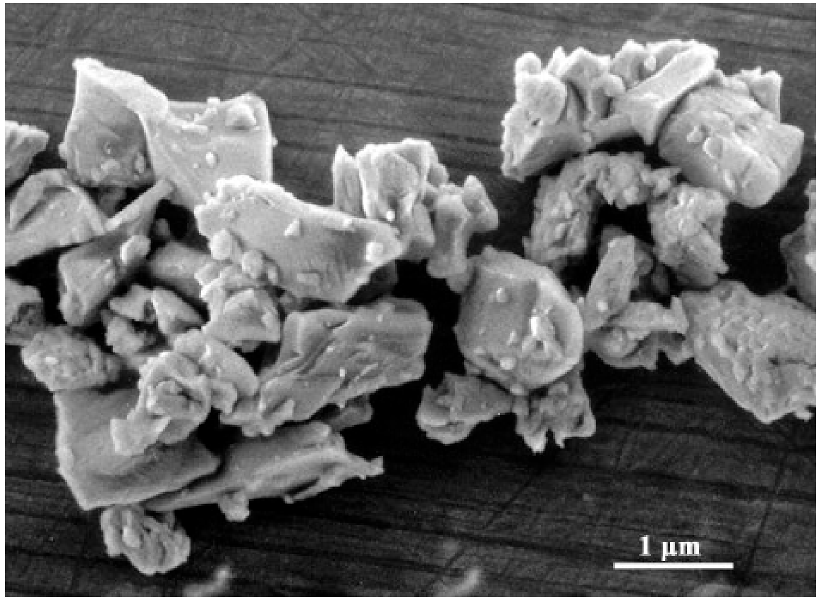
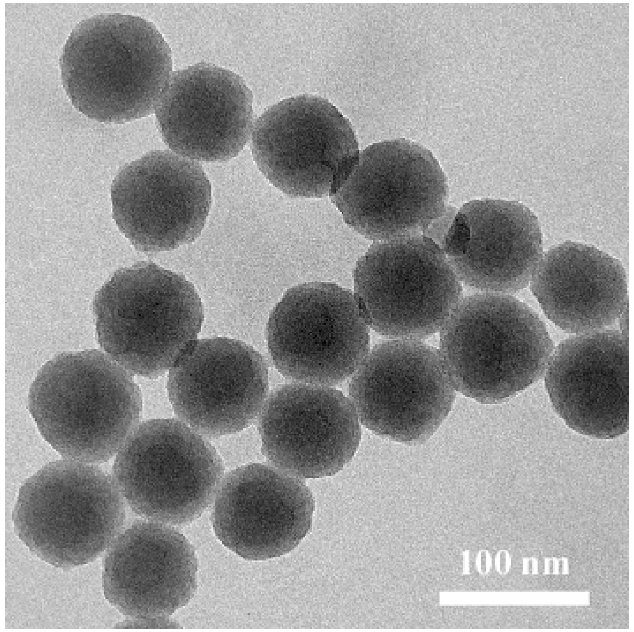
# Lesson 4

Dr. Andrea Testino

## 3.3 Raw materials and powder synthesis (p.81- 127*)




*Les Traité des Matériaux, Volume 16 « Les Céramiques »

# Summary

## 2.3 Matières premières et synthèse de poudres



La semaine passé

$$MgCO_3 \rightarrow MgO + CO_2$$

$K_{0.5}Na_{0.5}NbO_3$

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g)$$

cette semaine

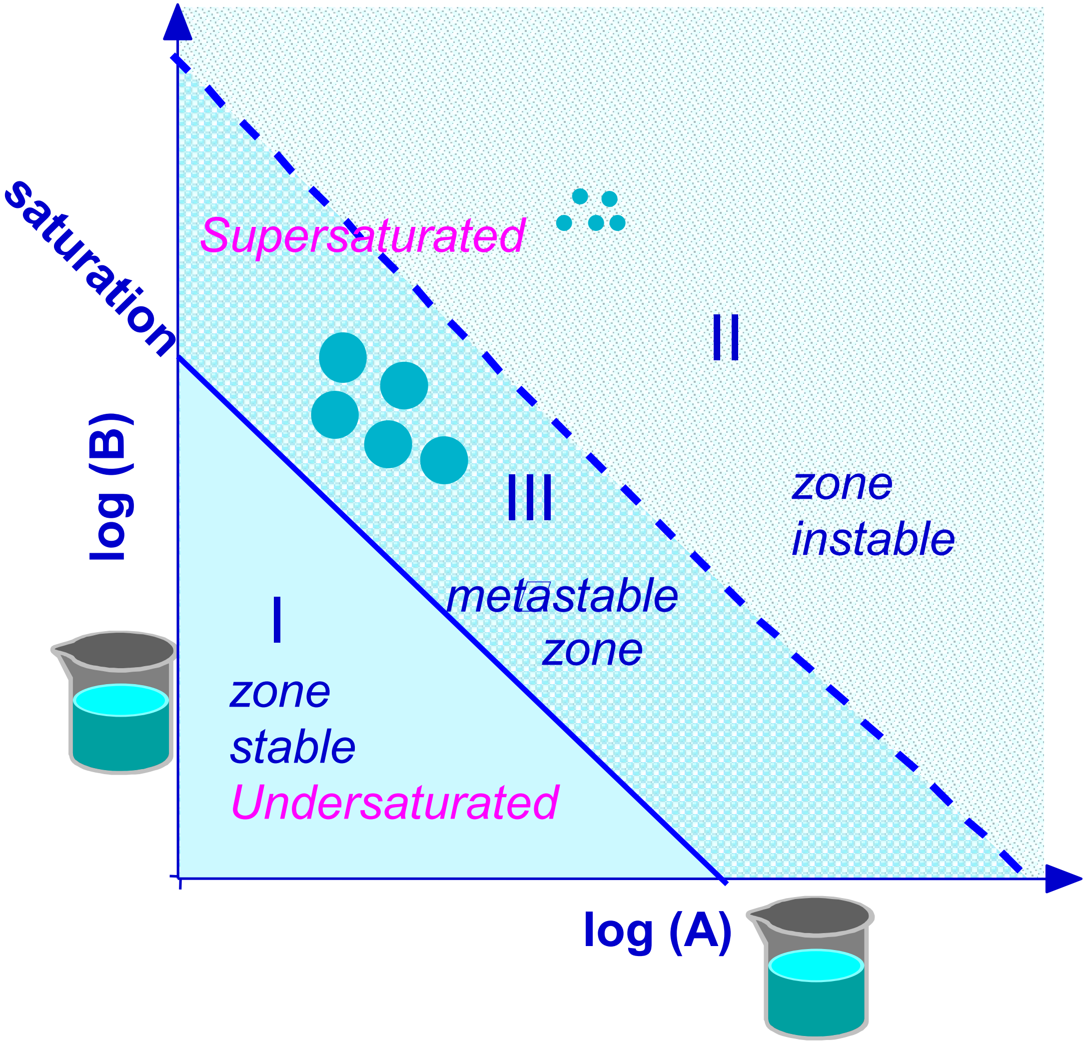
Thermodynamiques des solutions & exercises 2 Next week

# Evolution of a precipitation reaction

$A + B \leftrightarrows AB$

$K_s = (A)_s \times (B)_s$

$\frac{(A)\times(B)}{K_s}$ < 1 ⇨ under-saturation
= 1 ⇨ saturation
> 1 ⇨ super-saturation




**I** The material is dissolved in solution (one phase)

**II** Nucleation = formation of "solid entities" (embryo)

**III** Crystal growth and eventually agglomeration

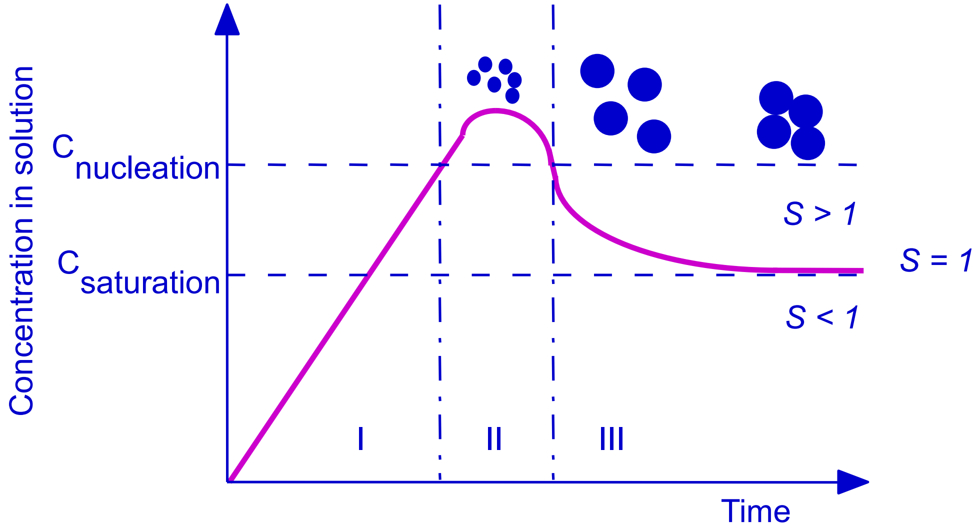
# Evolution of a precipitation process

$$S_R = \frac{C_l}{C_s}$$

= saturation ratio (other possible definition, pay attention on how it is defined!)

$C_l$ – conc. (activity) of the solute

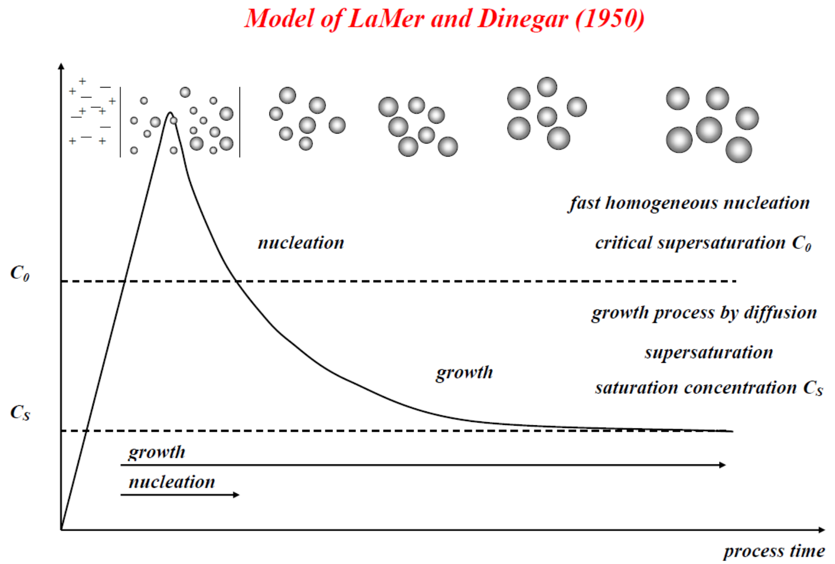
$C_s$ – conc. (activity) at the equilibrium (solubility product)




Zone I: The activity is to low to induce nucleation

Zone II: Nucleation = Formation of nuclei

Zone III: Crystal growth and eventually aggregation



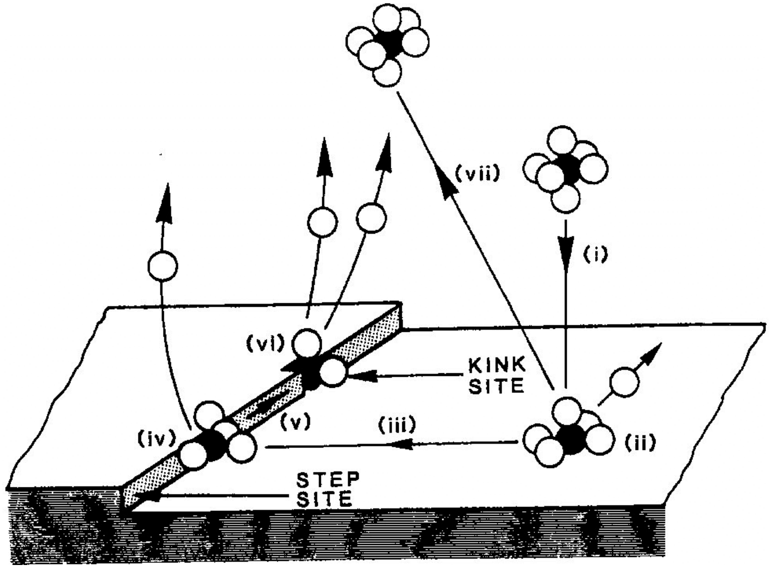

This partition of the precipitation in 3 zones (introduced in the '50) is a highly simplified view of a very complicated process, where the elementary sub-processes nucleation, growth, and aggregation can be convoluted. Such specific convolution defines the real **precipitation pathway** which is the object of an intense and controversial scientific research

PAUL SCHERRER INSTITUT PSI

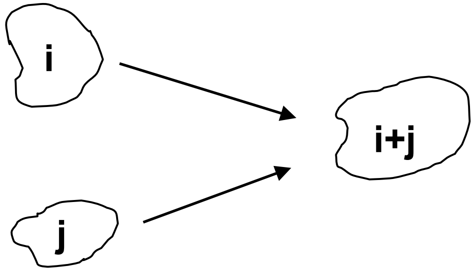
# Elementary processes: definitions

**Nucleation**
- **Primary**
  - **Homogeneous (no influence of any surfaces)**
  - **Heterogeneous (catalysed by a foreign surface)**
- **Secondary**
  - **True (initiated by the same phase)**
  - **Apparent (fragments)**
  - **Contact (reactor wall, stirrer, pump,…)**

**Growth: molecular growth. Incorporation of new building units of molecular size into the crystal surface.**



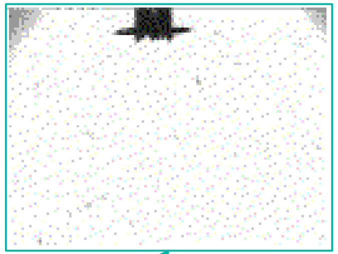

**Aggregation: interaction between 2 particles to form a bigger one**



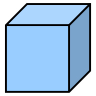

$$f_{i,j} = k(r_i, r_j) n_i n_j$$

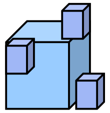
# Nucleation

2

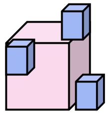


- Secondary nucleation: True, Apparent, Contact
- True (believed to be a rare event; recent research seems stating the opposite…)
  - Nucleation on the surface of a crystal (e.g. dendritic growth);
  - Close to a surface of a growing crystal - movement or structure of perturbed liquid – e.g. by an additive that limits the growth of a surface
  - Formation of germs in the boundary layer (higher concentration) which is detached



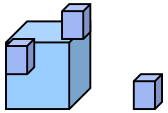


Sec. true

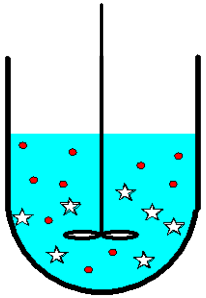


Hetero.

- Apparent
  - The **apparent** secondary nucleation refers to small fragments which are detached from the surface of pre-existing solid matter, generating additional small particles.

