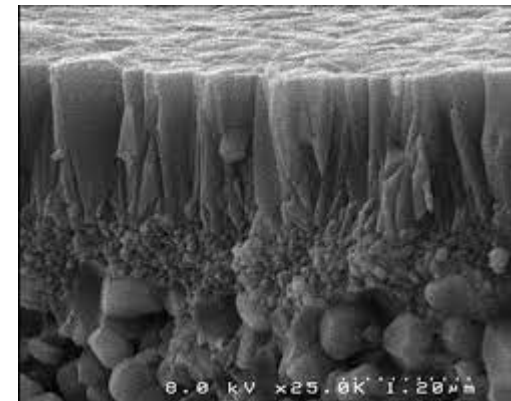




Zeolite membranes

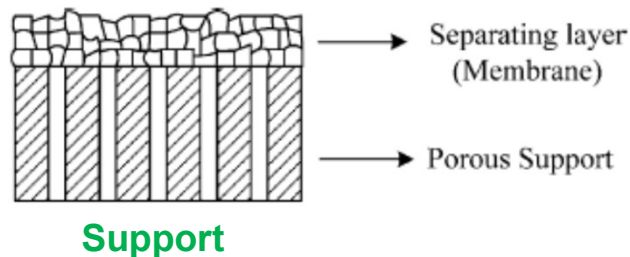


Applications : separation using membranes

development of selective zeolite membranes

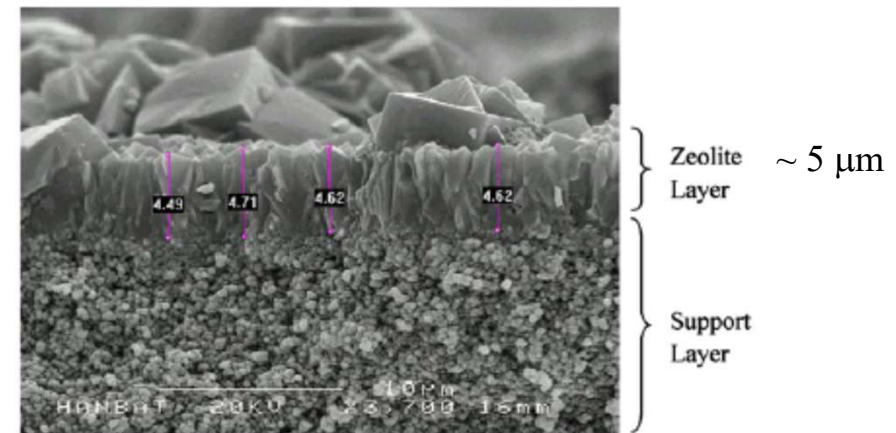
- Zeolite membrane specifications $\Rightarrow$ pure phases
 $\Rightarrow$ particles of small sizes
 $\Rightarrow$ uniform size distribution of particles

Most zeolite membranes are supported to $\nearrow$ mechanical strength



Al_2O_3 tube, $\varnothing$ pores 5 - 200 nm

Stainless steel, $\varnothing$ pores 0.5 - 4 μm



Cross section

$\rightarrow$ synthesis control difficult

- $\hookrightarrow$ the presence of impurities $\searrow$ the selectivity and the separative properties
- $\hookrightarrow$ an heterogeneous crystallite size creates multi scale porosity ($\Rightarrow$ favors leaks)

Applications : separation using membranes

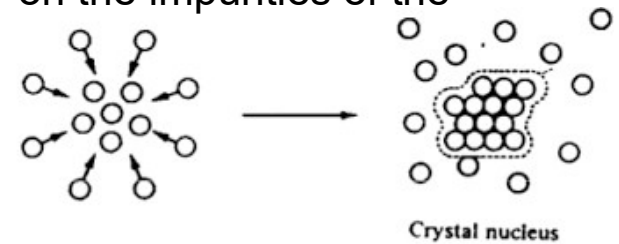
↳ Membranes preparation : nucleation - growth mechanism

- 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

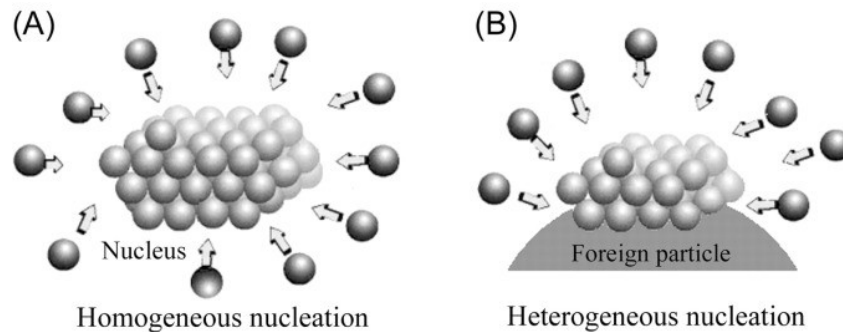
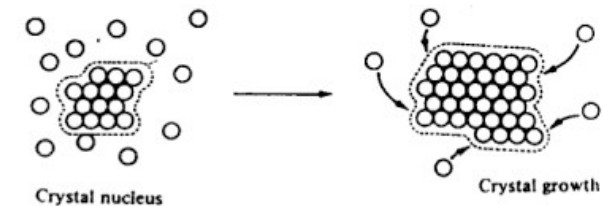
⇒ Support = impurity ⇒ the choice of the support is important



- Control of the growth step

search for a continuous, homogeneous film

⇒ control of the deposition rate of reactive species on the substrate, T, H₂O content, [reagents]



→ The presence of impurities $\supset$ the selectivity and the separation properties

→ A heterogeneous crystallite size creates meso and macroporosity

⇒ Synthesis is difficult

Membranes preparation

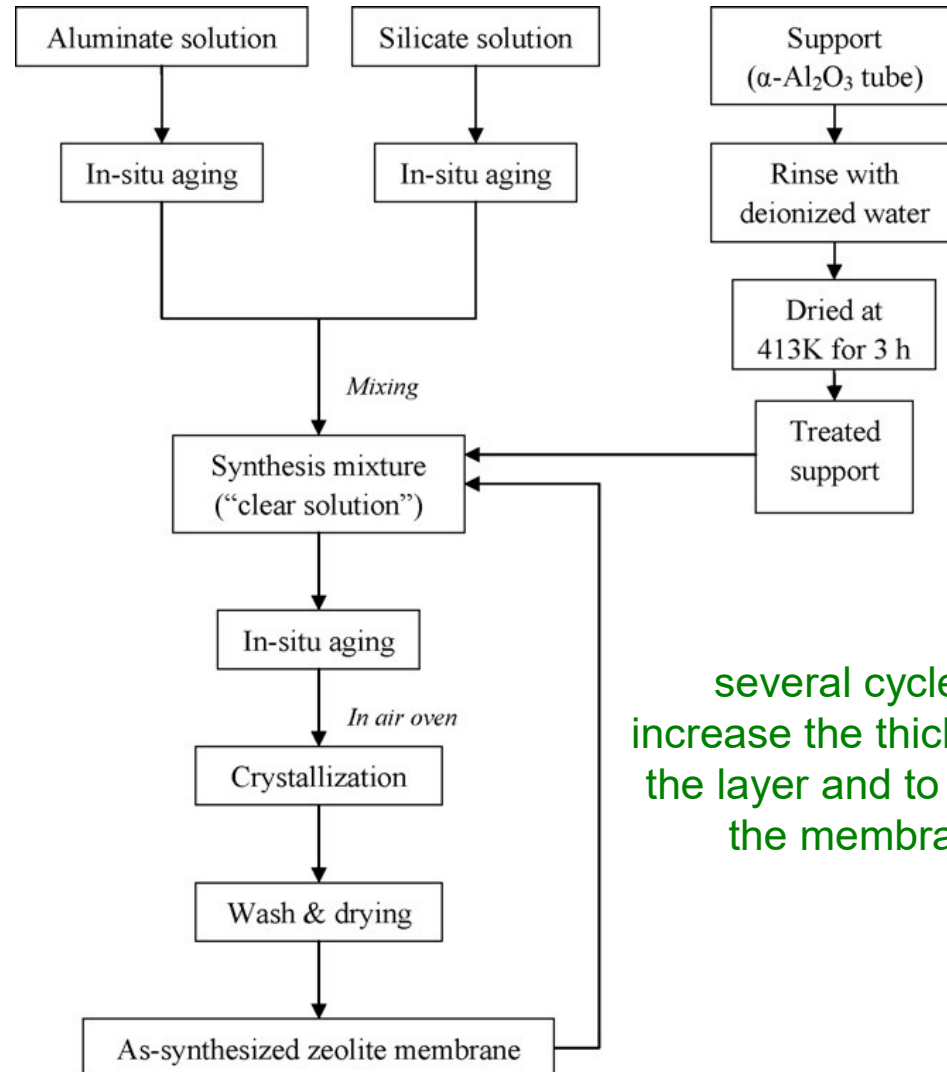
➤ Classical hydrothermal synthesis route

