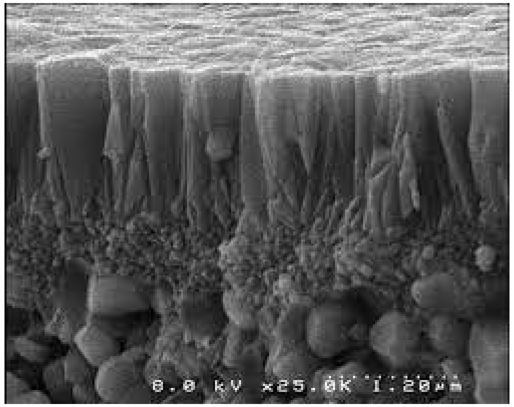
Zeolite membranes

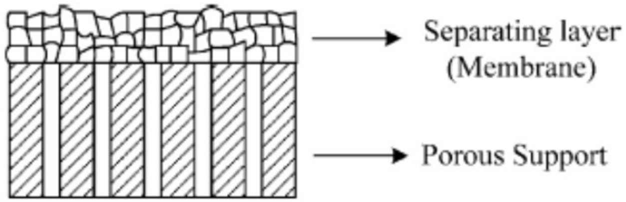


Applications : separation using membranes

↳ **development of selective zeolite membranes**

Zeolite membrane specifications ⇒ pure phases
⇒ particles of small sizes
⇒ uniform size distribution of particles

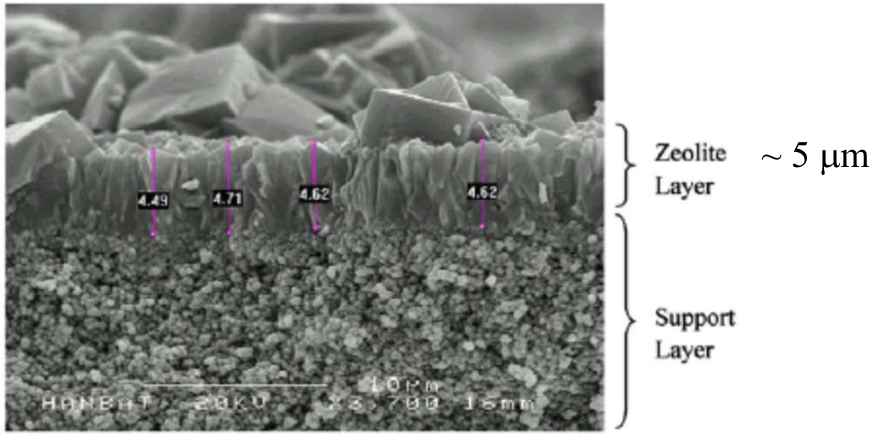
Most zeolite membranes are supported to ↗ mechanical strength



Support

Al_2O_3 tube, ∅ pores 5 - 200 nm

Stainless steel, ∅ pores 0.5 – 4 μm



Cross section

→ synthesis control difficult

↳ the presence of impurities ↘ the selectivity and the separative properties

↳ an heterogeneous crystallite size creates meso/macroporosity (⇒ induces leaks)

Applications : separation using membranes

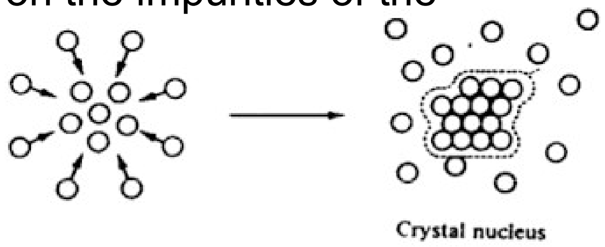
⇘ Membranes preparation : nucleation - growth mechanism

- Control of the nucleation (germination) step

  germination = formation of crystal nuclei = heterogeneous process

  ⇒ The nuclei of the future crystalline phase form preferentially on the impurities of the system

