



- **Webinar**
- **Membranes for Ammonia Separation**

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17th October, 2024

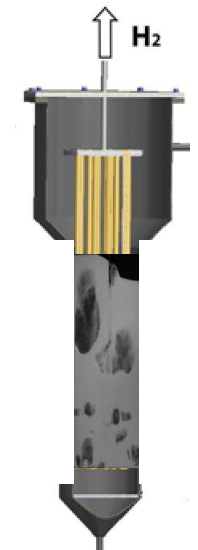
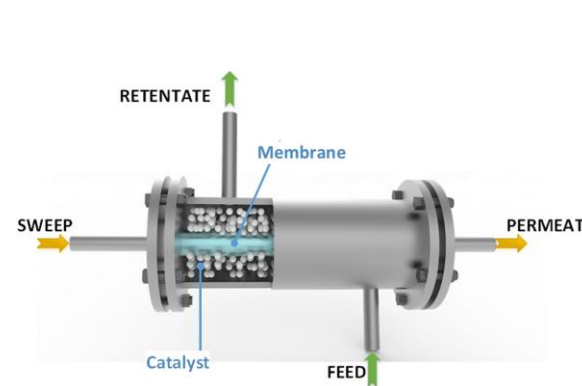
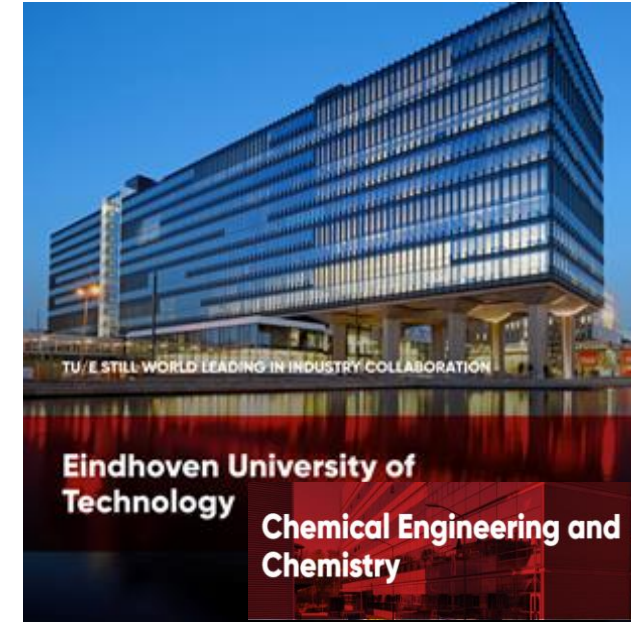


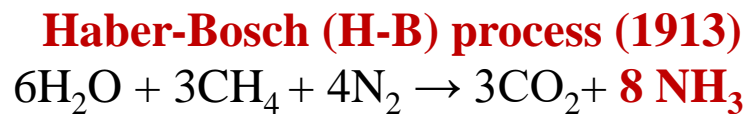
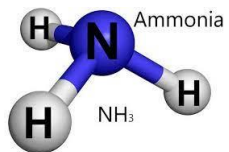


The largest applied research and technological development center in Spain
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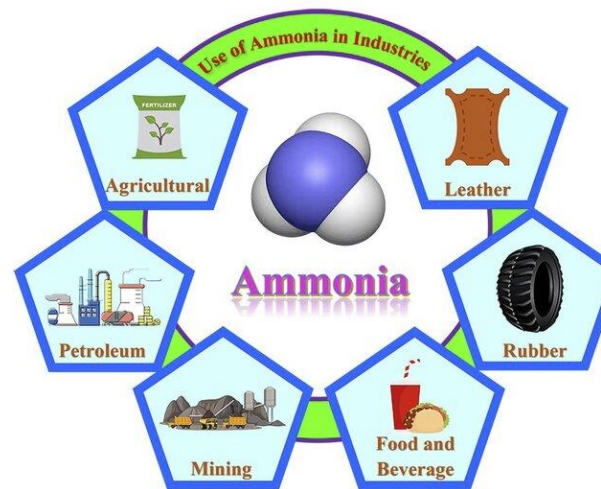


NH₃ at global scale

Consumes **55%** of H₂ produced

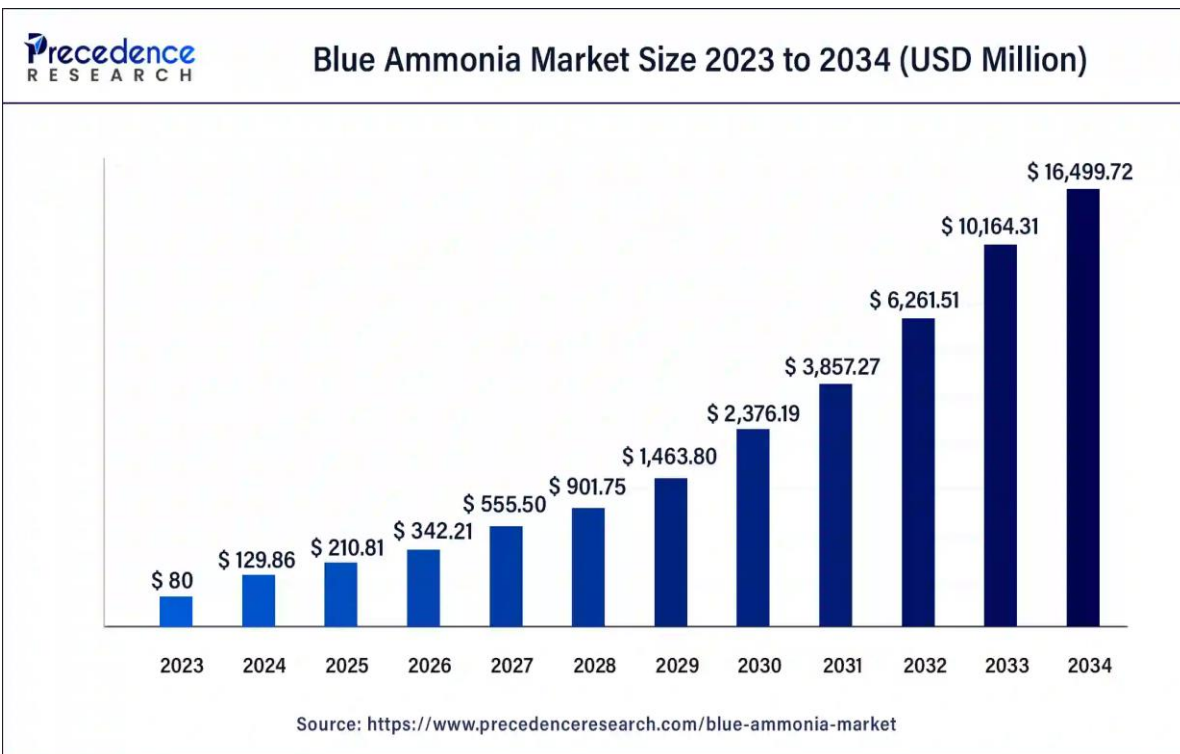
Consumes **1.8%** of all energy produced

1.8% of all CO₂ produced



RSC Adv., 2023, 13, 28211–28223
 DOI: 10.1039/d3ra05580a

85% Fertilizers
 NH₃, Nitrate



Typical ammonium concentration in various waste-water (ppm)

Wastewater source	Range (min ~ max)	Average
Municipal wastewater	10 ~ 200	40
Coking wastewater	41.44 ~ 120.32	314
Livestock wastewater (e.g., Chicken manure, swine wastewater)	1680 ~ 3940	2770
Textile dye wastewater	6 ~ 220	52
Leather tanning wastewater	98 ~ 168	132 ± 16
Landfill leachate	503 ~ 1671	1087
Produced water	0.017 ~ 6305	127
Coal gasification wastewater	166 ~ 684	384 ± 100
Anaerobic digestion	15 ~ 4000	991
Palm oil mill wastewater	35.2 ~ 631	227
Dairy wastewater	28 ~ 49	36
Seafood wastewater	35 ~ 120	100

