



UNIVERSITY OF ROME "LA SAPIENZA"
NANOTECHNOLOGIES ENGINEERING

NANOPARTICLES SYNTHESIS

SYNTHESIS IN LIQUID PHASE

- The synthesis in liquid phase are those most used for the nanoparticles production.
- The critical step to nanoparticles formation is performed in the liquid phase.
- The most common solvent is (pure) water, but also organic solvents in order to inhibit agglomeration may find application.
- A synthesis in liquid phase is also called “wet chemical synthesis”.

SYNTHESIS IN LIQUID PHASE

Compared to solid and gas phase, the synthesis in liquid phase has some advantages:

- a) The scale-up of the process is easy;
- b) The production process is more suitable for control since knowledge of chemical reactions in liquid phase is high;
- c) The operating conditions, that is low temperature and pressure, may be achieved at low costs and simple equipment;
- d) It is possible to address the production to a predetermined modal particle size;
- e) It is possible to add to the reaction other elements or compounds that may inhibit or eliminate agglomeration;
- f) The CSD is controlled by performing the nucleation in homogeneous systems, inhibiting growth and agglomeration.

SYNTHESIS IN LIQUID PHASE

These targets may be achieved:

- a. The modal dimension and particle shape;
- b. Uniform particles dimension;
- c. Purity, that is the chemical composition of the particles;
- d. crystallinity;
- e. The formation of core-shell particles, that is a composite particle characterized by a core and a shell made of different materials.

These properties sensibly changes the functionality of ceramics.

SYNTHESIS IN LIQUID PHASE

Classification:

- Chemical precipitation and co-precipitation;
- In sol-gel;
- hydrothermal;
- in microemulsions or inverted micelles;
- In non aqueous solutions;
- Assisted by microwaves or ultrasound;
- electrochemical;
- in supercritical fluids.

CHEMICAL PRECIPITATION AND CO-PRECIPITATION

- The nanoparticles are produced by the precipitation of solids after chemical reaction where the product is in supersaturated conditions.

Being M_1 e A the reactants, the reaction is:



- The presence of more metals may give rise to different solids composition, such as:



where M_1M_2A is a mixed metal oxide of two metals.

EXAMPLES

Nanoparticles	Carateristics	Purposes
CrO ₂	5nm, spherical	Raman shift
ZnO	1000 nm, agglomerated	Pigment
Fe ₂ O ₃	Spherical	Magnetic material
HAP	10 nm, prismatic	Medical prothesis
SbO ₂	200nm, polycrystalline	Flame retardant, optics, humidity sensors

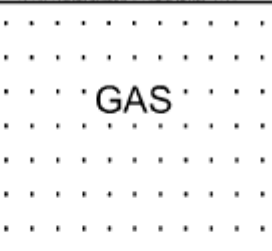
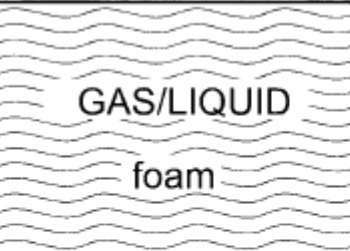
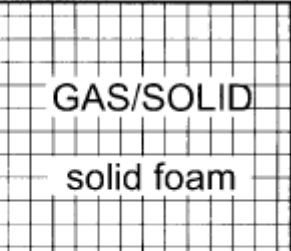
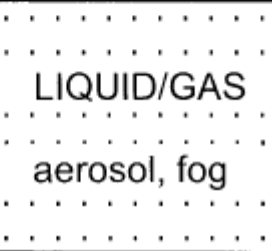
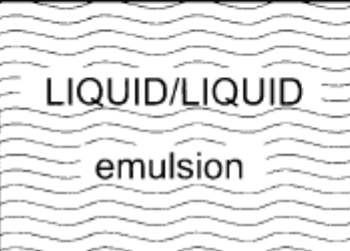
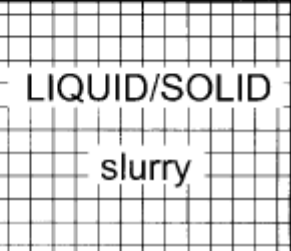
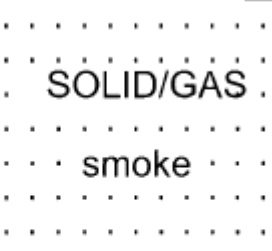
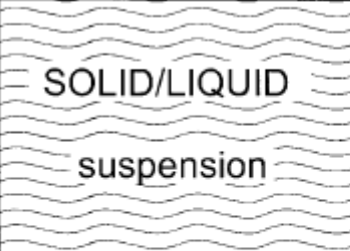
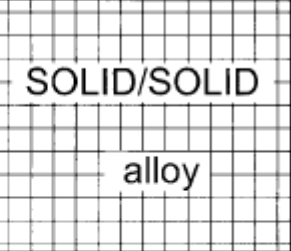
REDUCTION OF THE AGGLOMERATION PHENOMENA

Can be obtained by:

- Chemical stabilizers such as polyvinylpyrrolidone (PVP), polyvinylalcohol (PVA) and polyacrylic acid (PAA).
- Non aqueous solvents:
 - Aqueous solutions of ethanol and Ethylglycole (EG) are used to produce colloidal oxides of different morphology.
 - In particular EG offers two advantages: a high dielectric constant which increases the solubility of inorganic salts and a high boiling point (195 °C at 1 bar) which permits to work at relatively high temperatures

COLLOIDAL DISPERSIONS

- ❑ Colloids are biphasic systems where a dispersed phase, for example a powder, is homogeneously distributed in a bulk phase (gas or liquid).
- ❑ A “sol” and “emulsions” are the most relevant colloidal dispersions.
- ❑ A sol is a solid dispersion of particles less than 1000 nm stabilized in the bulk which do not allow any sedimentation.
- ❑ The emulsions are small liquid drops dispersed in a liquid, not miscible bulk.

disperse phase	gaseous	 <p>GAS</p>	 <p>GAS/LIQUID foam</p>	 <p>GAS/SOLID solid foam</p>
	liquid	 <p>LIQUID/GAS aerosol, fog</p>	 <p>LIQUID/LIQUID emulsion</p>	 <p>LIQUID/SOLID slurry</p>
	solid	 <p>SOLID/GAS smoke</p>	 <p>SOLID/LIQUID suspension</p>	 <p>SOLID/SOLID alloy</p>
		gaseous	liquid	solid
		continuous phase		

Examples	Class	Disperse phase	Continuous phase
<i>Disperse systems</i>			
fog, spray, vapor, tobacco smoke, aerosol sprays, flue gases	liquid or solid aerosols	liquid or solid	gas
milk, butter, mayonnaise, asphalt, cosmetic creams	emulsions	liquid	liquid
inorganic colloids (gold, silver iodide, sulfur, metallic hydroxides)	sols or colloidal suspensions	solid	liquid
clay, mud, toothpaste	slurry	solid	liquid
opal, pearls, colored glass, pigmented plastics	solid dispersions	solid	solid
foam	liquid foams	gas	liquid
meerschaum mineral, foamed plastics	solid foams	gas	solid
<i>Macromolecular colloids</i>			
jelly, glue	gel	macromolecules	solvent

SOL-GEL METHOD

- This method is known since the 17th Century and found industrial application from 1930.
- Colloidal sol is a suspension of tiny solid particles (10–1000 nm) where sedimentation occurs slowly but dominated by electrostatic forces such as Van der Waals.
- The synthesis by sol-gel has been developed recently due to the ease of production ceramic nanoparticles.
- Generally, a liquid phase is pushed to a transition to a gel phase, which is a organized structure similar to a solid by polymerized macromolecules which entraps the liquid suspensions containing the nanomaterial, which results to be suspended in the gel matrix characterized by a stable positions and avoiding agglomeration.

SOL-GEL SYNTHESIS

- The starting materials are commonly a organic salt of a metal (alkoxide) dissolved in organic matrix.
- Water and alkoxide are not miscible, therefore a organic matrix is required in order to permit mixing.
- The process requires the presence of a catalyst such as a mineral acid, HCl or HNO_3 or a base, ammonia.
 - The acid catalytic processes leads to the formation of structured polymers able to form the gel structure and/or capabilities for the coating.
 - The base catalytic processes forms clusters with many lateral chains which transforms to particles.

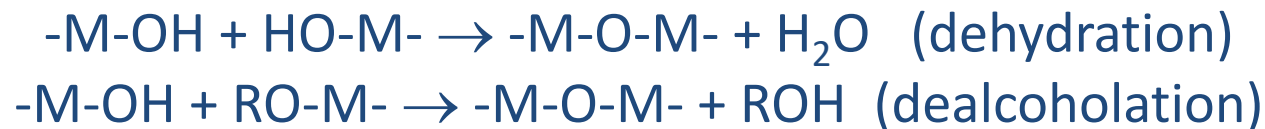
SOL-GEL

- Hydrolysis of an alkoxide giving rise by a hydrolysis reaction is the first step of the production process:



where R is the alchilic group.

- Following to this, the condensation reaction leads o the metal oxide by dehydration or dealcoholation:



- The condensation reactions may be controlled by modifying chemically the bulk, such as the addition of chelants (acetylacetone), acids, polyols and so on.

SOL-GEL

- The overall process is therefore given by these steps in series:
Hydrolysis → Polymerization (Condensation) → Nucleation → Growth
- The solute organizes small clusters (“sol”) in the matrix and parallel to this, condensation develops the produced sol in organized chains that entraps the liquid giving rise to a “gel phase. The sol is now entrapped by the gel structure and therefore sedimentation will not occur.
- The gel reactions will not stop at the gel point, since a certain amount of polymers will be formed during the metal oxide reaction process and thus adds to the polymer concentration., therefore promoting further network formation.
- The gel properties are a function of time, and depends from aging.

SOL-GEL

By aging the gel network develops to equilibrium, changing pore size, solid precipitation, shear, humidity and volume given by cross-links.

ACID



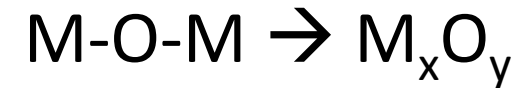
BASE



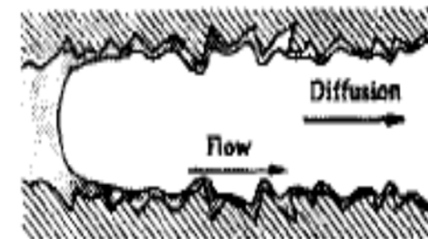
The sol-gel material may be used for coating purposes, or to the ceramic material by drying.