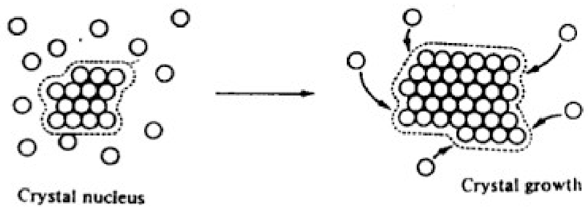
  ⇒ Support = impurity ⇨ the choice of the support is important

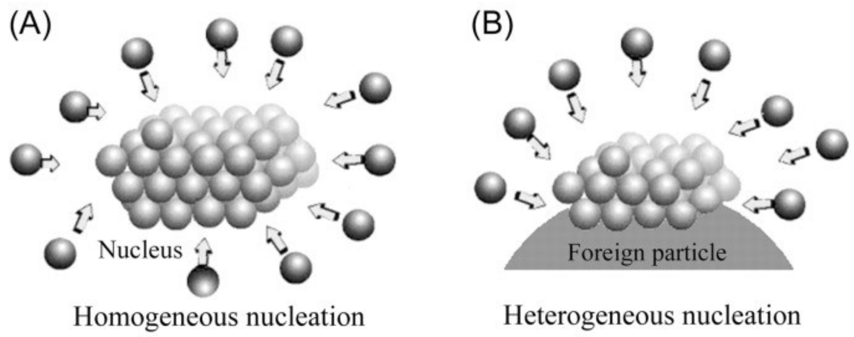


- Control of the growth step

  search for a continuous, homogeneous film

  ⇒ control of the deposition rate of reactive species on the substrate, T, H_2O content, [reagents]





→ The presence of impurities ↘ the selectivity and the separation properties

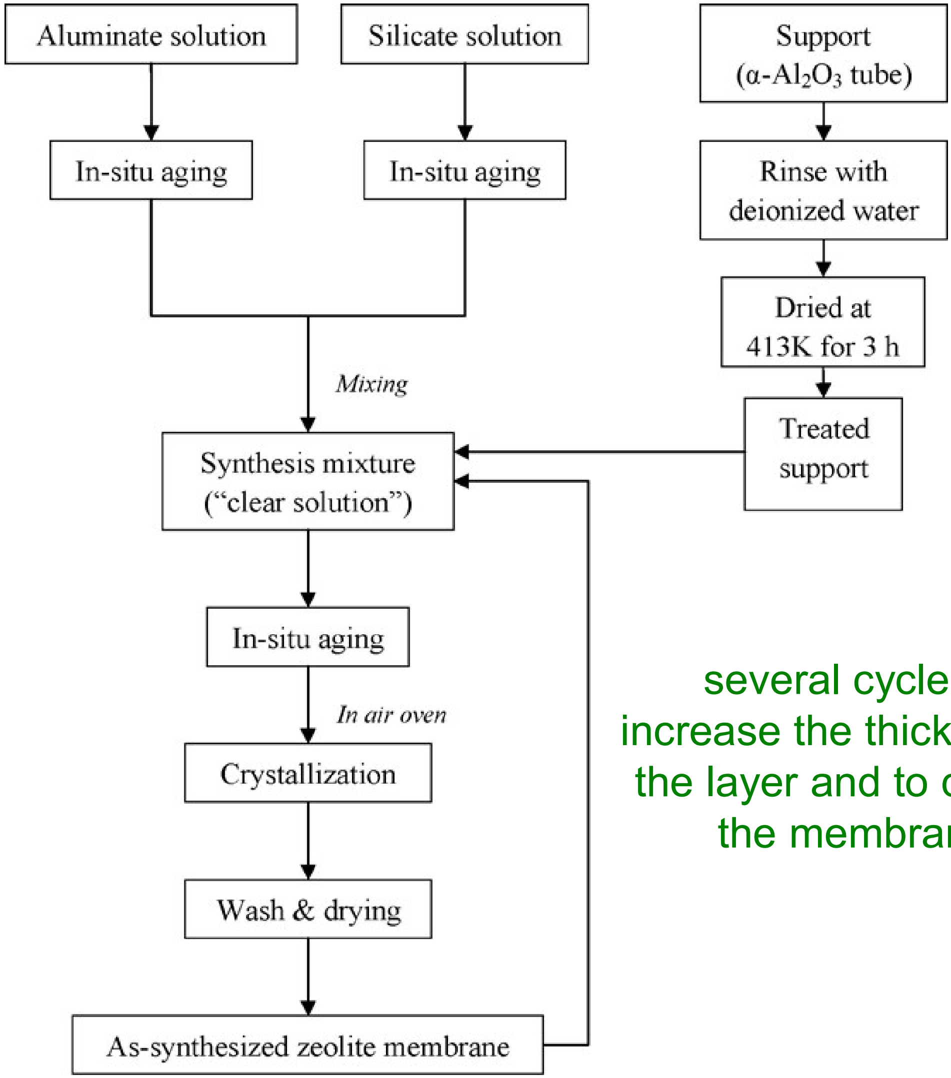
→ A heterogeneous crystallite size creates meso and macroporosity