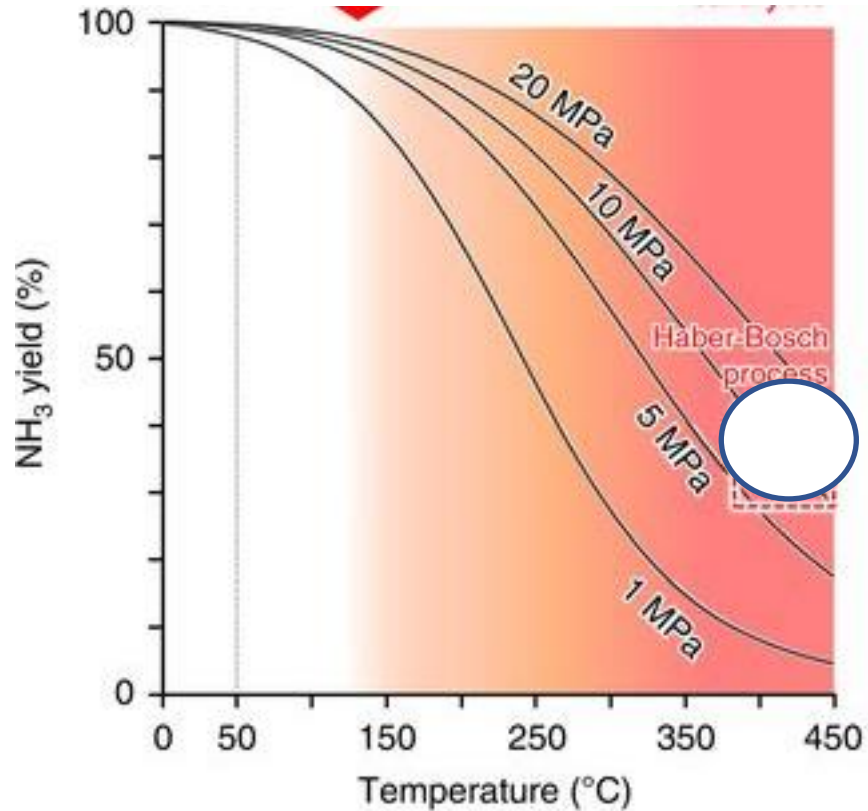
Green ammonia synthesis



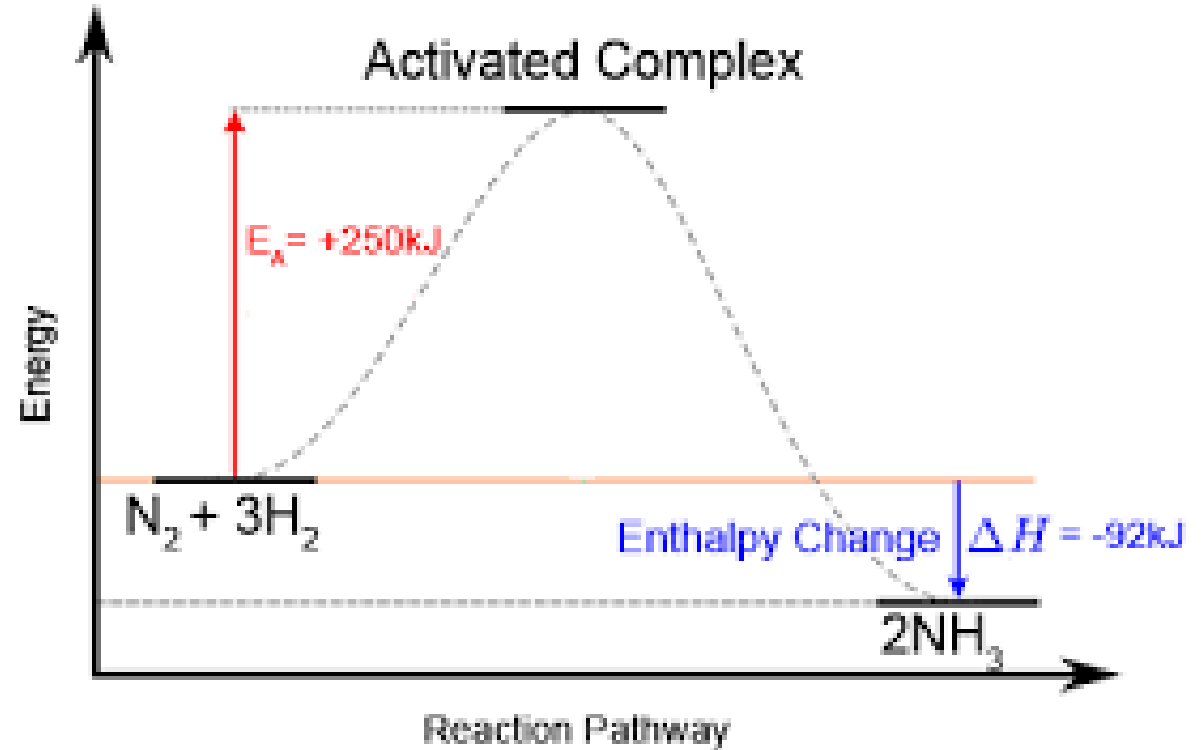
$$\Delta H = -46 \text{ kJ/mol}$$

Low temperature favour the NH_3 synthesis

NH_3 yield vs f (P, T)

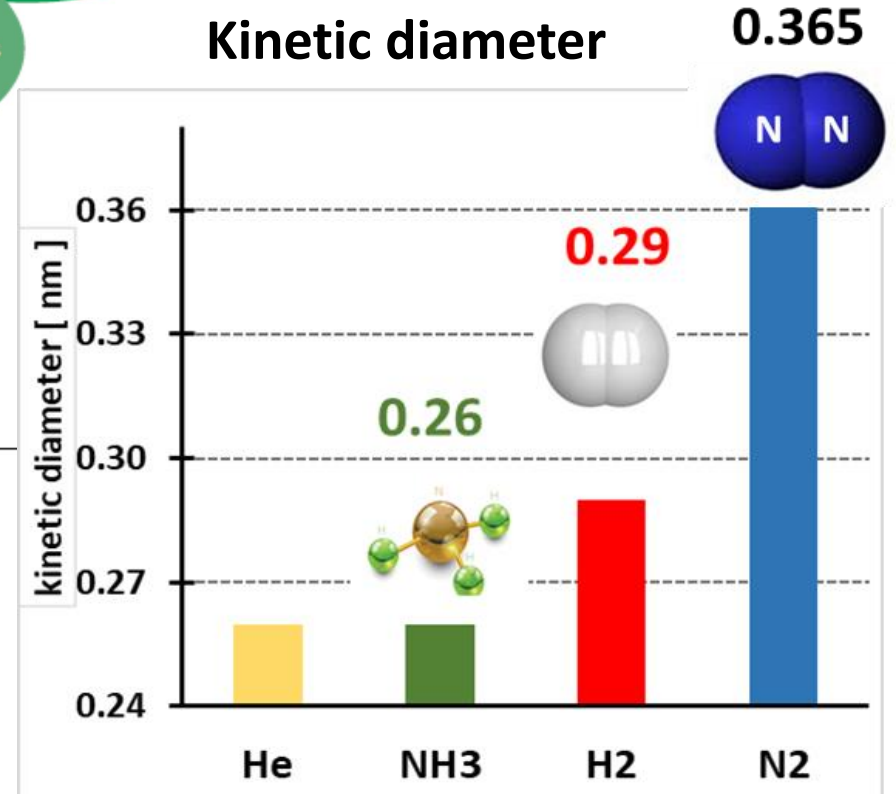
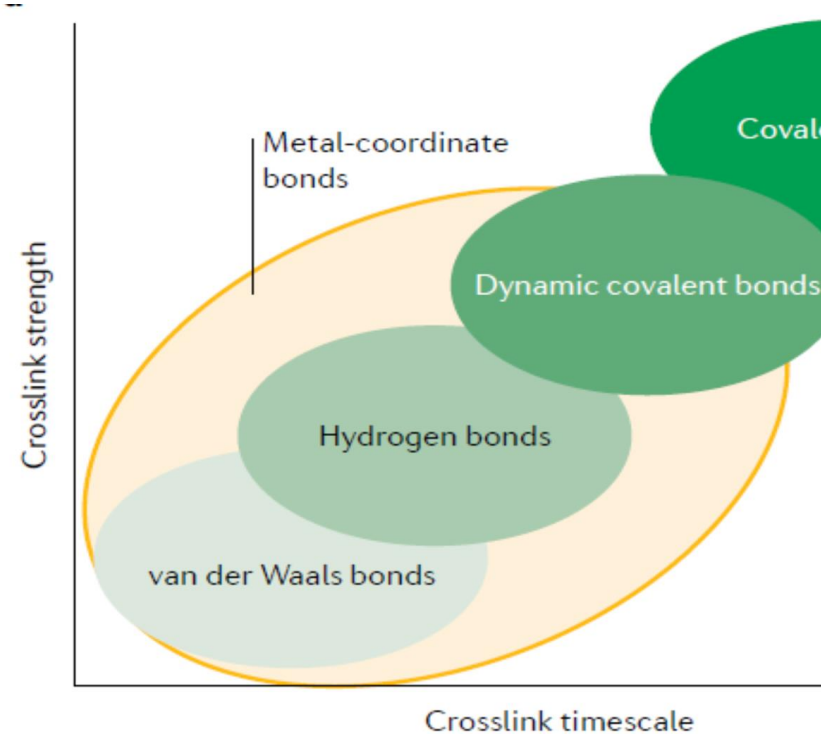
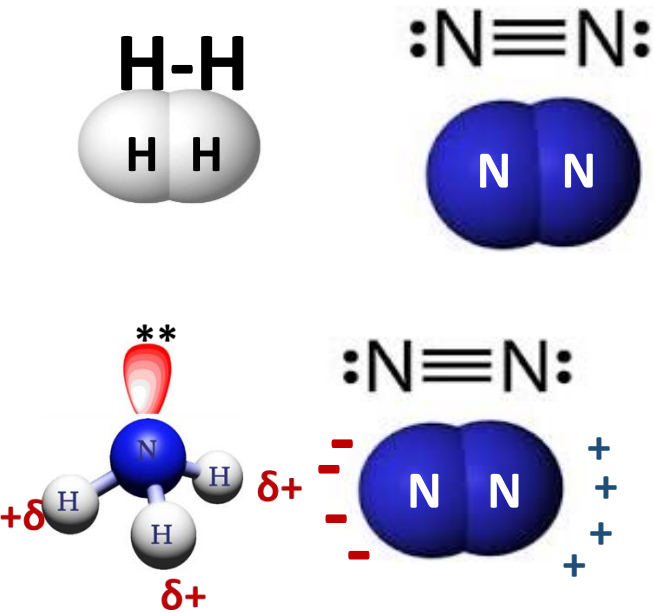