⇒ hydrothermal synthesis in the presence of the support



Disadvantages

- Low density membranes
- Long time synthesis (days)
- Frequent formation of impurities (nucleation step difficult to control)
⇒ reduced separation properties
- Crystalite size control difficult



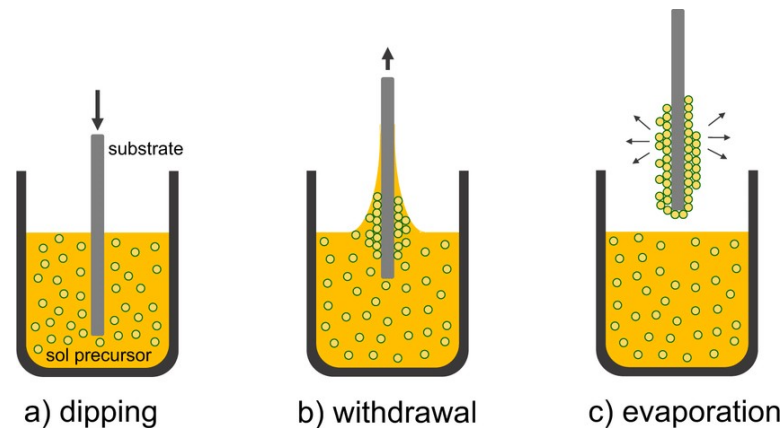
several cycles to increase the thickness of the layer and to densify the membrane

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

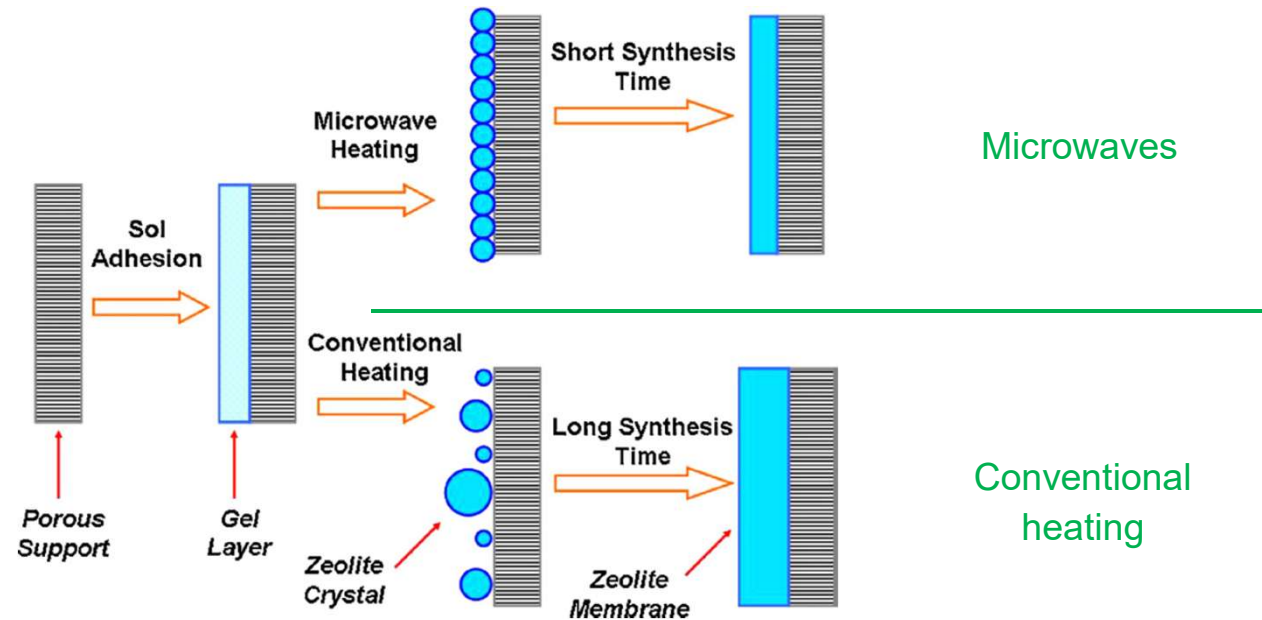
⇒ Better control of the membrane microstructure
(crystal thickness and orientation)

⇒ Better reproducibility

} Control of the nucleation step
= key step

Membranes preparation

➤ Microwave assisted synthesis



Advantages microwave synthesis vs conventional heating

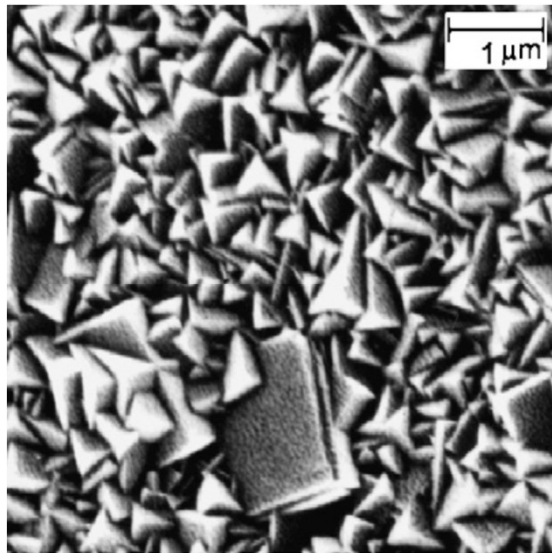
- Less time consuming (~ 10 min for crystallization) $\Rightarrow$ no conduction or convection: direct transfer of microwave energy to the core of the material
- Formation of smaller crystallites which are better stacked on the surface of the support, because of a rapid crystallization $\Rightarrow$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

$\Rightarrow$ Improved selectivity

Membranes preparation

↪ Microwave assisted synthesis vs conventional heating

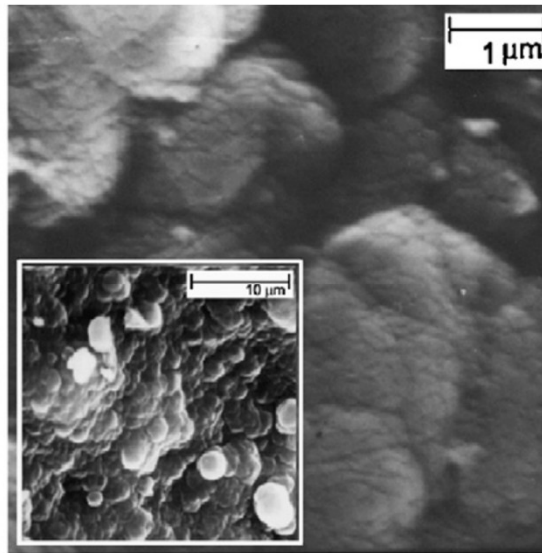
NaA membrane



Hydrothermal synthesis



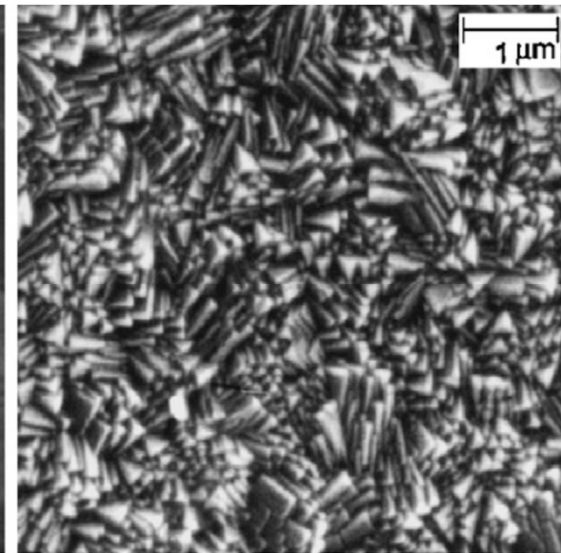
Micrometric size
crystals



Pulsed microwave



Particules with no
specific shape



Continuous microwave



Submicrometric
size crystals

→ 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)

$$\alpha_{A/B} = \frac{\left(\frac{x_A}{x_B}\right)_{\text{permeate}}}{\left(\frac{x_A}{x_B}\right)_{\text{feed}}} \quad x_A, x_B : \text{molar ratios}$$