⇨ **Synthesis is difficult**

Membranes preparation

↳ Classical hydrothermal synthesis route

⇨ hydrothermal synthesis in the presence of the support



several cycles to increase the thickness of the layer and to densify the membrane

Disadvantages

- Low density membranes
- Long time synthesis (days)
- Frequent formation of impurities
  (nucleation step difficult to control)

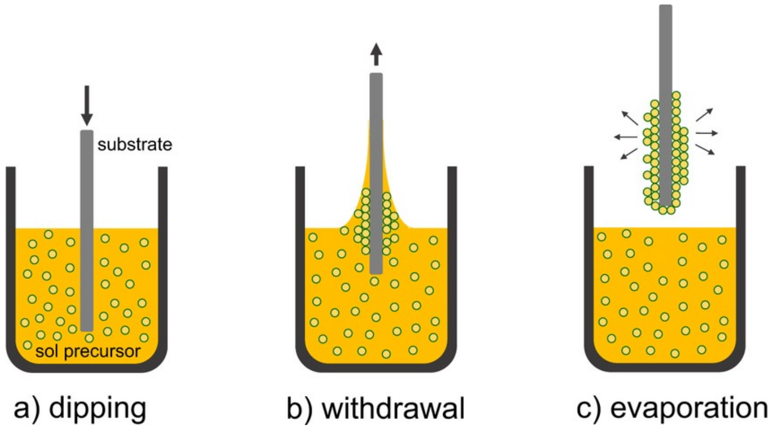
  ⇒ reduced separation properties
- Crystalite size control difficult

Membranes preparation

↳ Secondary growth synthesis of the material

1) Deposition of zeolite seeds on the support prior to hydrothermal synthesis

⇒ Deposition by dip-coating → a) Immersion of the substrate in a solution containing seeds
→ b) Formation of a continuous film on the surface of the substrate
→ c) Evaporation of the solvent: formation of crystal nuclei