DRYING OF SOL-GEL MATERIAL

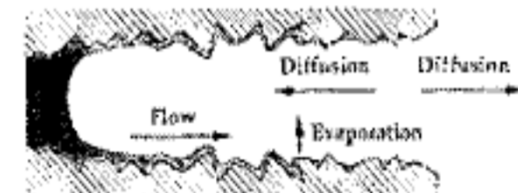
The drying process, required to take the liquid away from the gel network and to permit the solidification of the latter, is performed by some steps in series.



- 1) At the beginning the gel will shrink to a reduced volume, due to evaporation of the liquid near the surface and/or by internal shrinkage forces forcing liquid outside the gel mesh.
- 2) A critical point is reached where the liquid-ambient interface in the pores is in equilibrium with the driving forces.
- 3) At this point, the interface will travel back in the pore leaving a film that will continue to evaporate
- 4) Evaporation is finally limited internally to the gel.



Funicular Pendular



TiO₂ sol-gel production

- Hydrolysis:

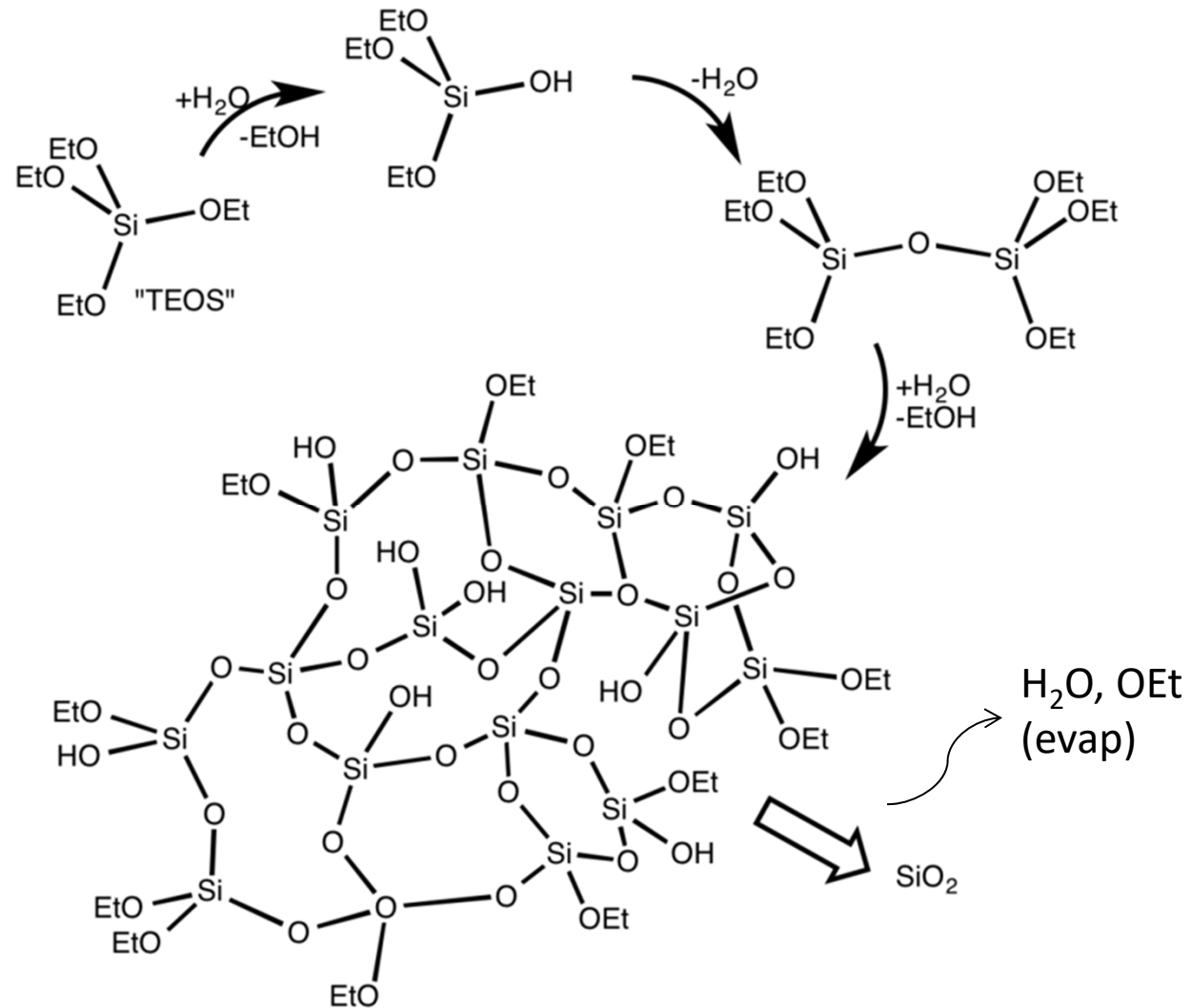


- Condensation:



After drying: TiO₂

SiO₂ sol-gel production



ADVANTAGES OF THE SOL-GEL PROCESS

- The parameters affecting the hydrolysis and condensation reactions and thus the sol-gel structure are: pH, T, t, reactant concentration, the ratio of the reactants, the nature of the catalyst, aging and drying. The process is therefore versatile.
- No dust and/or pollutants
- The formation of advanced materials at molecular level
- Organic-inorganic hybrid materials

EXAMPLES

Material	Characteristics	Process
SiO ₂	Amorphous	Hydrolysis by ammonia and condensation by hydroalkoholic solutions
TiO ₂	5-12 nm	Hydrolysis by Ti alkoxides
ZnO	3-5 nm, agglomerates	Diethyl zinc, ter-buthilalcohol, ethanol, water