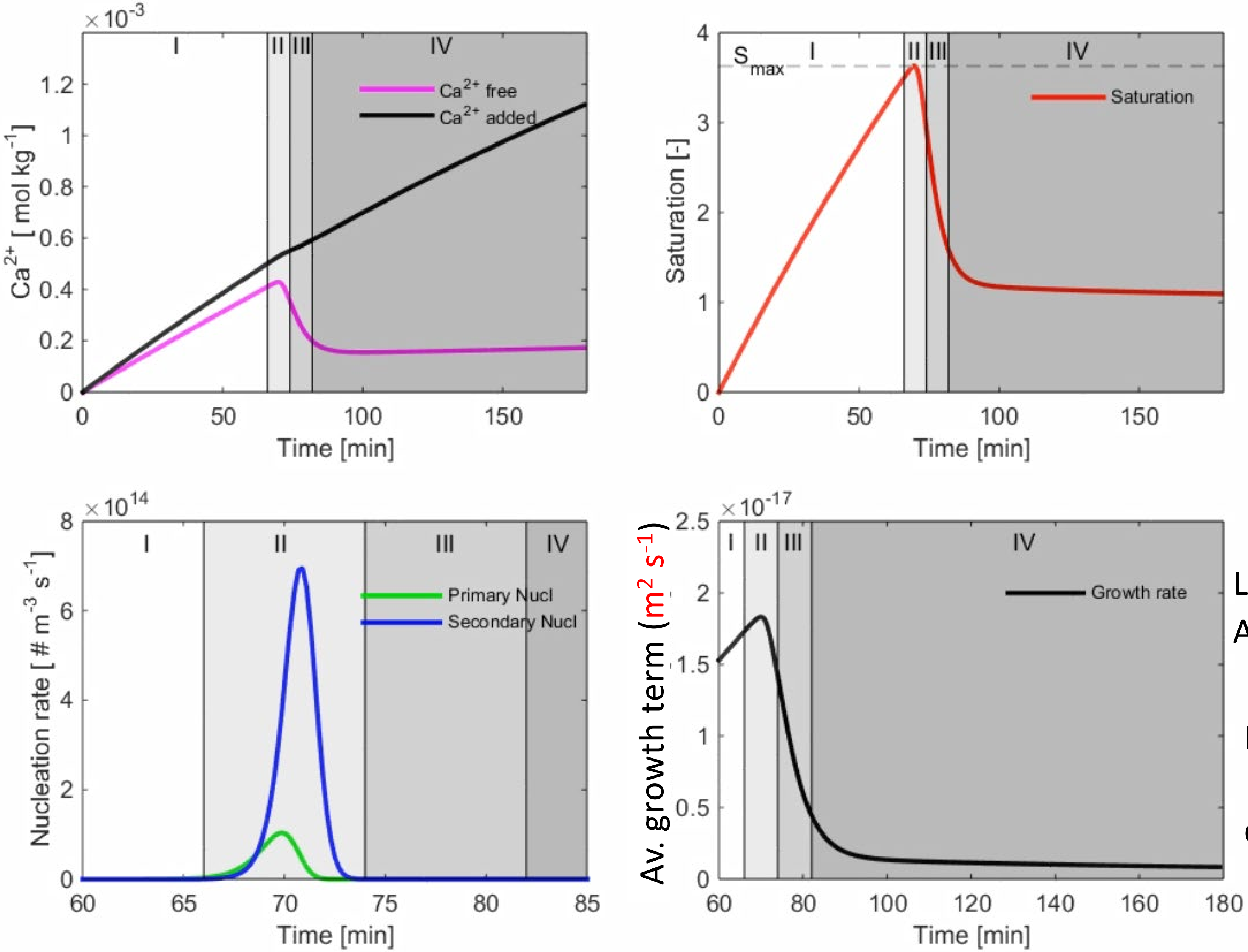


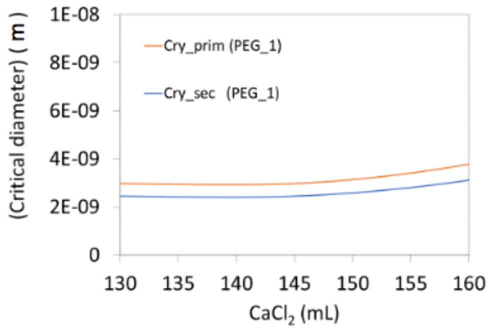
- Contact
  - Secondary **contact** nucleation refers to small fragment detached from the reactor wall or mixer or any other foreign surfaces in contact with the liquid into the reactor volume.

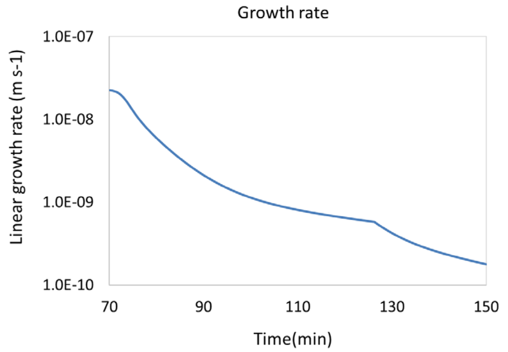


# Example of precipitation modelling ($CaCO_3$)






Linear growth rate (m $s^{-1}$)=
Av. growth term ($m^2$ $s^{-1}$) / size (m)

For particle 2 nm
= 2 $10^{-9}$ m
Growth rate ≈ 10 nm/s

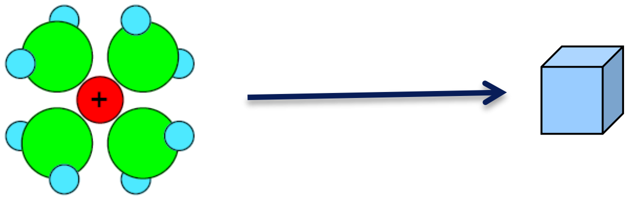
# Nucleation

- The Gibbs free energy – Chemical potentials – 5. Thermodynamics
  - Energy needed to generate new solid volume and the associated new surface is a function of the saturation ratio ($S_R$) and the surface tension ($\gamma$) (Nielsen, 1964).

$$\Delta G = \underbrace{-\left(\frac{V}{V_m}\right) \cdot k_B T \cdot \ln(S_R)}_{\text{volume}} + \underbrace{\gamma \cdot A}_{\text{surface}}$$

Where

- V: volume of the embryo;
- $V_m$: molecular volume of the solute (or building unit or growth unit)
- $k_B$: Boltzmann constant ($1.38064852 \times 10^{-23}$ $m^2$ kg $s^{-2}$ $K^{-1}$)
- T: temperature in K
- $\gamma$ : surface energy of the solid-liquid interface per surface unit (J $m^{-2}$)
- A: surface



Cation solvaté

Exercise: dimensional check of all equations

# Nucleation – Critical size

(Nielsen, 1964)

- Volume and Surface contribution to the Gibbs free energy as a function of size (R) and geometrical factors ($\beta_V$ and $\beta_A$)

$$\Delta G(R) = -\left(\frac{\beta_V R^3}{V_m}\right)\cdot k_B T \cdot \ln(S) + \gamma \cdot \beta_A R^2$$

$$V = \beta_V R^3$$

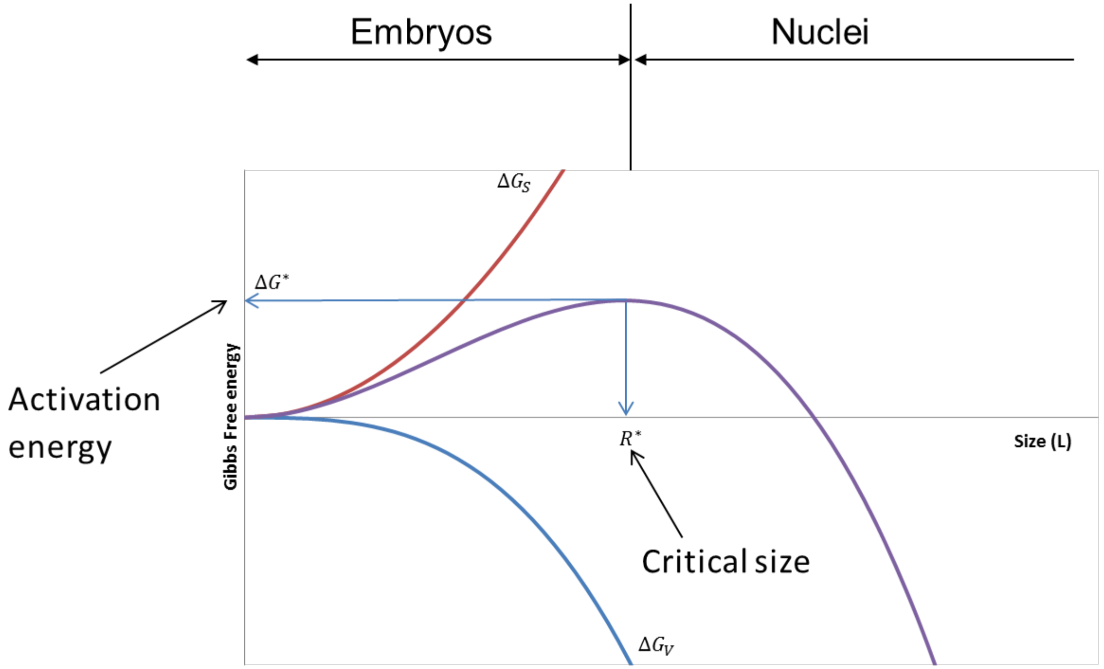
$$A = \beta_A R^2$$

$$R^* = \frac{2\cdot \beta_A \cdot \gamma \cdot V_m}{3\cdot \beta_V \cdot k_B T \cdot \ln(S)}$$

For spheres

$$\beta_V = \frac{4}{3}\pi$$

$$\beta_A = 4\pi$$




Exercise: how $\Delta G^*$ and R* can be deducted?

- Above the critical size, to a larger size corresponds a lower Gibbs free energy.
- Below the critical size…

… exercise. What does it mean?

# Nucleation – type and rate – as function of S

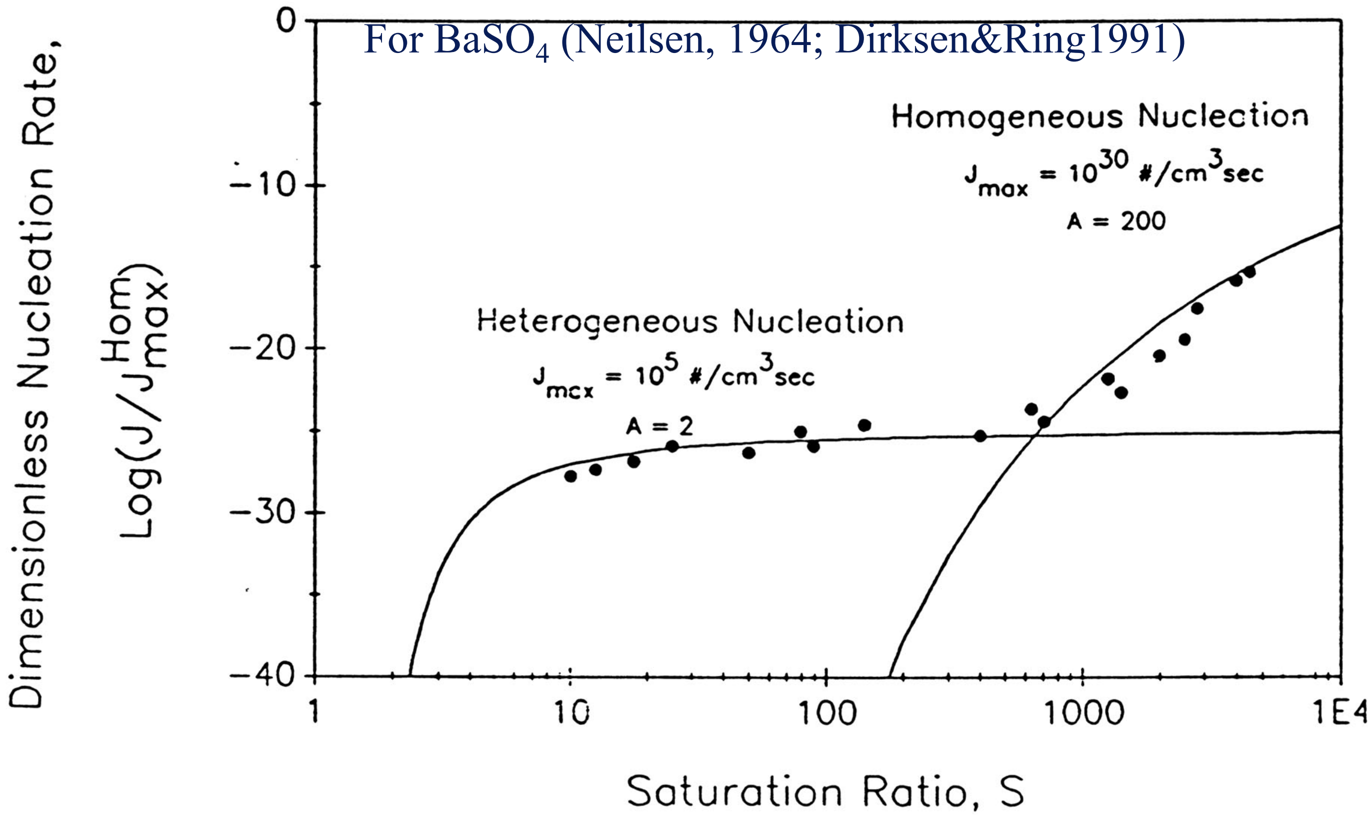
- Nucleation rate, J [ # $V^{-1}$ $s^{-1}$]. It is assumed that embryo grows by incorporation of growth units, one by one up to a critical size. $X_{(molec)} + X_{(r^*-molec)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X_{(r^*)}$

(Nielsen, 1964)

- $J_{homo}$, homogeneous nucleation rate: $\log\left(\frac{J_{homo}}{J_{homo}^{max}}\right) = \log(J) = -A\left[\log(S)\right]^{-2}$

where pre-exponential factor A or maximum nucleation rate, $J_{homo}^{max}$, can be estimated from the Einstein equation for diffusion (Eq. E1)

- $J_{hetero}$ , heterogeneous nucleation: lower activation energy because of the lower γ → higher rate

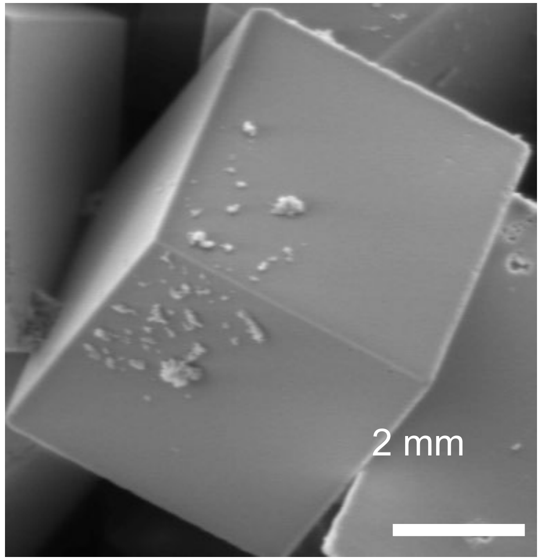



$$A = \frac{4}{27}\frac{\gamma^3\beta_A^3V^2}{\beta_V^2k_B^3T^3\ln(10)^3}$$

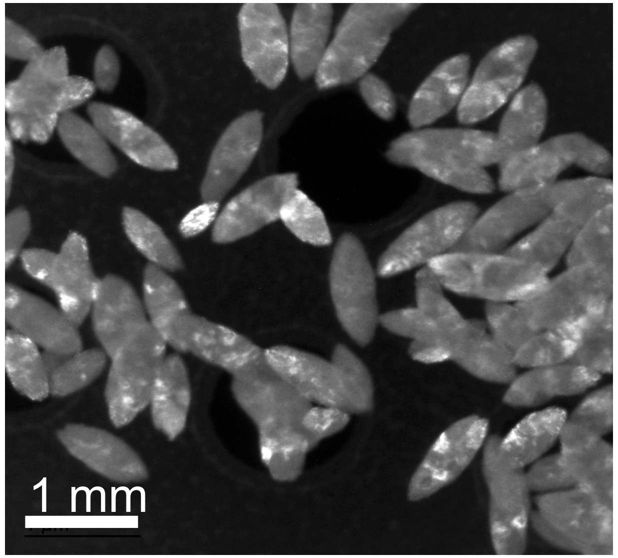
$$J_{homo}^{max} = \frac{2D}{d^5}$$ Eq. E1

