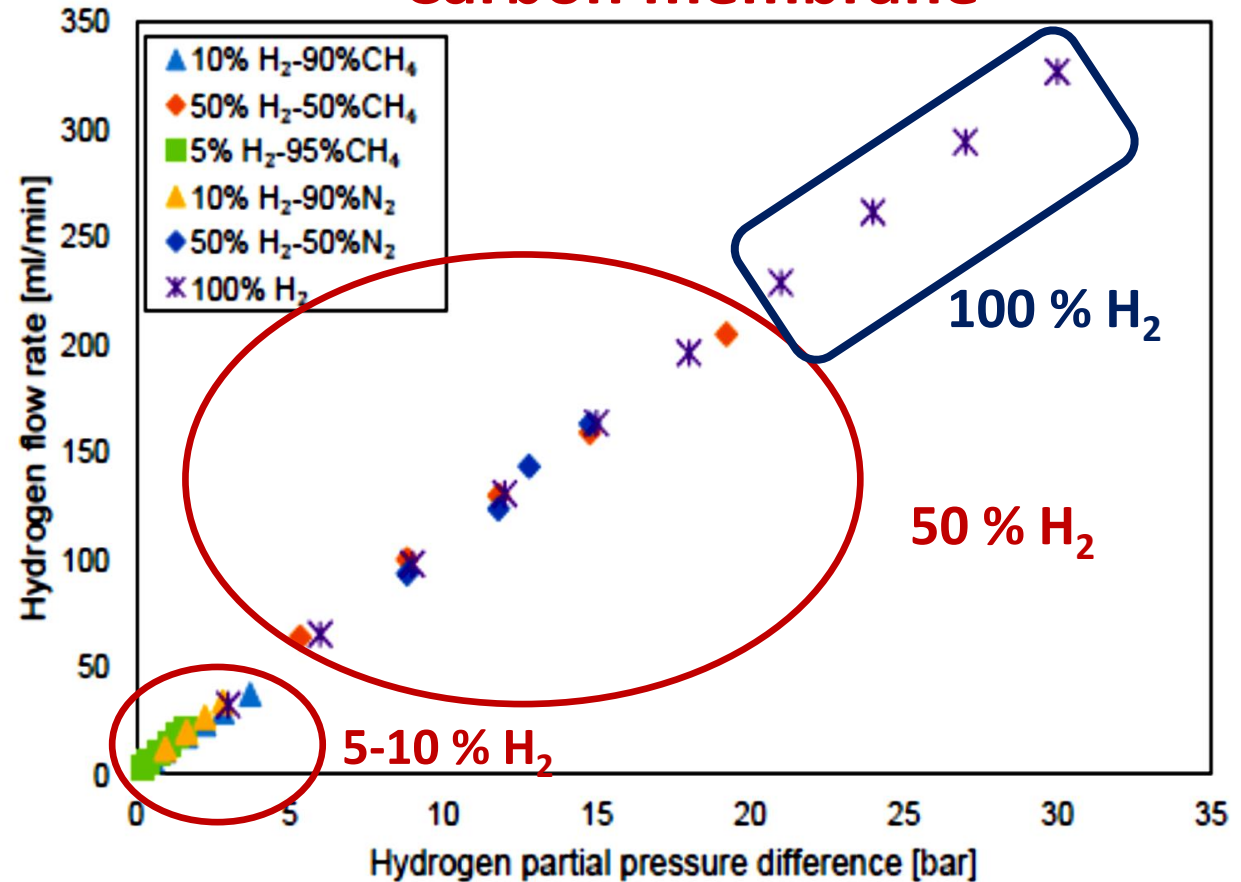


Pd-Ag double skin

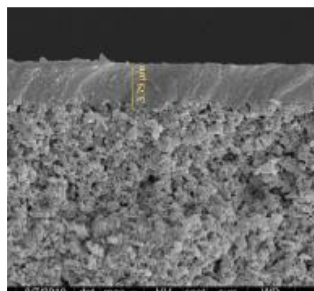
400 °C



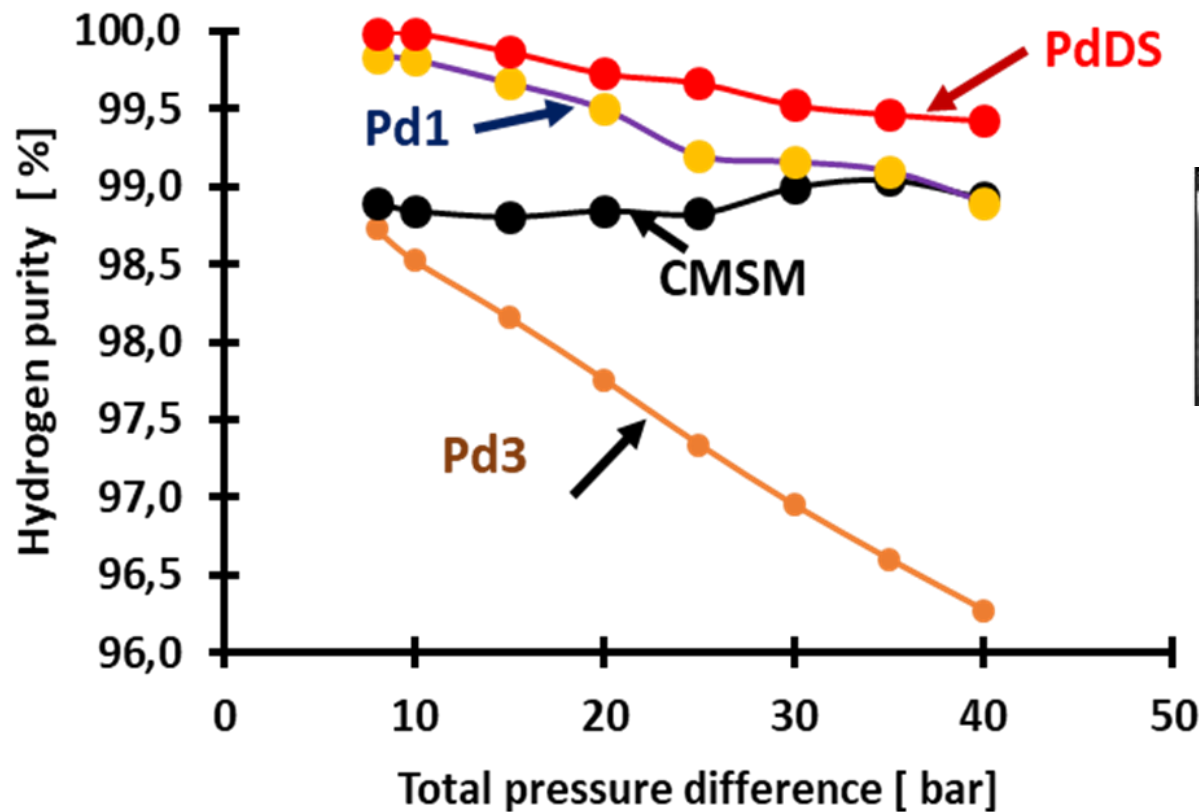
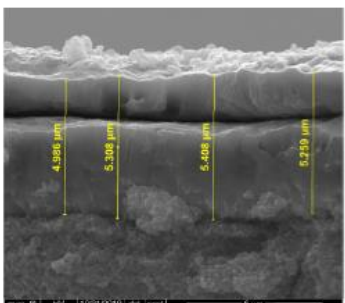
Carbon membrane



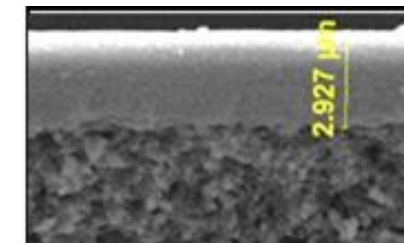
Pd 1 and Pd3



Pd 2 DS



CMSM



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

Comparison between carbon molecular sieve and Pd-Ag membranes in H₂-CH₄ separation at high pressure

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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 46(2021)23417