2) Hydrothermal synthesis on the support coated by the crystal nuclei

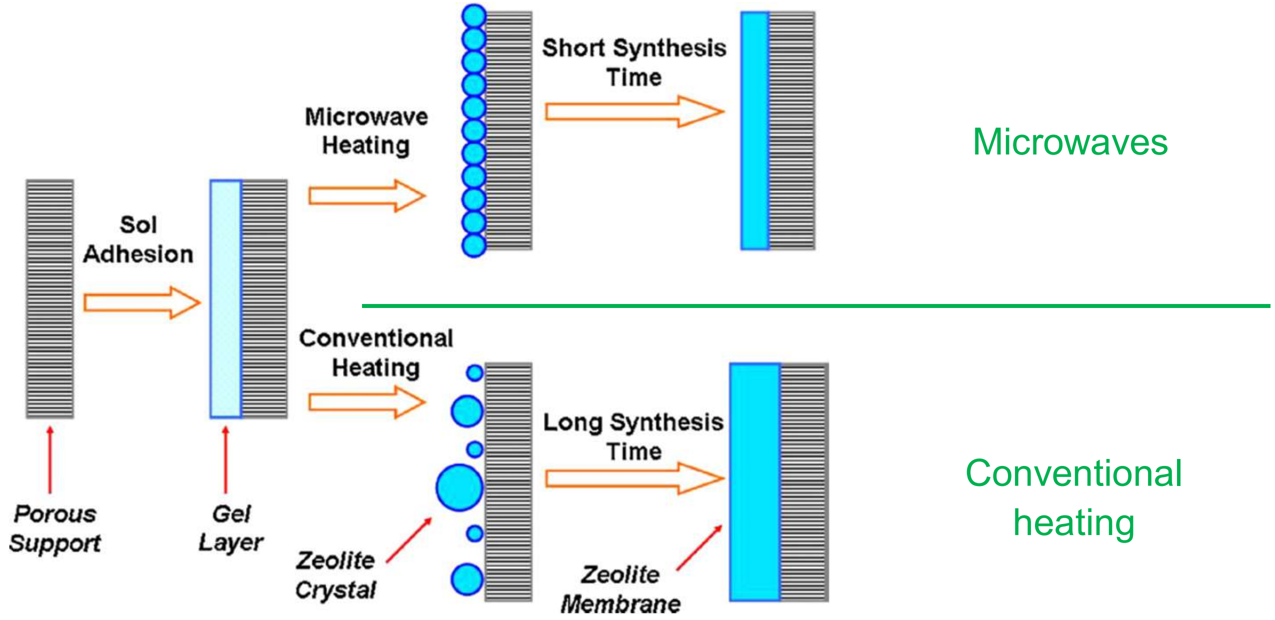
⇨ Better control of the membrane microstructure (crystal thickness and orientation)

⇨ Better reproducibility

} Control of the nucleation step = key step

Membranes preparation

↳ Microwave assisted synthesis



Advantages microwave synthesis vs conventional heating

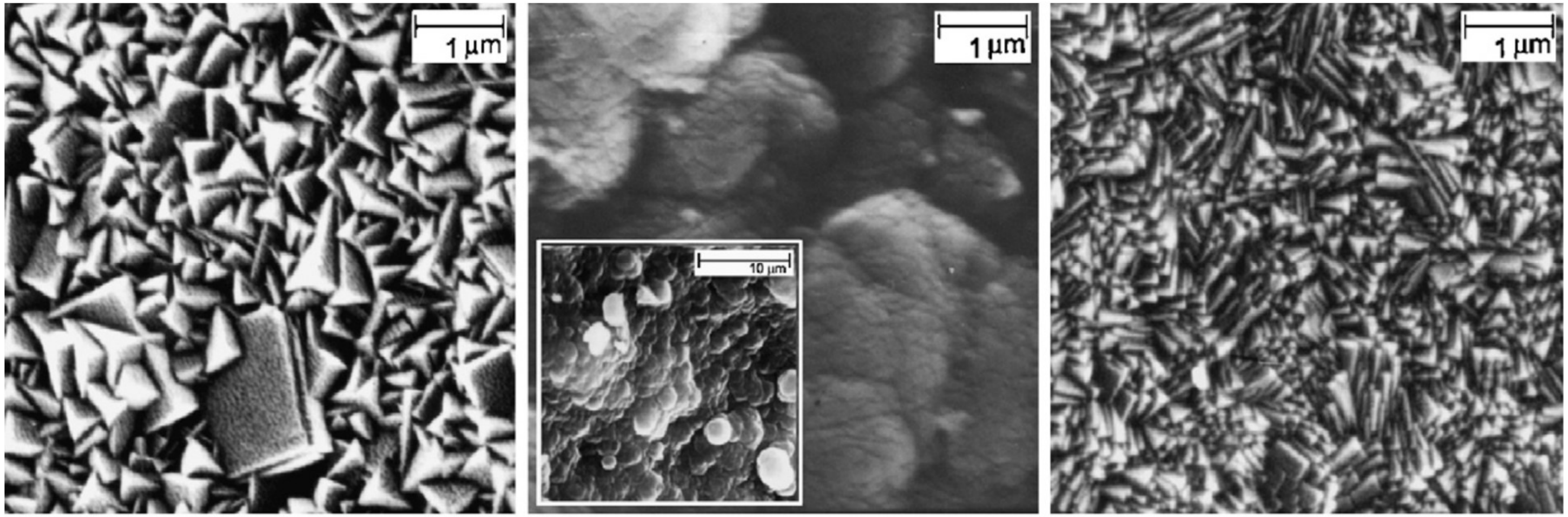
- Less time consuming (~ 10 min for crystallization) ⇒ no conduction or convection: direct transfer of microwave energy to the core of the material
- Formation of smaller crystallites which are better stacked on the surface of the support, because of a rapid crystallization ⇒ presence of fewer defects (↘ meso/macroporosity)
- Narrower pore size distribution ⇒ the thickness of the layer is well controlled
- High purity

