

## Chapter 9 Generation of (Nano)Particles by Growth

### 9.1 Nucleation

#### (1) Supersaturation

Thermodynamics assumes a phase change takes place when there reaches

Saturation of vapor in a gas,

Saturation of solute in a solvent or

Saturation of solute in a solid solution....

\* Vapor pressure and solubilities indicate the saturation...

In real world, the phase change requires a certain degree of supersaturation, accompanying a formation of nuclei in the media...

Supersaturation of growth species,  $S$

$$S = \frac{p}{p_0} > 1$$

$$S = \frac{c}{c_0} > 1$$

where  $p$ : partial pressure of the species  $i$  in the gas phase  $> p_0$

$c$ : concentration of species  $i$  in the solution

$p_0, c_0$ : vapor pressure and saturation concentration of the species  $i$

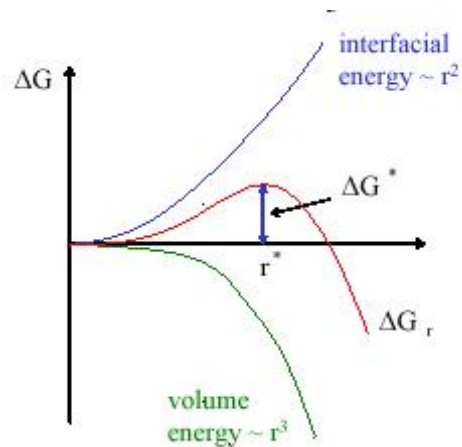
#### (2) Formation of Nuclei (Nucleation)

##### 1) Critical Nuclei and Energy Barrier

Gibbs free energy change for a sphere of the growth species from molecules

$$\Delta G = \underbrace{\pi x^2 \sigma}_{\text{interfacial energy}} + \underbrace{\frac{\pi x^3}{6} \Delta G_v}_{\text{volume energy}}$$

$$\text{where } \Delta G_v = -\frac{kT}{v_m} \ln S$$



Newly formed nucleus is stable only when its radius exceeds a critical size  $r^*$ (or  $x^*$ )...

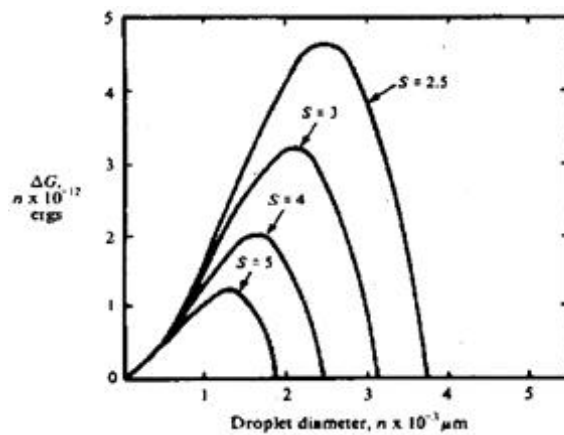
At critical size  $r^*(x^*)$

$$\left. \frac{d\Delta G_v}{dx} \right|_{x=x^*} = 0$$

By some manipulation

$$x^* = -\frac{4\sigma}{\Delta G_v} = -\frac{4\sigma v_m}{kT \ln S} \quad (*) \quad \text{Diameter of critical nucleus}$$

$$\Delta G^* = \frac{16\pi\sigma}{(3\Delta G_v)^2} \quad \text{Energy barrier against nucleation}$$



$\Delta G_v$  for formation of water droplet

\* From (\*)

$$\ln S = \ln \left( \frac{p_x}{p_0} \right) = \frac{4\sigma v_m}{kTx}$$

Kelvin equation

- Vapor pressure elevation (or boiling point lowering) of small particles

## 2) Nucleation rate [number of nuclei formed / (time volume of medium)]

### Homogeneous nucleation

- For vapor-to-droplet in gas

$$R_N = \frac{p^2}{(2\pi m)^{1/2} (kT)^{3/2}} (\pi x^2) \exp\left(-\frac{\Delta G^*}{kT}\right)$$

where  $m$ : molecular mass

- For solute-to-particles in solution

$$R_N = \frac{C_0 kT}{3\pi x_m^3 \mu} \exp\left(-\frac{\Delta G^*}{kT}\right)$$

where  $C_0$ : initial concentration

$x_m$ : molecular diameter

\* Critical saturation ratio,  $S$  at  $R_N = 1.0$

For water vapor at  $300^\circ\text{C}$ ,  $S_{crit} = 3.1$

### Heterogeneous nucleation

- Formation of nuclei on existing foreign surface

$$\Delta G_{het}^* = \Delta G^* \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4}$$

where  $\theta$ : angle of contact

Since  $\Delta G_{het}^* \leq \Delta G^*$ ,

- Heterogeneous nucleation is easier than homogeneous nucleation in most cases...