D: diffusion coefficient;
d: root-mean-squared displacement, estimated as the molecular diameter

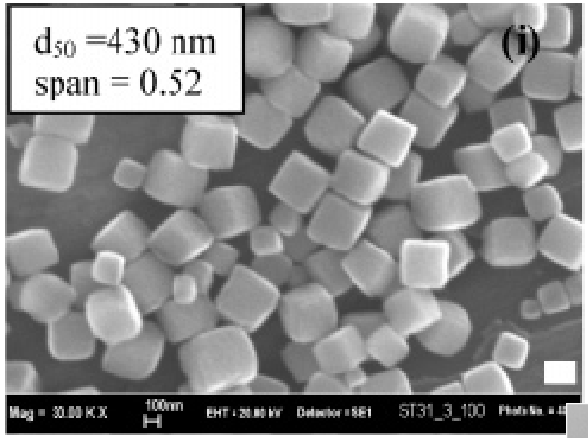
# Examples Monocrystal - Polycrystal

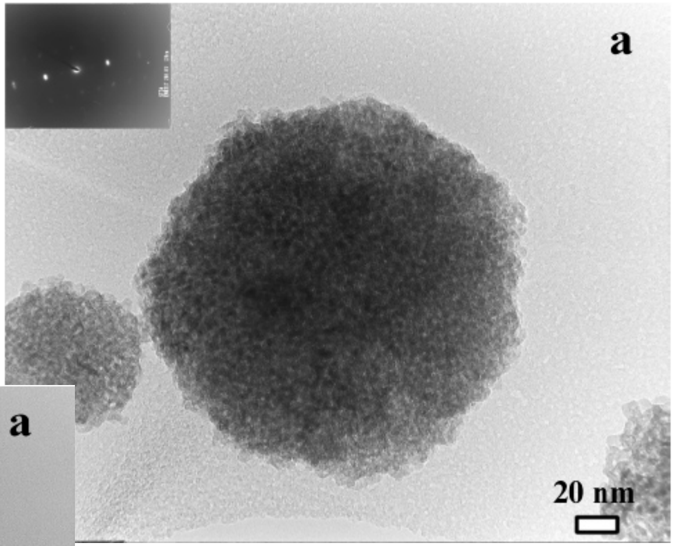


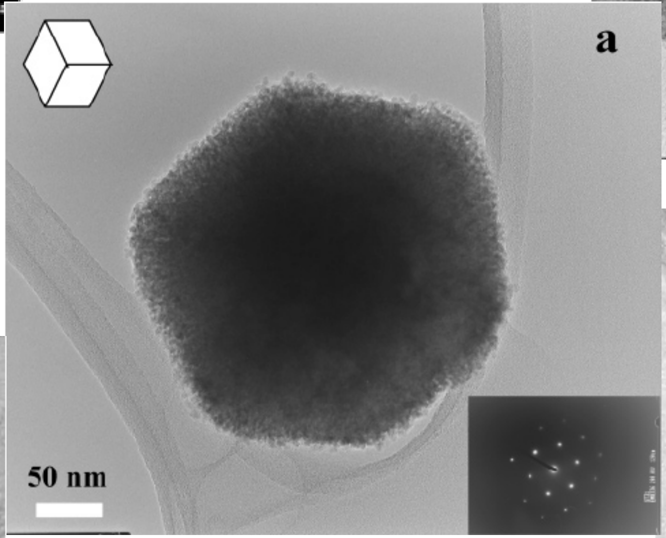

- Calcite Monocrystal
- Calcite - Polycrystal

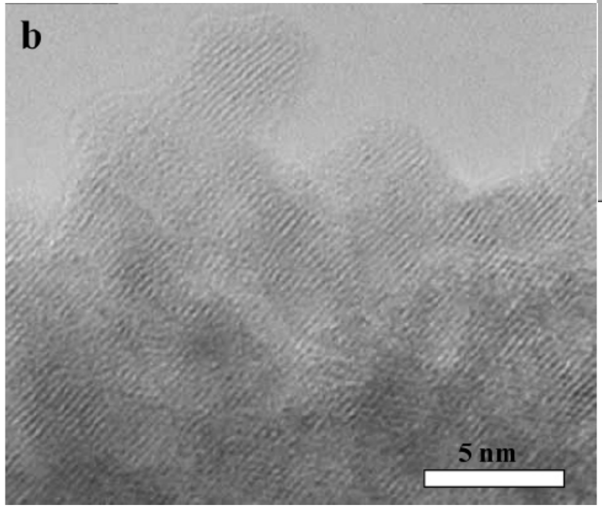



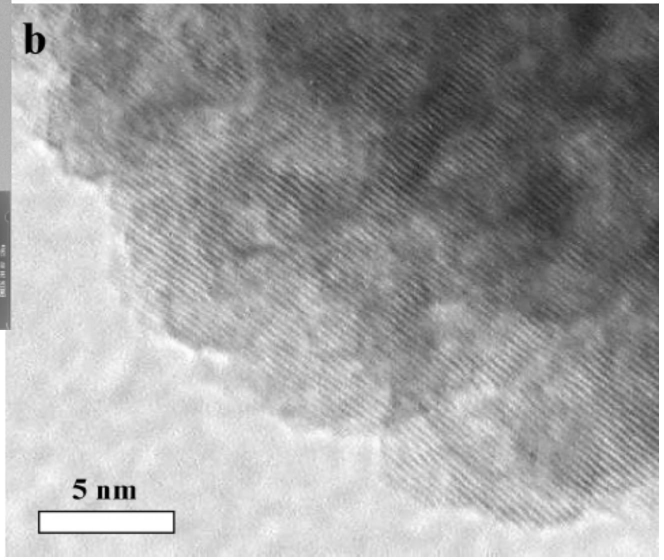
# Examples Monocrystal – Polycrystal



# Crystal growth

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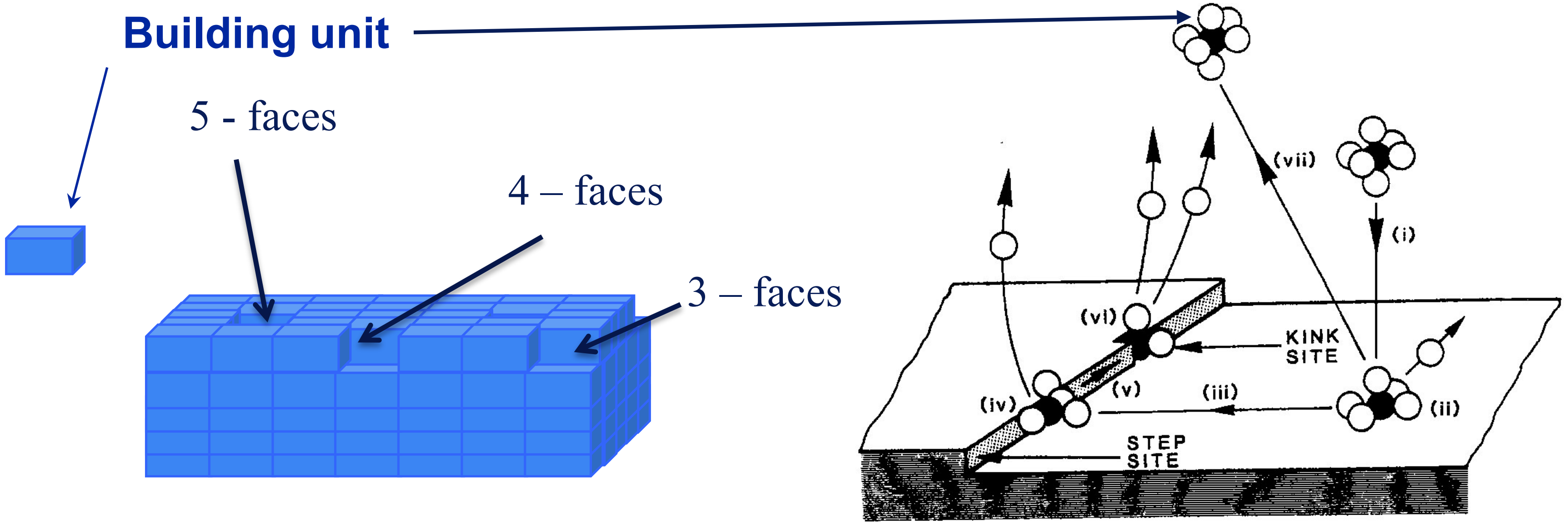
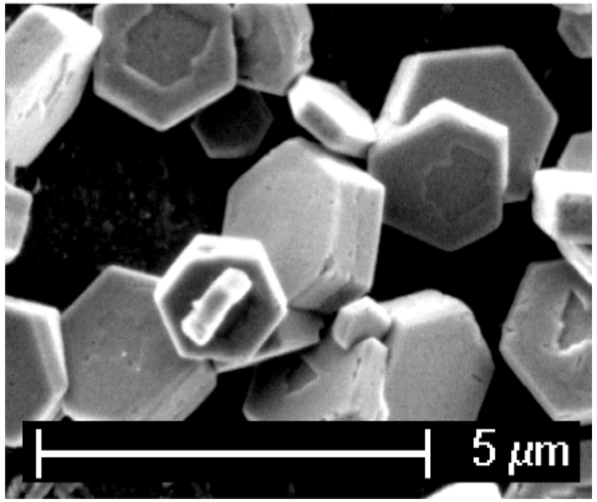



Terrace – Ledge - Kink (TLK) Model

- The crystal habit (shape) is dominated by the surface energy, which may be different for different surfaces. The lower the surface energy of a specific face, the faster the growth of that face. Always the same principle at work: energy minimization (Wulff's theorem). Thus, every substance (additive) that changes the surface energy, may induce a different crystal habit (e.g. from spheres to platelets or needles).



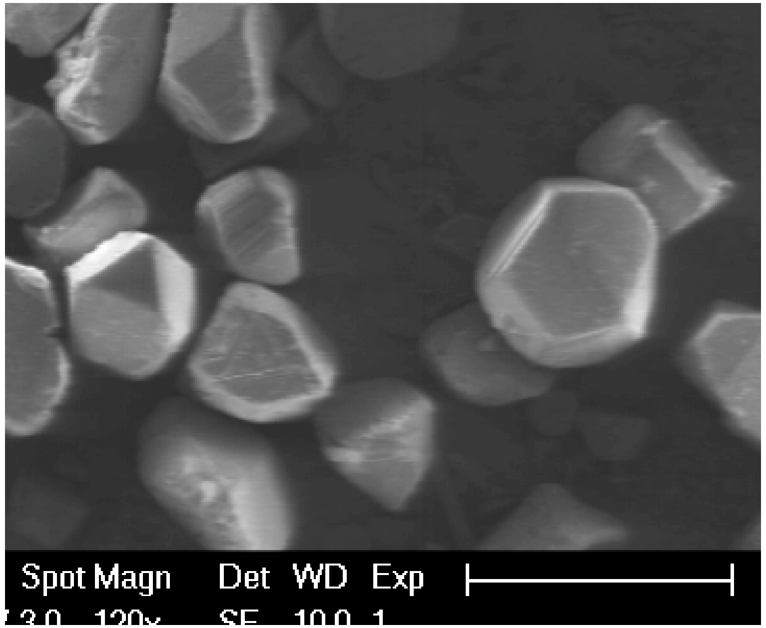

$Ca(OH)_2$ - platelets

in the presence of sulfate ions ($SO_4^{2-}$)

# Simulation – Molecular dynamic - S. Galmarini*

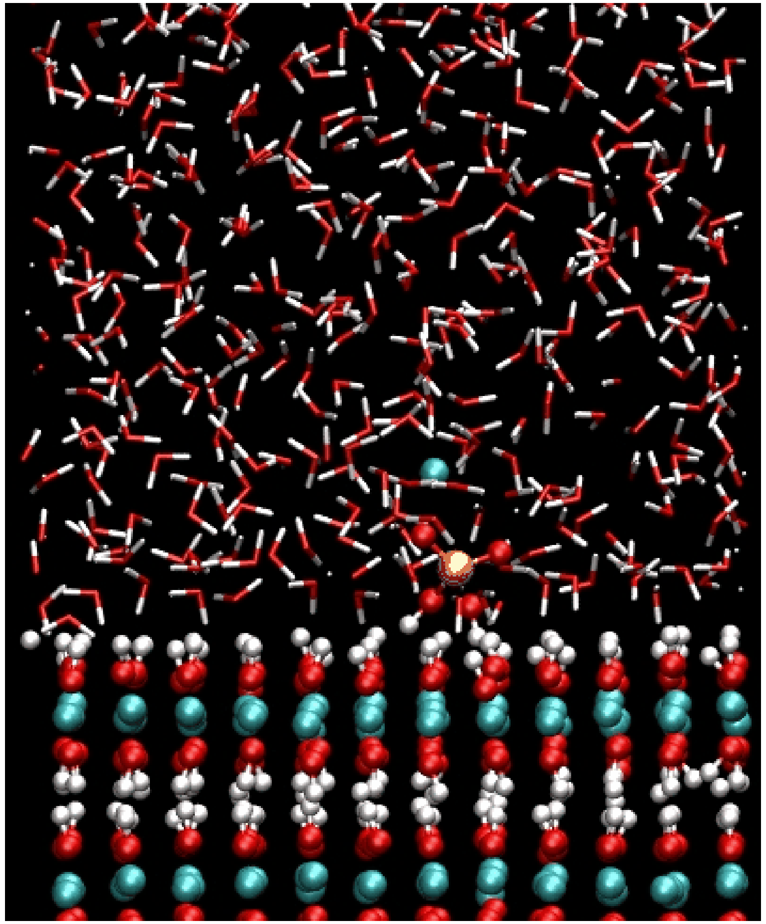
- $Ca(OH)_2$ growth (Portlandite)
- 25% in Portland cement
- 70% calcium silicate hydrate
- Effect of ions and other species on growth
- $CaSiO_2(OH)_2$ can act as inhibitor

  see 5. Thermodynamic….