Int. J. hydrogen energy 45(2020)28876

H₂ vs NH₃



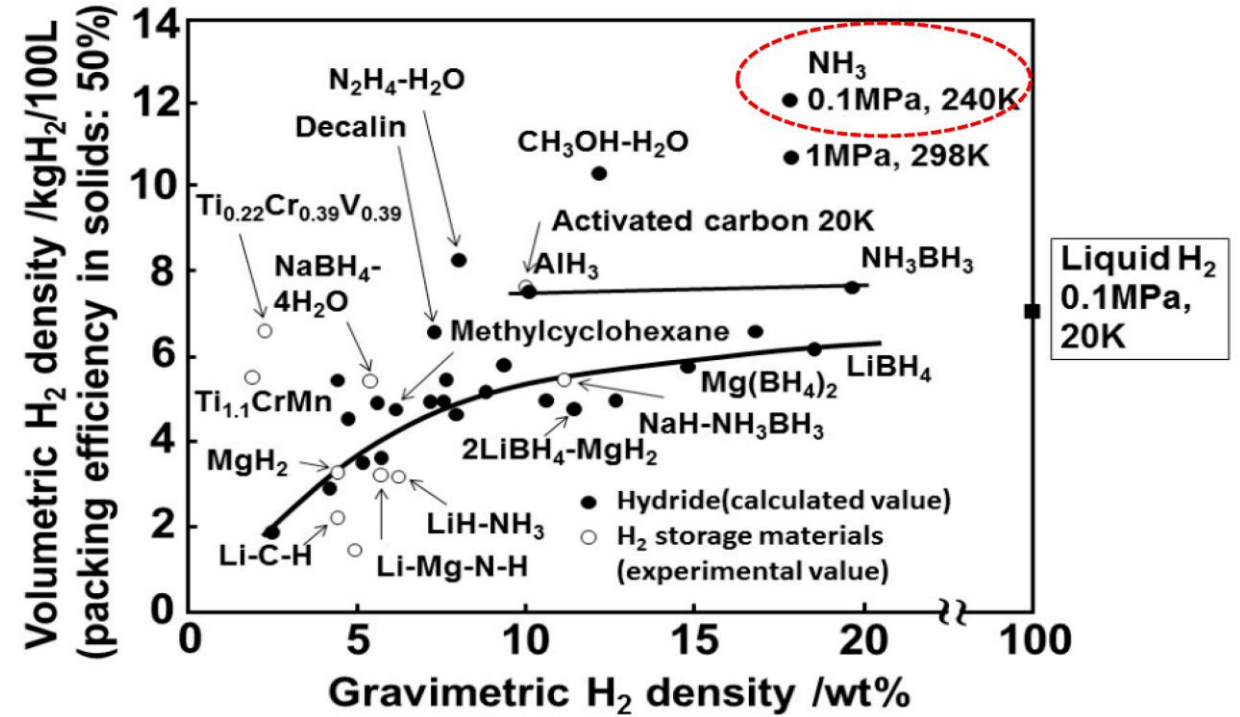
Liquid H₂ is at least 10 times more expensive to produce and store than NH₃ because it requires high pressure and low temperature