\* Criteria for homo or heterogeneous nucleation

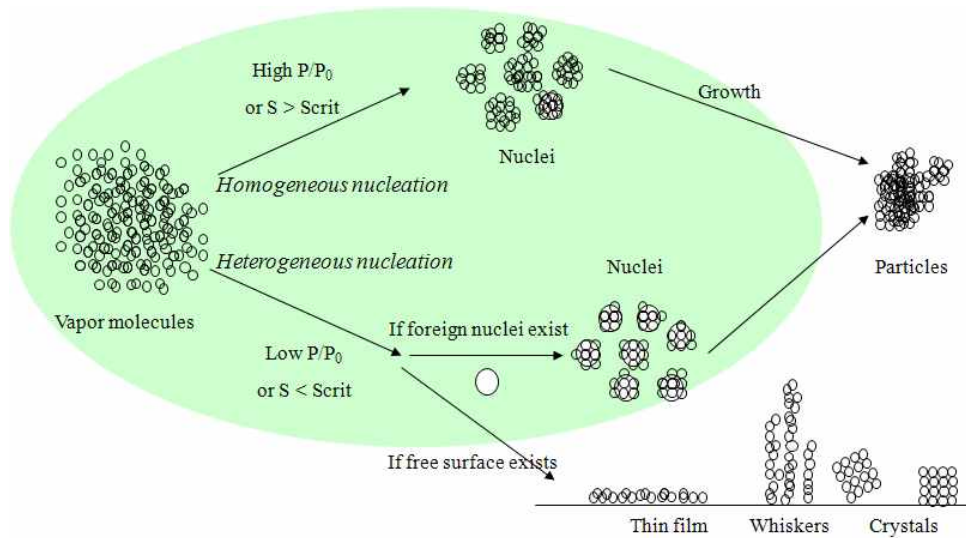
For  $S > S_{crit}$ , homogeneous nucleation

For  $S < S_{crit}$ , heterogeneous nucleation

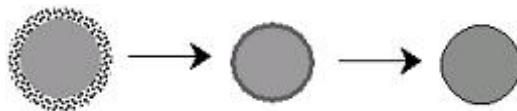
\* If foreign surface is supplied by foreign nuclei (ions, clusters...), particle growth on the existing nuclei after homogeneous nucleation. This resulted in the growth of monodisperse particles...

ex. artificial rain formation

\* If the foreign surface is supplied by the plain surface, thin film or whiskers will grow...



## 9.2 Growth by Condensation



- Condensation : growth of particles by collision of individual molecules followed by sticking...

### (1) Growth Law

- In general condensation occurs in diffusion limited condition...

In free molecule regime

$$\frac{dx}{dt} = \frac{2v_m}{(2\pi mkT)^{1/2}} (p - p_x)$$

In continuum regime

$$\frac{dx}{dt} = \frac{4Dv_m}{kTx} (p - p_x)$$

In terms of particle volume,  $v$

$$\frac{dv}{dt} = \frac{d\left(\frac{\pi x^3}{6}\right)}{dt} = \frac{\pi}{6} 3x^2 \frac{dx}{dt} = \frac{\pi}{2} x^2 \frac{4Dv_m}{kTx} (p - p_x) = \frac{2\pi Dv_m x}{kT} (p - p_x)$$

- If  $p < p_x$ , evaporation occurs..

- For growth from liquid phase

$$\frac{dx}{dt} = \frac{4Dv_m}{x} (c - c_x)$$

\*  $\frac{dx}{dt}$  is called "growth law".

\* Variation in size decreases as growth by condensation proceeds!

## (2) Ostwald ripening

From Kelvin equation

$$\ln S = \ln\left(\frac{p_x}{p_0}\right) = \frac{4\sigma v_m}{kTx}$$

For the two particles,  $x_1 \gg x_2 \rightarrow c_{x_1} \ll c_{x_2}$

Solute will deposit onto the surface of the larger particle, whereas the small particle has to continue dissolving...

### Example.

A 30- $\mu\text{m}$ -diameter water droplet is evaporating in a chamber. The chamber temperature is 20°C, and the pressure is 760mmHg. The chamber relative humidity is 50%. Find the droplet evaporation rate in grams of water lost per second. Diffusion coefficient of water vapor in air is 0.251cm<sup>2</sup>/s and vapor pressure at 20°C is 17.50 mmHg.

$$k := 1.38 \cdot 10^{-16} \frac{\text{erg}}{\text{K}}$$

$$p_x := \frac{17.5}{760} \text{atm}$$

$$p := p_x \cdot 0.5$$

$$x := 30 \times 10^{-6} \text{m}$$

$$v_m := \frac{18 \text{gm}}{6.023 \cdot 10^{23}}$$

$$D := 0.251 \frac{\text{cm}^2}{\text{s}}$$

$$T_w := 293 \text{K}$$

+

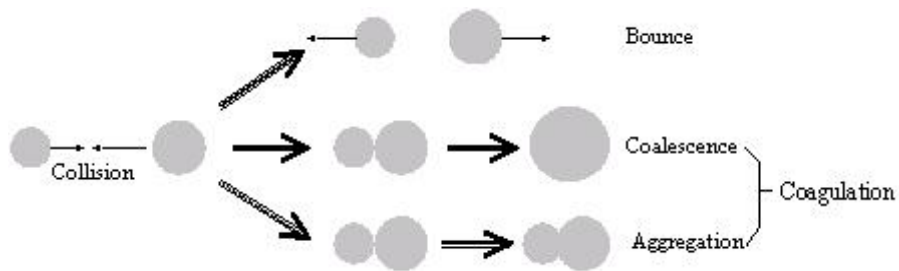
$$I := \frac{2\pi D \cdot v_m \cdot x}{k \cdot T} (p - p_x)$$

$$I = -4.079 \times 10^{-11} \frac{\text{kg}}{\text{s}}$$

### 9.3 Growth by Coagulation

#### (1) Introduction

- Growth as a result of collision of a particle with other particle and subsequent sticking with each other...