Company

CHEMAT TECHNOLOGY

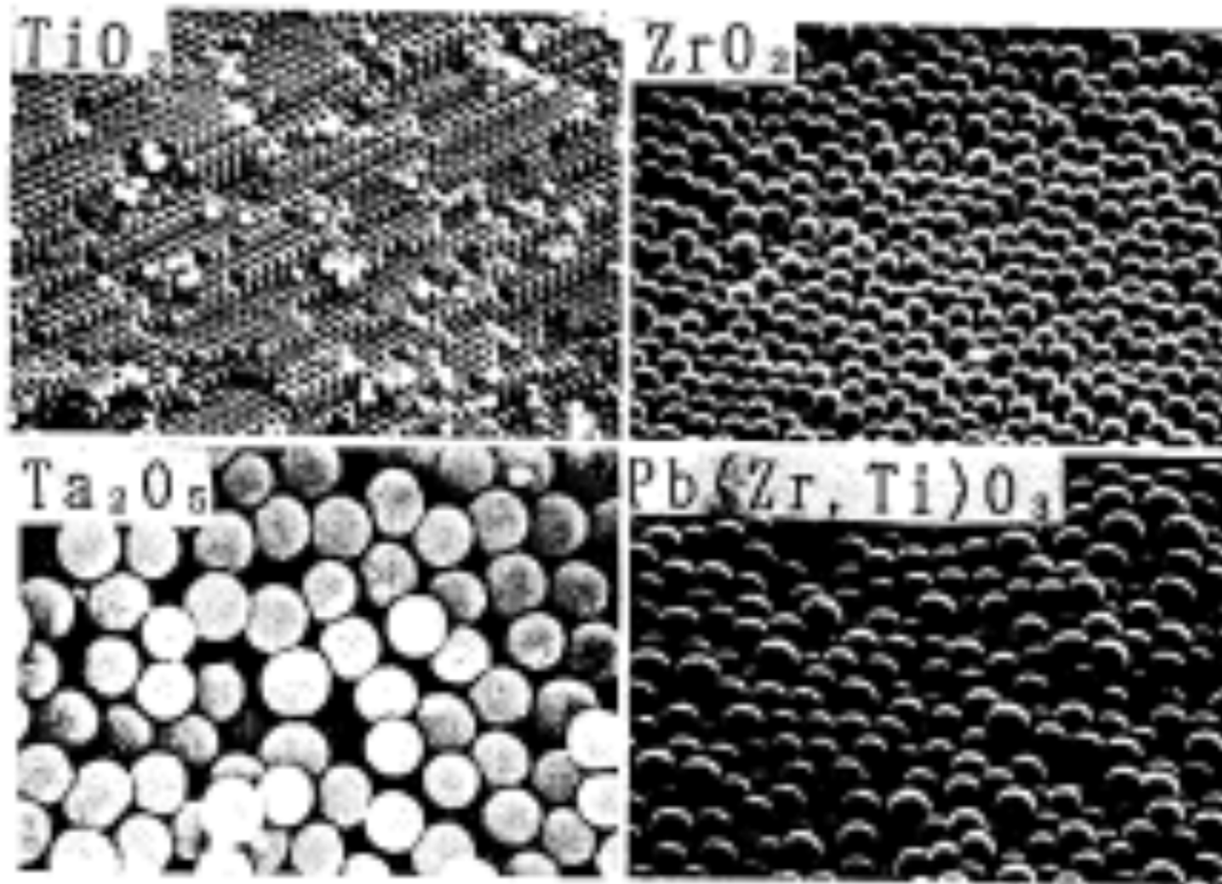
NANO-X

Market

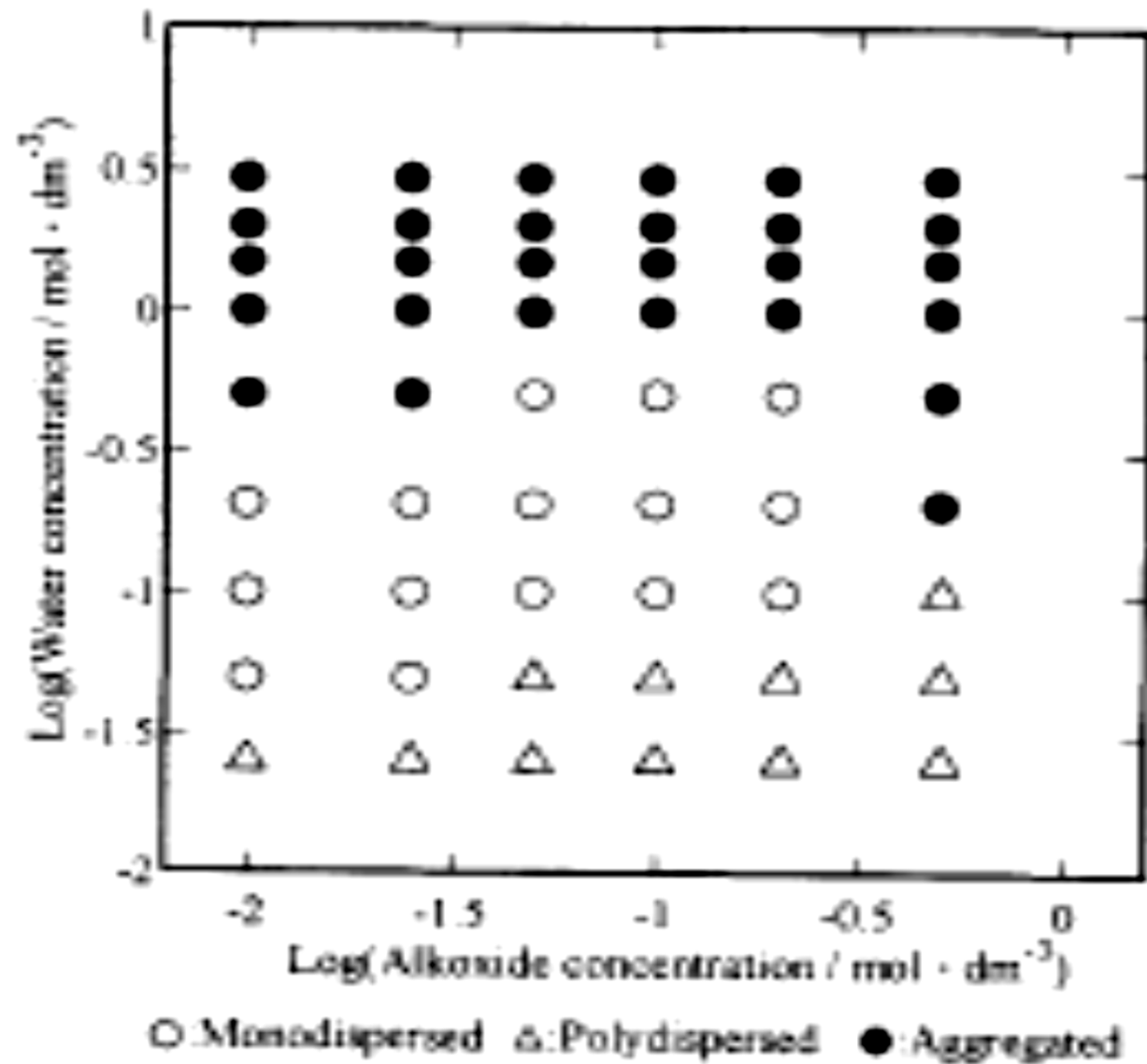
Production of many sol-gel precursors. Has developed processes to coat anti reflective glasses.

Coating by sol-gel methods.

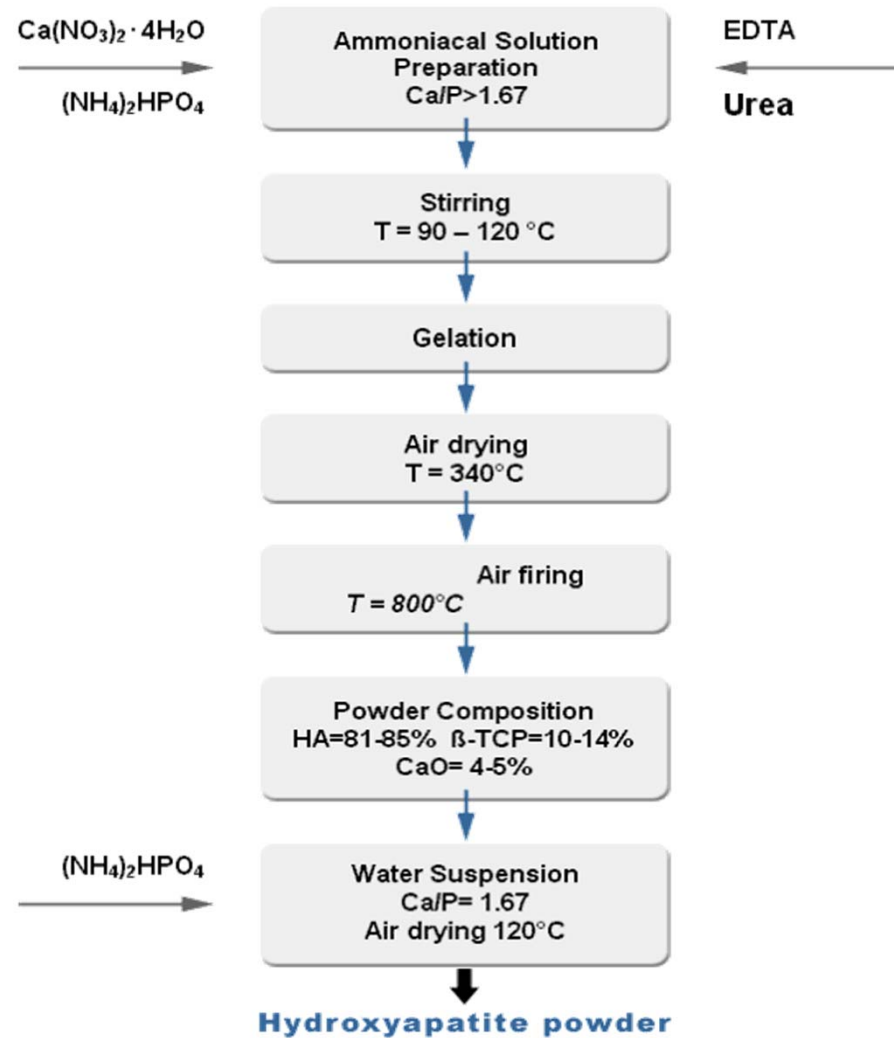
PARTICLES PRODUCED BY SOL-GEL



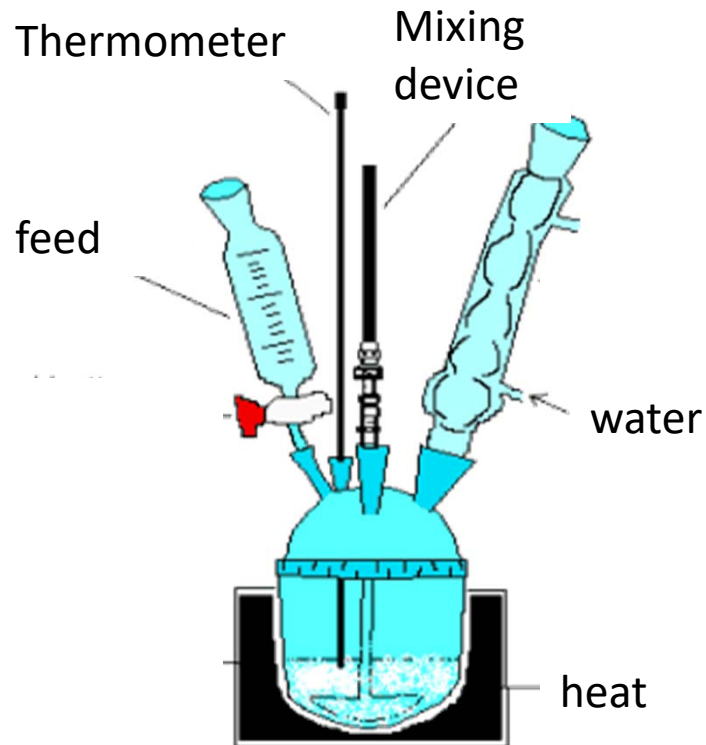
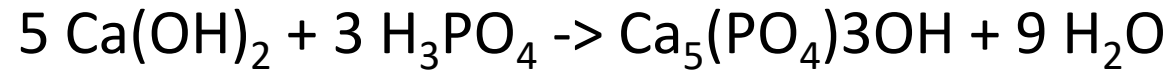
EFFECT OF REACTANT CONCENTRATION ON GEL PHASE



SOL-GEL FOR HAP PRODUCTION



HAP SYNTHESIS



Production steps

1. Reaction (precipitation)
2. Filtration
3. Freeze drying

SOL-GEL: APPLICATIONS

- **Coating:** of granules for adsorption processes, glass (anti reflex, hydrophobic), support for photocatalysis...
- **Nanoparticles:** pure or composite for chemical and medical applications.
- **Solar cells:** a micron tall layer is used for the production of Die Sensitized Solar Cells.
- **Catalysis:** production of high quality catalysts.

GLASS COATING BY SOL-GEL TiO_2

OBJECTIVES:

- Production of self cleaning glasses (contact angle at 90°)
- Production of hydrophobic surfaces (contact angle greater than 90°)



1. TTIP in isopropanol in a ratio of 1/5 is prepared. Glass is put in contact (bath) with this solution.
2. dip-coating of the surface is performed taking care about the humidity (presence of water) in the atmosphere.

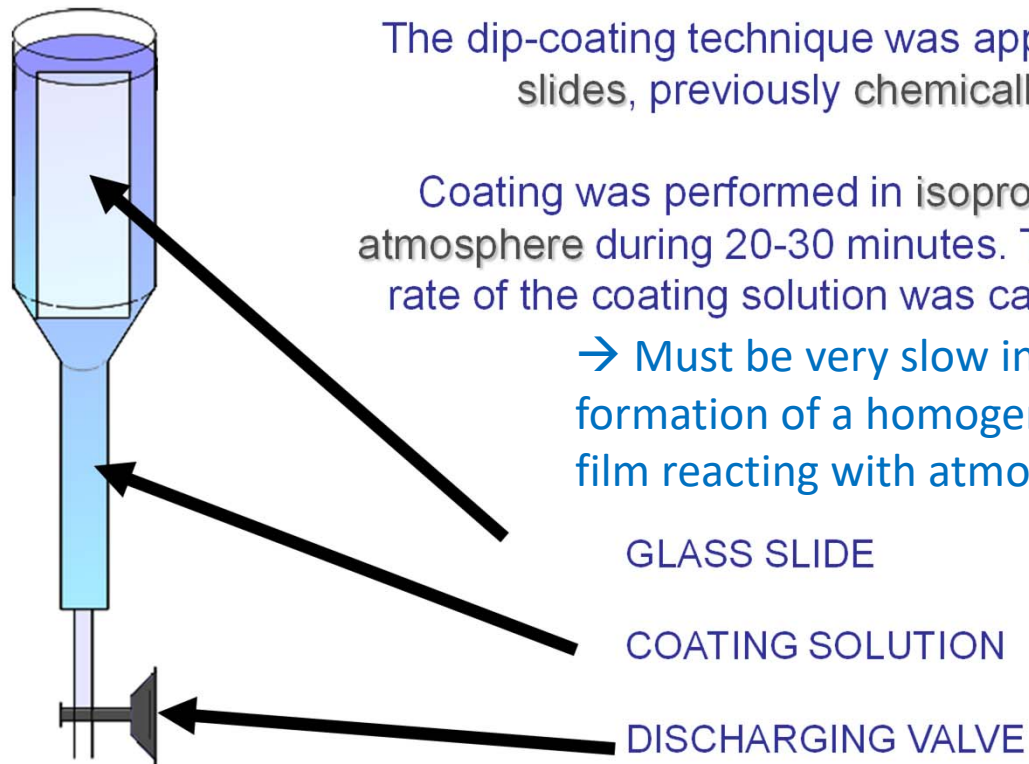
DIP-COATING

DIP-COATING OF GLASS

The dip-coating technique was applied to coat glass slides, previously chemically cleaned.