⇒ **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/m²/h

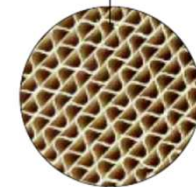
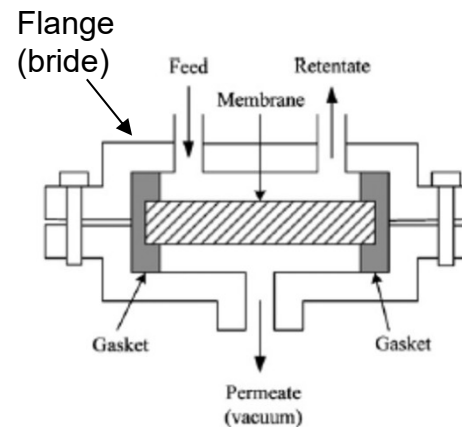
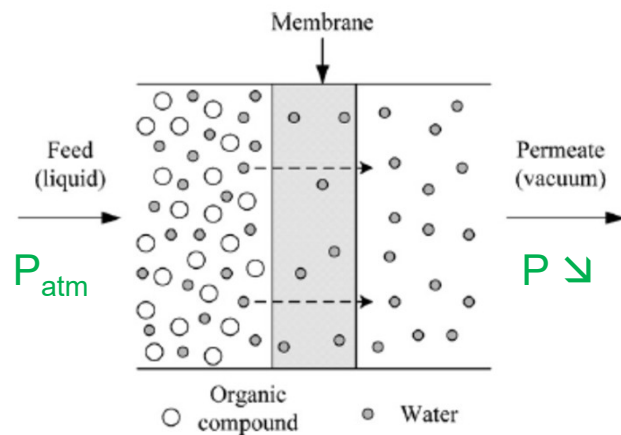
⇒ **The Productivity must be as high as possible**

⇒ **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)**

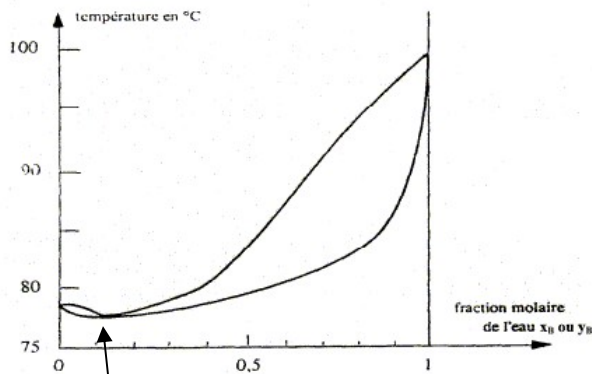
Application : separation on membranes

↳ 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**
- To obtain **absolute ethanol** (99.9%): → azeotropic distillation ($Az = 95.6\%$)
→ drying

But: long/difficult process (especially as constituents have close volatilities)

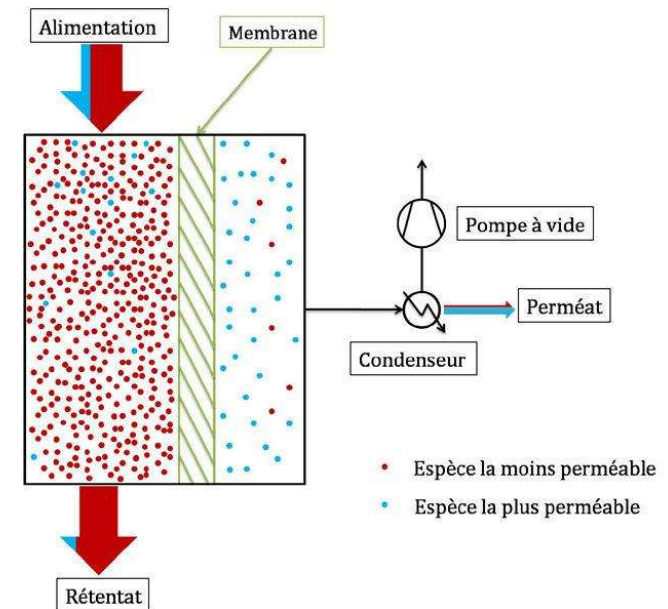
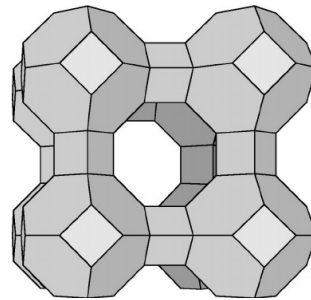
⇒ Possibility of separation **by pervaporation on hydrophilic membranes**



95.6%
(Az)

Ex : Na-A hydrophilic zeolite membrane

- Adequate properties for H_2O diffusion
- Obtention of absolute EtOH
- Flux $\sim 2.3 \text{ kg/m}^2/\text{h}$



Application : separation on membranes

↪ Pervaporation membranes at industrial scale

- Advantages

- Low energy consumption compared to distillation (only the extracted liquid fraction is evaporated: 10 to 150 kWh/m³)
- Flexibility and compactness of the plant (can be easily adjusted)
- High purity of the obtained products and absence of polluting emissions
- Easy to operate and to control

- Disadvantages

- The investment cost is high compared to other technologies (distillation, molecular sieve adsorption)
- The choice of industrial membranes is insufficient : does not cover all types of separations
- Many preliminary tests must be carried out before sizing
- Membranes are very sensitive to variations in composition of the liquid

Application : separation by pervaporation

↪ Acetic acid / water mixture on a Sn-substituted MFI-type zeolite

- Polymeric hydrophobic membranes present poor performances for CH₃COOH/H₂O separation

→ Separation Factor $\alpha \sim 2$

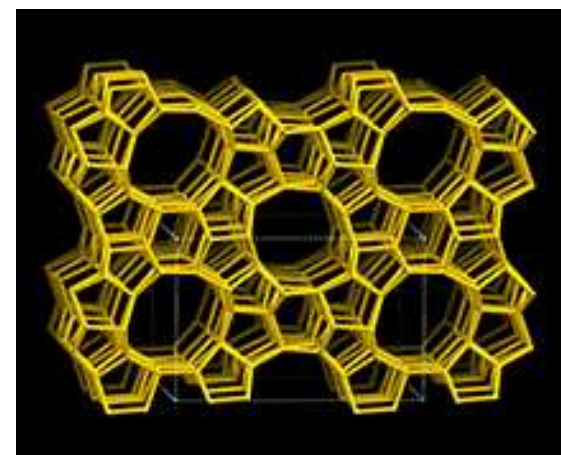
→ flux < 0.15 kg/m²/h

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

- Aim of the study : comparison of the separation properties of:

→ a silicalite (MFI, Si/Al = ∞)

→ a Sn-substituted MFI

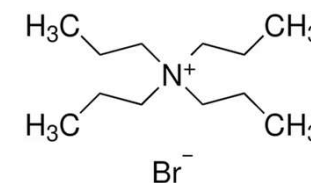


MFI viewed along [010]