- Sources of collision

*Brownian motion*

*External force fields*

*Particle-particle interaction (polar, coulombic)*

- Coalescence

*Spherical growth: liquid-phase growth*

*Occurs for most liquid particles and for rapid sintering solid particles*



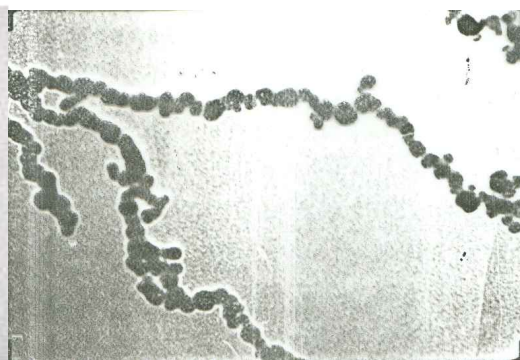
- Aggregation (Agglomeration)

*Nonspherical growth keeping identities of primary particles*

*Solid-phase growth*



Aggregation of TiO<sub>2</sub> nanoparticles



Aggregation of iron nanoparticles

## (2) Mathematical Description for Coagulation

Let

$N_{i,j}$  : Number of collisions occurring per unit time per unit volume of medium between the particles having diameters (volumes)  $d_i(v_i)$  and  $d_j(v_j)$  respectively.

$$N_{i,j} = b_{i,j}n_in_j$$

where

$n_i, n_j$ : number concentration of colliding particles  $v_i, v_j$ , respectively  
(no./cm<sup>3</sup>)

$i, j$ : number of basic units making particles (e.g.  $i$ -mer and  $j$ -mer)

In terms of continuous size distribution

$$N(v_i, v_j) = b(v_i, v_j)n(v_i)n(v_j)dv_idv_j$$

where  $b_{i,j} = b(v_i, v_j)$ : collision frequency function

"Coagulation coefficient"

- Coagulation resulted in the increase in size but decrease in the number concentration of particles...

In discrete notation

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k}^{N_{i,j}} - \sum_{i=1}^{\infty} N_{i,k} = \frac{1}{2} \sum_{i+j=k}^{N_{i,j}} b_{i,j}n_in_j - n_k \sum_{i=1}^{\infty} b_{i,k}n_i$$

In continuous notation

$$\frac{dn(v)}{dt} = \frac{1}{2} \int_0^v b(v', v-v')n(v')n(v-v')dv' - n(v) \int_0^{\infty} b(v, v')n(v')dv'$$

## (3) Brownian coagulation

For continuum regime

$$\begin{aligned} b_{i,j} &= \left( \frac{2kT}{3\mu} \right) \left( \frac{1}{v_i} + \frac{1}{v_j} \right) (v_i^{1/3} + v_j^{1/3}) \\ &= \left( \frac{2kT}{3\mu} \right) \left( \frac{1}{x_i} + \frac{1}{x_j} \right) (x_i + v_j) \end{aligned}$$

For polydisperse particles

When  $x_i > x_j$ ,  $b_{i,j} > b_{i,i}$  or  $b_{j,j}$

$\therefore$  Different-size coagulation occurs faster than that between similar size coagulation...

Monodisperse particles becomes polydisperse...

Polydisperse particles becomes monodisperse..

\* Self-preserving,  $\sigma_{g,ultimate} \approx 1.4$

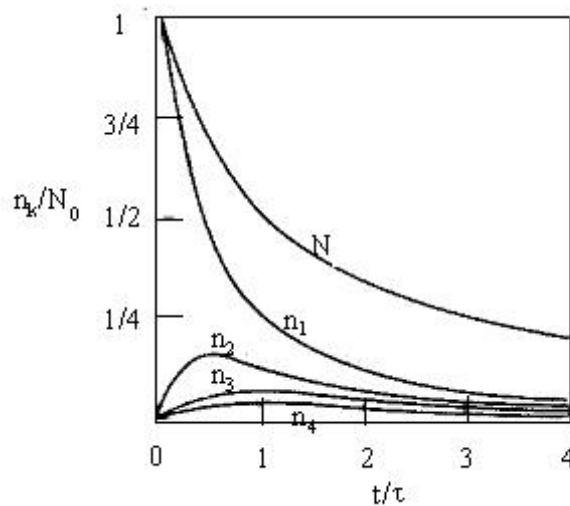
For monodisperse particles in air at 1atm and 20°C

$$b = \frac{8kT}{3\mu} = K = 3.0 \times 10^{-16} C_c, \quad \frac{m^3}{s}$$

Then

$$\frac{dn_i}{dt} = \frac{K}{2} \sum_{i+j=k} n_i n_j - K n_i \sum_{j=1}^{\infty} n_j$$