Coating was performed in isopropanol saturated atmosphere during 20-30 minutes. The downward flow rate of the coating solution was carefully controlled.



→ Must be very slow in order to permit the formation of a homogeneous, continuous liquid film reacting with atmosphere.



COMPARISON OF THE SOL-GEL MATERIAL FROM DIFFERENT REACTORS

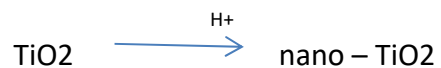
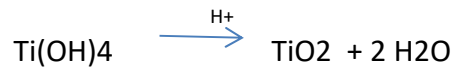
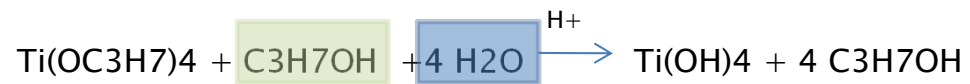
	SPINNING DISC REACTOR	STIRRED TANK REACTOR
Operating conditions	1440 RPM	1500 RPM
Contact angle without UVB radiation	83°	65°
Contact angle after UVB radiation	58°	43°

COMPARISON OF THE SOL-GEL MATERIAL FROM DIFFERENT REACTORS

	SPINNING DISC REACTOR	STIRRED TANK REATOR
Operating conditions	1440 RPM	1500 RPM
The coated layer observed with an optical microscope (zoom 40x)		

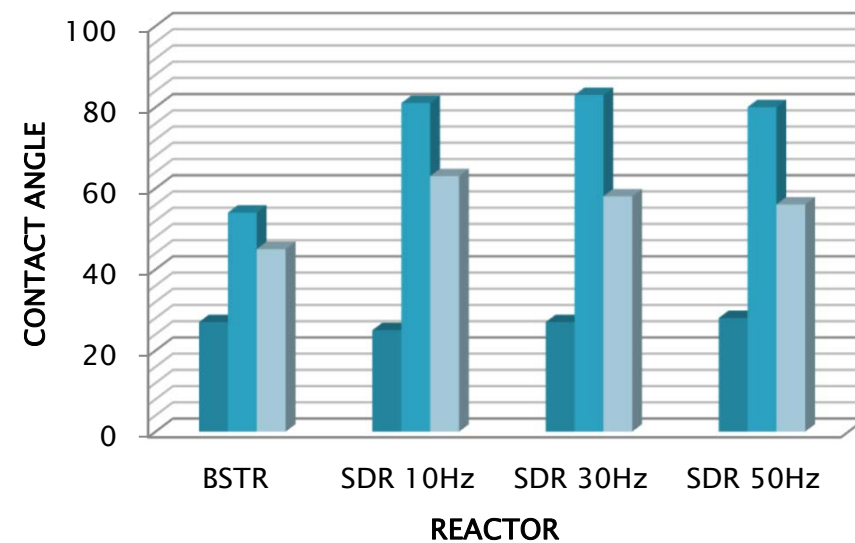
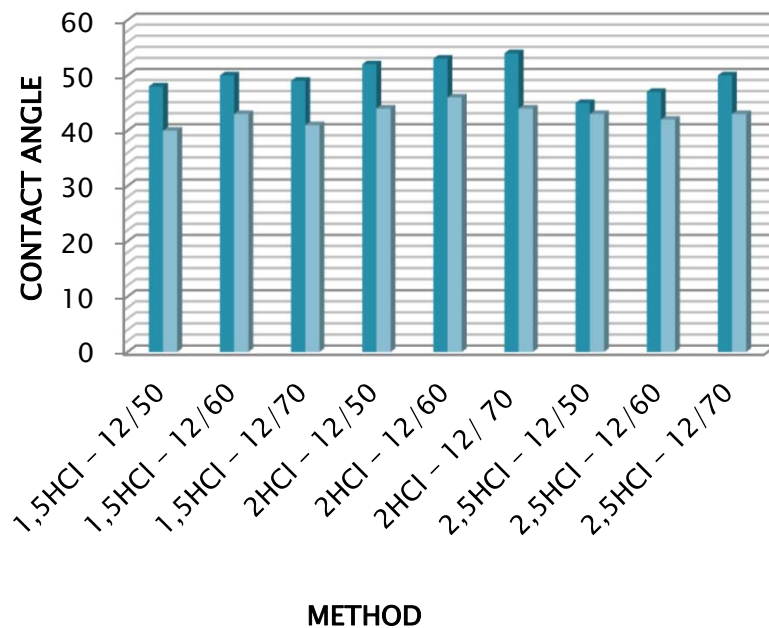
SELF CLEANING GLASSES

sol gel for coating:



Coated glass:

no UV
with UV



HYDROTHERMAL SYNTHESIS

- The hydrothermal process, called thermal hydrolysis process, concerns:
 - an aqueous solution with a metallic salt or metallic organic;
 - the heating in an autoclave of a precursor such as sol-gel material.
- The hydrothermal reaction of metallic ions is as follows:



- In detail, the relevant reaction follows the stoichiometry of a particular reaction of forced hydrolysis, coordinated by the presence of the metal ion and forces water to divide:



- After this, the hydroxide divides in water and the oxide:
 $M(OH)_z \rightarrow MO_z + z H_2O$

HYDROTHERMAL SYNTHESIS

- At high temperatures, the forced hydrolysis may happen even without the presence of an acid or a base.
- A moderate temperature increase with a fixed initial pH value have influence of the reaction of the metal ion and the subsequent complex formation.
- The pH value normally decreases due to the deprotonation of the metal ion and metal oxides may form by oxidation of the hydroxides.
- There is a continuous production of ions during the hydrothermal process.

OPERATING CONDITIONS

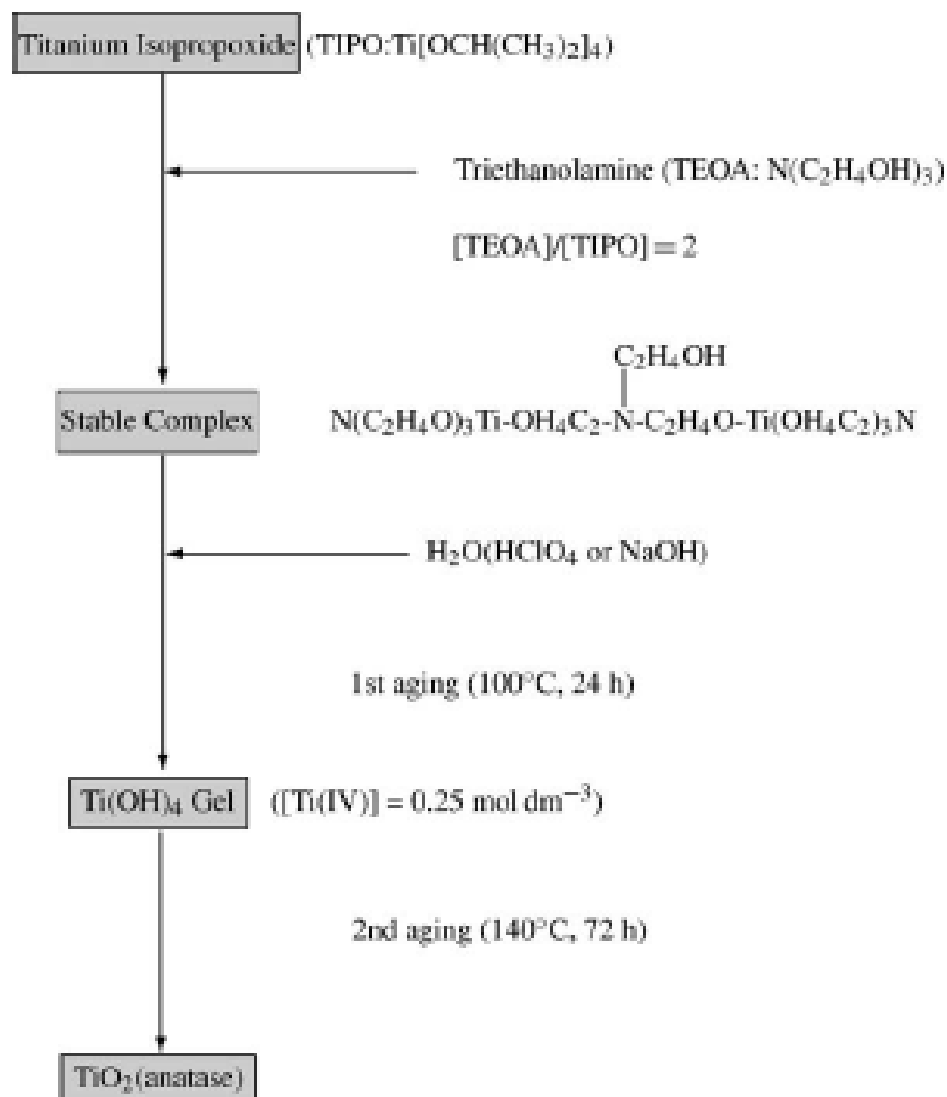
- The forced hydrolysis requires an acid solution of a metallic salt at a certain concentration, which will be heated in order to promote hydroxides by deprotonization of water.
- The coagulation of the particles is avoided by the electrostatic forces due to the low ionic force of the solution.
- The process is dependant of the pH values, the concentration of the reactants, T and the presence of anions: the latter ones are the main responsible of the morphology of the produced particles.
- Cations may hydrolyze weakly, and requires the addition of weak base such as urea in order to promote and accelerate the reactions.