$Ca(OH)_2$ – in pure water - 10 μm

Silicate complex – $Ca^{2+}SiO_2(OH)_2^{2-}$



Surface adsorption – relevant for solid formation and for colloidal stability

*Thèse EPFL, n° 5754 (2013)

# Evolution de la morphologie

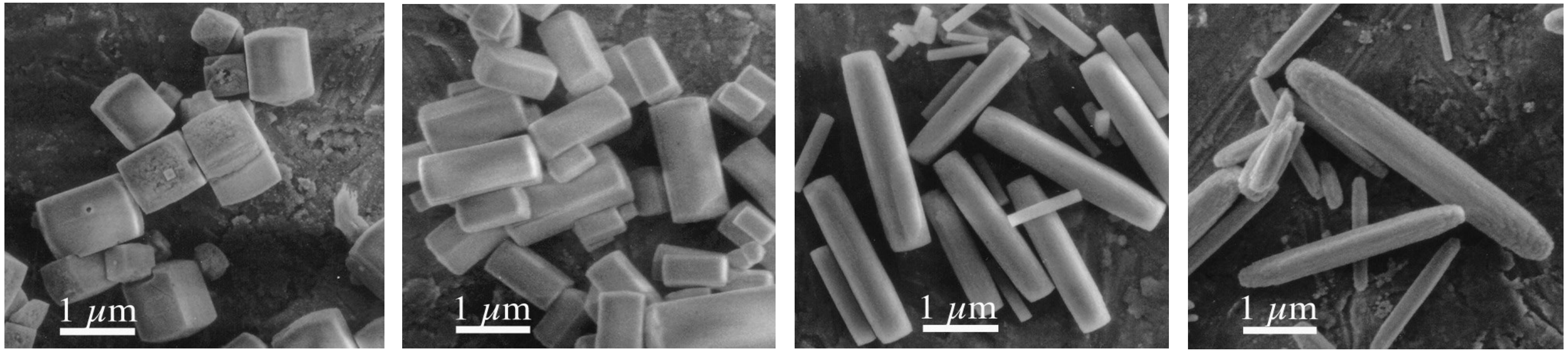


- Specific adsorption on one face → the relative growth rate of faces is modified → different crystal habit

$$Cu(NO_3)_2 + Na_2C_2O_4 + H_2O \Rightarrow CuC_2O_4.xH_2O + 2Na^+ + 2NO_3^-$$

Concentration HPMC increase* (HPMC = Hydroxy Propyl Methyl Cellulose)

*0.005 g/L* *0.020 g/L* *0.156 g/l* *0.625 g/l*




*h/b* = *1.2* *2.5* *5.0* *7.5*

*Jongen, N. Bowen,P. Lemaître,J. Valmallette and Hofmann,H. "Precipitation of self-organised copper oxalate polycrystalline particles in the presence of Hydoxypropylmethylcellulose (HPMC) : control of morphology" J. Coll. Interf. Sci. **226** 189-198 (2000).

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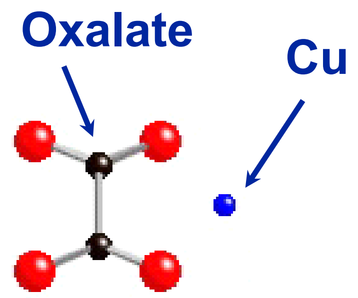
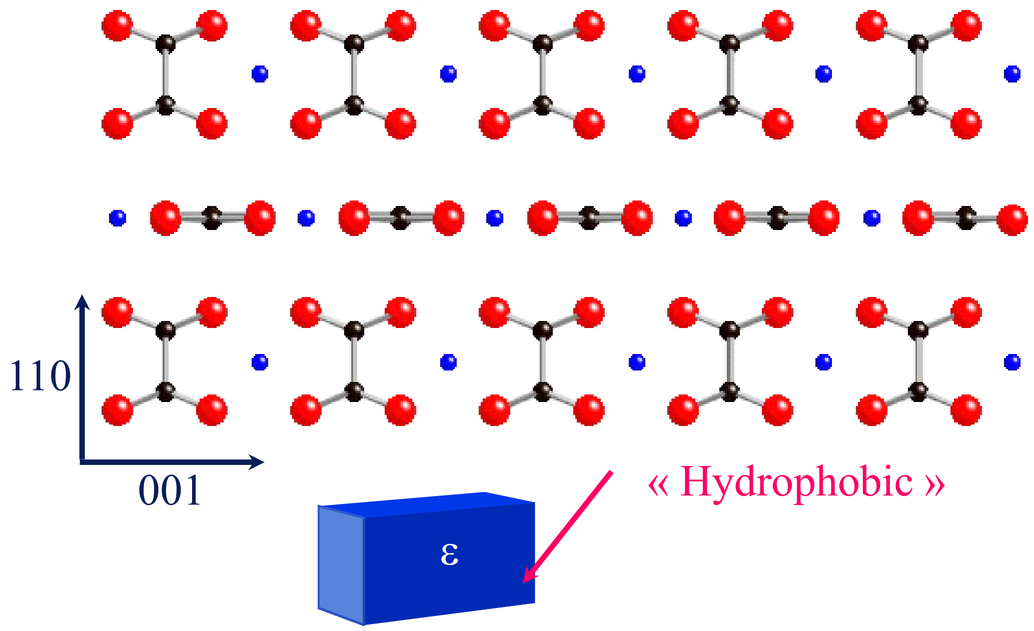
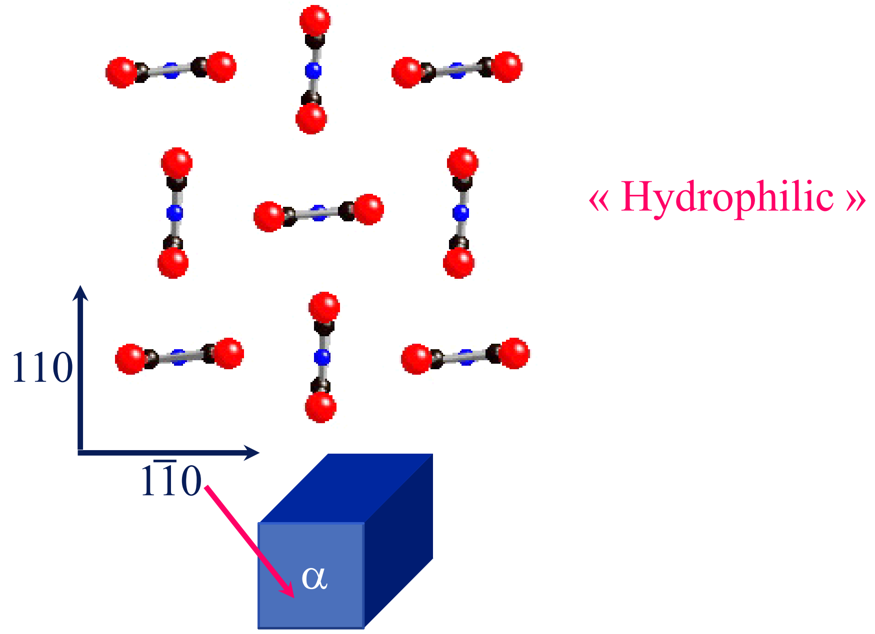
# Copper oxalate structure




- Stacking of...**Cu-Ox-Cu-Ox**... ribbons
- Each **Cu** bound to 4 **O** in same ribbon + 2 **O** in lower and upper ribbons

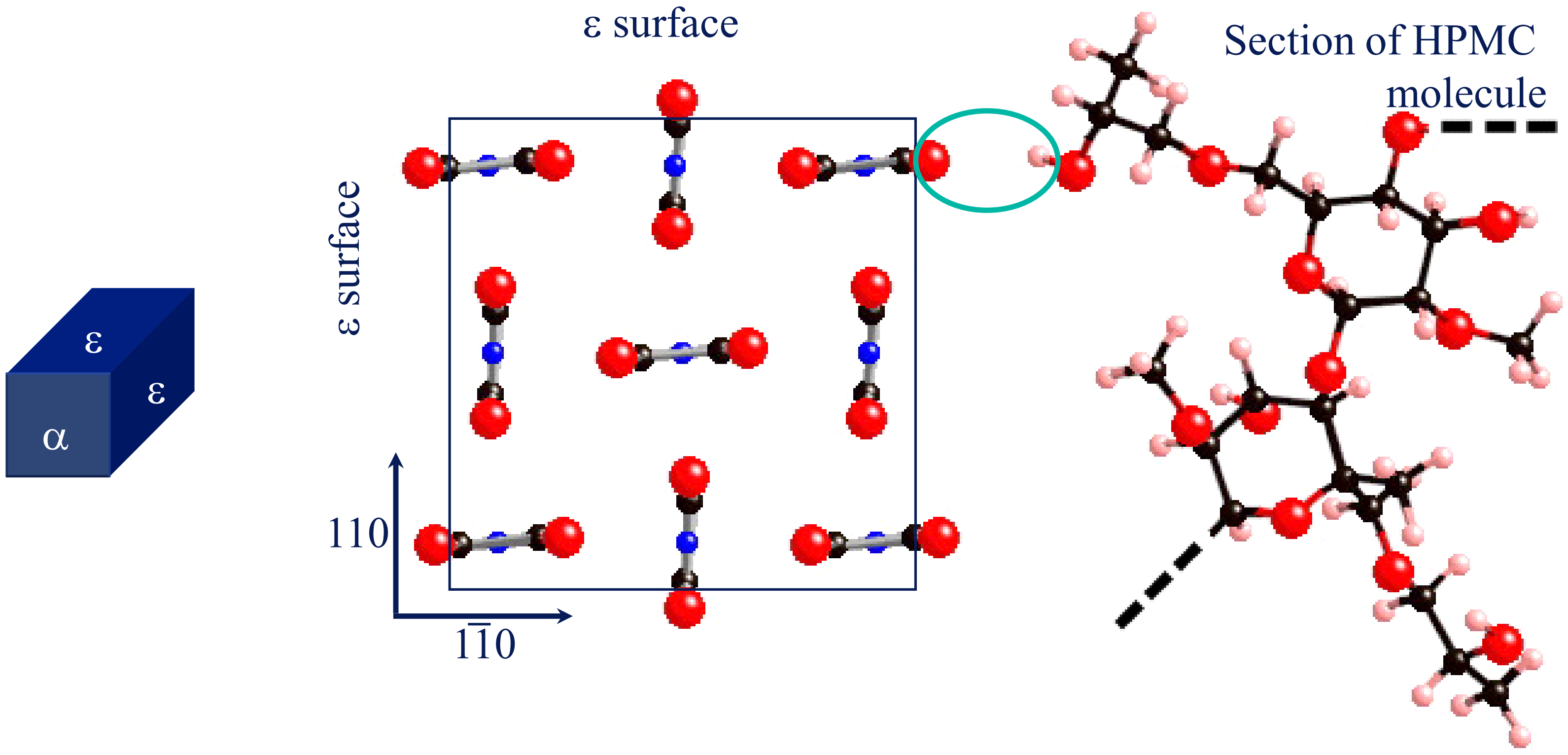



Structure built after H. Schmittler, *Monats. Deutsch. Akad. Wissenschaften Berlin* **10**(8), 581 (1968)

# Interaction between HPMC and crystallites

- Hydrogen bond possibly formed between $-CH_2-CHOH-CH_3$ (HPMC) and $-Cu-O_2C-CO_2-$



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# Different possible growth mechanisms

- Dirksen and Ring (1991) – many possible growth mechanisms
- Use of population balance modelling methods – identify most probable

$$\frac{dR}{dt} = Cf(S)g(R)$$

Table 4. The effect of supersaturation and particle size on the crystal growth rates for various types of growth mechanisms: crystal growth rate $dR/dt = Cf(S)g(R)$

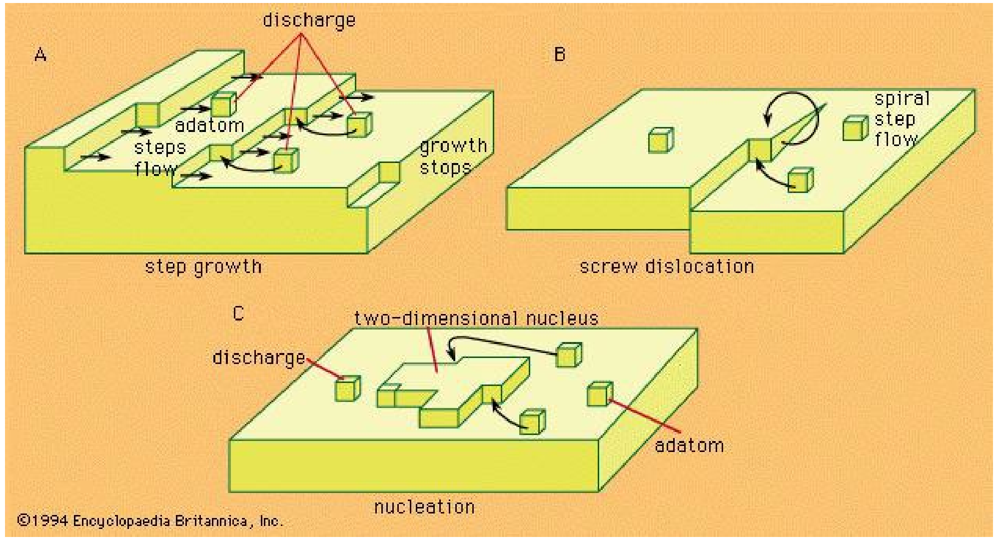
| Growth mechanism | $C$ | $f(S)$ | $g(R)$ | Ref. |
|---|---|---|---|---|
| Monosurface nucleation | $\beta_A D/d^3$ | $\exp[-\Delta G^s_{max}/k_B T]^\dagger$ | $R^2$ | 5 |
| Mono/poly crossover point | $0.2\hat{V}DC_{eq}$ | $S-1$ | $1/R$ | 5 |
| Polysurface nucleation | $(Dd/3)(\hat{V}C_{eq})^{2/3}$ | $(S-1)^{2/3}\exp[-\Delta G^s_{max}/k_B T]^\dagger$ | 1 | 5 |
| Screw dislocation | $D_s n_{se}\beta/(y_s^2\rho)$ | $(S^2/S_1)\tanh[S_1/S]^\ddagger$ | 1 | 30 |
| Bulk diffusion | $\hat{V}DC_{eq}$ | $S-1$ | $1/R$ | 48 |

$^\dagger\Delta G^s_{max} = \beta_L^2 \gamma_e^2 d^2/(4\beta_A k_B T \ln S)$.
$^\ddagger S_1 = (y_0/y_s)S$.

$y$ distance traveled along a surface, L
$y_0$ distance between steps, L
$y_s$ mean distance traveled to arrive at a step, L

$D_v$: solute surface concentration, $D_s$: surface diffusion coefficient, D: solute/growth unit diffusion coefficient, d: diameter of diffusing species

Different competing mechanisms may dominate the growth process and the **dominant one can change with the saturation of the system**.