Integration yields



Summing up over  $i = 1, \infty$

$$\sum_{i=1}^{\infty} \frac{dn_i}{dt} = \frac{K}{2} \sum_{i=1}^{\infty} \sum_{i+j=k} n_i n_j - K \sum_{i=1}^{\infty} n_i \sum_{j=1}^{\infty} n_j$$

Therefore

$$\frac{dN}{dt} = -\frac{K}{2} N^2$$



Integration yields

$$N(t) = \frac{N_0}{1 + N_0 K t}$$

Since  $N\left(\frac{\pi}{6}x^3\right) = \text{constant}$  and  $N_0 x_0^3 = N x^3$

$$\frac{x(t)}{x_0} = \left(\frac{N_0}{N(t)}\right)^{1/3}$$

*Example.*

The initial number concentration of a magnesium-oxide fume is  $10^7/\text{cm}^3$ , and the particles are  $0.2\mu\text{m}$  in diameter. Determine the time required for the concentration to decrease to  $10^6/\text{cm}^3$ . Assume simple monodisperse coagulation at  $20^\circ\text{C}$  with a constant  $K$  of  $5 \times 10^{-16} \text{m}^3/\text{s}$  [ $5 \times 10^{-10} \text{cm}^3/\text{s}$ ]. What is the average particle diameter at the end of this period?

$$10^6 \text{ cm}^{-3} = \frac{10^7 \text{ cm}^{-3}}{1 + 10^7 \text{ cm}^{-3} \cdot 5 \cdot 10^{-10} \frac{\text{cm}^3}{\text{s}} t} \quad \text{solve} \rightarrow 1800 \text{ s}$$

$$t = 1800 \text{ s}$$

$$t = 0.5 \text{ hr}$$

+

$$\bar{x}_n = 0.2 \cdot 10^{-6} \text{ m} \cdot \left( \frac{10^7 \frac{\text{cm}^3}{\text{cm}^3}}{10^6 \frac{\text{cm}^3}{\text{cm}^3}} \right)^{\frac{1}{3}} = 4.309 \times 10^{-7} \text{ m} \quad 0.439 \mu\text{m}$$

+

## 9.4 General Dynamic Equation

Population balance for particles

$$\frac{dn(v)}{dt} = D \nabla^2 n(v) - \bar{U} \cdot \nabla n - \nabla \cdot (n \bar{V})$$

Accumulation      Diffusion      convection      migration

$$+ \left( \frac{dn(v)}{dt} \right)_{nucl} + \left( \frac{dn(v)}{dt} \right)_{coag} + \left( \frac{dn(v)}{dt} \right)_{cond}$$

where

$$\left( \frac{\partial n(v)}{\partial t} \right)_{nucl} = R_N \cdot \delta(v^*)$$

$$\left( \frac{\partial n(v)}{\partial t} \right)_{coag} = \frac{1}{2} \int_0^v b(v', v-v') n(v') n(v-v') dv' - n(v) \int_0^\infty b(v, v') n(v') dv'$$

$$\left(\frac{\partial n(v)}{\partial t}\right)_{cond} = -\frac{\partial I}{\partial v}$$

where  $I$ : particle current

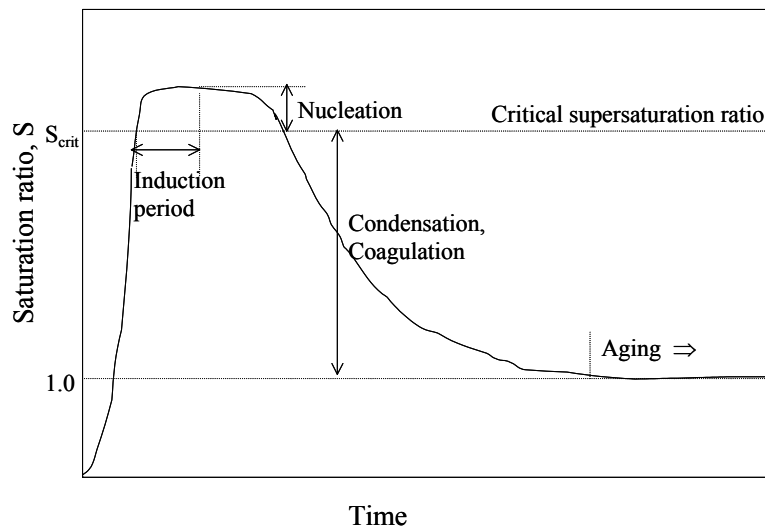
the number of particles per unit time per unit volume of gas passing the point  $v$

Since  $I(v) \approx n(v) \frac{dn}{dt}$

$$\left(\frac{\partial n(v)}{\partial t}\right)_{cond} = -\frac{\partial \left( n(v) \frac{dn}{dt} \right)}{\partial v}$$

## 9.5 Some Comments on Particle Growth

### (1) Overall Growth



### (2) Effect of Growth Mechanisms on Particle Size Distribution

#### Nucleation

- Increase of particle number concentration
- Gives delta function in particle size distribution in given condition
- May cause accelerating the rate of coagulation

#### Condensation

- No effect on particle number concentration
- Results in monodisperse size distribution.