⇒ Elaboration of MFI membranes supported on α -Al₂O₃ tubes

Hydrothermal synthesis route : TEOS + SnCl₄.5H₂O + NaOH + TPABr

Si/Sn = ∞ , 100, 50, 30 and 25



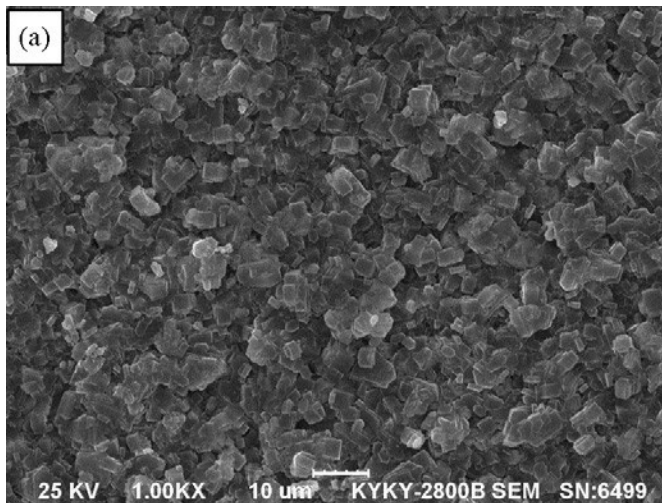
Water adsorption tests ⇒ the substitution of Si by Sn led to an increase in hydrophobicity

Application : separation by pervaporation

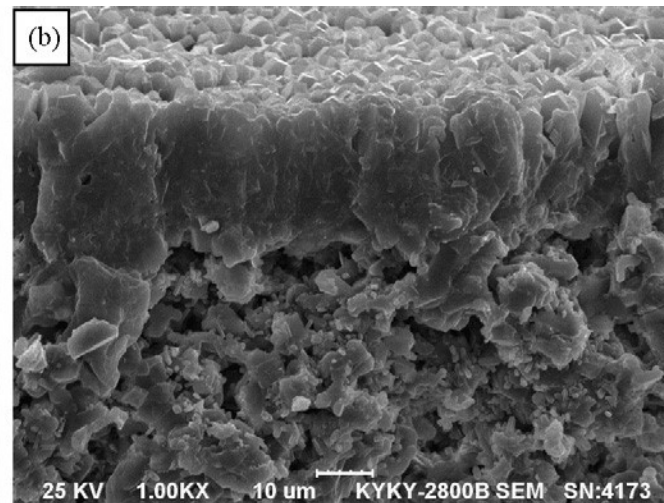
↪ **Acetic acid / water mixture on a Sn-substituted MFI-type zeolite**

Characterization of Si/Sn substitution :

- **FTIR** : shift of the Sn-O vibration bands compared to Si-O ones
- **XRD** : increase of the lattice parameters after substitution
- **SEM** : high density of crystals, no crackings



α -Al₂O₃ support



support + MFI

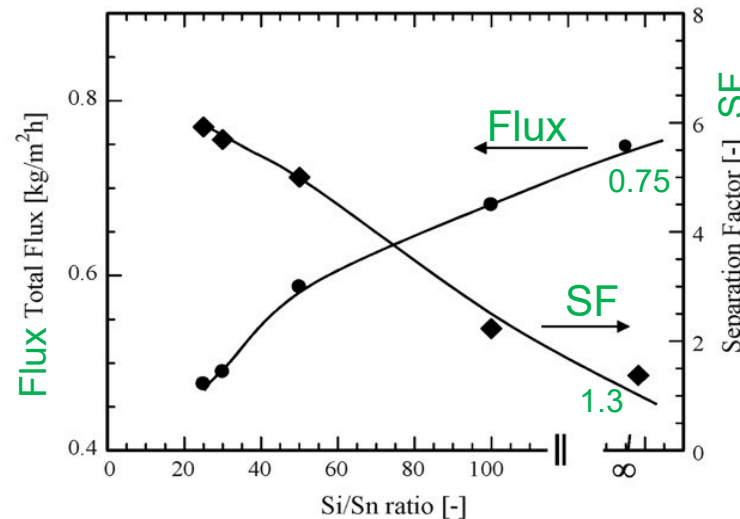
e ~ 15 μ m

Application : separation by pervaporation

Acetic acid / water mixture on a Sn-substituted MFI-type zeolite

- For silicalite (Si/Al = ∞) : SF ~ 1.3 , flux ~ 0.75 kg/m²/h

[CH₃COOH]
5 wt.%
70°C



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

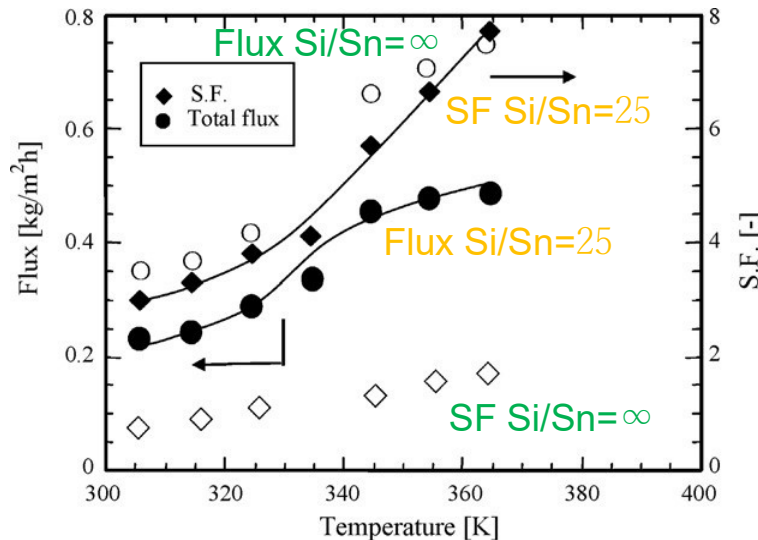
- When Si/Sn $\searrow$, the SF $\nearrow$
 - $\Rightarrow$ the increase in Sn content leads to a better separation
 - $\Rightarrow$ the increase in Sn content increases hydrophobicity
 - $\Rightarrow$ the zeolite does not retain H₂O
 - $\Rightarrow$ H₂O (permeate) is better separated from the acid
- When Si/Sn $\searrow$, the total flux $\searrow$
 - $\Rightarrow$ the increase in Sn content increases hydrophobicity
 - $\Rightarrow$ the zeolite has a low affinity for H₂O
 - $\Rightarrow$ H₂O passes through it slowly
 - $\Rightarrow$ The separation kinetic is slow

When Si/Sn $\searrow$, the separation is better but the kinetic of separation is slower: compromise needed

However: the Sn content is limited by the precipitation of SnO₂

Application : separation by pervaporation

↪ Acetic acid / water mixture on a Sn-substituted MFI-type zeolite : effect of T



Comparison $\text{Si/Sn} = \infty$ and $\text{Si/Sn} = 25$
(highest/lowest ratios)

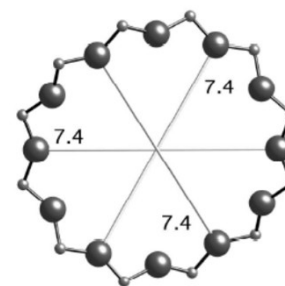
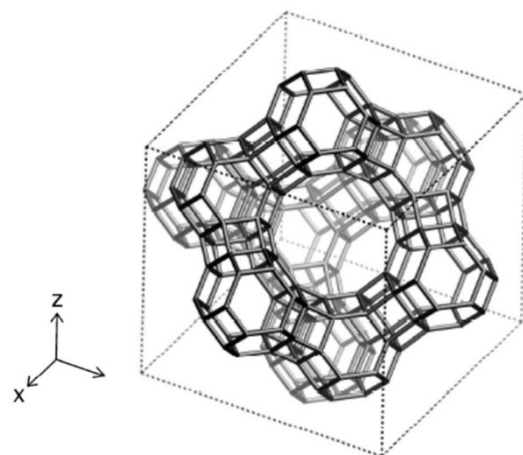
- When $T \nearrow$, Flux $\nearrow$
 $\Rightarrow$ The diffusion rates of H_2O and CH_3COOH increase with the increase in T
- When $T \nearrow$, SF $\nearrow$
 $\Rightarrow$ The diffusion rate of H_2O increases more than the one of CH_3COOH
- $\Rightarrow$ for $\text{Si/Sn} = 25$ (25/75 wt.% $\text{CH}_3\text{COOH}/\text{H}_2\text{O}$), the Sn-substituted MFI has a better performance than the silicalite ($\text{Si/Sn} = \infty$) and also than classical polymeric membranes
- $\Rightarrow$ However : $\searrow$ in performance as $[\text{CH}_3\text{COOH}] \nearrow$, which limits the applications