# Aqueous – Bayer# process – $Al_2O_3$

Bauxite* – Milling - Washing

↓

Dissolution (NaOH – 250°C, 6 bar)

↓ $\{Na^+ (AlO_2)^-\}_{aq}$

Dilution – Filtration

↓ *cooling* $Al(OH)_3$

Precipitation / Crystallization - « seeding »

↓

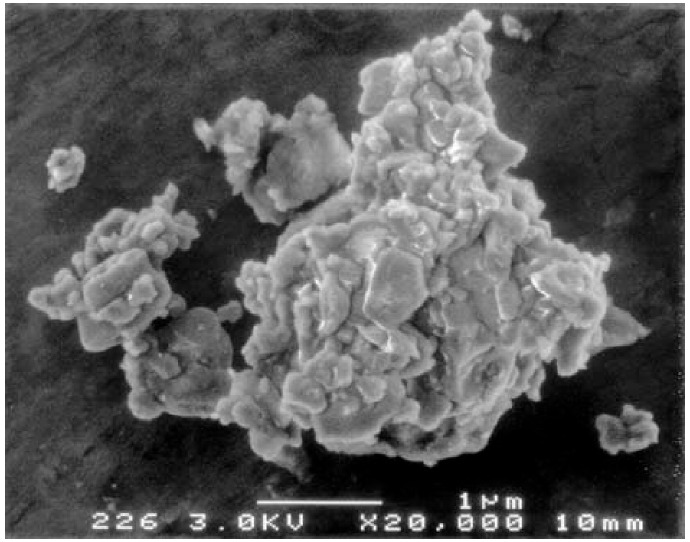
Gibbsite – $Al(OH)_3$

↓

Washing – filtration

↓

Thermal decomposition: Alumina ($Al_2O_3$) - Milling




**100ppm de Fe, Na 800 ppm,**
5-20 CHF/kg

Alum precipitation ($NH_4Al(SO_4)_2.12H_2O$)
**Fe 4-8 ppm, Na 8-10 ppm,**
75-100 CHF/kg

Bayer process is followed by Hall–Héroult process (for electrolytic Al)

#Invented by 1888 by Carl Josef Bayer

*Bauxite: different Al oxide-hydroxide-silicate + Fe, Ti,…

# Non-aqueous synthesis: $Si_3N_4$

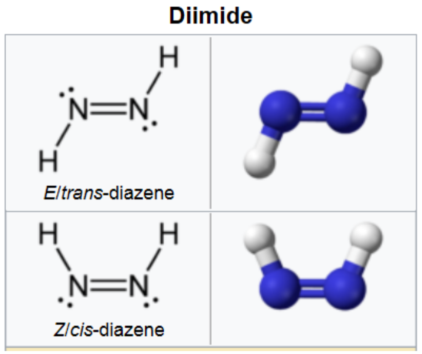
- Silicon nitride, $Si_3N_4$, can be produce in different way. A non-aqueous method in solution is the so-called diimide*, $Si(NH)_2$ , route.

$$SiCl_4 + 6NH_3 \rightarrow Si(NH)_2\downarrow + 4NH_4Cl \qquad \text{Eq.3.3.28}$$

- Silicon diimide is formed by reaction between liquid ammonia and $SiCl_4$ in hexane @ T=–50 °C

- At such temperature, $NH_4Cl$ is soluble into the solvent (hexane-liquid ammonia) and the solid diimide is separated by filtration

*Diimide:



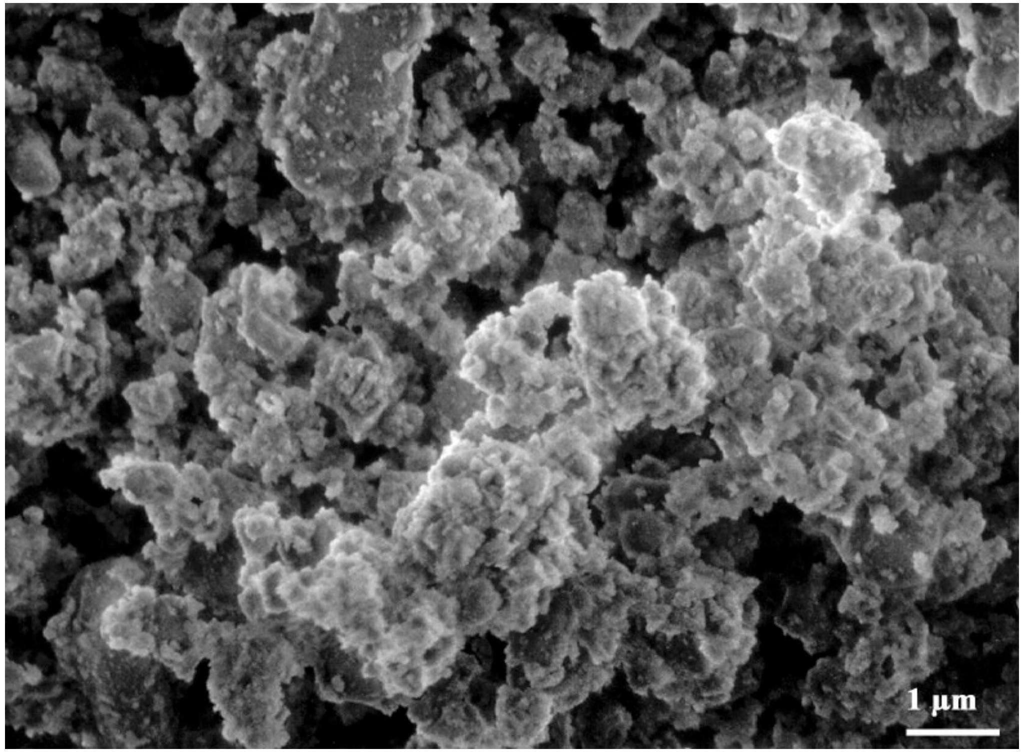
# Non-aqueous synthesis: $Si_3N_4$

- In a second step, silicon diimide is thermally decomposed under controlled atmosphere (inert or $N_2$-rich) at about 1000 °C

$$3Si(NH)_2 \rightarrow Si_3N_4 + 2NH_3 \qquad \text{Eq.3.3.29}$$

At such temperature $2NH_3 \leftrightarrows N_2 + 3H_2$

- High purity (<130 ppm metals) and relatively high surface area (10-20 $m^2/g$) powders are produced with this method
- e.g. 12 $m^2/g$, $D_{v50}$ – 0.65μm
- $d_{BET}$ - 0.156 μm
- $F_{ag}$ – 4.2
- 98%α-2% β



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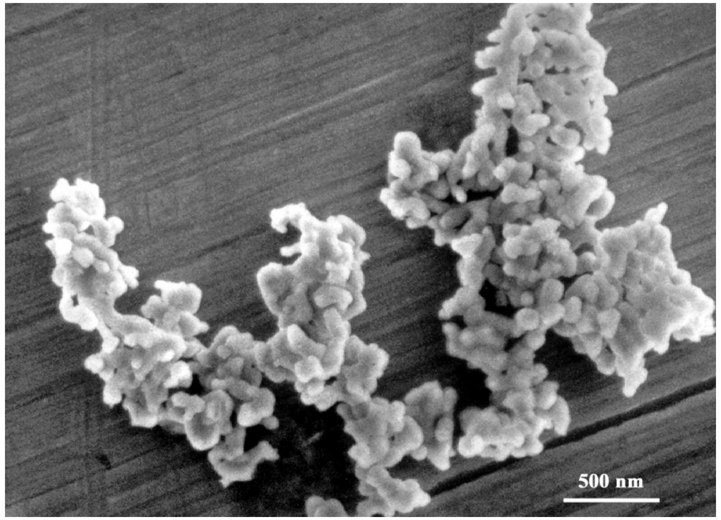
# $Al_2O_3$ doping

- "Doping" means addition of limited amount (generally <1wt%) of foreign element(s) in order to modify the material properties. Optical, electronic, and mechanical properties as well as phase stability, grain boundary movement, sintering, etc… can be modified by doping, opening infinite combination among materials and dopants for a plethora of applications in every field. Doping can be done at different stage of the material processing, e.g. during precipitation.

- Synthetic ruby ($Al_2O_3$)
  - Cr-doping
  - Added during the precipitation step, e.g. as nitrate
  - Synthesis of high purity $\gamma$-$Al_2O_3$


Ruby – Cr-doped corundum ($\alpha$-$Al_2O_3$)
Sapphire – (Fe,Ti,Cr,Cu,Mg)-doped corundum

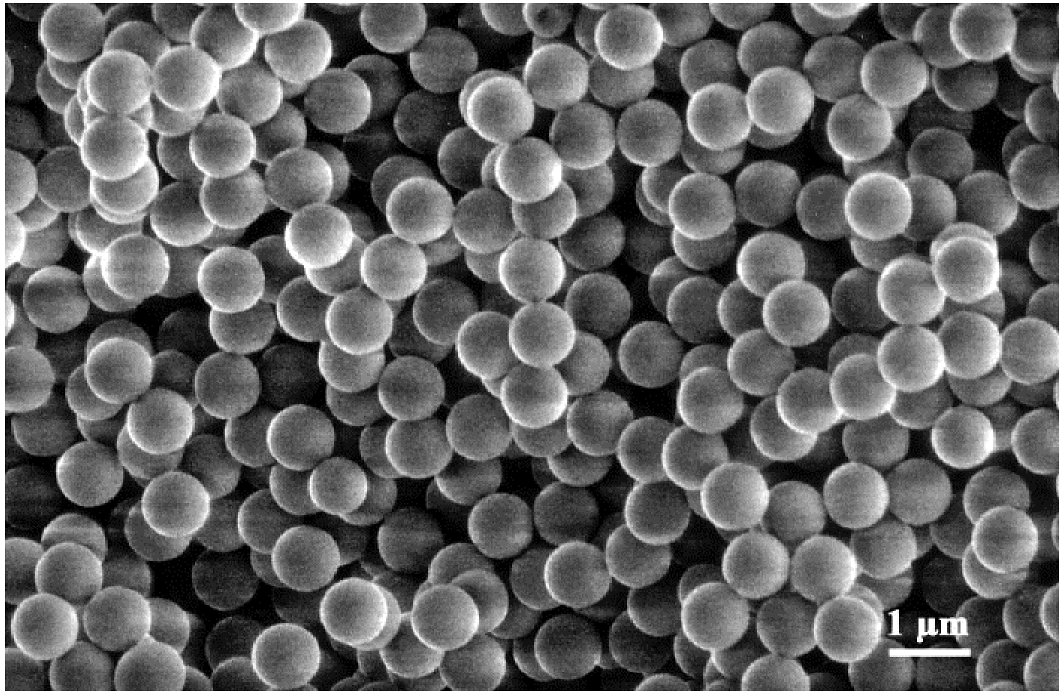
# Sol-Gel synthesis

- Alkoxides hydrolysis

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \qquad \text{Eq.3.3.30}$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \qquad \text{Eq.3.3.31}$$

- If the reaction is catalyzed with a **base**, the alkoxide is fully hydrolyzed, forming silicic acid ($Si(OH)_4$ or $H_4SiO_4$).
- By polycondensation* reaction, as for polymers, hydrated $SiO_2$ is formed.
- Depending on the operative condition, spherical particles can be produced with a narrow PSD.

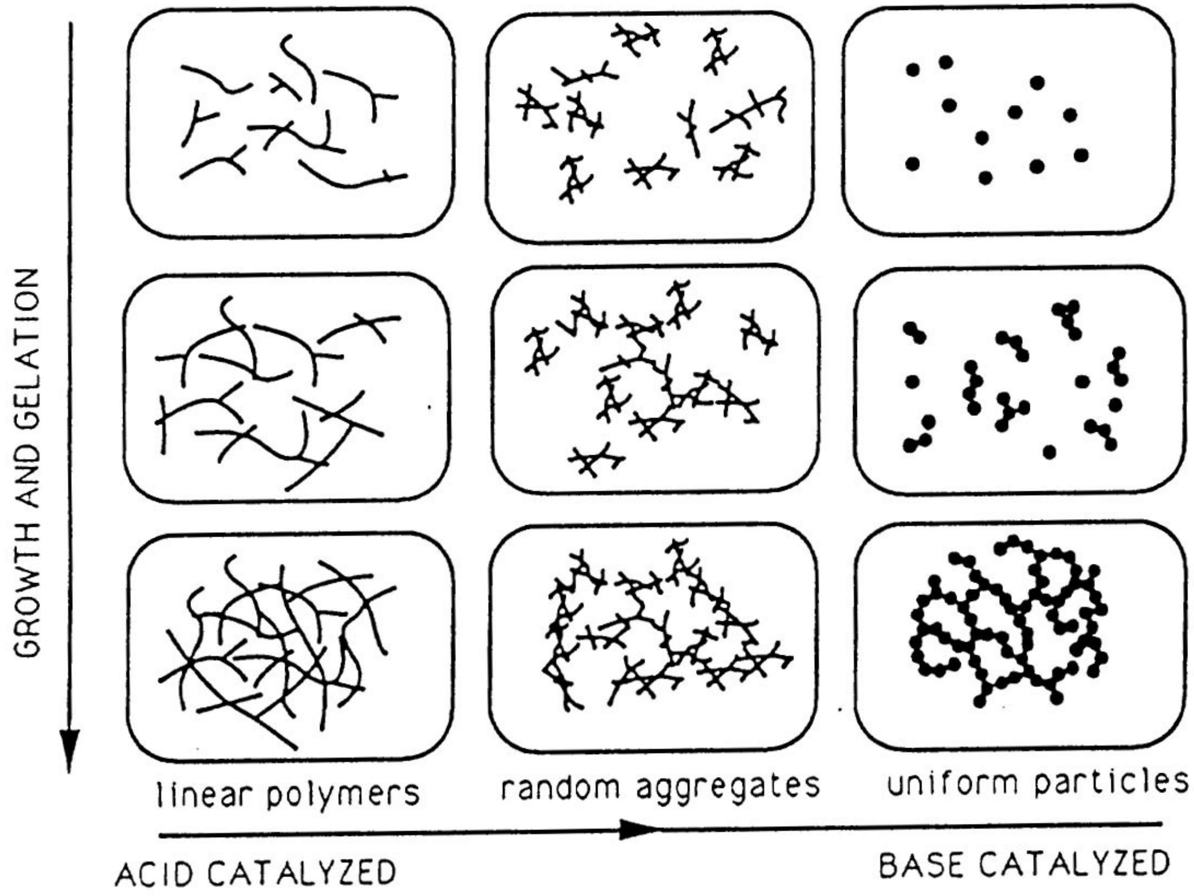



CHEMIE UETIKON GMBH - HPLC

*concept to remember:
condensation polymer vs. addition (or chain-growth) polymer

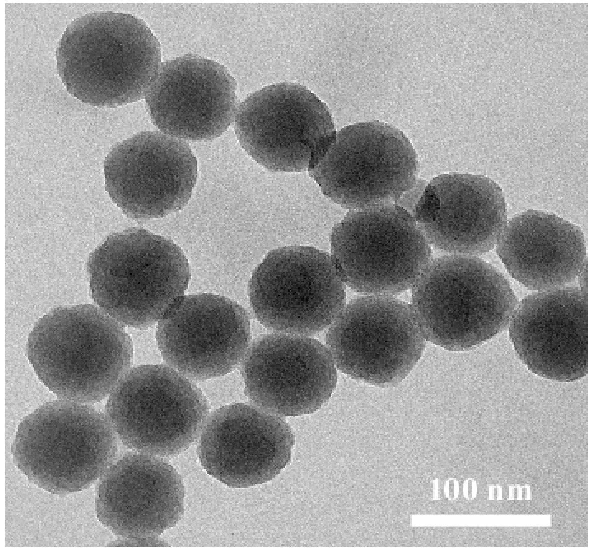
# Sol-Gel

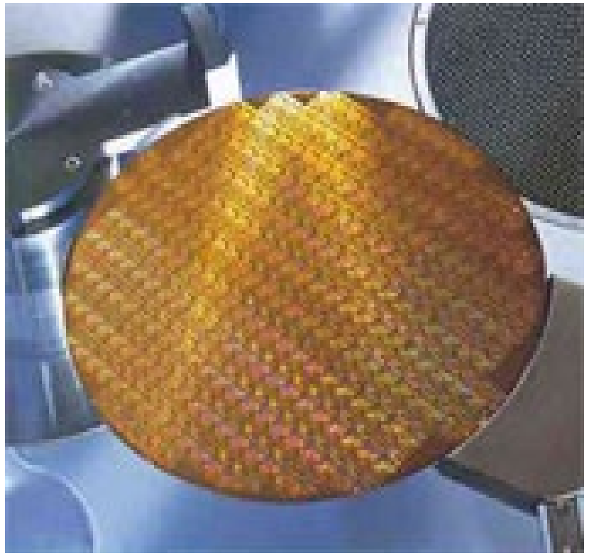
- If the reaction is catalyzed by an **acid** – the polycondensation reaction produces an alcohol-gel with a certain amount of residual alkoxy groups in the polymeric structure generating a continuous network