### Coagulation

- Decreases in particle number concentration
- Gives polydisperse size distribution in growth process

### **(3) Formation of Monodisperse Particles**

- Maintain low rate of nucleation using low supersaturation
- Induce heterogeneous nucleation
  - \* Matijevic's method
- Allow the same growth time for all the particles by shortening the time of nucleation
- Suppress coagulation
  - Using electrostatic repulsion (electrical double layer)
  - Using adsorption of surfactants and macromolecules
  - Rapid cooling followed by rapid dilution
- Use of Ostwald ripening (not for oxides)

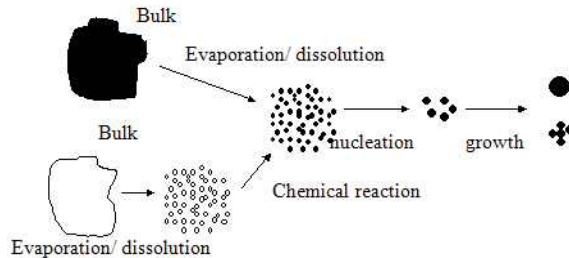
## **9.5 Formation Methods of Nanoparticles**

### **(1) Introduction**

- \* Keys for NP preparation
  - Formation of high-degree supersaturation in narrow time or space
  - Suppression of aggregation
  - Monodisperse growth- diffusion-controlled growth/Ostwald ripening
- \* Classification of preparation methods
  - In terms of phase of medium for preparation
    - Gas / liquid / aerosol / solid phases
  - In terms of method of "monomer" preparation

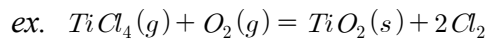
Physical/ chemical

**(2) Gas-phase preparation**



- Rapid increase in concentration of condensable vapor component by

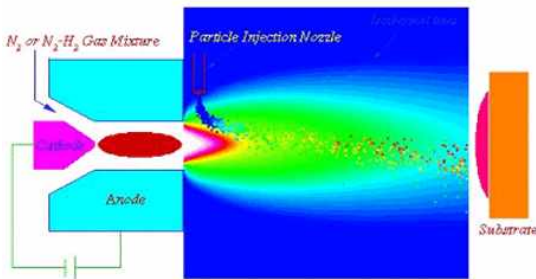
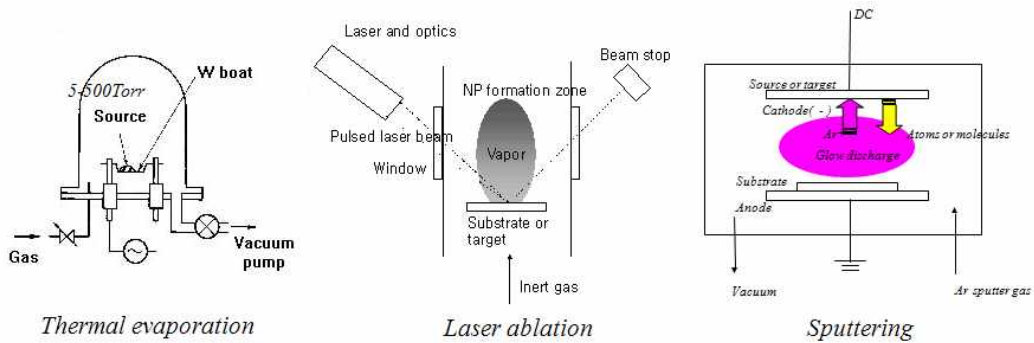
- Vaporization/Sublimation: physical
- Chemical reaction



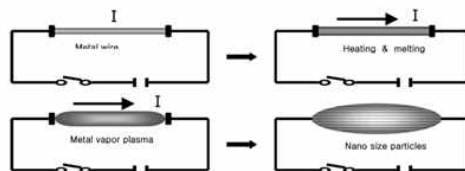
· Needs energy from hot wall, flame, laser, plasma...