Adsorption / ozone decomposition coupling

✚ VOC adsorption and in-situ regeneration of zeolites by simultaneous O_3 adsorption

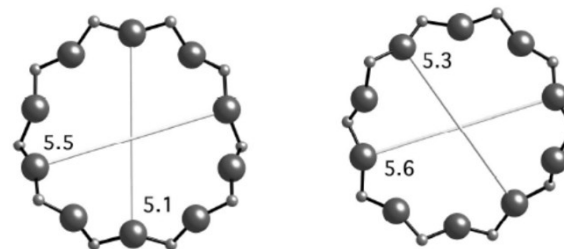
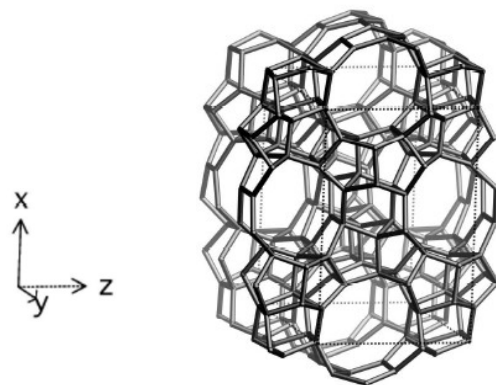
- Comparison of the adsorption properties of a **faujasite (FAU)** and a **silicalite (MFI)**
- Adsorption of **toluene (1 g.cm^{-3})** and **methyl ethyl cetone (2.15 g.cm^{-3})** present in a gaseous effluent

Faujasite
FAU



12T along [111]

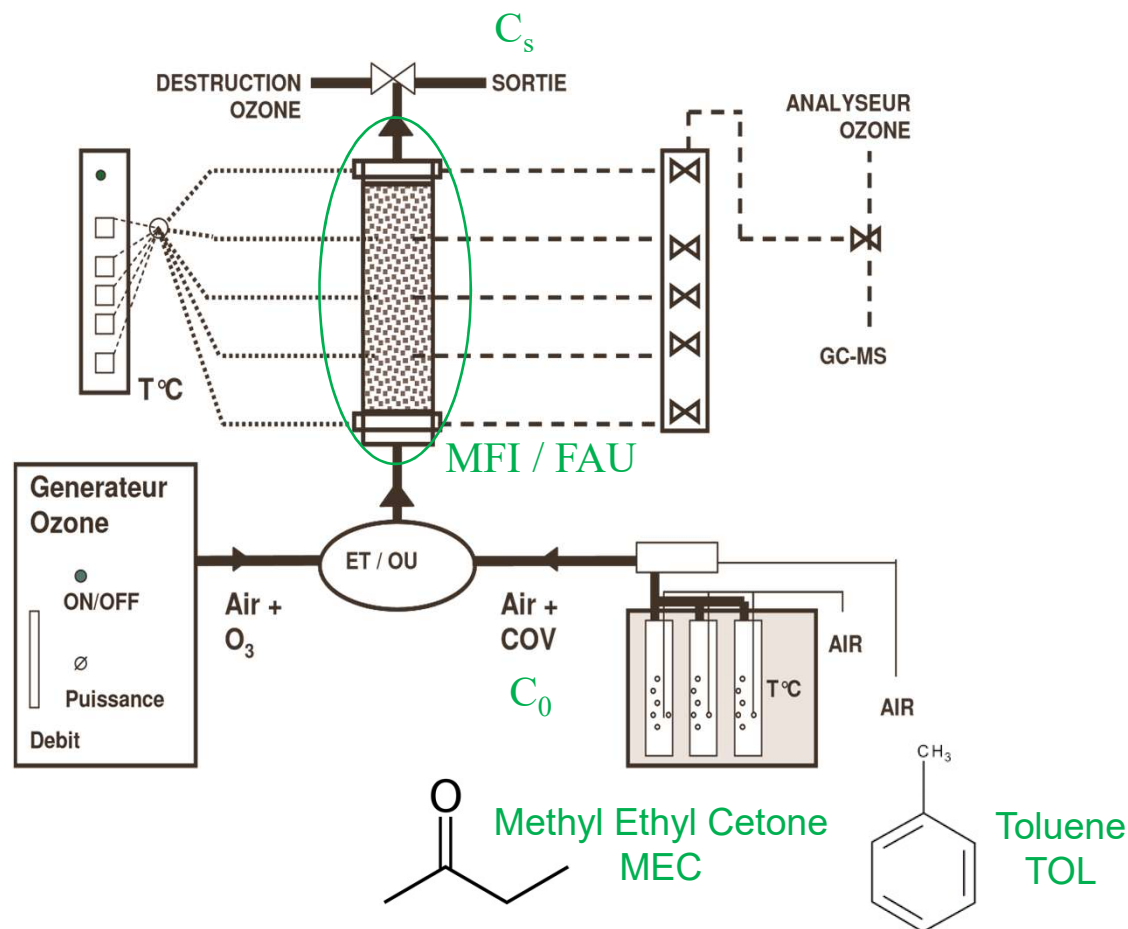
Silicalite
MFI



10T along [100] et [010]

Adsorption / ozone decomposition coupling

Experimental bench

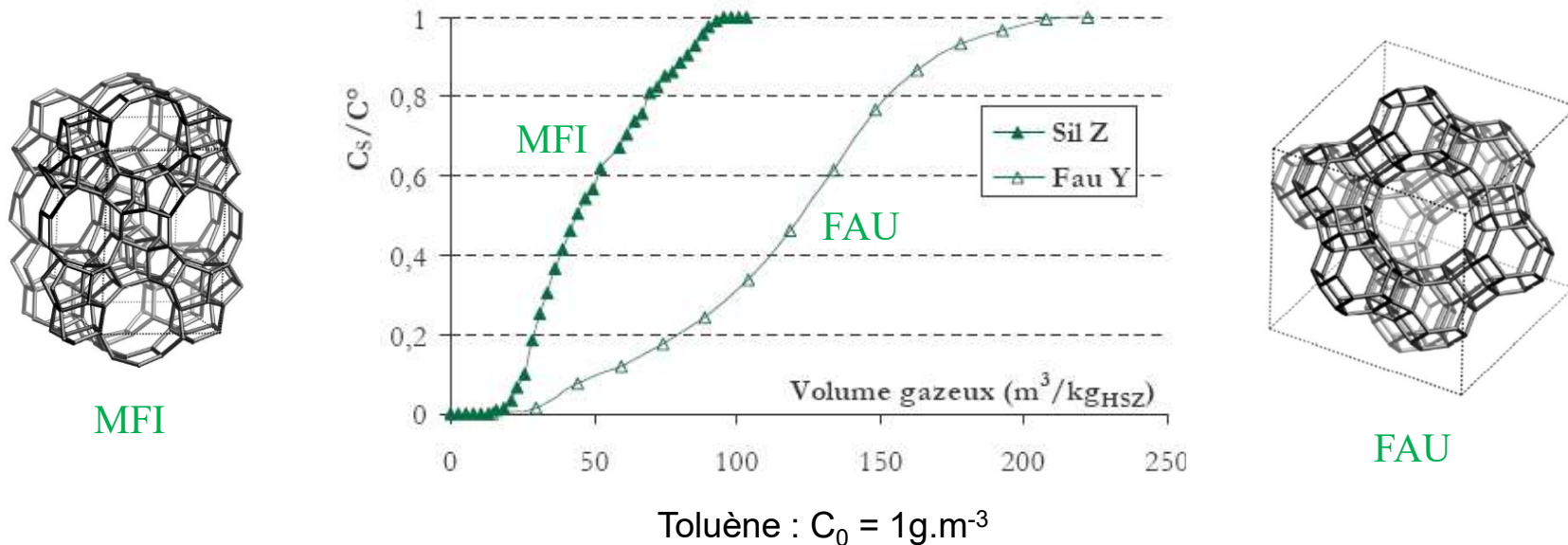


⇒ Saturation of the zeolites by the gaseous effluent

⇒ Study of the breakthrough curves : $C_s/C_0 = f(\text{Volume of gas treated per unit mass of adsorbent})$