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

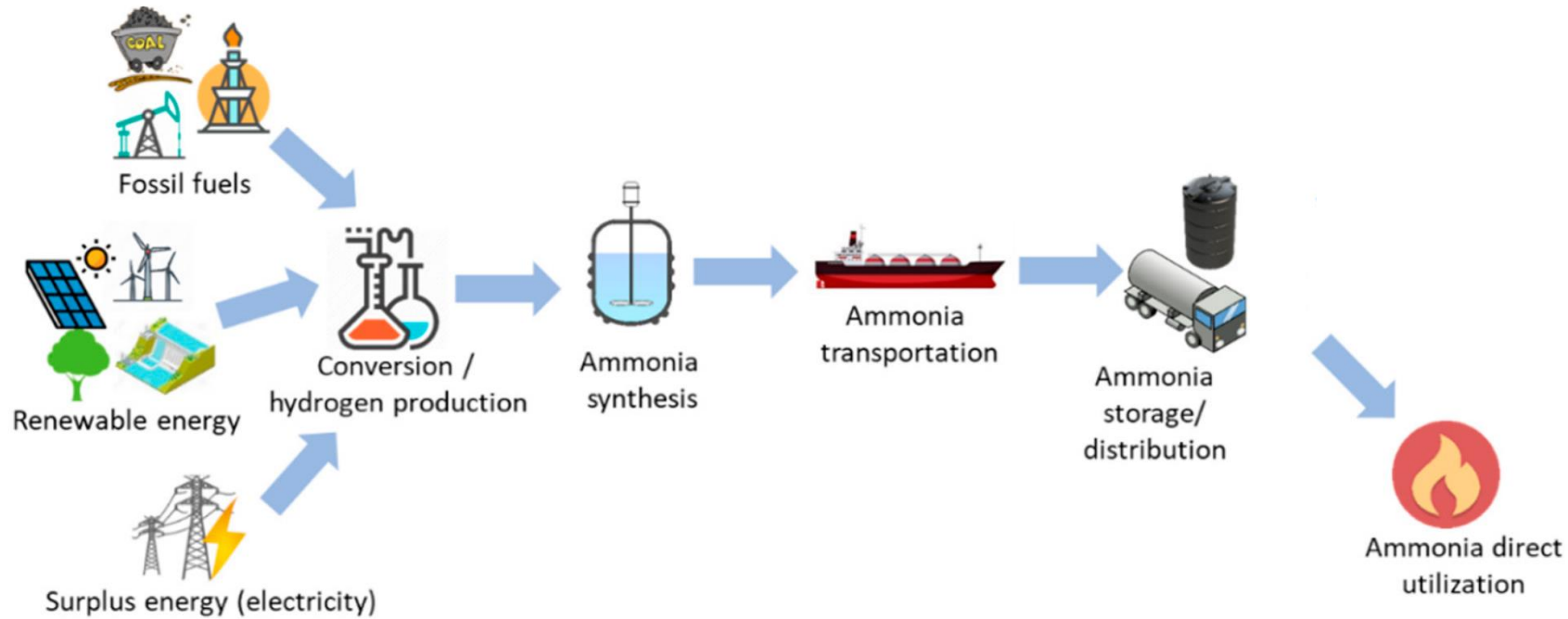
NH₃ was used in internal combustion engines since 1800

The density of hydrogen in hydrogen carriers

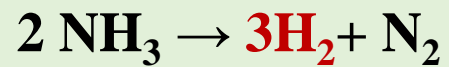


Energies 2021, 14(13), 3732

NH₃ as transport and storage of H₂



Descomposition of ammonia

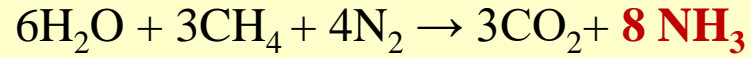


areNH₃a



NH₃ Synthesis

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

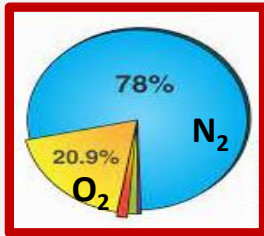


1.8% energy consumed 1.8% CO₂ produced in the world

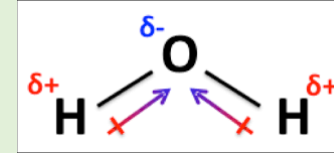
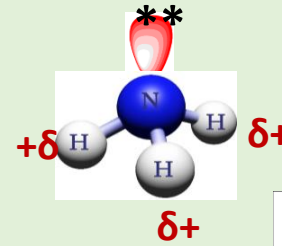
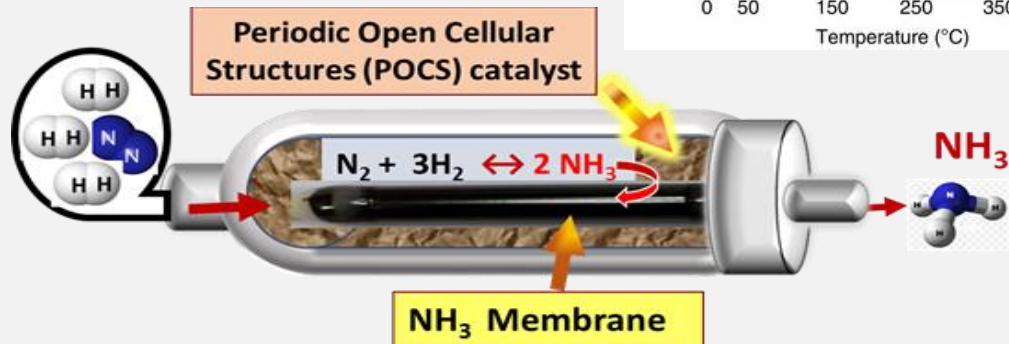
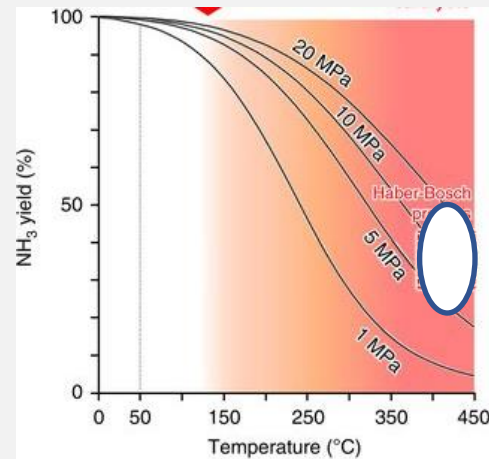
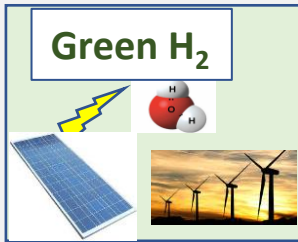
Catalytic Membrane Reactor (CMR)