OPERATING CONDITIONS

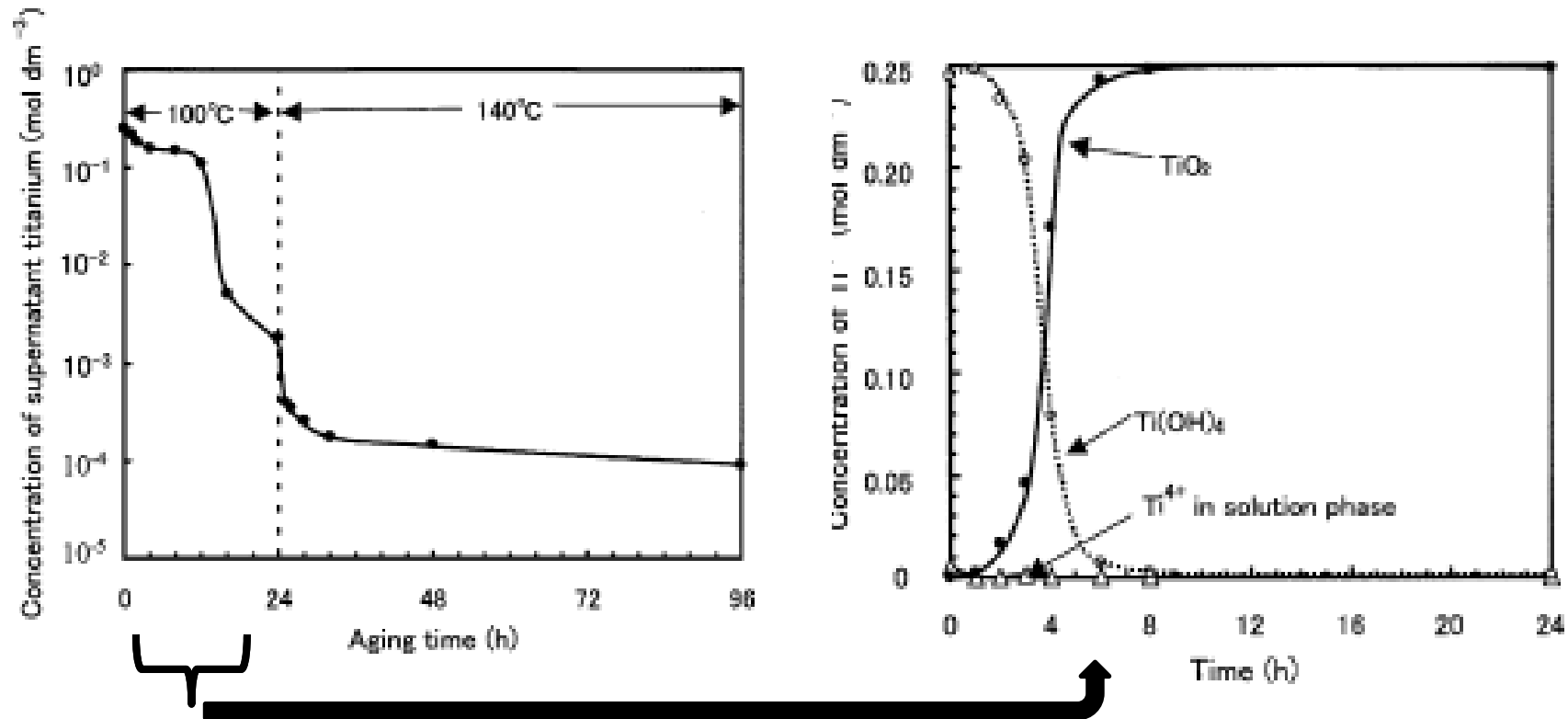
Most processes uses water as a solvent!

- But: the process may be used in the presence of other solvents such as pioils or hydroalcoholic solutions. The addition of alcohol has an effect on the formation of the particles (nucleation and growth) and, as a consequence, on the morphology.
- The heating for this process may be provided by microwaves, which normally increases the temperature very fast and thus increases the precipitation kinetics.

TiO₂ PRODUCTION PROCESS



TiO₂ TRANSFORMATION DURING THE HYDROTHERMAL PROCESS



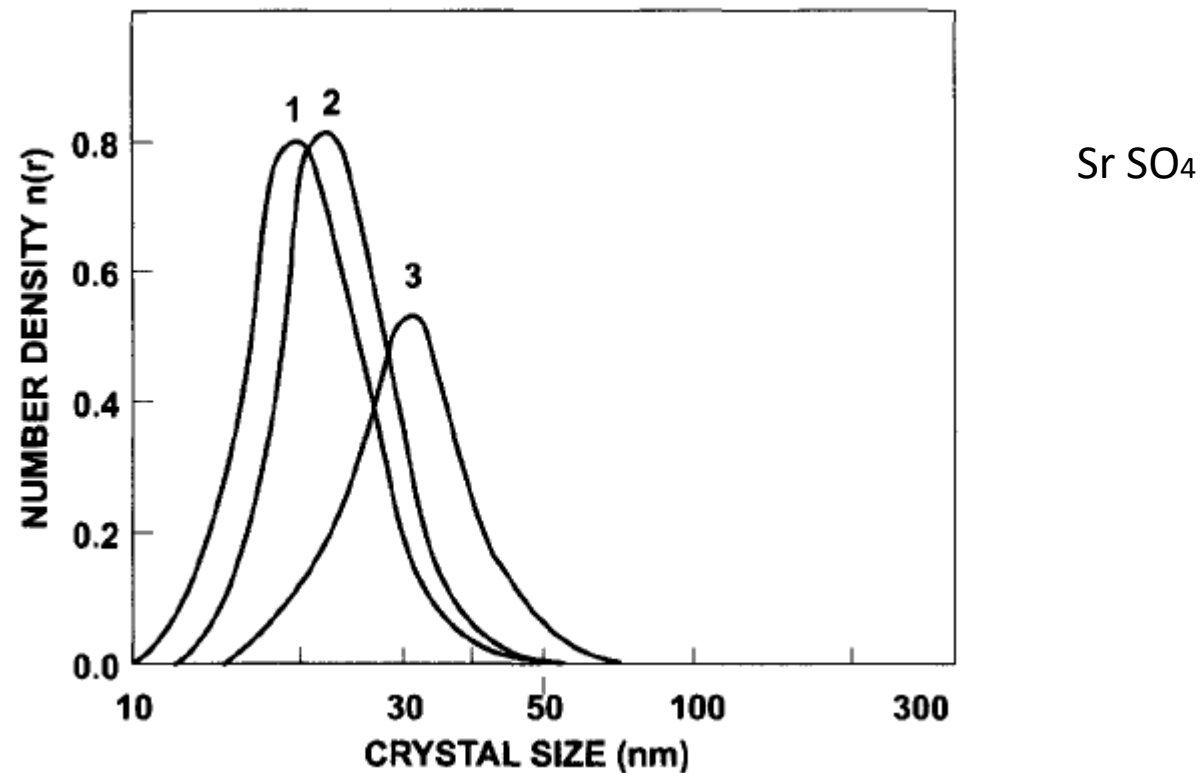
The transformation of TTIP is strictly connected to the reduction of the supersaturation value of Ti⁴⁺

Hydrothermal processes for suspension stabilization

- The hydrothermal process can also be used to homogenize the particle size distribution of a sol-gel material.
- As ease of an example, a suspension of titania for coating purposes can be treated by a hydrothermal process at 200°C for some hours. At the end of the process, a stable colloidal solution is obtained, and the particle size is around 100nm. The phenomena underlying the process is that of particle repining, that dissolves the smaller particles to permit the growth of the larger ones.
- If the solvent has a boiling point less than the operating temperature, a pressurized reactor must be used. At 200°C water reaches a pressure of 20 ata.

OSTWALD RIPENING

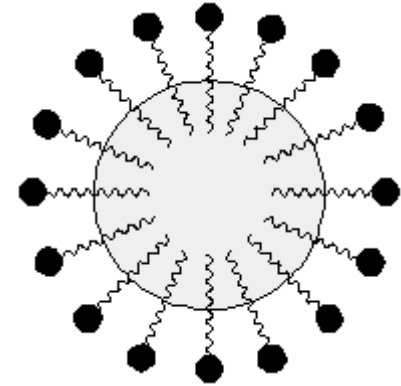
When smaller crystals are dissolved (again), the relative small supersaturation forming assists the crystal growth of bigger crystals in the solution.



1 CSD initial, 2 after 45 minutes, 3 after 60 days,

MICELLES

A micelle is an aggregate of molecules in colloidal phase, with surfactant properties, having both hydrophilic and hydrophobic functional groups.



The aggregates may form at temperatures equal or higher than those required to critically dissolve the surfactant, that is at such a concentration required to form micelles (CMC – critical micelle concentration)