Adsorption / ozone decomposition coupling

⇒ Breakthrough curves of toluene (“courbes de percée”)



⇒ Both zeolites present different adsorption properties

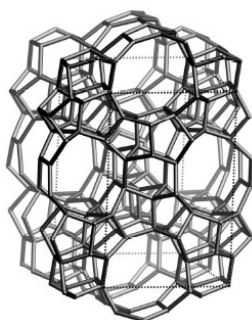
- Silicalite adsorbs toluene more rapidly (breakthrough more vertical)
- Silicalite is more quickly saturated ($V_{\text{gas at saturation}} \sim 100 \text{ m}^3.\text{kg}^{-1}$ vs $225 \text{ m}^3.\text{kg}^{-1}$)
- Qads (FAU) > Qads (MFI)

⇒ The cavity of FAU is more suitable for the adsorption of TOL than the channels of MFI

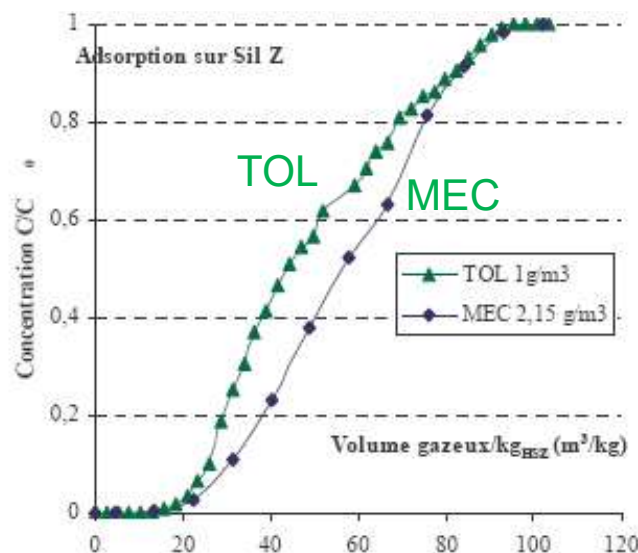
⇒ **Good match of shape**

Adsorption / ozone decomposition coupling

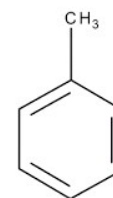
⇒ Breakthrough curves of MEC and TOL on silicalite



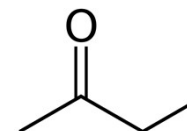
MFI



Breakthrough curves on silicalite



TOL



MEC

Silicalite adsorbs more MEC :

→ The saturation is obtained for a similar gas volume but for a more concentrated effluent (1 g.m⁻³ for TOL vs 2.15 g.m⁻³ for MEC)

⇒ The channels of MFI are more suitable for the adsorption de MEC than the cavities of FAU

⇒ **Good match of shape**

Adsorption / ozone decomposition coupling

Zeolites regeneration

- a dry air/O₃ (18 g.m⁻³) flow is passed through the saturated adsorbent
- Measurement of C_{O₃} et C_{VOC} at the outlet of the column

∀ zeolite ∀ VOC → highly exothermic reaction

→ formation of by-products : organic molecules + H₂O + CO₂

→ no trace of O₃ detected at the outlet of the column

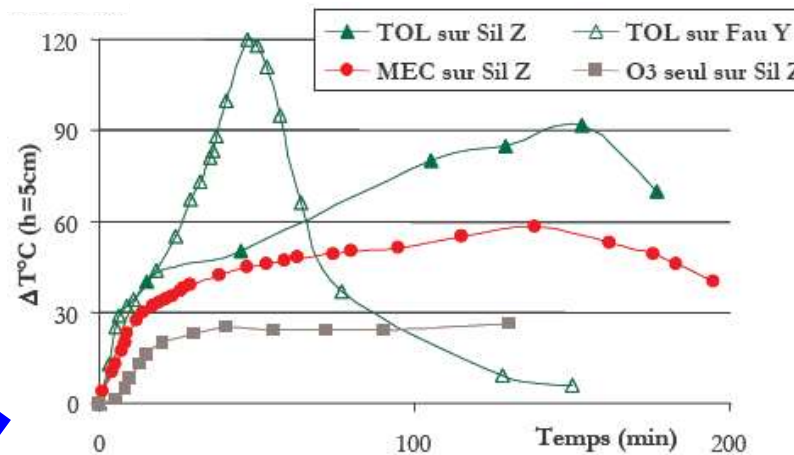
oxidation on the zeolite surfaces

Measure of the T ⤴ during the oxidation by ozone

→ the more exothermic the reaction is

→ the more T ⤴

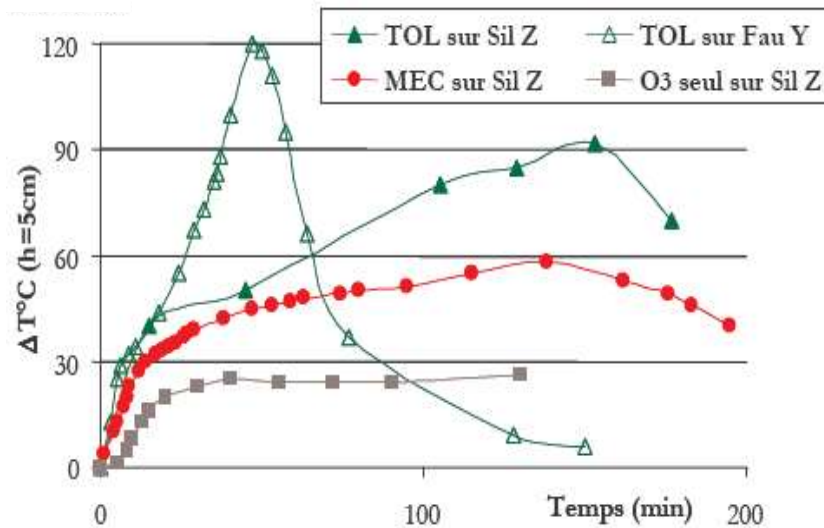
→ the more efficient the oxidation is



Concentration profiles inside the bed during ozonation of pristine and VOC-saturated zeolites

Adsorption / ozone decomposition coupling

Zeolites regeneration



Concentration profile inside the bed during ozonation of pristine and VOC-saturated zeolites

- For the oxidation of TOL on SIL (▲) and FAU (△) → different thermal effect
→ higher temperature increase for FAU

⇒ $\varnothing_{\text{pores}}$ FAU ($\sim 13 \text{ \AA}$) > $\varnothing_{\text{pores}}$ MFI ($\sim 5-6 \text{ \AA}$) : this favors the diffusion of reactants and products

⇒ V_{pores} FAU > V_{pores} MFI ⇒ FAU can adsorb a higher amount of TOL

- For the oxidation on silicalite (MFI) → lower T increase for MEC (●) than for TOL (▲)
→ incomplete oxidation and formation of stable by-products
- Detected by-products → TOL : oxalic, acetic, formic acids, formique and acetaldehyde
→ MEC : acetic acid, butan-2,3-dione

Adsorption / ozone decomposition coupling

↪ Reaction mechanisms (TOL)

1st hypothesis – classical oxido-reduction mechanism

- Adsorption of toluene onto the zeolite surface
- O_3 = strong oxidizing gas $\Rightarrow$ pollutant's degradation by oxidation

2nd hypothesis- Radical mechanism

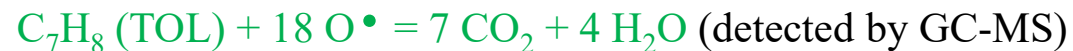
- Adsorption of O_3 onto the Lewis acid sites of the surface (s : aluminium)



- Decomposition into O_2 and atomic active oxygen : $O^\bullet$



- Decomposition of toluene by par atomic active oxygen



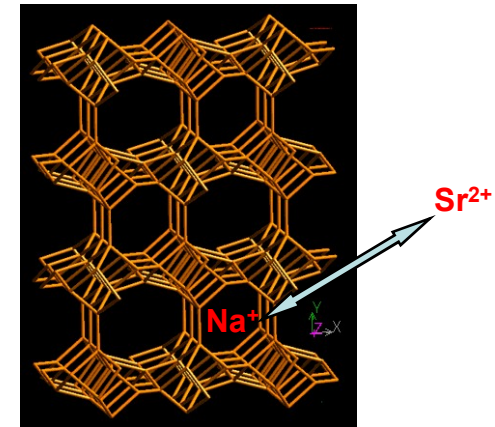
- $\Rightarrow$ Possibility of in-situ regeneration of the zeolite
- $\Rightarrow$ Zeolites can be used for continuous pollution control