Inert



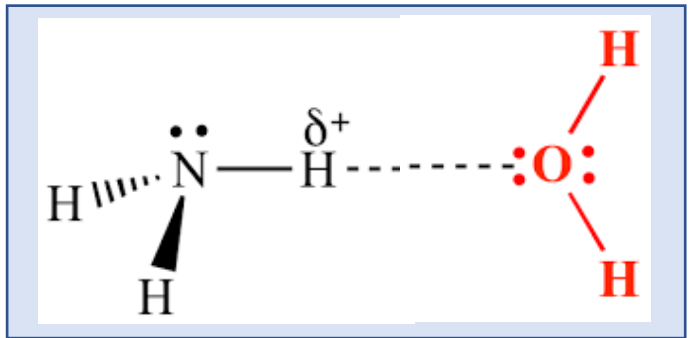
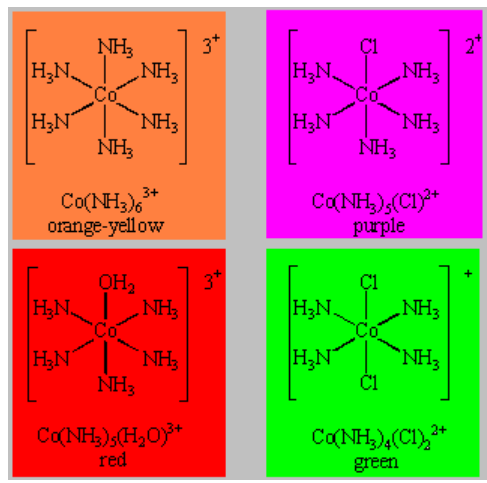
High temperature to overcome activation energy

NH3 separation technologies

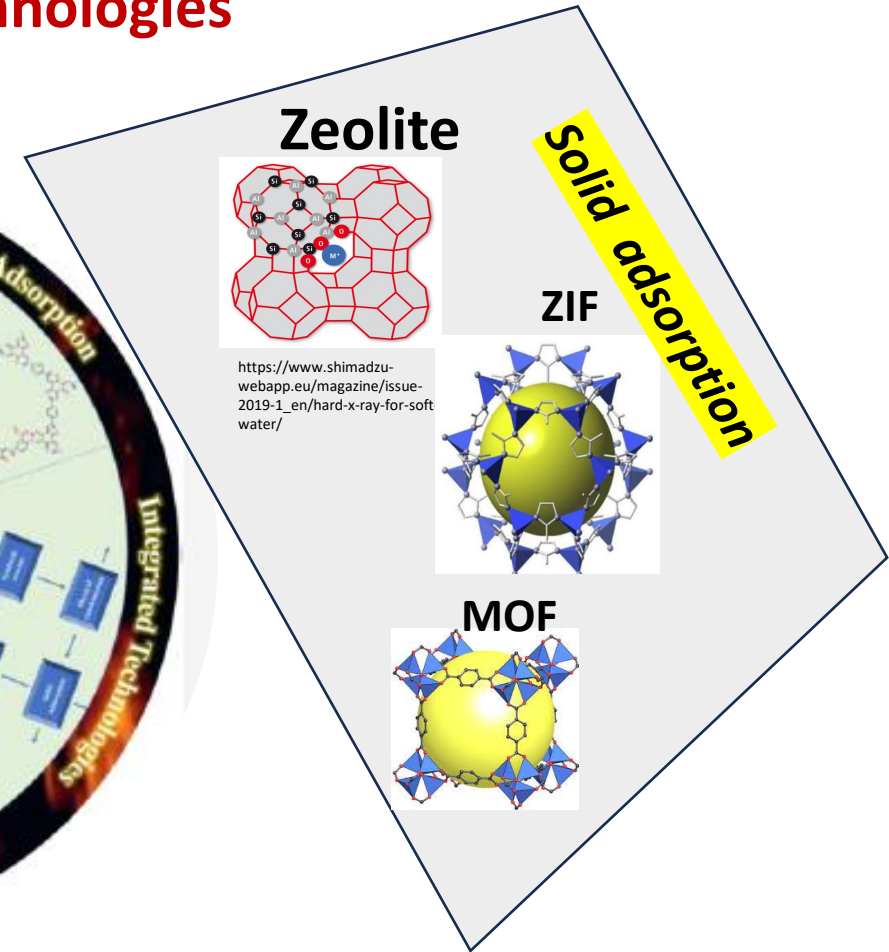
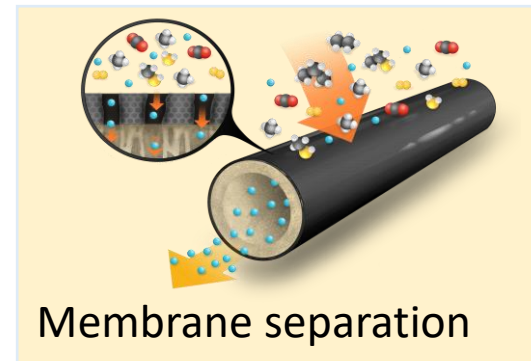
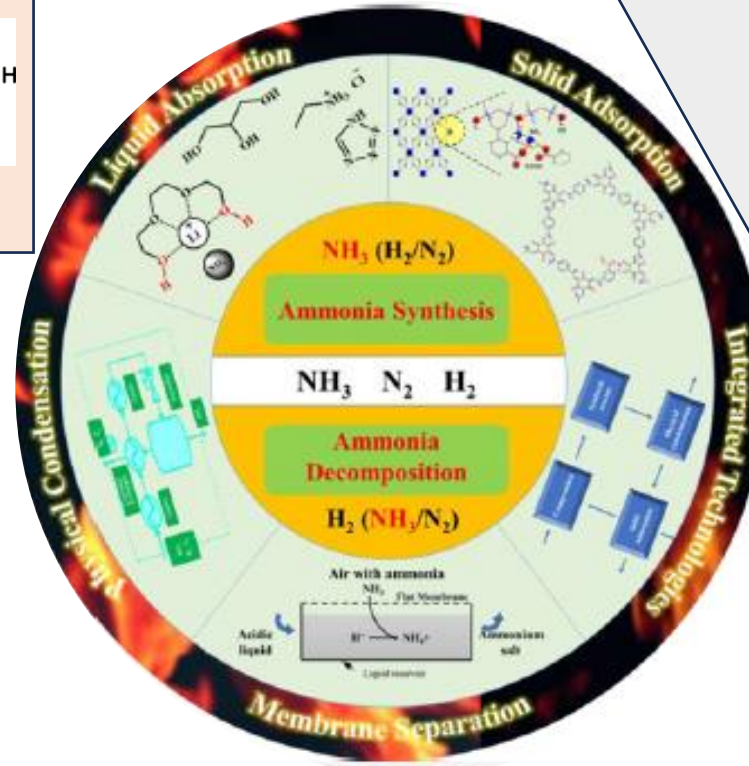
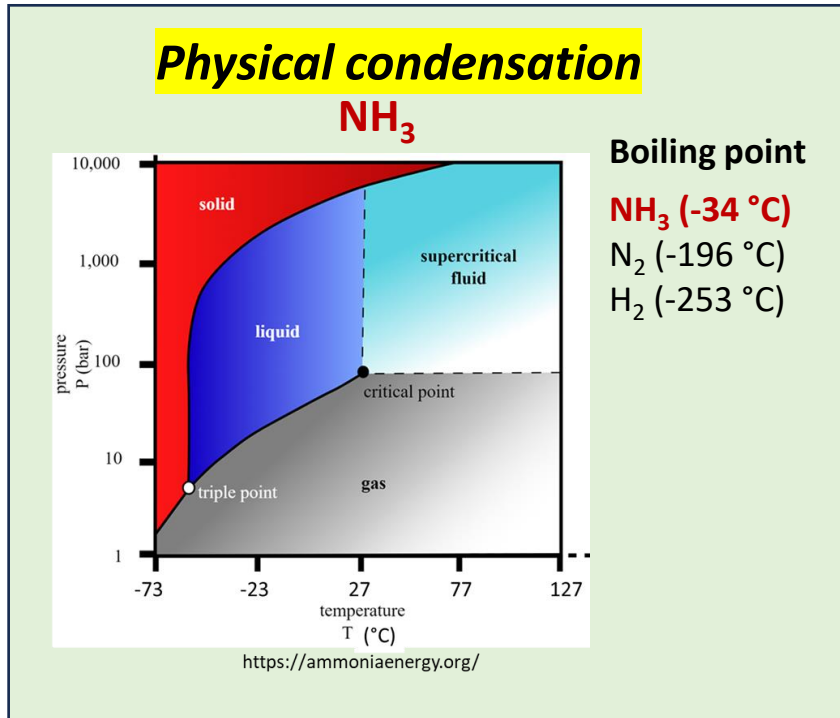
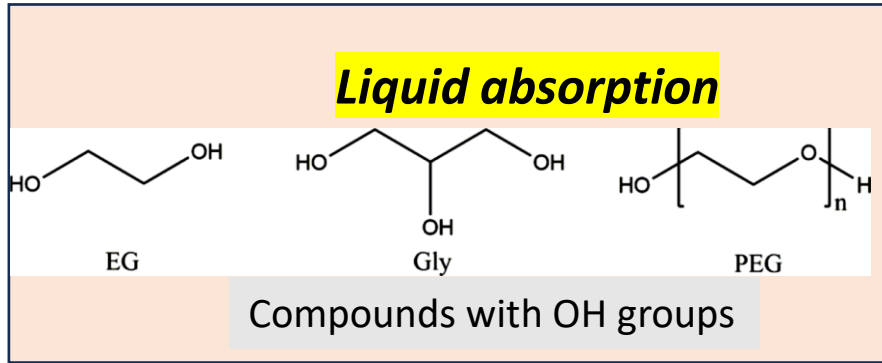