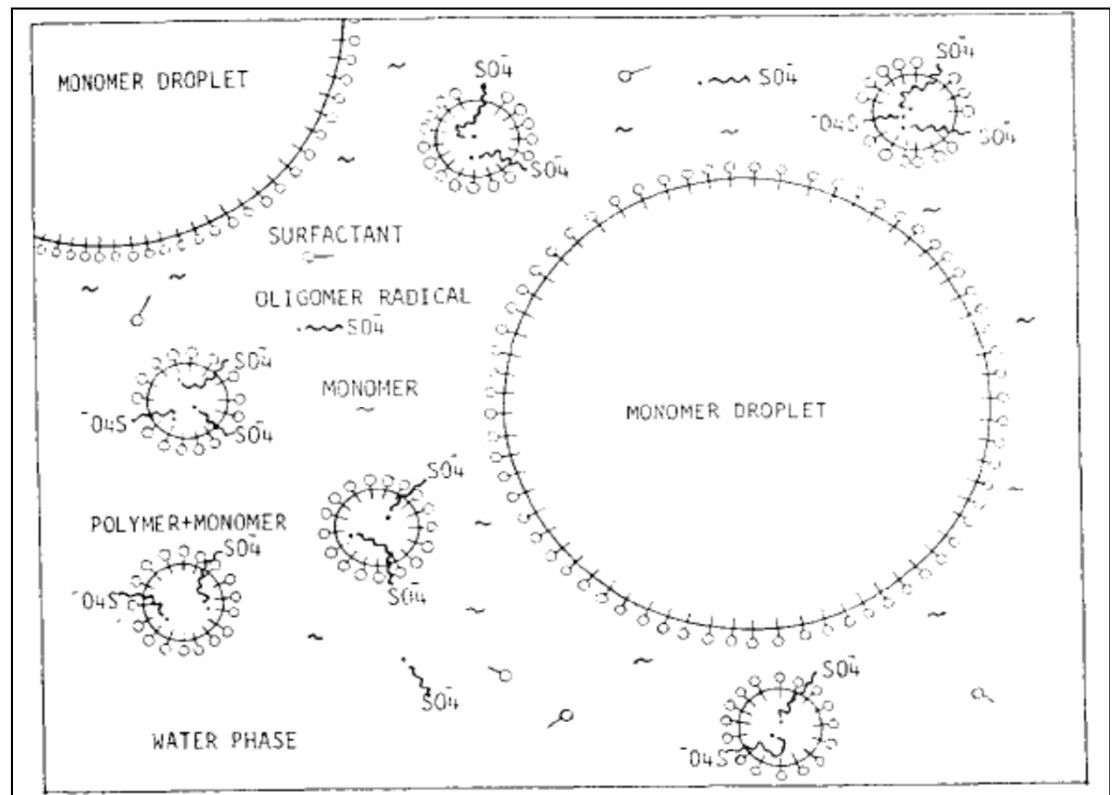
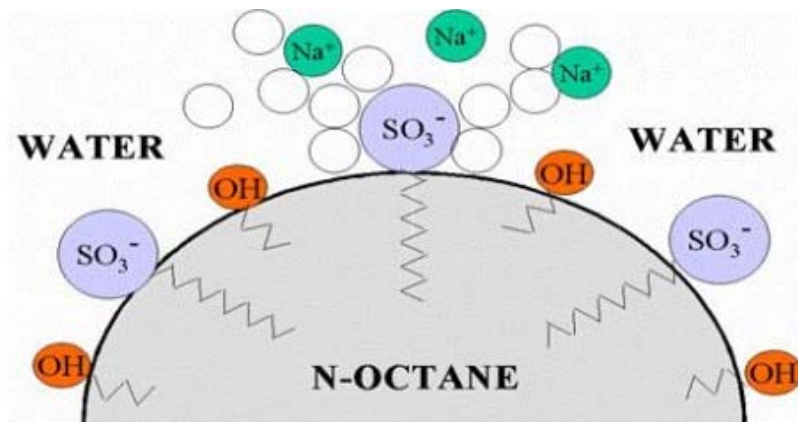
In a first step, adding to water a surfactant, micelles are not immediately formed if the CMC value is not exceeded. In this case, the surfactant will concentrate on the water-air interface, pointing with the hydrophobic group outside the water in air. Once the CMC is overcome, the surfactant will form the emulsion and are capable to include other molecules (oil, grease) in or in contact with the water, thus promoting the elimination of these particles.

MICROEMULSION SYNTHESIS

- The microemulsion is a stable dispersion of two immiscible liquid phases (10-100 nm) from a thermodynamic point of view, isotropic and not visible (such as oil in water or water in oil).
- The microemulsion take place as soon as a surfactants (or a mix of surfactants) assists the reduction of the surface tension to values which allows the spontaneous dispersion of the two phases by simple thermal effects.
- Conventional microemulsions such as micelles oil/water there is a constancy in the dimension and shape of the dispersed phase.
- In case of microemulsions, the dispersed phase exhibits changes in morphology by continuous breakage and coalescence motions.
- If the dispersed phase is given only by shear forces, the emulsion is called miniemulsion.

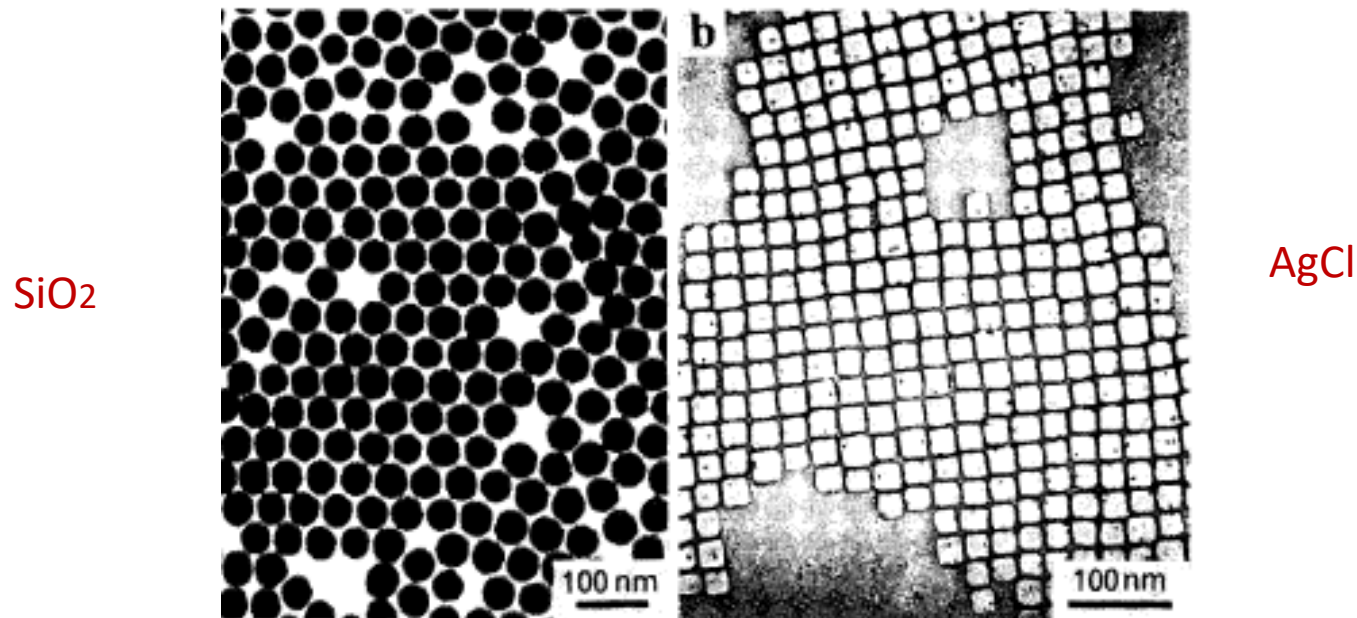
INVERSE MICELLES

- In the case of water in oil emulsions, the micelles will be inverted: the hydrophilic part will point the core (dispersed phase), whereas the hydrophobic part the bulk.
- Using for example oligomers in a oil in water emulsion, both structures may be observed: the surfactant giving rise to micelles, whereas the oligomer an inversed one, both co-existing. The philoorganic part of the oligomer will point to the core, whereas the hydrophilic part to the bulk, capable to polymerize.



MICROEMULSION SYNTHESIS

- The microemulsion synthesis is a recent technique in the framework of micro- and nanoreactors: it is possible to produce nanoparticles of metal oxides, coated nanoparticles, semiconductors and so on.
- The application permits to obtain very small nanoparticles.
- The success of this operation is the confined reaction volume that do not allow particle growth outside the nanoreactor, where the micelle represent the reactor wall.



MICROEMULSIONS

- The transfer of the solute in the micelle is permitted from the bulk, as long as the adsorbed layer on the micelle surface permits the passage.
- The surfactant forming micelles avoid a contact between the particles produced in single micelle, thus avoiding agglomeration.
- Productivities are very low.

- The process is a function of temperature, the concentration of surfactant and the ratio between the dispersed phase and the bulk.
- The required concentration of surfactant exceeding the CMC sensibly influences the morphology of the produced nanoparticles.

MICROEMULSIONS: EXAMPLES

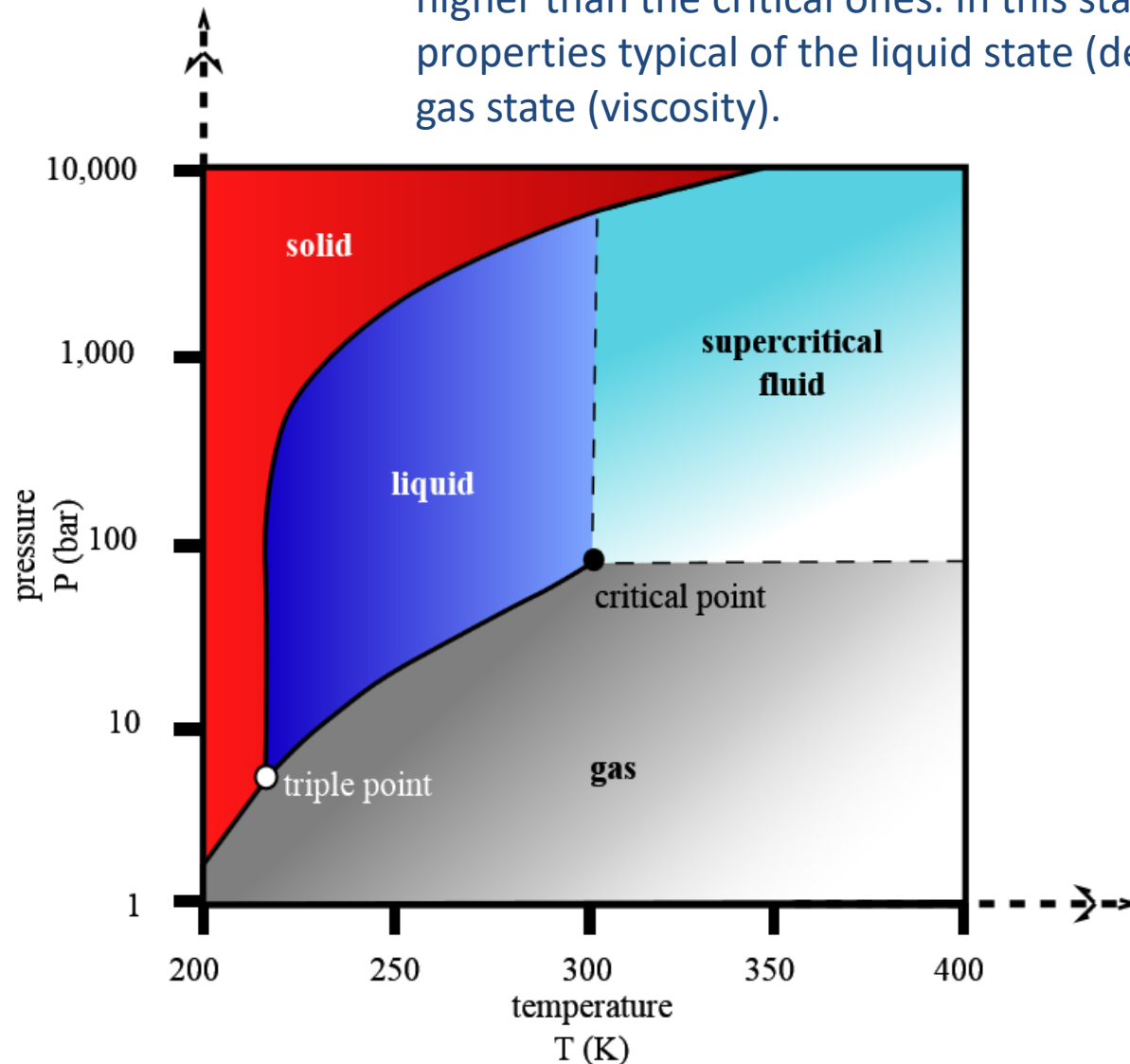
- Typically, a organic metal or salt as precursor is dissolved in the dispersed phase, which will form the core of the micelles. The other reactant is then added to the bulk (liquid or gas).
- Results obtained by this technique are:
 - Metal nanoparticles for catalyst use such as Pt, Rh and Pd, of 3-5 nm, by reduction of salts in water/oil and hydrazine or hydrogen.
 - Magnetite nanoparticles, Fe_3O_4 , by ferric ions in oil, water in oil emulsion and ammonia in water.