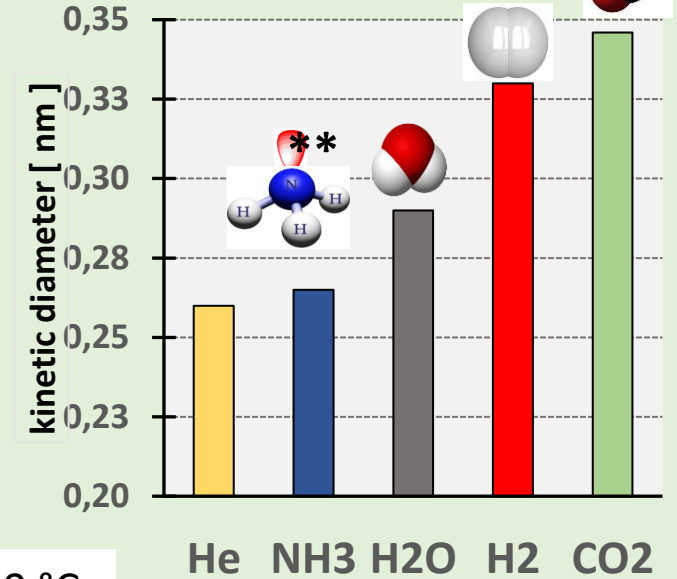
Air



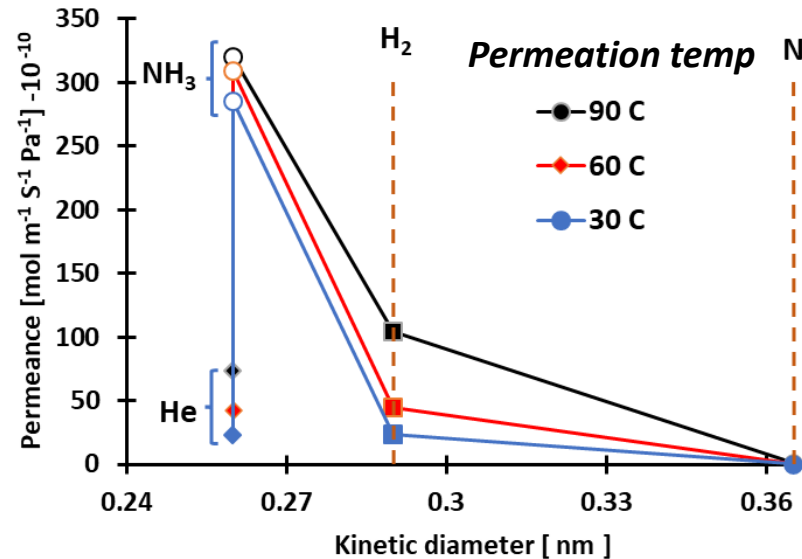
Green H₂



NH₃ Dipole, pair electrons (H-bonding)



Al-CMSM carbonized 500 °C

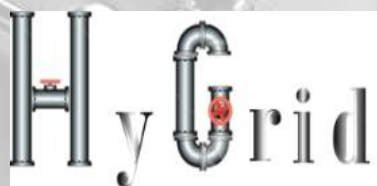


tecnal:a

MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

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Many thanks