<https://doi.org/10.1038/s41578-020-00270-z>

Metal coordination

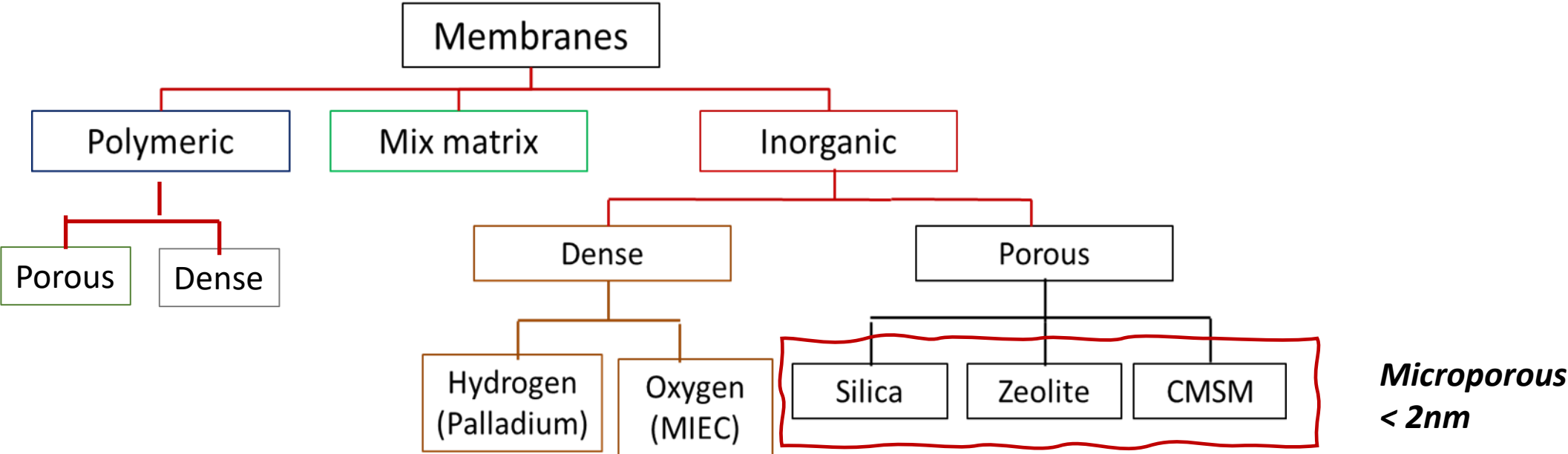
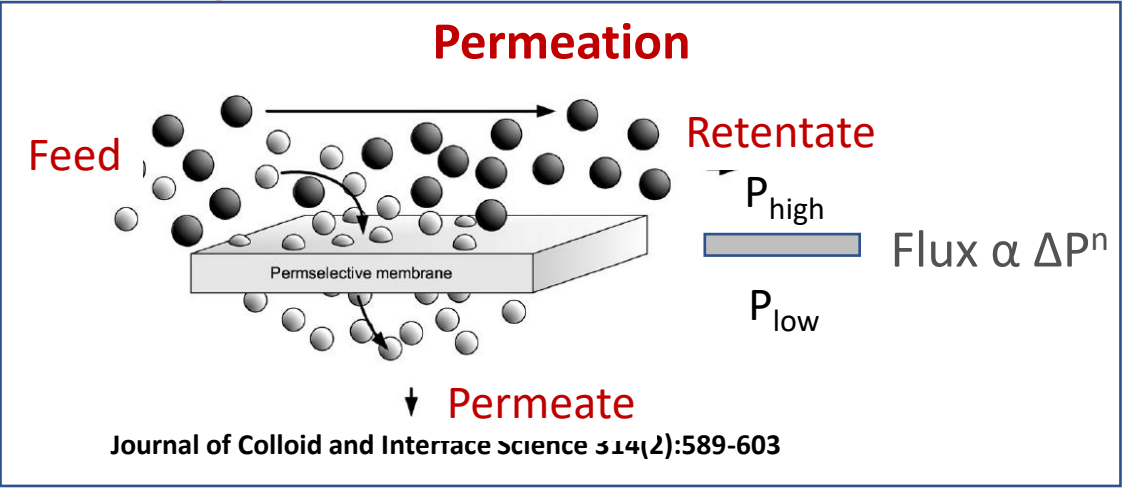


NH3 separation technologies



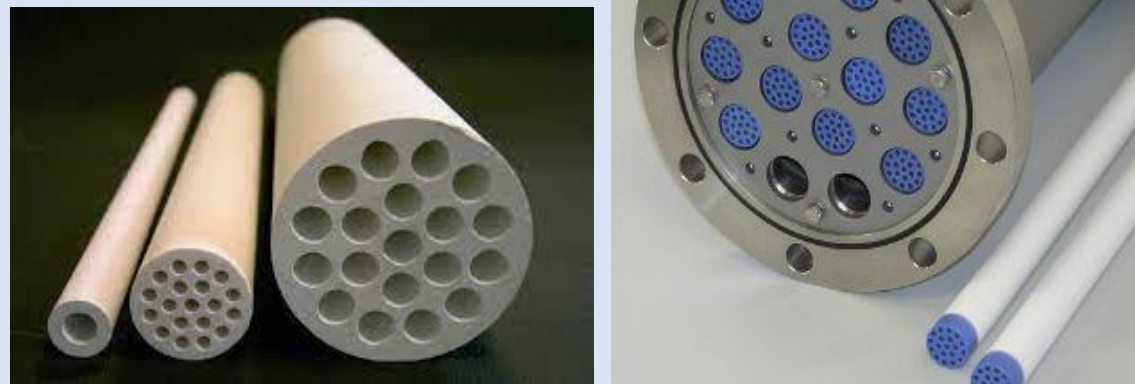
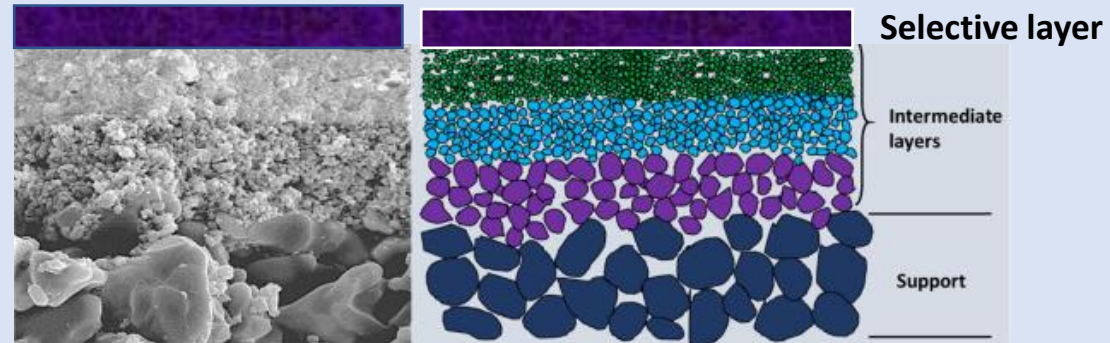
Membranes for gas separation