- Followed by rapid cooling, expansion and dilution

**1) Physical Methods**

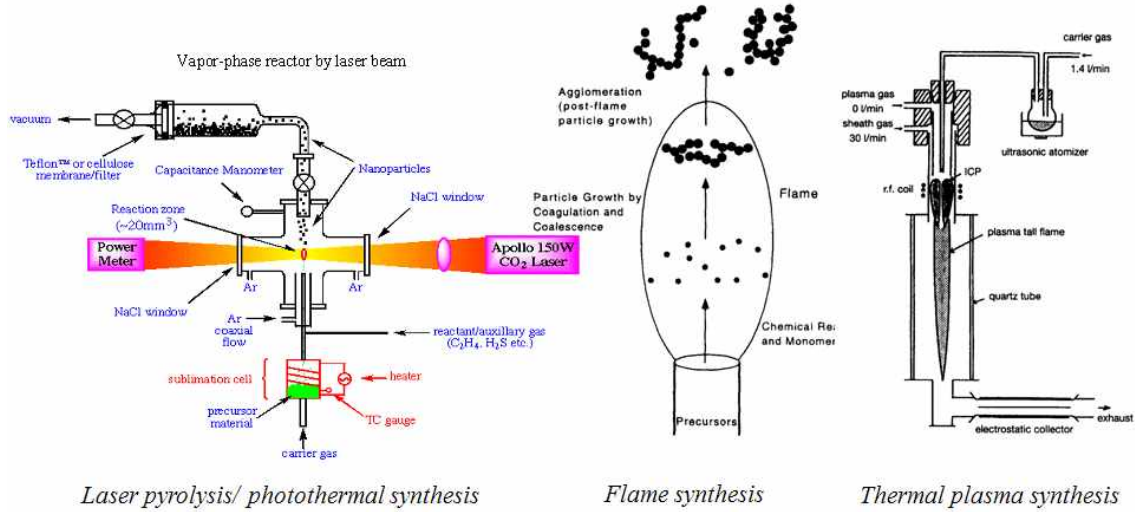
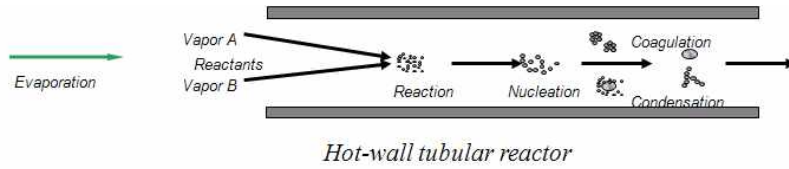


Arc plasma



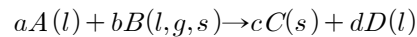
Electrical wire explosion

## 2) Chemical Methods



### (2) Liquid-Phase Preparation

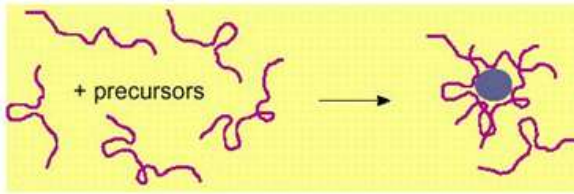
Mostly by chemical methods...



- If C: highly insoluble, high chances to form very small and so many nuclei
- Results in giant aggregates composed of nanoparticles due to its high concentration and low mean free path in liquid phase.
- Requires to suppress aggregation of the nanoparticles
  - Electrical double layer
  - Surfactants
  - Polymers
- Liquid-phase preparation:
  - Delicate close to art...but robust...
  - Involves many chemicals, many processes

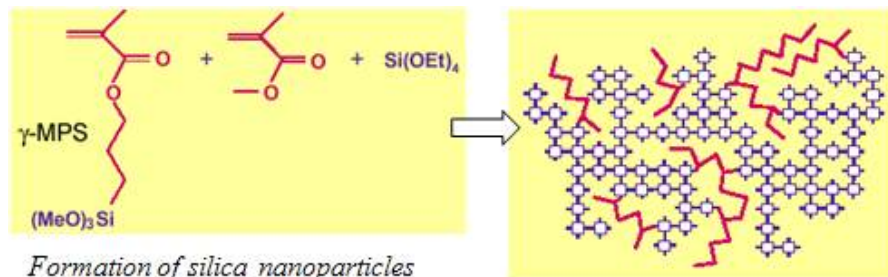
## 1) Formation with polymeric stabilizer