⇒ Improved selectivity

Membranes preparation

↳ Microwave assisted synthesis vs conventional heating

NaA membrane



Hydrothermal synthesis	Pulsed microwave	Continuous microwave
⬇	⬇	⬇
Micrometric size crystals	Particules with no specific shape	Submicrometric size rystals

→ characterisation of the porosity by gas permeation (presence of defects ?)

→ Measure of BET surface area (S_{BET}) : characterisation of the microporosity

Application : separation on membranes

↳ Efficiency criteria for membranes

⇨ Selectivity

It is expressed by a parameter called « retention » or by the « Separation Factor » : $\alpha_{A/B}$ (SF)

$$\alpha_{A/B} = \frac{\left(\frac{x_A}{x_B}\right)_{\text{permeate}}}{\left(\frac{x_A}{x_B}\right)_{\text{alimentationfeed}}}$$

x_A, x_B : molar ratios

⇒ The Separation Factor must be as high as possible

⇨ Productivity

It is expressed by a parameter called « flux »

It is the volume of fluid separated, per unit of membrane surface, per unit of time

→ in $L/m^2/h$

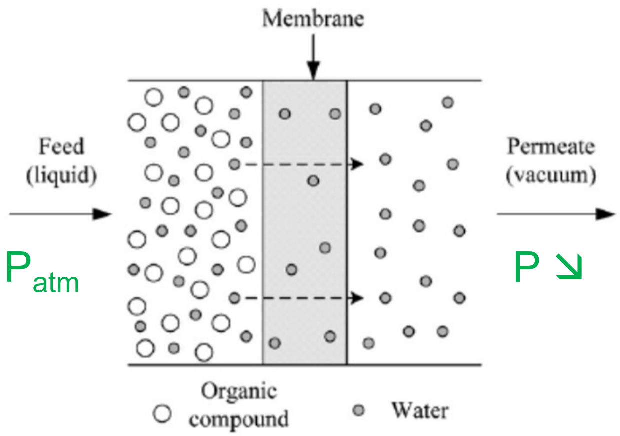
⇒ The Productivity must be as high as possible

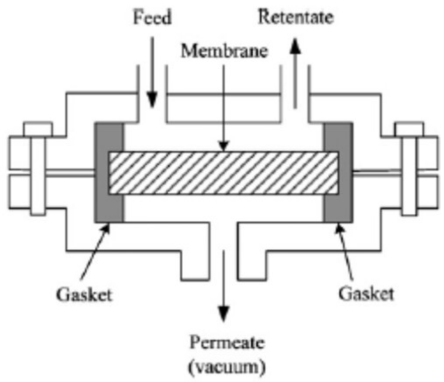
⇨ A good compromise must be found between the two factors