Adsorption by cationic exchange

↪ Treatment of aqueous nuclear effluents

- Removal of radioactive waste from nuclear power plant effluents before discharge into the environment

- retention of ^{90}Sr , ^{137}Cs , ^{60}Co , ^{45}Ca by ionic exchange with the zeolite cations (Na^+ , K^+) $\Rightarrow$ size match
- use of clinoptilolites and mordenites (good resistance to soil acidity)
- zeolites containing « non-harmful » waste are buried



Clinoptilolite
10T et 8T
(natural, synthetic)

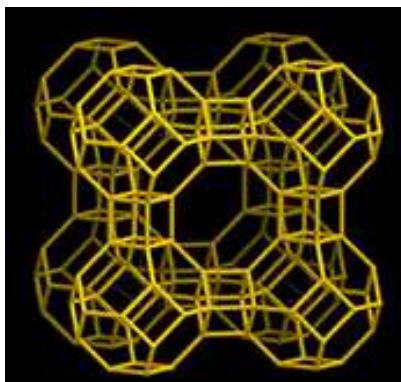
- reduction of radioactive contamination

- Three Mile Island, 1979
- cleaning up after the Tchernobyl disaster, 1986 (> 500 000 t)
- Limiting the pollution of the marine environment, Fukushima, 2011

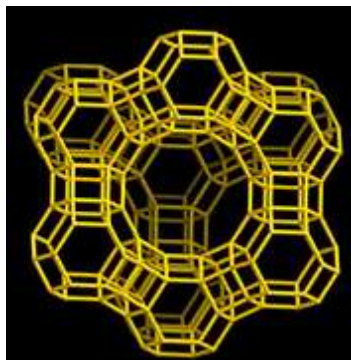


Adsorption by cationic exchange

↪ Comparative adsorption of ^{137}Cs and ^{90}Sr on different zeolites

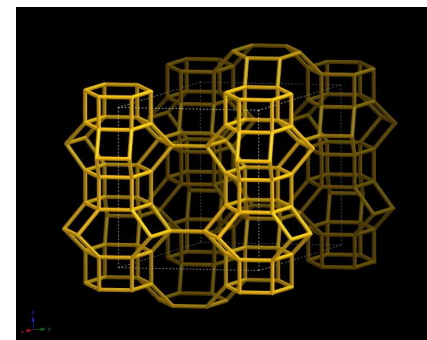


NaA (LTA)



NaX/NaY (FAU)

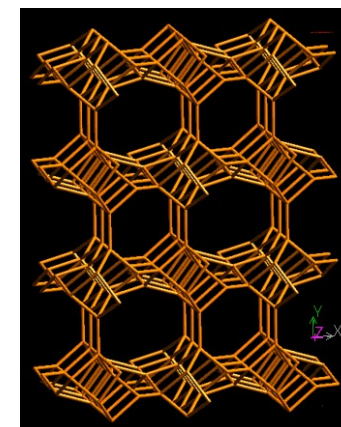
Zeolite	Si/Al	Structure	Ouverture
NaA	1	LTA	8T
NaX	1.25	FAU	12T
NaY	2.4		
Erionite	3.5	ERI	8T
Clinoptilolite	> 4	HEU	10T and 8T