- In polymer solution



Iron oxide (left) without (right) with dextran

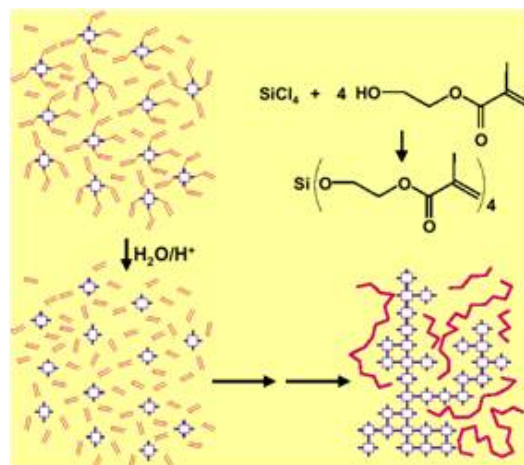
- With simultaneous polymerization



Formation of silica nanoparticles

$\gamma$ -MPS =  $\gamma$ -methacryloyloxypropyl-trimethoxysilane

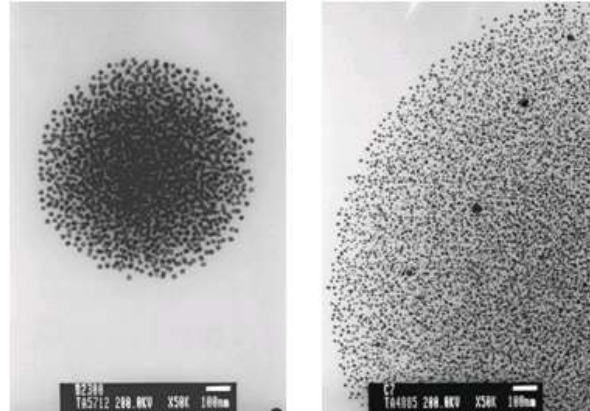
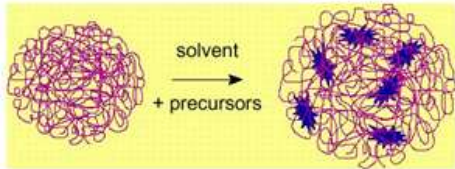
- From a single precursor for nanoparticles and polymer



Formation of silica nanoparticles

## 2) Confined growth

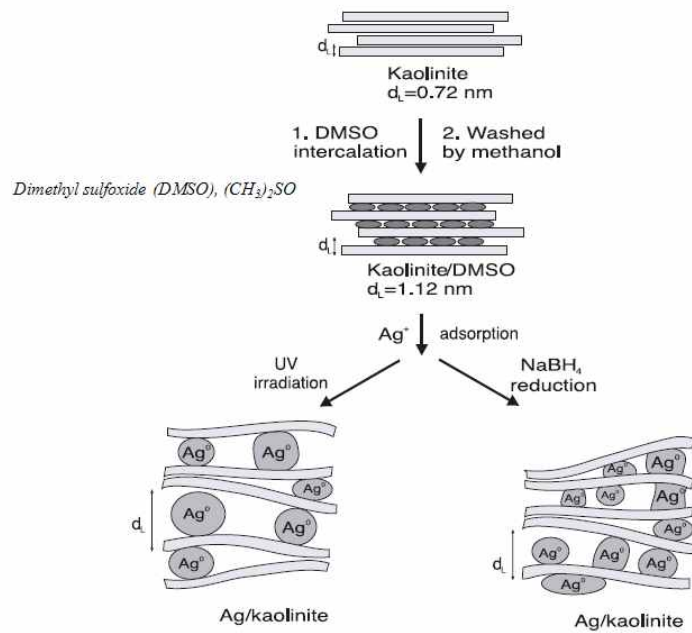
- In polymer matrix



Silver NP in PVP matrix

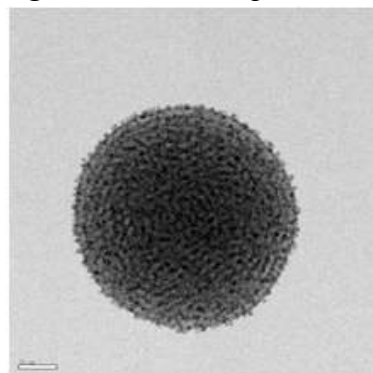
- In layered materials

e.g. kaolinite ( $Al_2Si_2O_5(OH)_4$ )



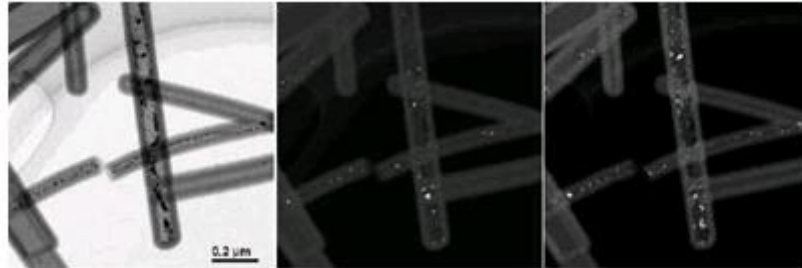
- In porous materials

e.g. zeolites, mesoporous silica



Silver NP in mesoporous silica

- In nanotubes



*BF, DF and conical DF image of Pt particles inside of SiO<sub>2</sub>-NTs*

- Preparation of nanoparticles in microemulsion

### **3) Sol-Gel Methods**

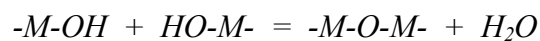
#### Precursors

- Metal alkoxides,  $M(OR)_z$ , in organic solvent
- Metal salts (chloride, oxychloride, nitrate..) in aqueous solution