Application : separation on membranes

⇘ Pervaporation (= pervaporative separation)

= process for the separation of liquid mixtures by partial vaporization through a membrane





Stainless steel module + 12m² Na-A

- Membrane = selective barrier between several phases
- A pressure difference (ΔP) is applied between both sides of the membrane
  - → the phase able to pass through the membrane (size match) is vaporised, diffuses through the membrane and is recondensed into liquid phase ⇨ permeate
  - → the mismatched phase remains in liquid form upstream

⇒ transfer possible due to the difference in vapour pressure of the compounds

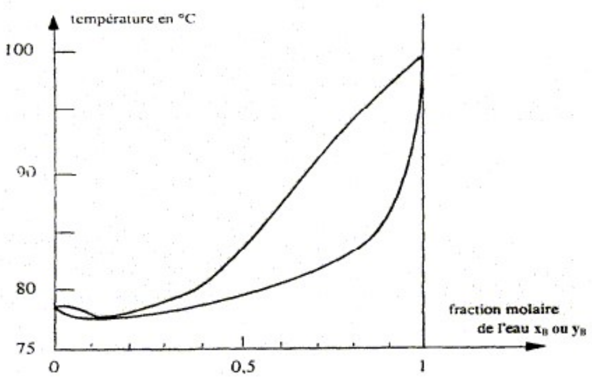
Ideal material: ⇨ good selectivity
⇨ high productivity (L/m²/h)

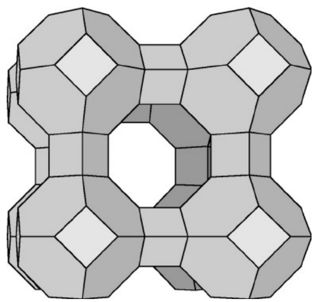
Application : separation on membranes

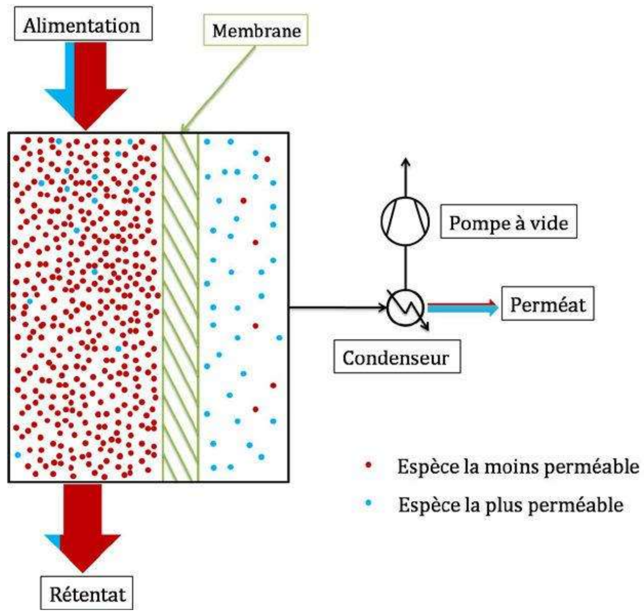
⇘ Pervaporation : separation of water – ethanol mixtures

- Used in bio-ethanol production units
- Bioethanol production (by fermentation of sugars/starch) produces large amounts of aqueous ethanol solutions
- Absolute ethanol (99.9%) can be obtained by azeotropic distillation → long/difficult process (especially for constituentsif of close volatilities)

⇒ Possibility of separation by pervaporation on hydrophilic membranes







Ex : Na-A hydrophilic zeolite membrane

→ Adequate properties for H_2O diffusion

→ Obtention of absolute EtOH

→ Flux ~ 2.3 kg/m^2/h