MICROEMULSIONS: EXAMPLES

Material	Size	Process
SiO ₂	30-70 nm	TEOS in water/polyoxymethylene, ciclohexan and NH ₄ OH
ZrO ₂		Water and cyclohexsanhexsanol, Triton (as dispersion agent)
Al ₂ O ₃	1-2,4 nm	ATIP in alcohol mixed to water and acetylacetone
TiO ₂	Less than 10nm	Tetrabuthtitanate in water and Tween 80

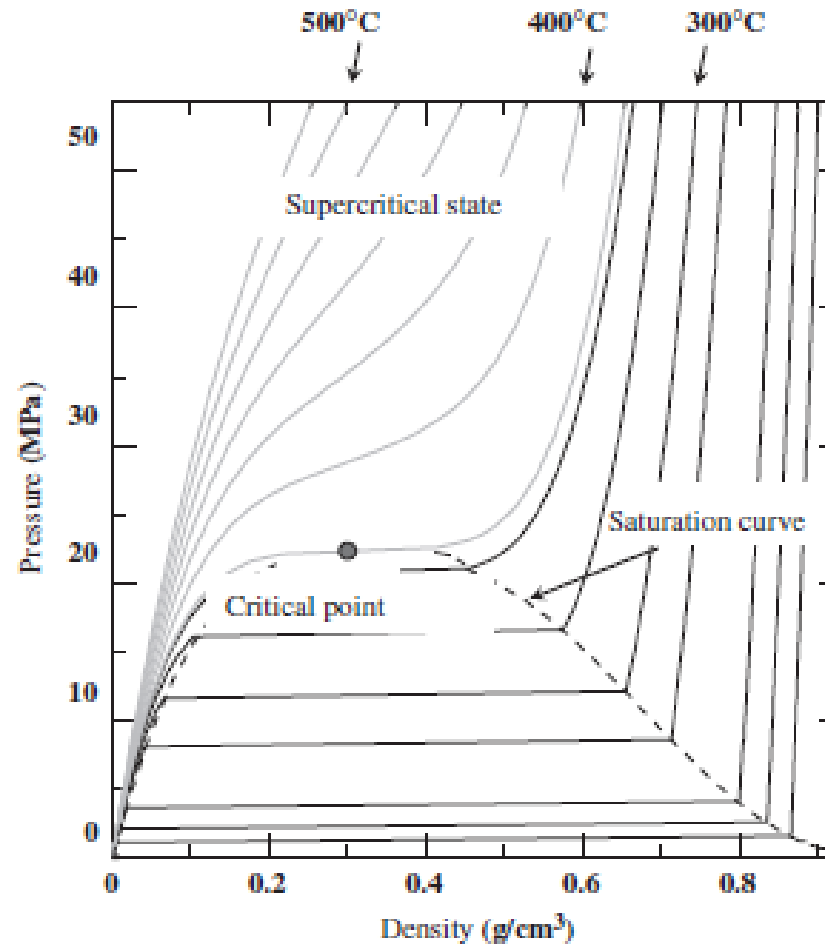
SUPERCRITICAL FLUIDS

A fluid is in a supercritical state once both temperature and pressure is higher than the critical ones. In this state, the fluid has some properties typical of the liquid state (density) and other typical of the gas state (viscosity).



CO₂

WATER



Above the critical point ($T=374\text{ }^{\circ}\text{C}$, $P = 221\text{ kg/cm}^2$) water sensibly reduces solubility towards inorganic materials but can dissolve organic ones.

SUPERCritical FLUID SYNTHESIS

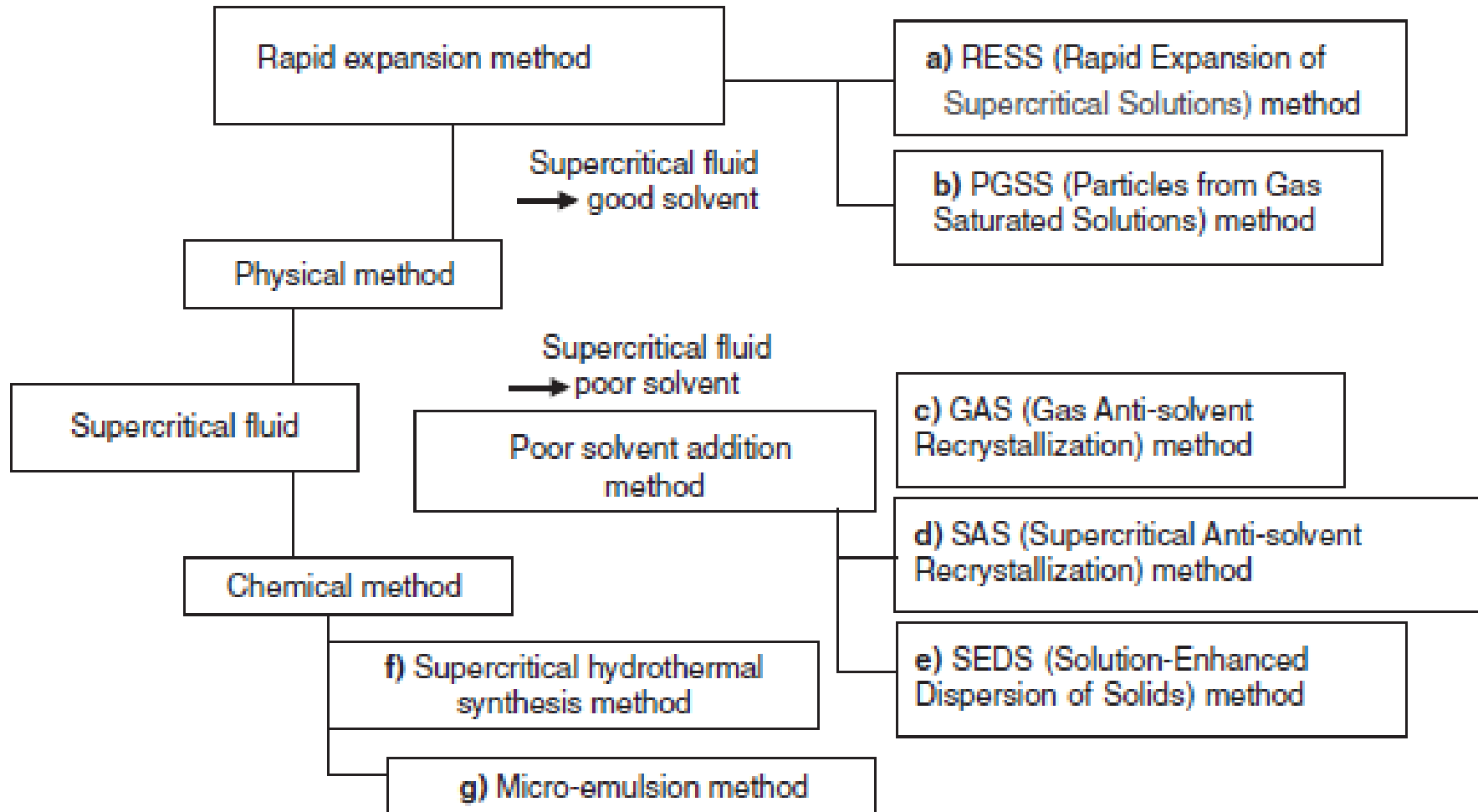
- These kind of fluids may be used for the production of nanoparticles by reaction processes.
- There are many advantages:
 - High efficiency and yield of the process;
 - size and morphology may be controlled by P,T changes;
 - The possibility to use particular atmospheres capable to oxidize or reduce precursors (O_2 , H_2 , H_2O_2).
- Mostly used solvents: H_2O and CO_2 .

SUPERCRITICAL HYDROTHERMAL SYNTHESIS

For water: $T_c = 374\text{ }^{\circ}\text{C}$ and $P_c = 221\text{ bar}$

- The reduction of the dielectric constant of water in supercritical conditions boosts the hydrothermal reaction kinetics drastically.
- The solubility of inorganic salts is greatly reduced, leading to high supersaturation values and a sensibly reduction of the Ostwald ripening phenomenon.
- The improved solubility of organics allows to use this molecules as ant agglomeration agents.
- Example: production of copper oxide nanoparticles in presence of 1-hexandihol and metal oxides starting from nitrates.