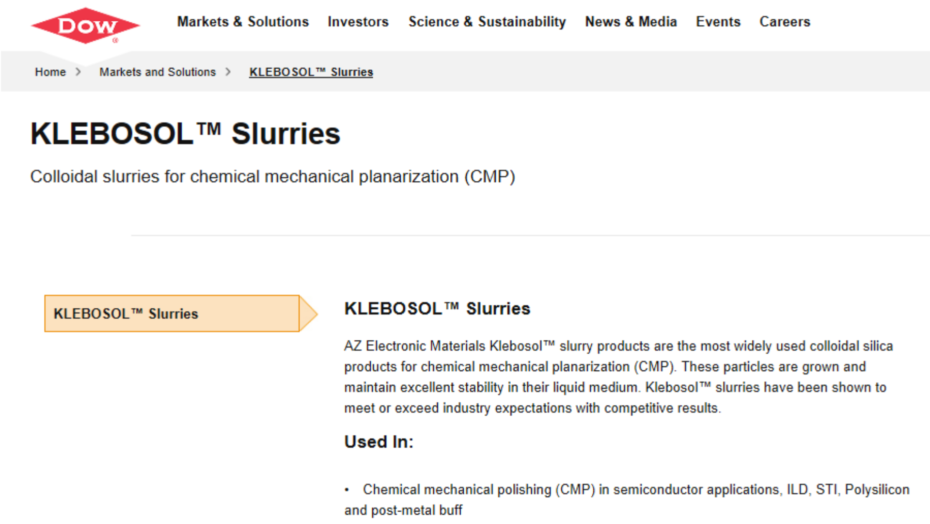
# Spherical Silica – Application - CMP

- Klebosol – A-Z chemicals – Klebosol used for chemical mechanical polishing (CMP) of silicon wafers (20cm wafer – 10-15,000 CHF!), no aggregates!



http://www.grace.com/EngineeredMaterials/ProductsAndApplications/Electronics/WaferPolishing.aspx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KLEBOSOL™ Slurries

Colloidal slurries for chemical mechanical planarization (CMP)

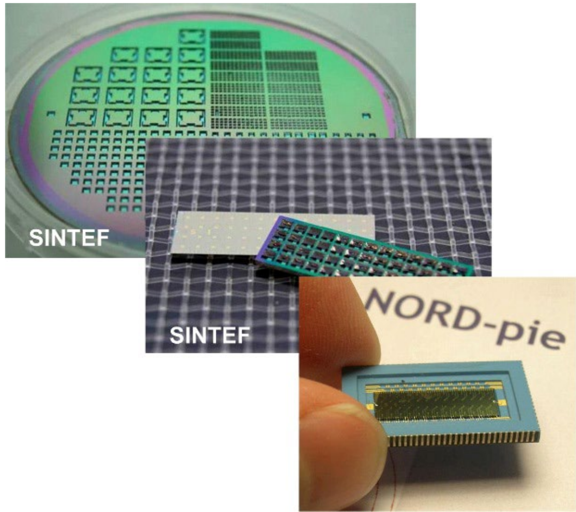
KLEBOSOL™ Slurries

KLEBOSOL™ Slurries

AZ Electronic Materials Klebosol™ slurry products are the most widely used colloidal silica products for chemical mechanical planarization (CMP). These particles are grown and maintain excellent stability in their liquid medium. Klebosol™ slurries have been shown to meet or exceed industry expectations with competitive results.

Used In:

- Chemical mechanical polishing (CMP) in semiconductor applications, ILD, STI, Polysilicon and post-metal buff

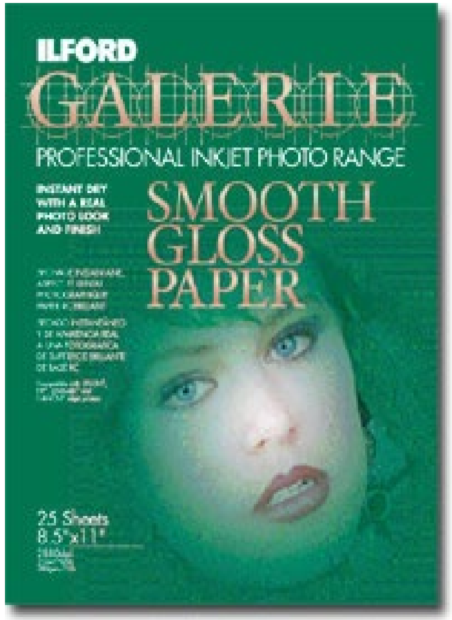


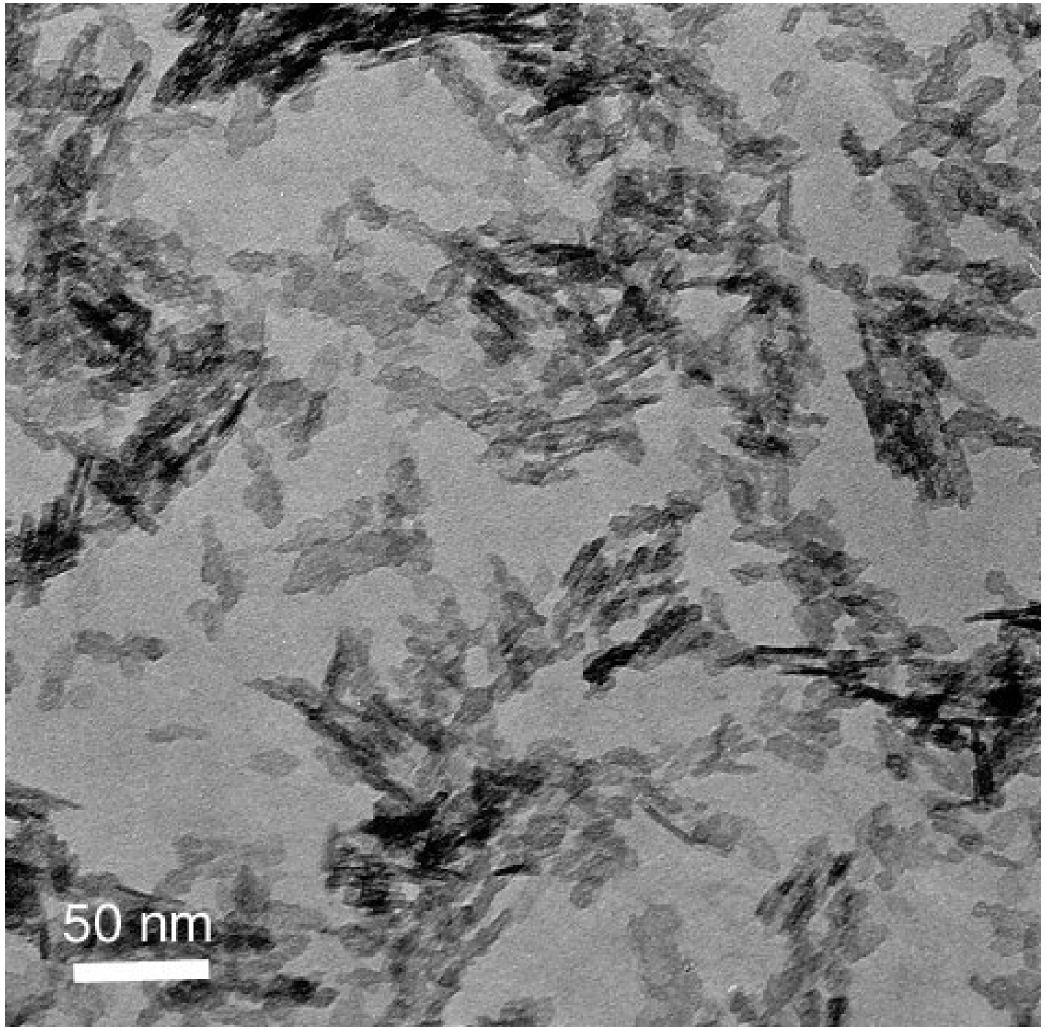

low temperature co-fired ceramics (LTCC) embedded piezoelectric actuator

http://www.infotech.oulu.fi/empart

# Sol-Gel – Boehmite (AlOOH) precipitation

- Produced from Aluminum Iso-propoxide $Al(OC_3H_7)_3$
- Spay dried and re-dispersible (20 nm)
- $d_{BET}$ =9.3 nm $F_{ag}$ = 1.7
- Applications as porous coating
- Ink-jet paper (ILFORD)
- Commercially available, Instant Dry

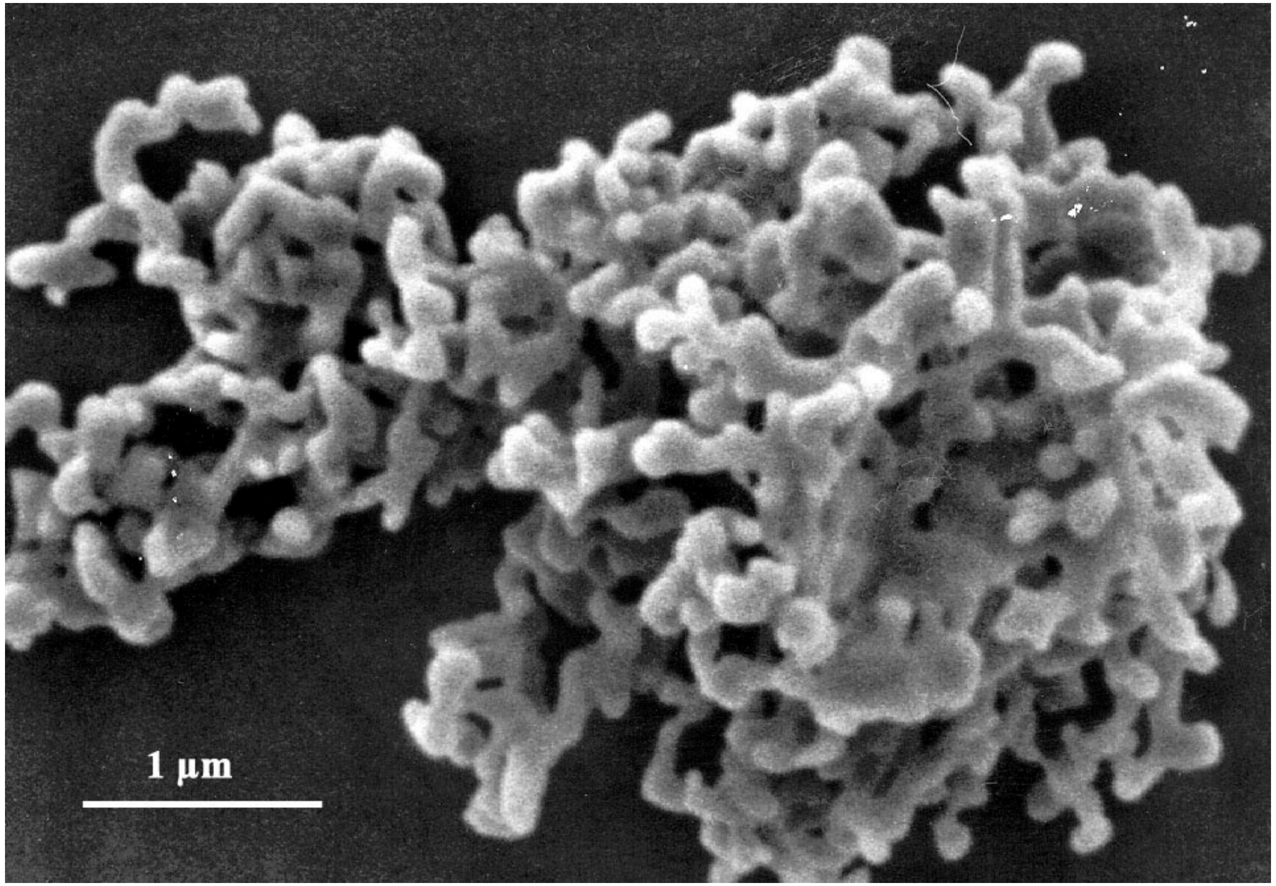



$$Al(OC_3H_7)_3 + 2H_2O \xrightarrow{H^+} Al(OOH) + 3C_3H_7OH$$

# Sol-Gel –Transformation AlOOH → γ-$Al_2O_3$

- $2AlOOH \rightarrow Al_2O_3 + H_2O$ ( 500-1000°C)
- Agglomeration $D_{v50}$ = 1.22 µm, SSA = 147 $m^2/g$
- $d_{BET}$ =12.2 nm $F_{ag}$ = 100




Micrograph of gamma alumina produced by thermal treatment of boehmite

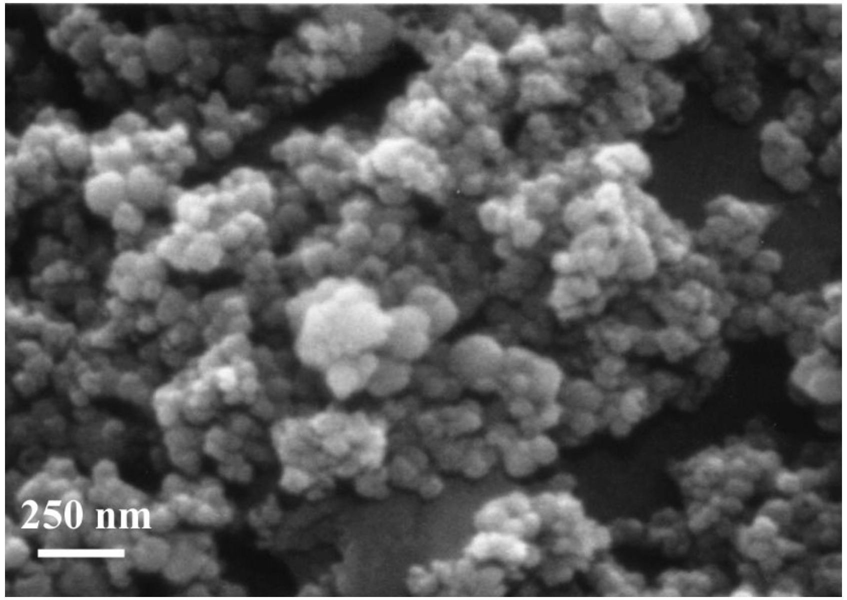
# Hydrothermal synthesis

- High pressure and temperature (1-50 bars, 80-350°C)
- Zeolites (aluminosilicate with a complex and controlled porous structure) are produced with this method.
- It is used for several relevant industrial products such as catalysts.
- On the advantage is the direct preparation of high purity fine ceramic powders and not a precipitate that needs to be thermally treated.
- On the other hand, the powders need to be dried in a controlled manner in order to limit the formation of hard aggregates.

# Hydrothermal synthesis

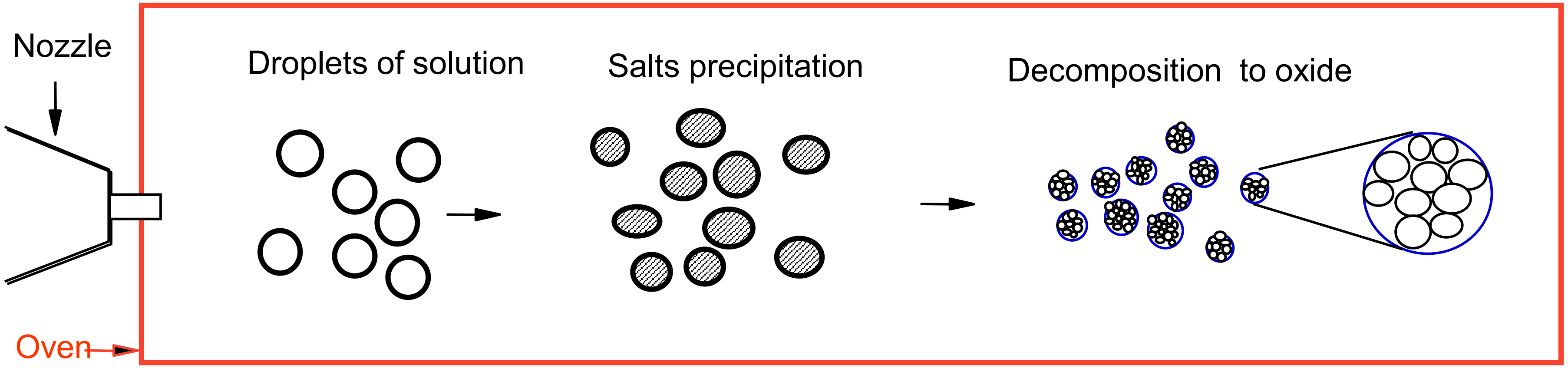


- In general, a process that makes use of high T and P might be accepted if the product shows peculiarities which are difficult to be achieved with other method. It is a market decision: if the added value of the product is sufficient to compensate the higher production costs, expensive processes might be considered. A working example is the hydrothermal production of ultra-fine high-purity $BaTiO_3$ for electronic industry (mainly capacitors).