ERI

} synthetic

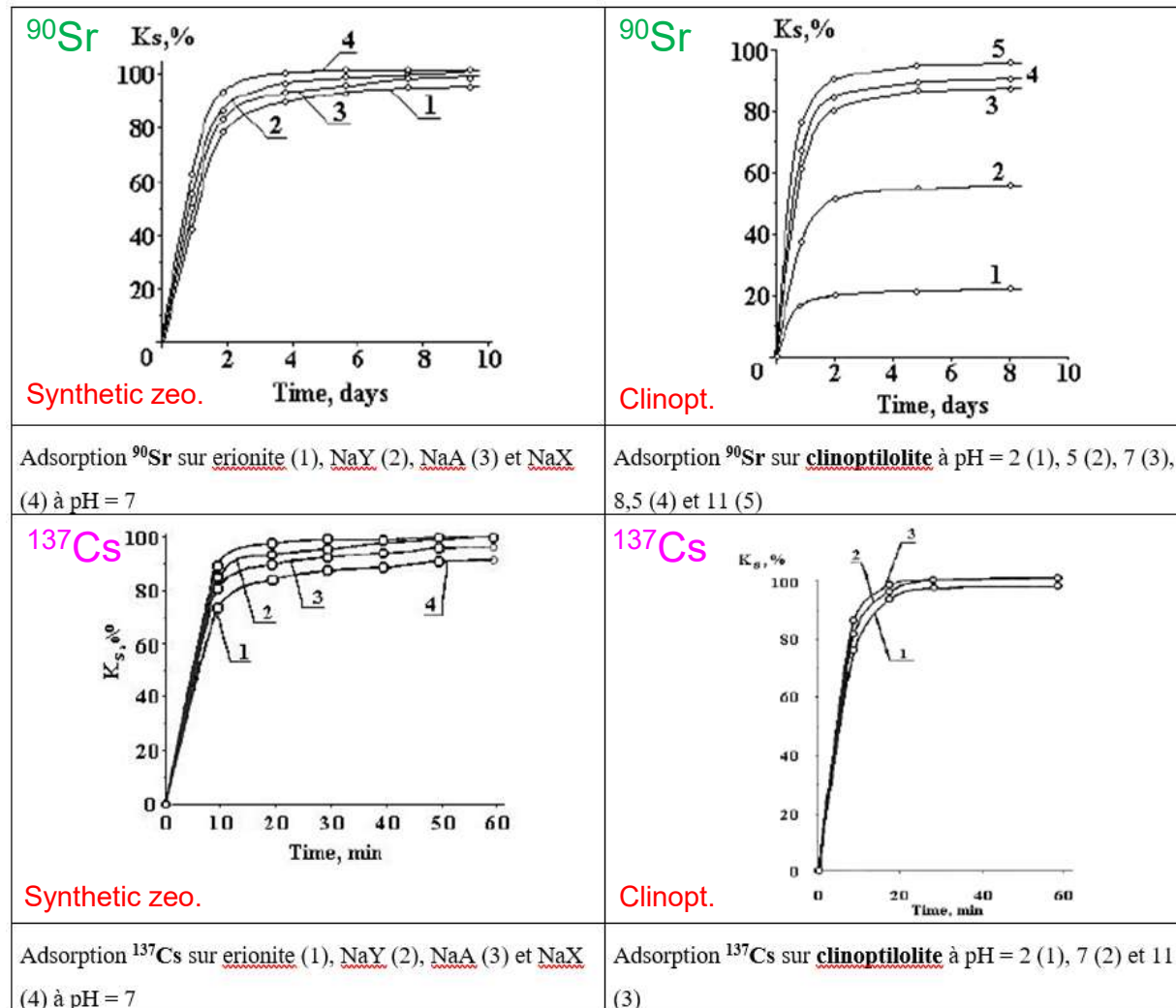
} natural



Clinoptilolite

Adsorption by cationic exchange

Adsorption kinetics

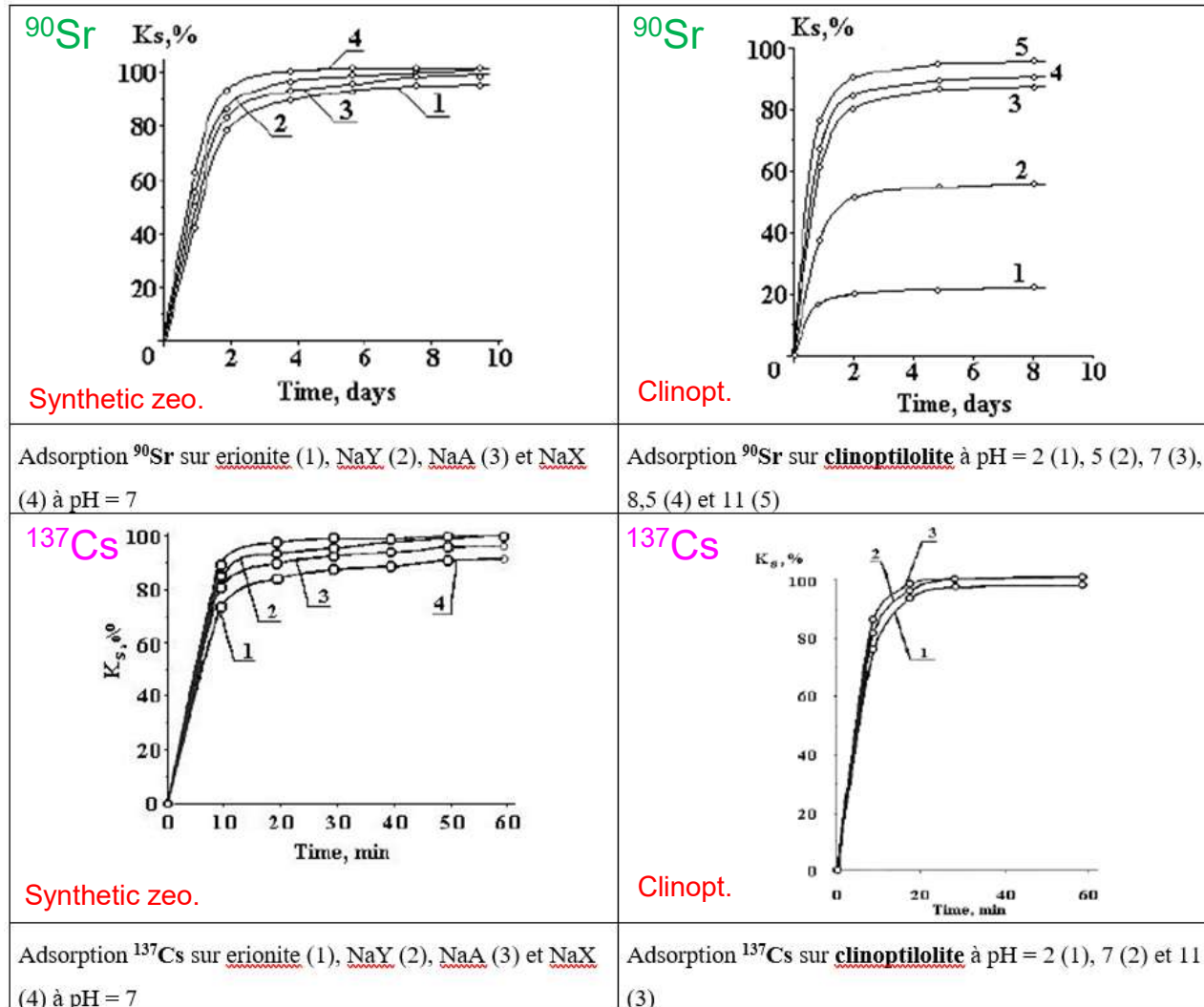


∀ zeolite, ∀ the pollutant ⇒ adsorption in 2 steps :

- 1st step, very quick → saturation of the sites by the pollutant : fast diffusion due to accessible porosity
- 2nd step, slower → steric hindrance ⇒ decrease in diffusion speed

Adsorption by cationic exchange LR1

➤ Adsorption kinetics



^{90}Sr : Adsorption equilibrium → 2 days for clinoptilolite (pH dependent)

→ 4 days for the synthetic zeolites

^{137}Cs : ≠ adsorption phenomena : adsorption equilibrium reached more quickly (< 20 min) $\forall$ zeolite

⇒ Adsorption of **^{137}Cs** favored compared to **^{90}Sr**

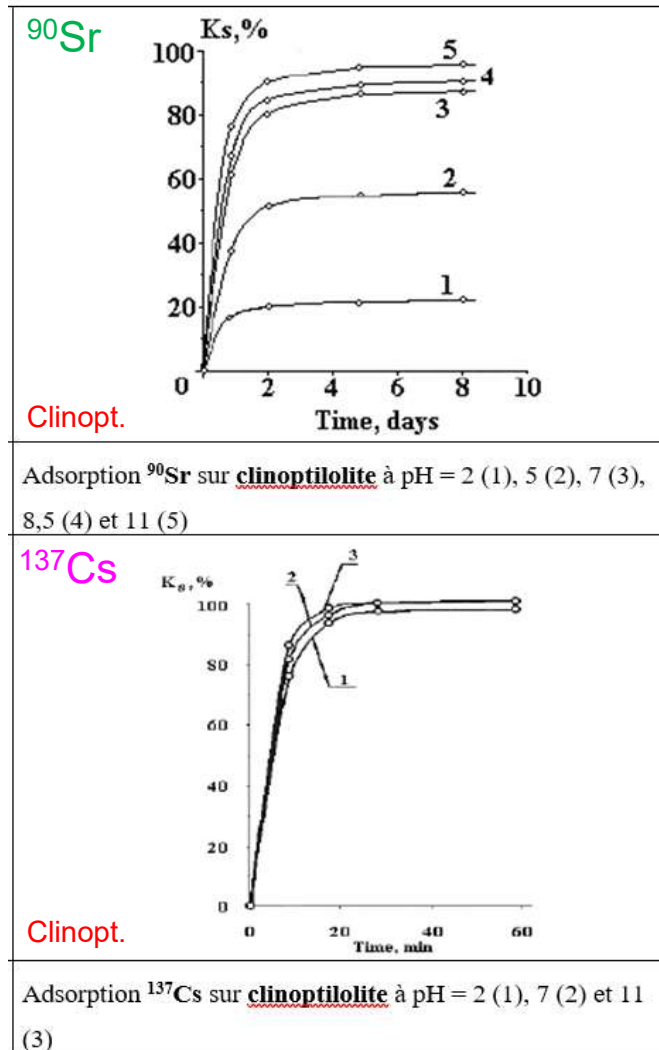
Diapositive 28

LR1

Laurence Reinert; 12/11/2024

Adsorption by cationic exchange

↳ Adsorption kinetics : effect of pH (clinoptilolite)



⁹⁰Sr → adsorption highly dependent of the pH of the initial solution

→ Maximal adsorption from pH 7

¹³⁷Cs : adsorption independent of the pH

⇒ adsorption sites different for Cs⁺ and Sr²⁺

At acidic pH : competition between H⁺ and Cs⁺/Sr²⁺

⇒ Protonation of the O⁻ groups of the framework

⇒ ↓ of the negative charge of the framework

⇒ ↓ of the adsorption capacities

Adsorption by cationic exchange

↳ Adsorption mechanisms on clinoptilolite

- $Q_{\text{ads}}^{137}\text{Cs} > Q_{\text{ads}}^{90}\text{Sr}$

Or $r\text{Sr}^{2+} \sim 127 \text{ pm}$ and $r\text{Cs}^+ \sim 167 \text{ pm} \Rightarrow r\text{Cs}^+ > r\text{Sr}^{2+}$

$\Rightarrow \text{Sr}^{2+}$ is probably adsorbed under an hydrated form $\Rightarrow$ increase in ion size

(Sr^{2+} : small and highly charged $\Rightarrow$ PP $\nearrow \Rightarrow$ is easily surrounded by a hydration sphere)

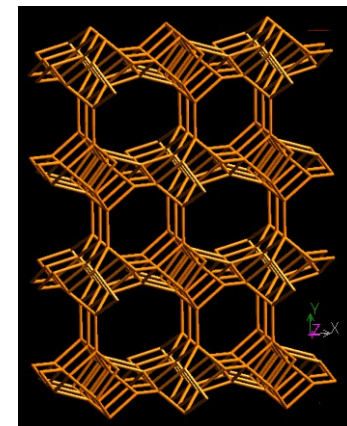
$\Rightarrow \text{Cs}^+$ fits the 8T clinoptilolite cycle with the right size

- Clinoptilolite possesses a high Si/Al ratio

$\Rightarrow$ low charge compensation required

$\Rightarrow$ specific zeolite for low-charge cations

$\Rightarrow$ Clinoptilolite is selective for low hydrated mono/divalents cations



Clinoptilolite