#### Basic mechanism



- Polycondensation

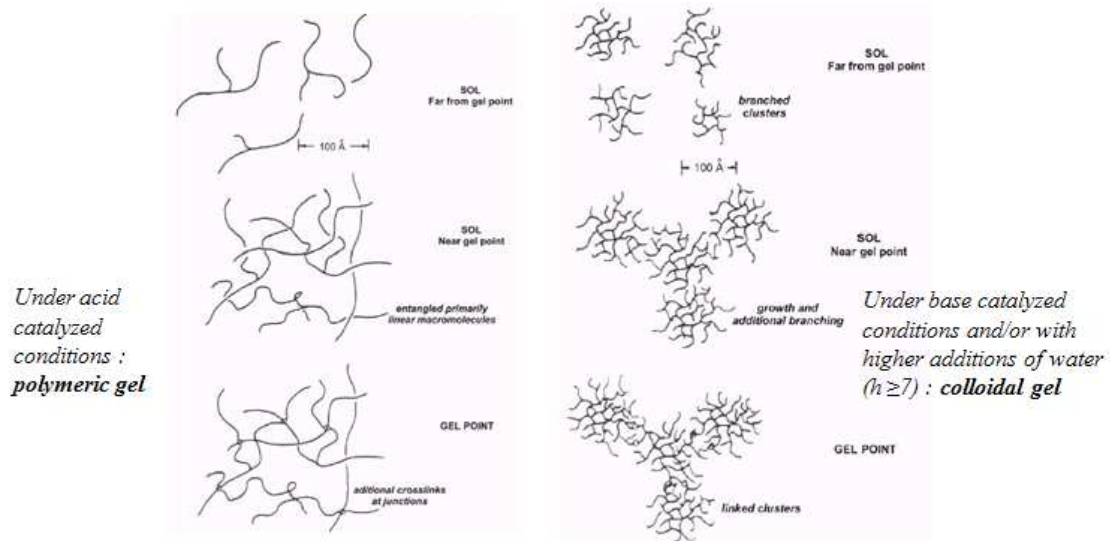


- Occurs sequentially and in parallel
- Usually  $M(OR)_n$ ,  $n > 1 \rightarrow$  three-dimensional structures...

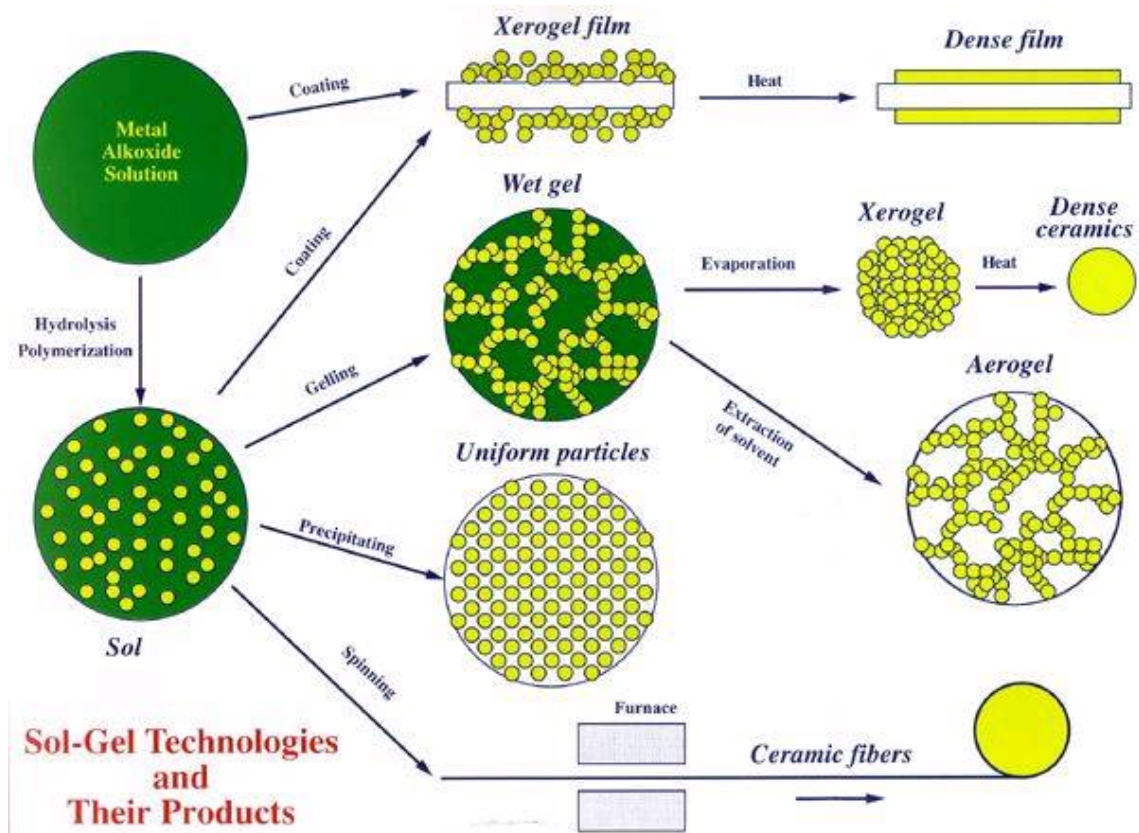
#### Gel formation

e.g. Sol-gel transformation for silica





Supercritical extraction → aerogels  
 cf. xerogels



### Characteristics of aerogels

*Porosity: 75-99%*

*Specific surface area:  $\sim >1,000\text{m}^2/\text{g}$*

*cf. porosity of xerogel: 1-50%*

- *Very light, transparent*
- *Used in catalysts, sensor, electrodes, thermally and/or electrically insulating materials*