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




CMSM : Carbonization of polymer 7

Porous Ceramic supports



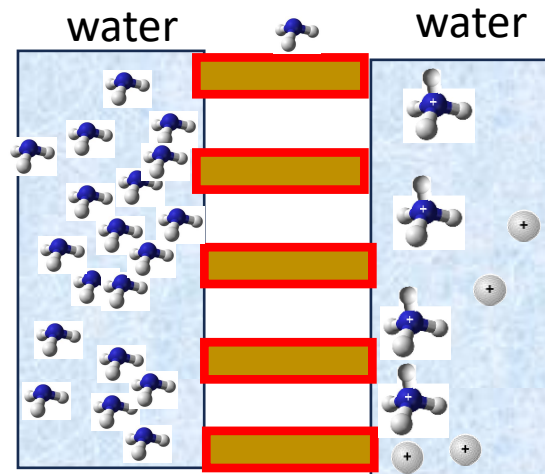
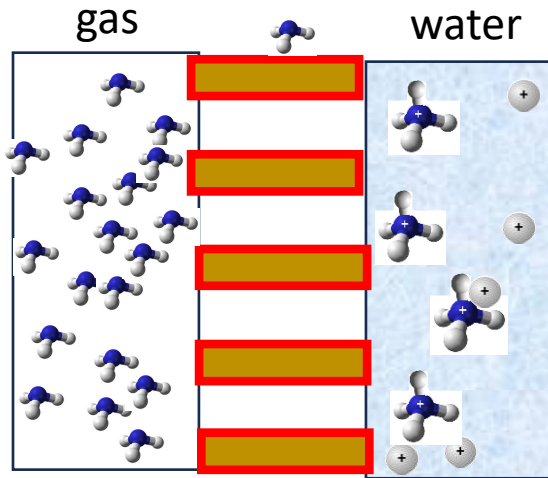
Permeation depends on thickness of membrane

 Hydrophobic porous membrane
pores >100 nm

Membrane contactor

membrane separates two fluid phases

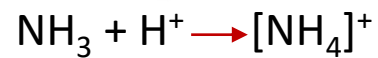
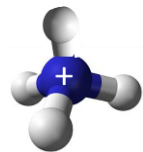
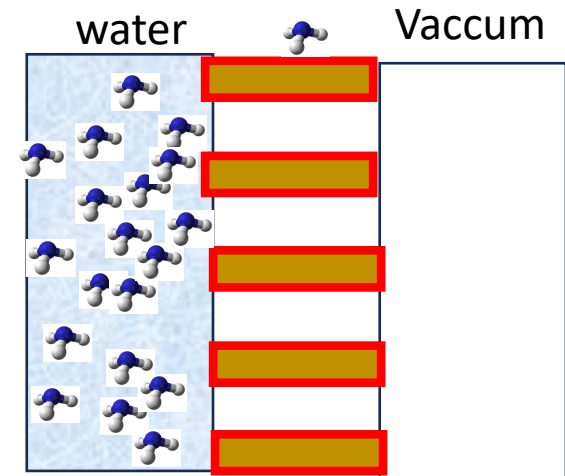
The membrane acts as a mere barrier between the two fluids



Membrane distillation

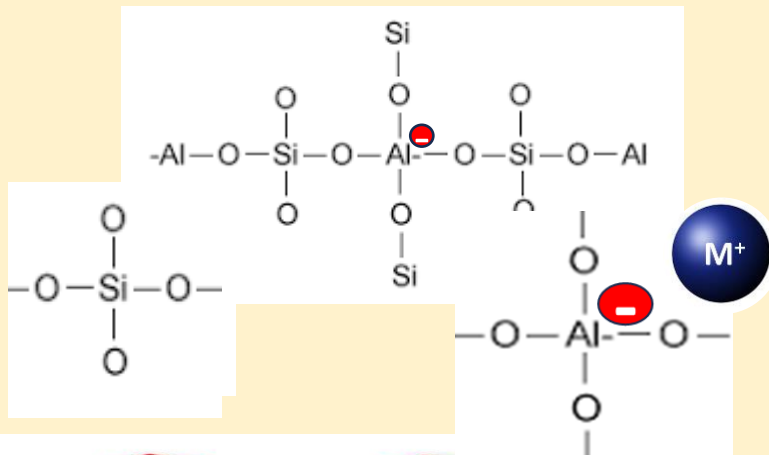
Gas pass through the membrane

Driving force vapor pressure

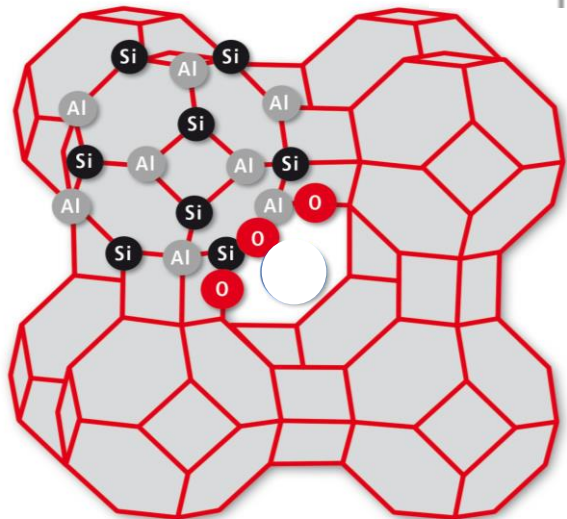
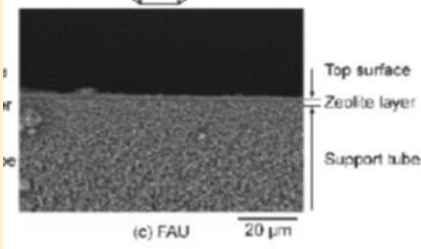
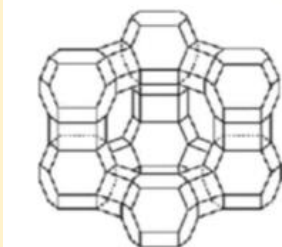


Zeolites

3D Aluminosilicate
Well defined pore size and shape



0,74 nm
FAU

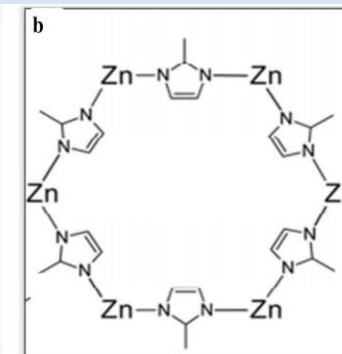
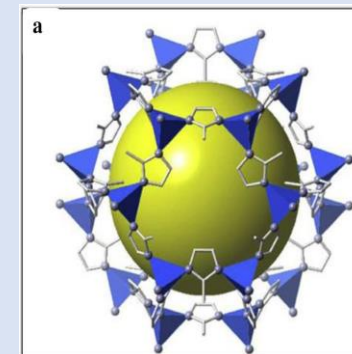
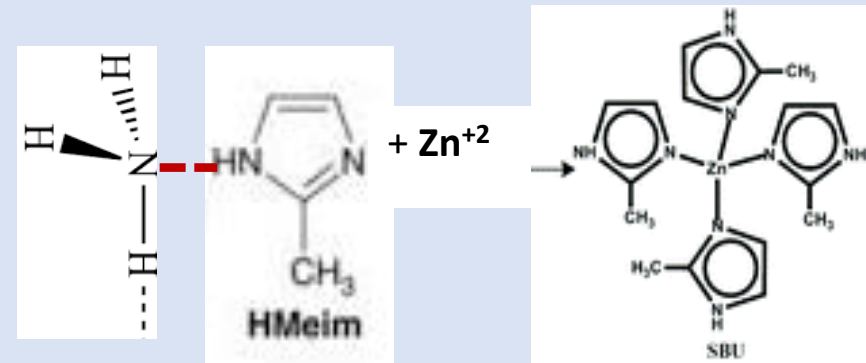


NH_3/N_2 710
 NH_3 $3.4 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}$
Temp 27°C

Membranes 2021, 11, 348

MOF

Zeolitic Imidazolate Frameworks (ZIF)



NH_3/N_2 6-35, NH_3/H_2 1-12
 NH_3 $3.6 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}$
Temp 27°C

<https://doi.org/10.1016/j.memsci.2021.119078>

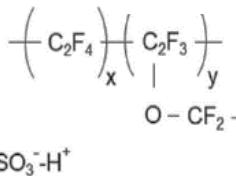
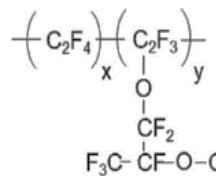
DOI: 10.1039/d0cc07217f



Ammonia permeation of fluorinated sulfonic acid/ceramic membrane

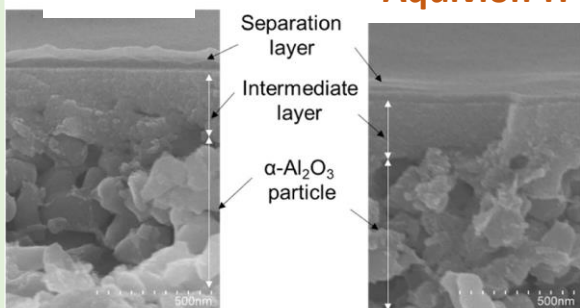
Nafion

Aquivion

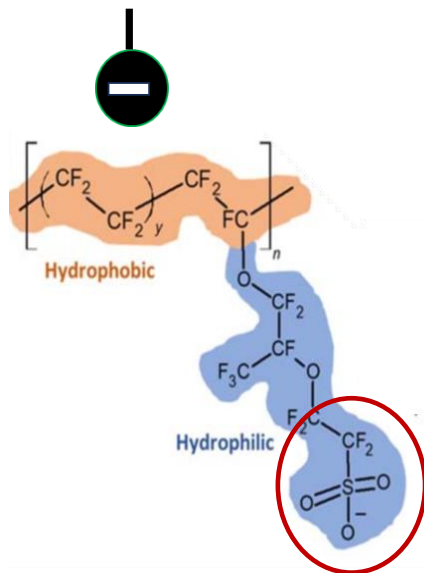
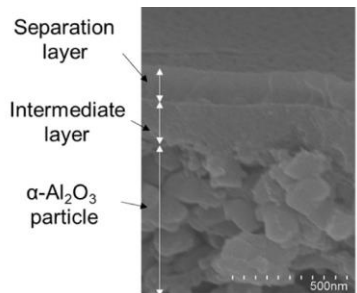