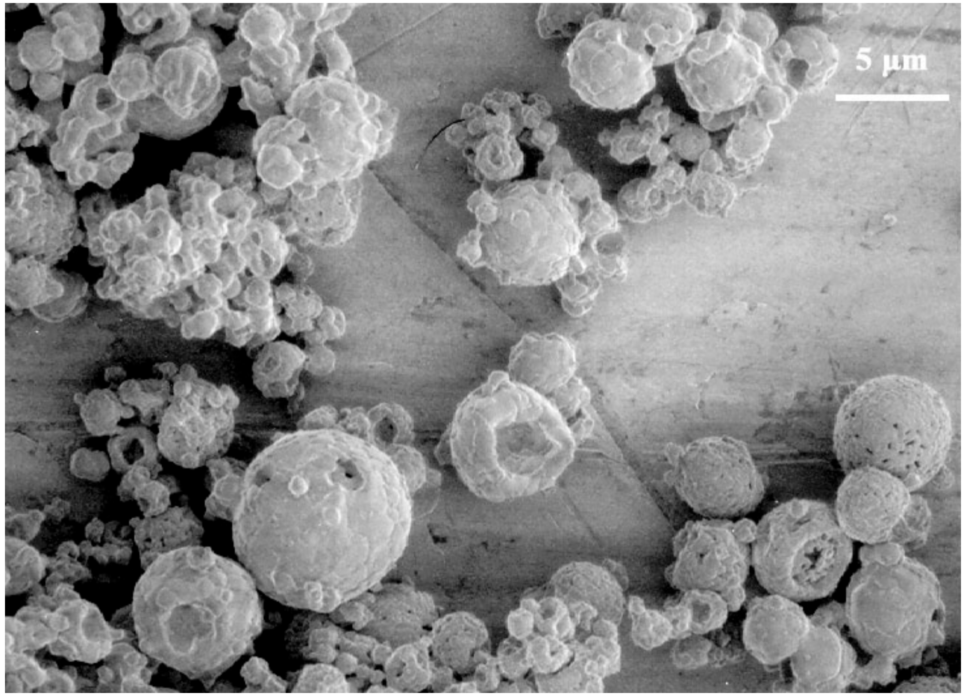

| Powder | SSA $m^2/g$ | $d_{BET}$ nm | PSD (nm) $d_{v16}$ | $d_{v50}$ | $d_{v84}$ | $F_{ag}$ $(d_{v50} / d_{BET})$ |
|---|---|---|---|---|---|---|
| Batch | 37.6 | 30.9 | 54.1 | 86.3 | 328 | 2.8 |

# Spray-pyrolysis – principles

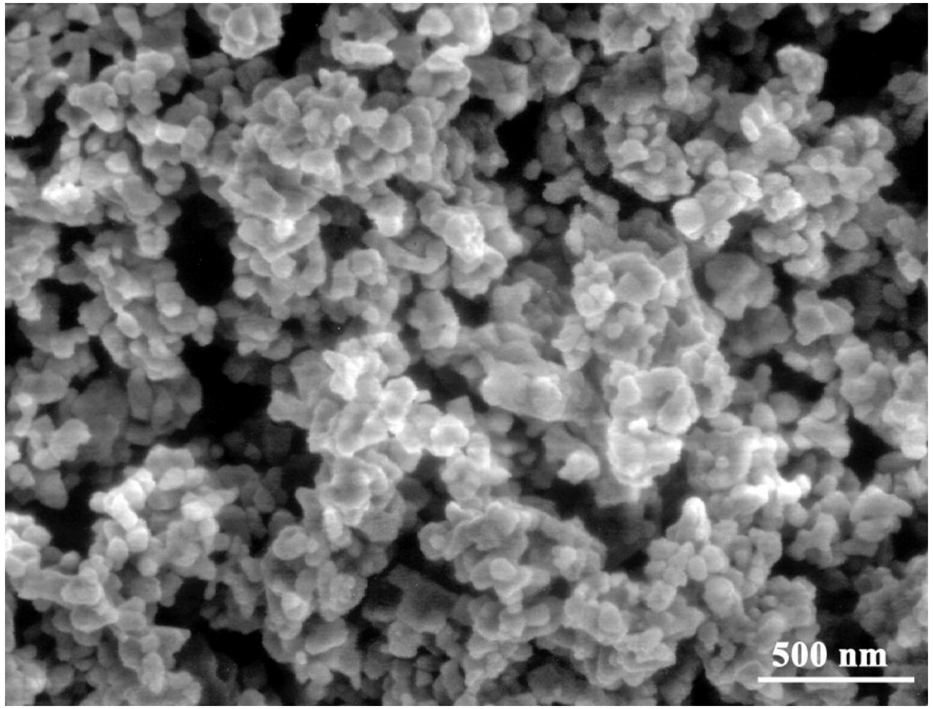



- Suitable for complex mixed oxides and at large production several hundred tons per year
- Often nitrates or chlorides salts (easy to decompose but with corrosion implications…)
- In complex matrix, if the saturation levels of the precipitating salts are too different, segregation occurs and
- The molecular homogeneity cannot be achieved.

# Spray-pyrolysis – powders

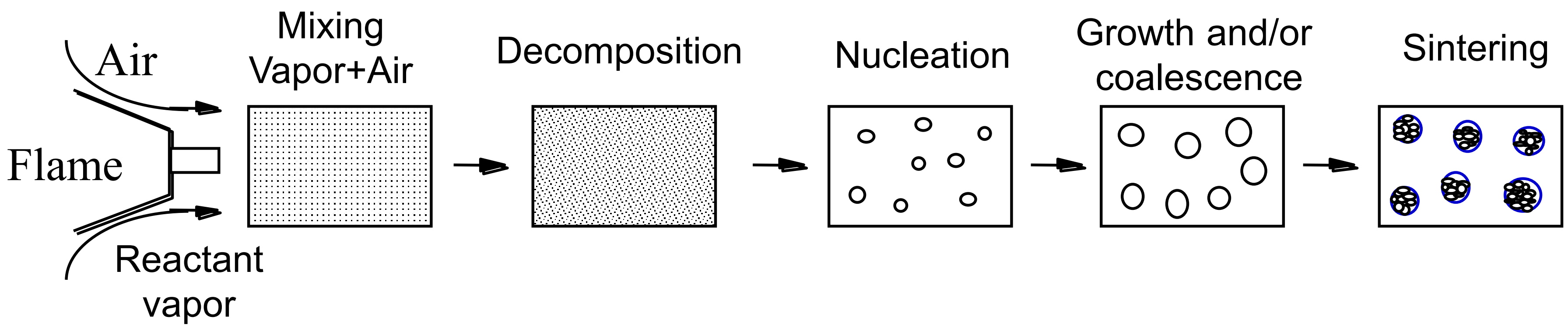



Strontium aluminate chromate $[Sr_8(Al_{12}O_{24})(CrO_4)_2]$ prepared by spraying – LTP Application as luminophore (doped with Eu, Dy) – watches and aircraft




$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}$ oxide prepared by spray-pyrolysis - commercial. Used in solid oxide fuel cells (SOFCs)

# Vapor Phase Synthesis - principles




- Reactants can be metal chlorides
- The required heating can be provided by

- a flame (up to 2500 K),

- an oven (up to 2300 K),

- a laser (up to 1800 K),

- or a plasma (up to 10000 K).

# Vapor Phase Synthesis - principles

- The particles formation is similar to the precipitation in liquid phase but instead of concentration (activity) of the solutes…

- … the partial pressures of reactant vapors or gasses (fugacity) are driving the nucleation and growth mechanisms. Anyway, the process can be reduced to the chemical potentials, similar to precipitation in solution.

- Two dominant mechanisms take place during the particles in gas phase:

    1. Condensation and 2. Coagulation

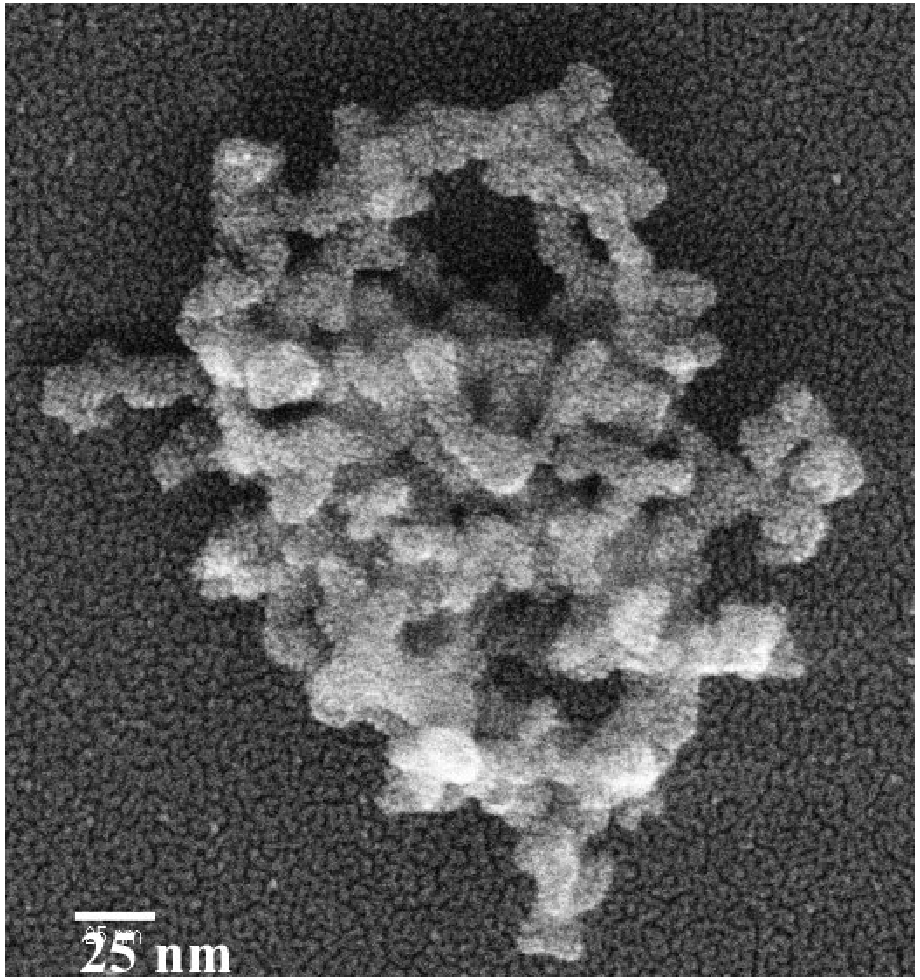
# Vapor Phase Synthesis – mechanism

- **Coagulation** dominates when

- the critical size of the embryo is of the dimension of molecular or atomic species and

- the particles form because of coalescence among atoms or molecules.

- Fume silica *(cement)*, alumina *(catalyst support)* and titanium dioxide *(photocatalyst e.g. for water purification)* are typical examples




Gamma alumina,
$d_{v50}$ =40 nm
$F_{ag}$ = 2.5

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

# Vapor Phase Synthesis – mechanism

- **Condensation** dominates when the critical size is larger than the growth unit.
- The nucleation rate defines the particle formation rate
- Then, the particles growth by:

  - condensation of molecular growth units on stable nucleolus (as growth mechanism in solution)

  - or by direct chemical reaction on the nucleolus/particle surface

  - an example is carbon black used in car tires:

- 14 million tons/y (2016)!
- Improved mechanical properties (reinforcing phase)
- Increase conductivity (thermal)
- Minimize tire wear, increasing tire life
- Primary particles: 20-25 nm!

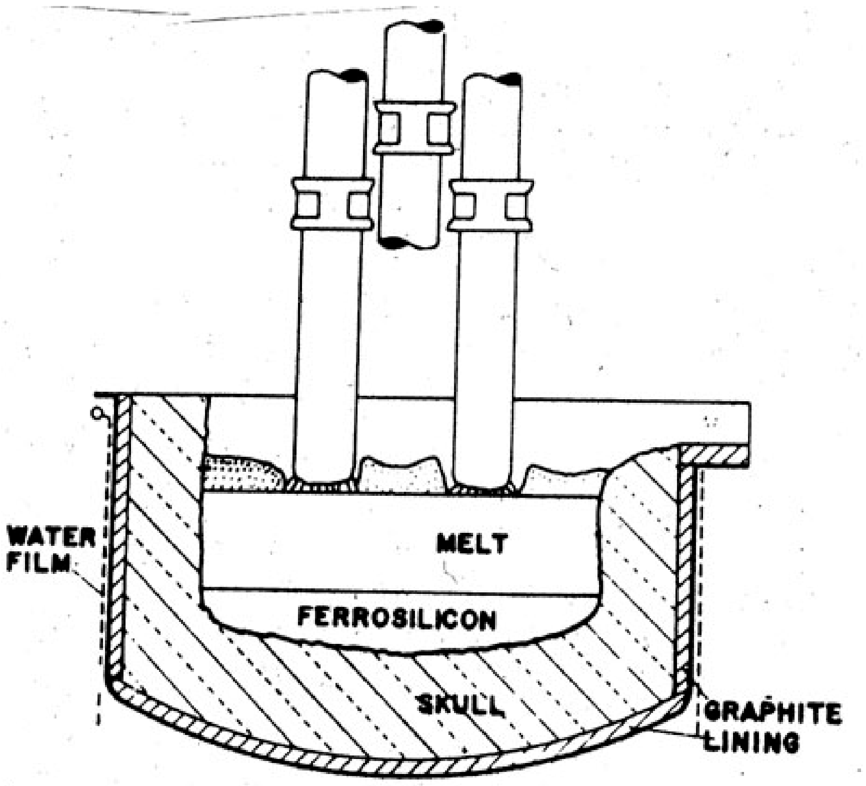
# Other methods

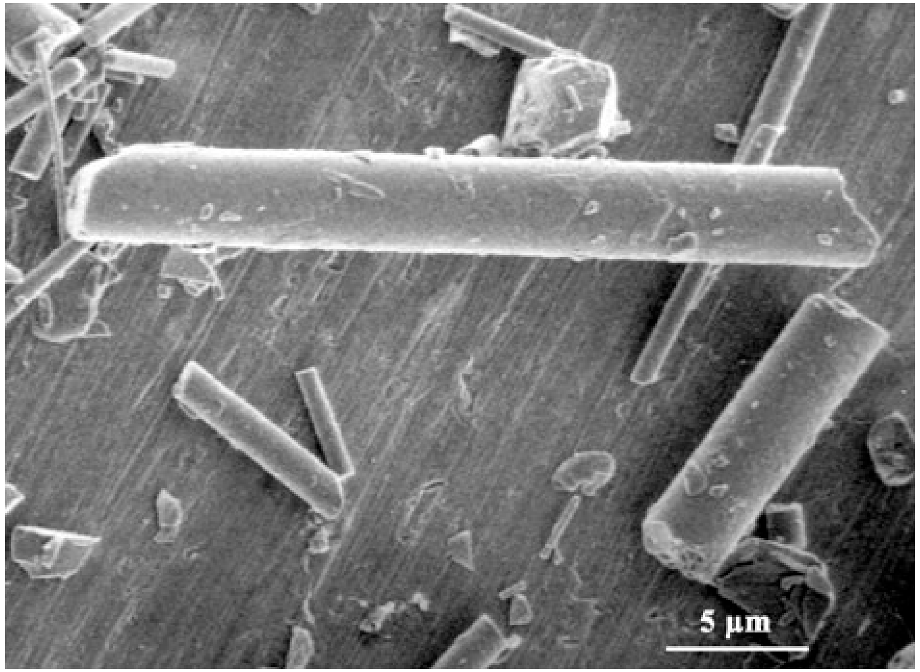
**Electrofusion**

- The production of molten alumina for abrasive and refractories industries is carried out by melting calcined bauxite or alumina in an arc-furnace.
- Coke (or anthracite) is mixed with bauxite to reduce impurities such as $Fe_2O_3$, $SiO_2$ and $TiO_2$.
- Once melted, an alloy of variable composition FeSiAlTiC is separated from alumina because of its higher density.
- The molten alumina is then casted in a mold and solidified.
- The solidified mass is then broken and milled and the residual FeSiAlTiC alloy is magnetically removed.
- This material undergoes additional milling and sieving for use as an abrasive.
- These method can also be used to produce glasses, calcium aluminate cements and aluminosilicate fibers (by adding about 40% $SiO_2$)