SUPERCritical TECHNOLOGIES



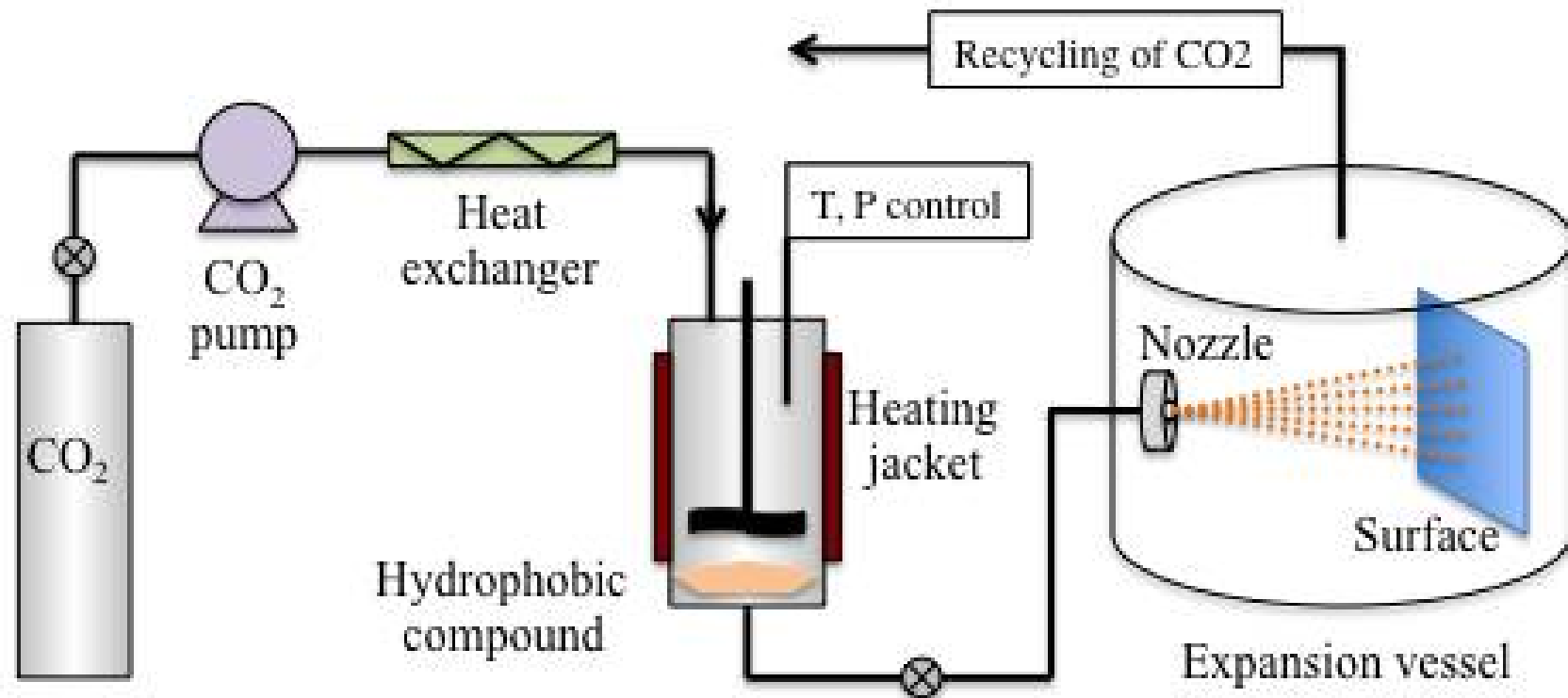
SUPERCritical TECHNOLOGIES

Method	Description
RESS	Production by flashing the fluid in SC conditions down to atmospheric pressure
PGSS	Production of particles by cooling of the CO ₂ SC decompression
GAS	The SC fluid is used as anti solvent in gas phase
SAS	The SC fluid do not dissolve the solute added to the solution which contains the material to be precipitated
SEDS	Increases the turbulence within the T mixer devices
Hydrothermal	Hydrothermal process with water in SC conditions.
Micro-emulsions	Production of nanoparticles in water drops in CO ₂ SCF.

The SCF can be used also to dissolve a reactant for the active solution: in this case, the SFC have both the purpose to lead to the product by chemical reaction of the two streams, and to promote the required supersaturation conditions of the product for the formation of the nanoparticles.

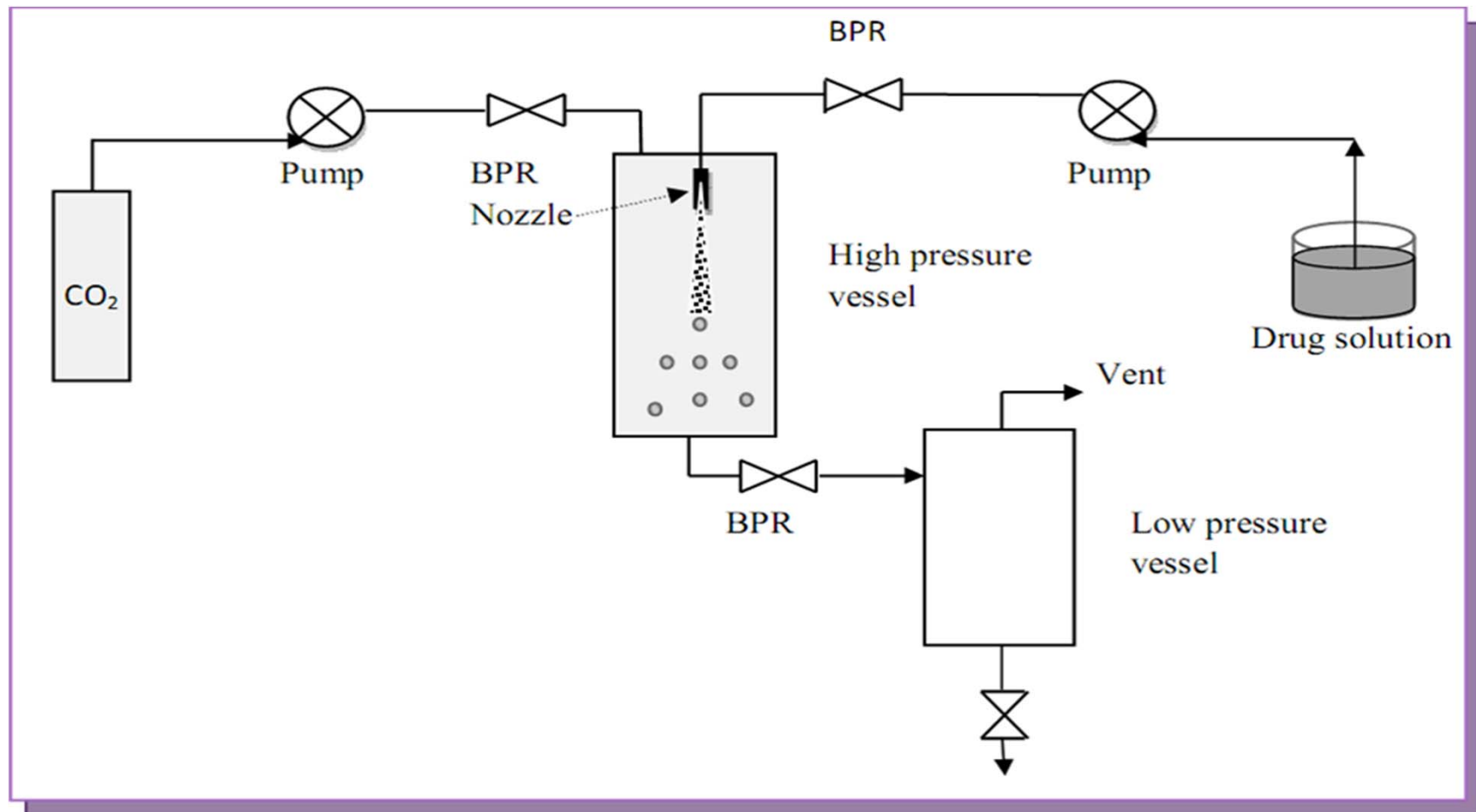
SUPERCritical TECHNOLOGIES

Method	Description
RESS	Production by flashing the fluid in SC conditions down to atmospheric pressure



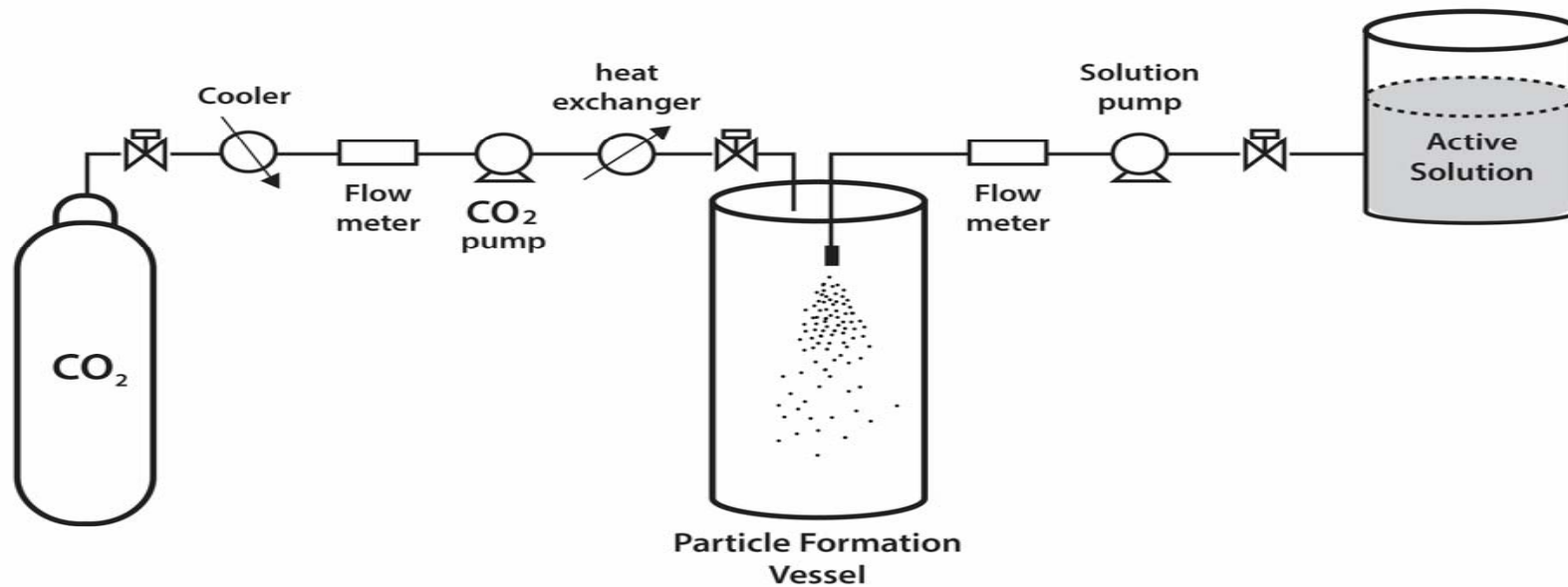
SUPERCritical TECHNOLOGIES

Method	Description
GAS	The SC fluid is used as anti solvent in gas phase



SUPERCritical TECHNOLOGIES

Method	Description
SAS	The SC fluid do not dissolve the solute added to the solution which contains the material to be precipitated



NANOCOMPOSITES

Wang et al. Have produced nano capsules of SiO₂ coated by a polymer by the SAS technique:

1. The polymer is dissolved in acetone, and SiO₂ were added to this solution.
2. CO₂ SC was added to the dispersion: in this case, the polymer is not capable to keep its dissolved state, thus precipitating on the existing seed and therefore forming nano capsules of SiO₂/polymer.

The starting size of silica was 16-30 nm, the final size of the nano capsules 50-100 nm.