Nafion

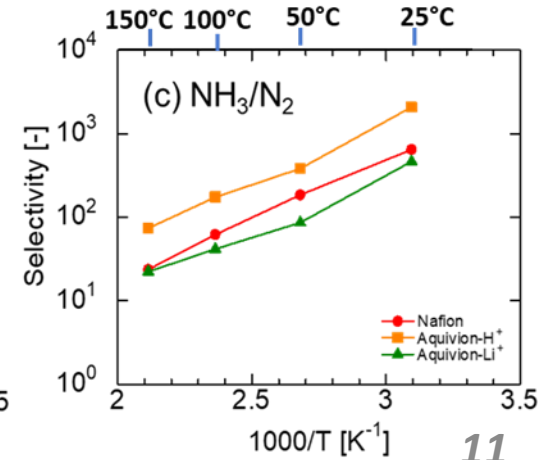
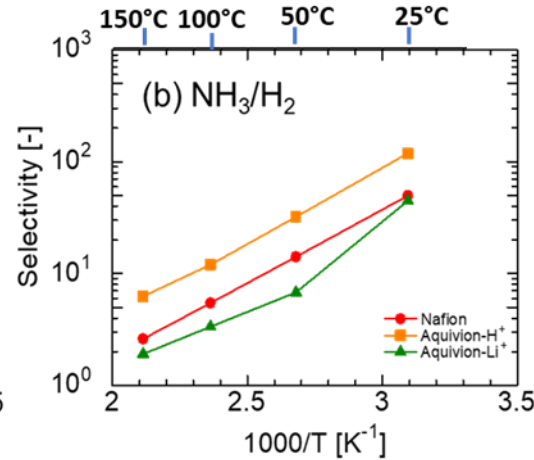
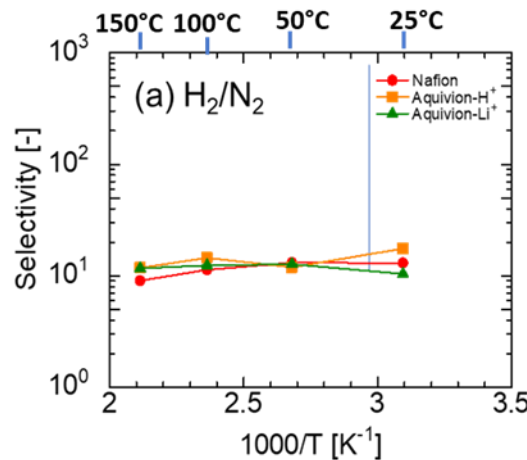
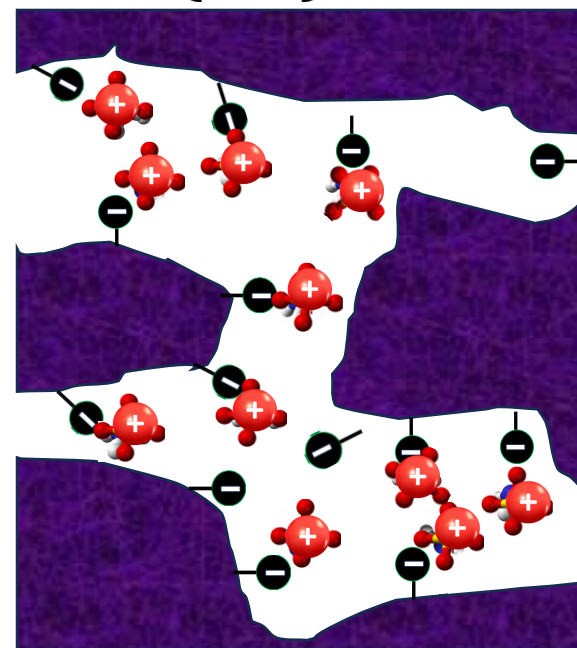
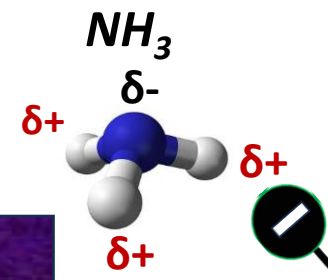
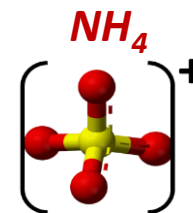
Aquivion-H⁺



Aquivion-Li⁺



PEM Proton





• Carbon molecular sieves membrane

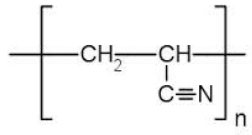
• CMSM

tecnal:a

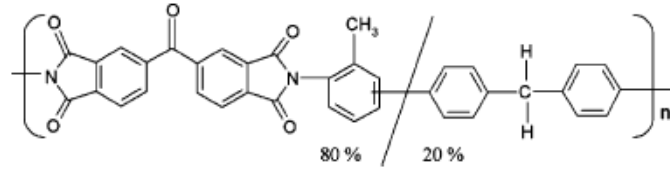
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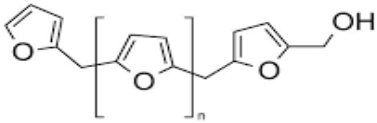
Polymeric precursors for CMSM