# Other methods- Fibers

- A $Al_2O_3$-$SiO_2$ melt is blown by pressurized air during casting from the crucible
- An amorphous product with limited properties is obtained. Working temperature < 1400°C



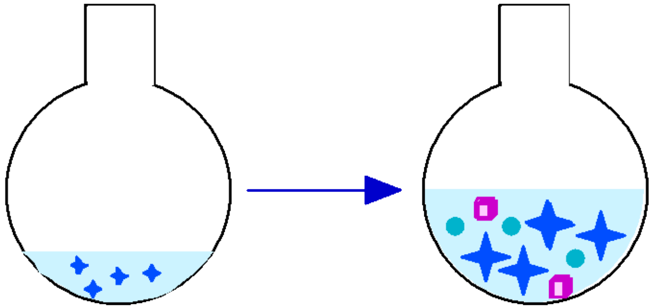



3

# Scaling-up strategies – Tubular Reactor

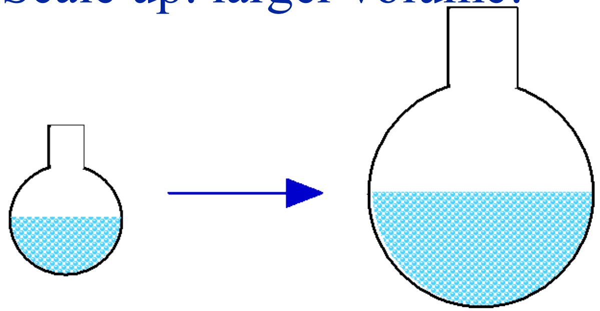
## Batch reactor

- Accumulation of unreacted chemicals
- Poor Mixing



Prone to heterogeneous nucleation

- Scale up: larger volume!

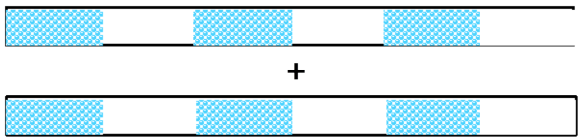


## Tubular reactor

- Efficient reactant mixing
- Reduced reactor volumes

Higher chemical selectivity
Narrower PSD

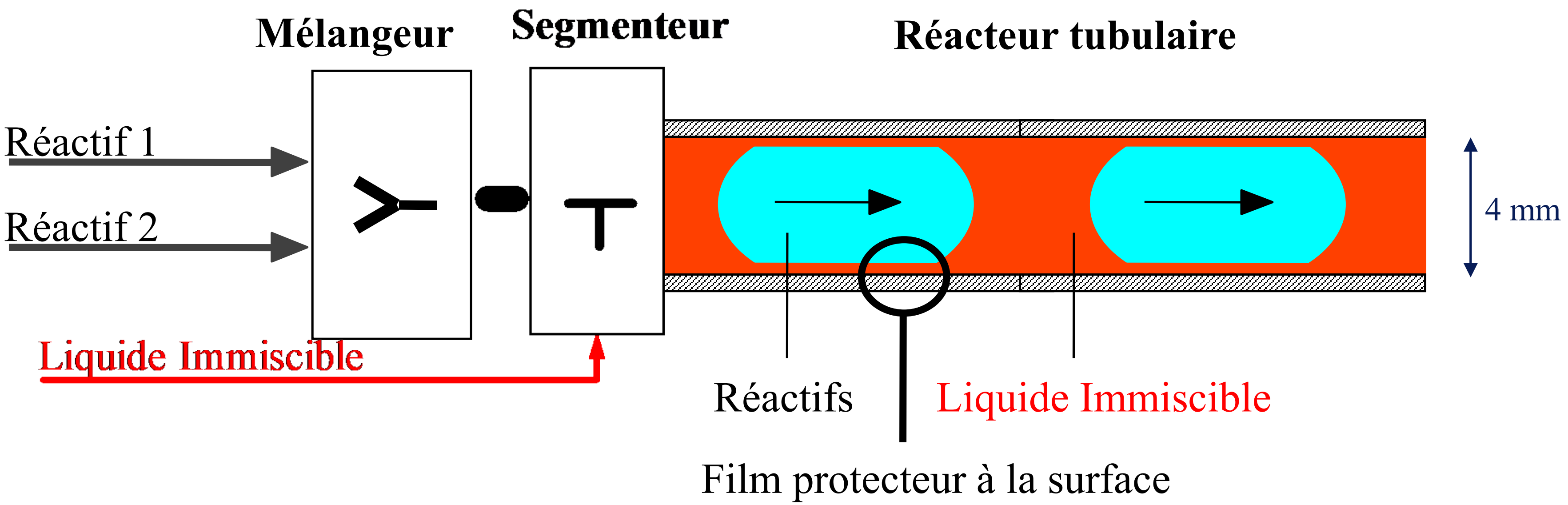
- Scale up: several tubes!




Risk of fouling: deposition of material on the internal tube surface

# Segmented flow tubular reactor (SFTR)

The reactive fluid which contains the chemicals is segmented into a series of small droplets.

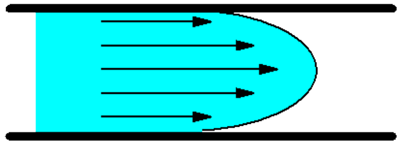



➔ Controlled mixing ⇒ **improved powder quality**
➔ Each droplets (reactor) has identical "*history*" (residence time and heat exchange)
➔ Continuous process

3

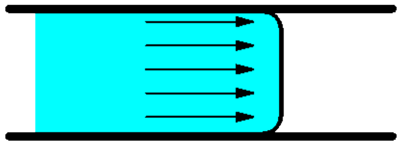
# Why segmentation?

Parabolic flow



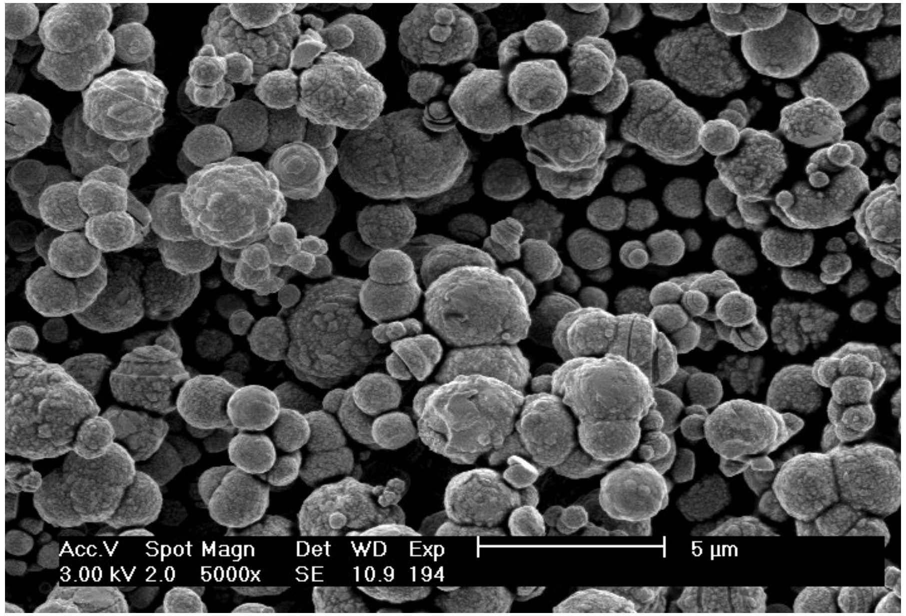
Ag nanoparticles

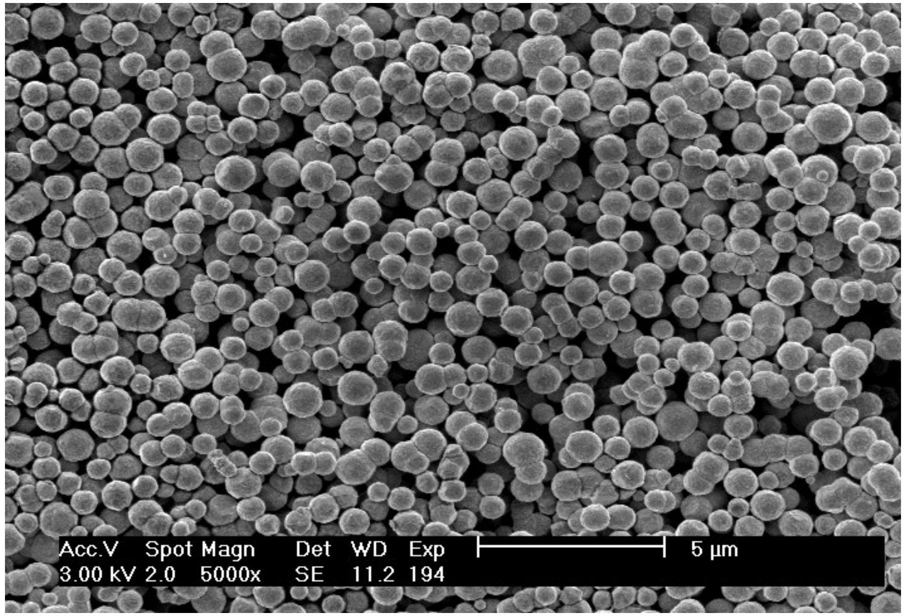
Ideal plug-flow



Without segmentation

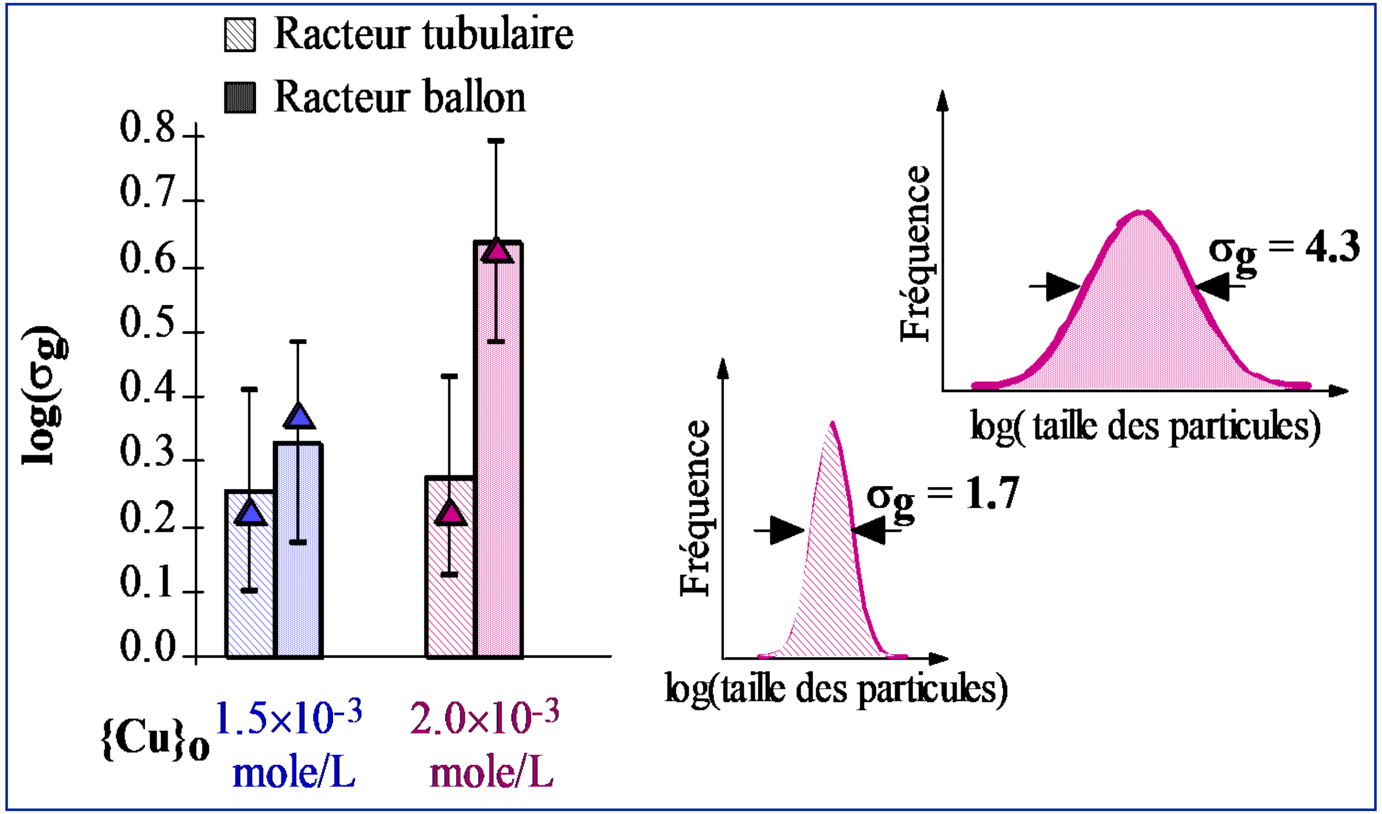
With segmentation

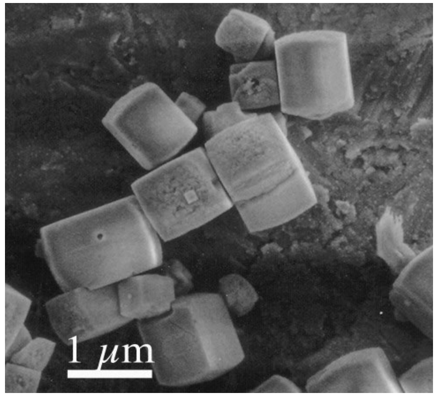


# Copper oxalate:
PSD broadening (e.g. FWHM, normalized width,…)






- **Narrower** PSD with tubular reactor
- Tubular reactor is **more robust** (e.g. higher reproducibility of the produced powders) at high saturation level