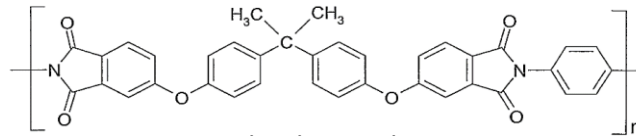
Polyacrylonitrile



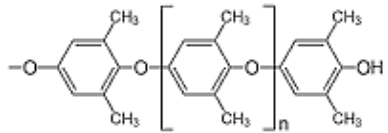
P84 co-polyimide



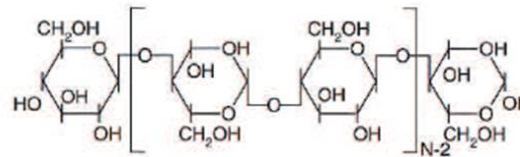
Polyfurfuryl alcohol



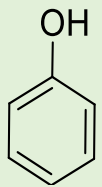
Polyetherimide



Polyphenylene oxide



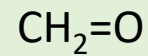
Cellulose



Phenol

Phenolic resins

+

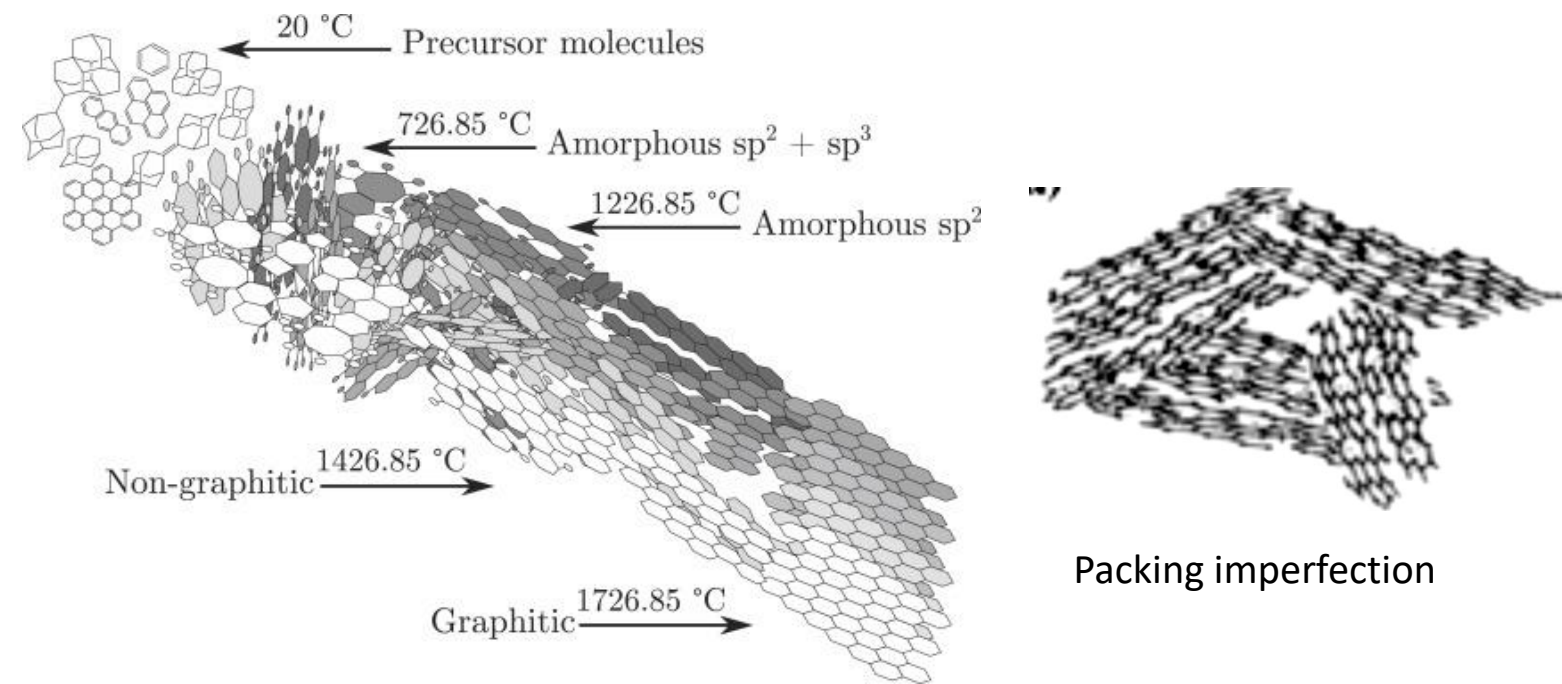


Formaldehyde

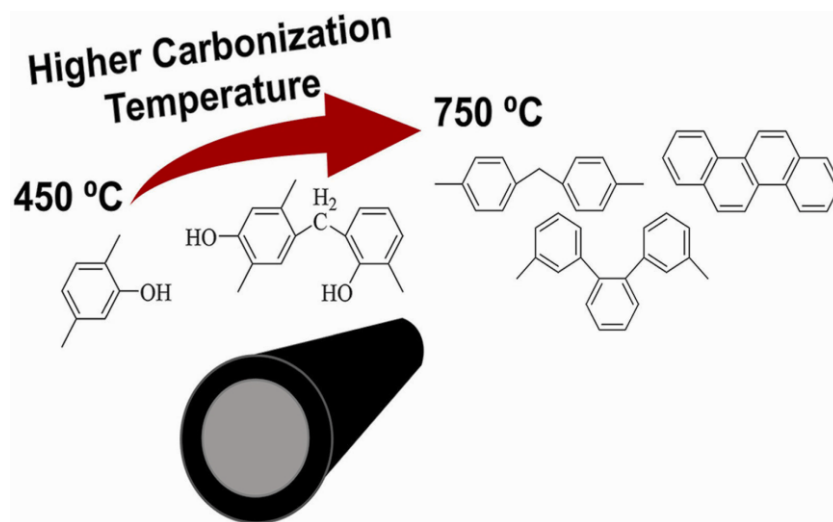
Resol : basic media and Formaldehyde /Phenol > 1
the polymerization occurs with the time

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

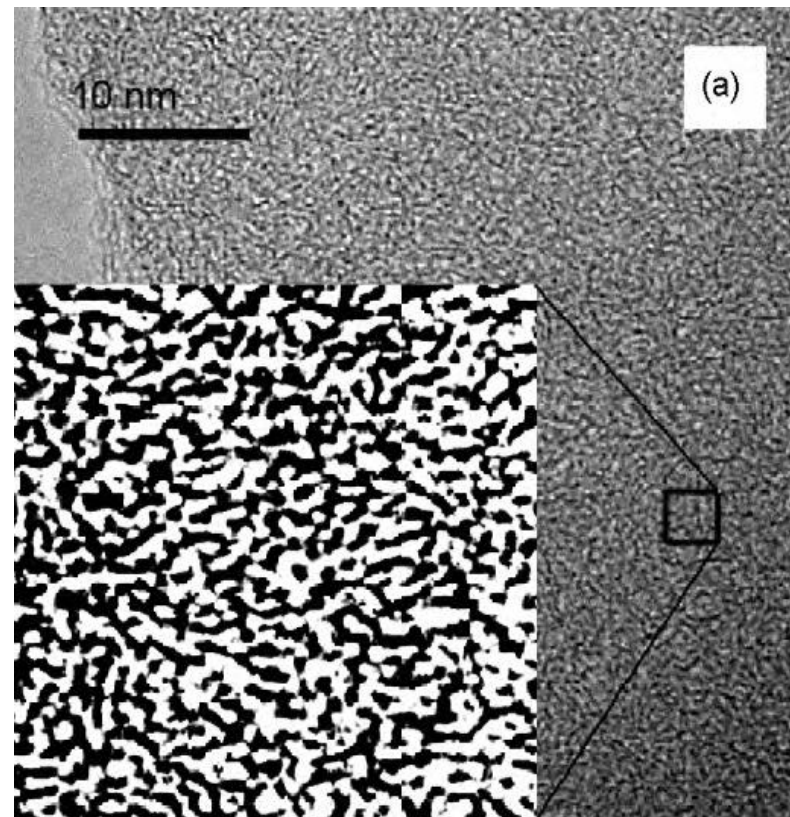
Carbonization



Carbon 161 (2020) 359-372



TEM Carbon Membrane

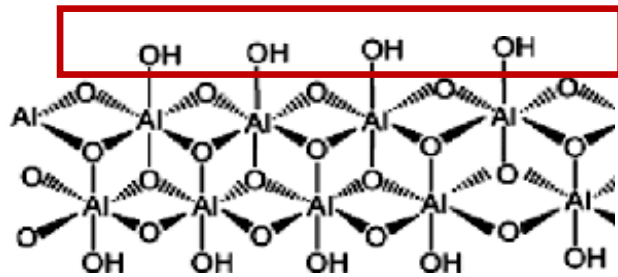


Chengwen S., Tonghua W., Huawei J., Xiuyue W., Yiming C., Jieshan Q., *J. Membr. Sci.*, 361, 22-27, 2010.

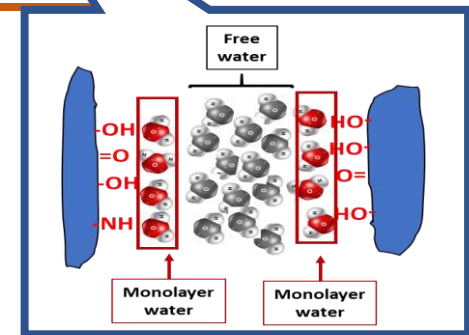
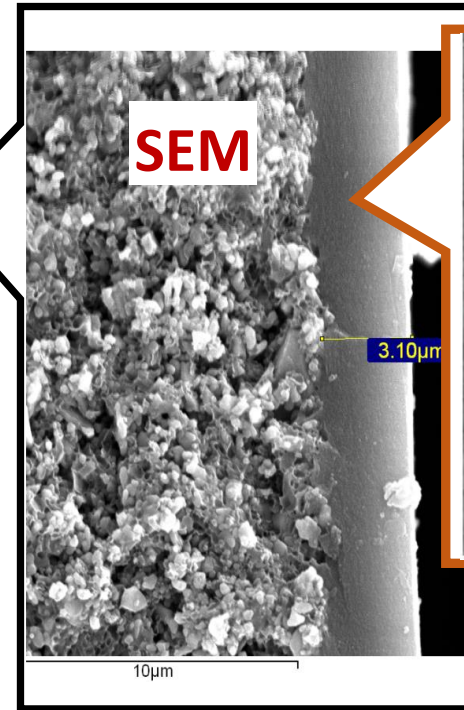
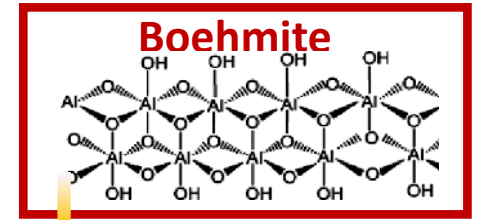
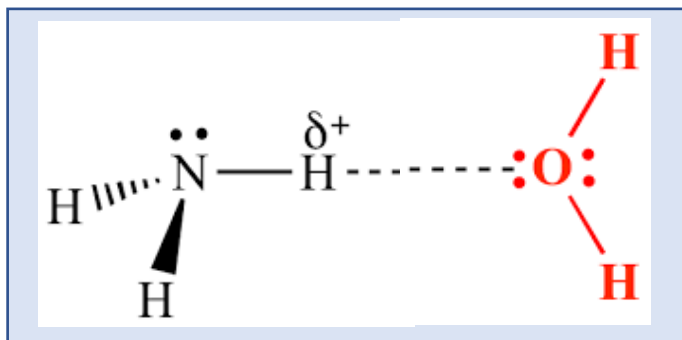
Dipping solution

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

Boehmite

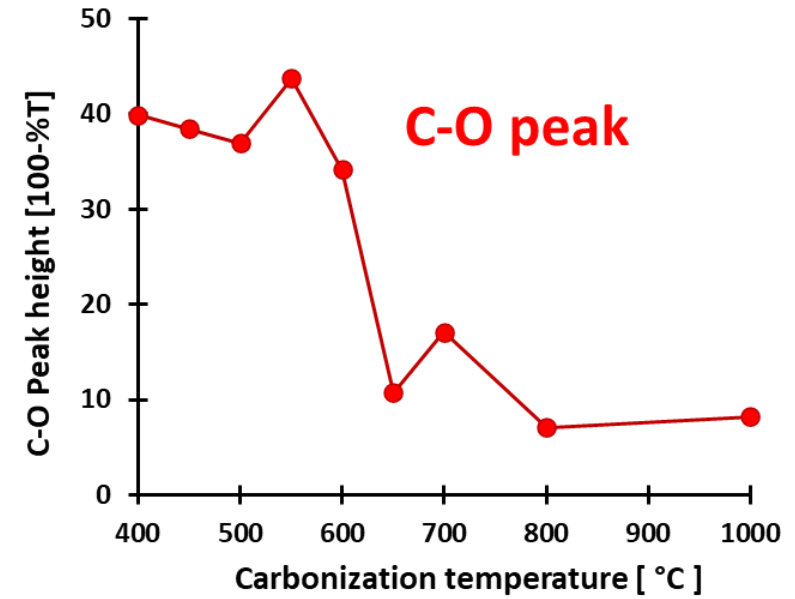
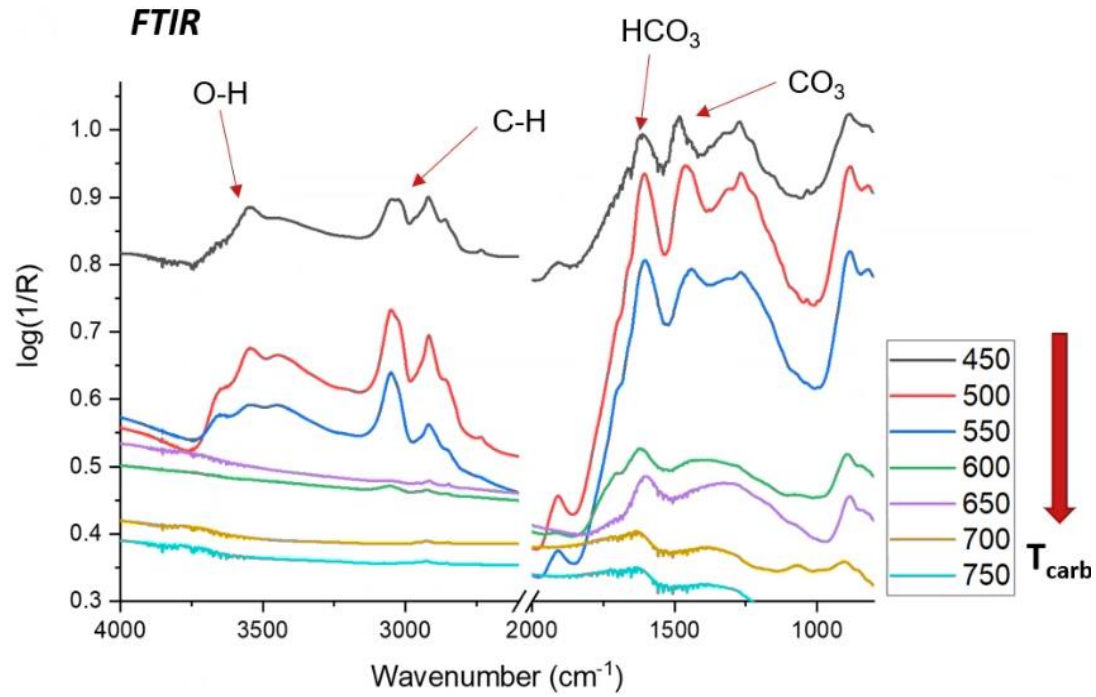


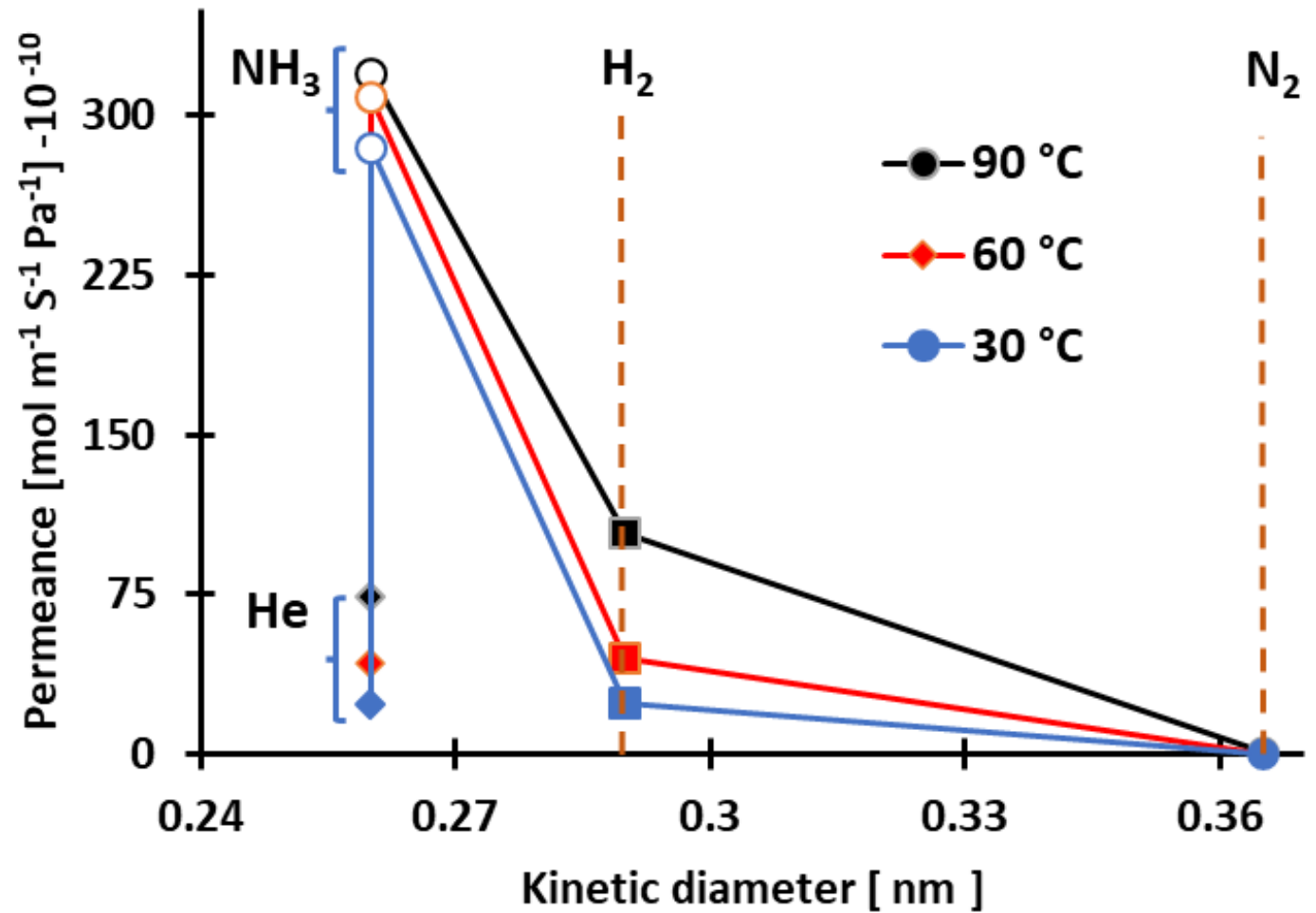
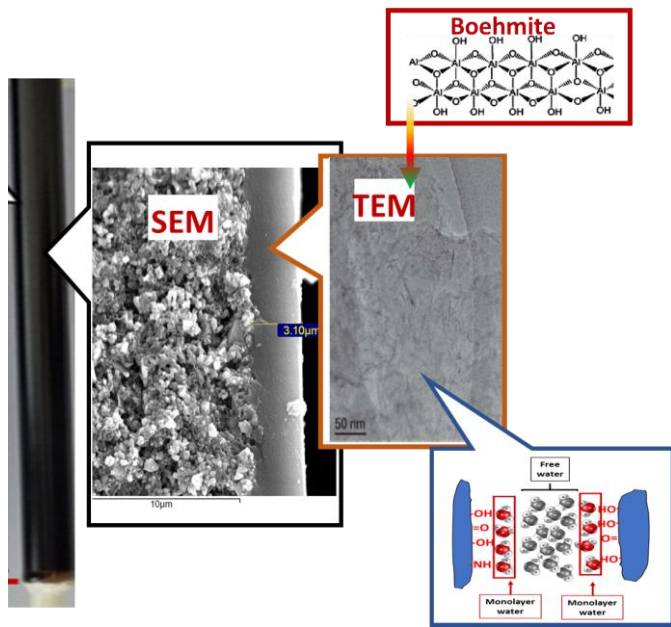
10 x 50 nm



Effect of the temperature of carbonization

FTIR





Acknowledgements



Funded by the European Union under grant agreement N° 101058565



Funded by the European Union under grant agreement N° 101112118

Many thanks

