

# DICP Course - Dalian, 2012

## Preparation of solid catalysts

### Part 4

Supported by the Chinese Academy of Sciences

Charles Kappenstein, Professor Emeritus, University of Poitiers, France



DALIAN INSTITUTE OF CHEMICAL PHYSICS,  
CHINESE ACADEMY OF SCIENCES



中国科学院  
CHINESE ACADEMY OF SCIENCES



# Outline

Introduction and general aspects

Interfacial chemistry – Electrostatic adsorption

Impregnation, drying, calcination and/or reduction

 Sol-gel chemistry processing

Deposition – Precipitation – Coprecipitation

Shaping of solid catalysts – Monolith-based catalysts

## Zeolite-based catalysts

## Characterization – High throughput experimentation

### Case studies:

- Noble metal catalysts
- Methanol catalysts
- Hydrotreating catalysts
- .....

## Sol-gel chemistry processing

- 
- 1) The physics of sols**
  - 2) Sol-gel processing of silicate materials**
  - 3) Sol-gel chemistry of metal oxides**
  - 4) Aerogels**

## The physics of sols

**Sol gel process → creation of a network by condensation reactions**

**Definitions:**

**Sol: stable suspension of colloidal solid particles (or polymers) in a liquid  
particles amorphous or crystalline, size 1 to 1000 nm**

**Gel: porous 3-D solid network supporting a continuous liquid phase (wet gel)**

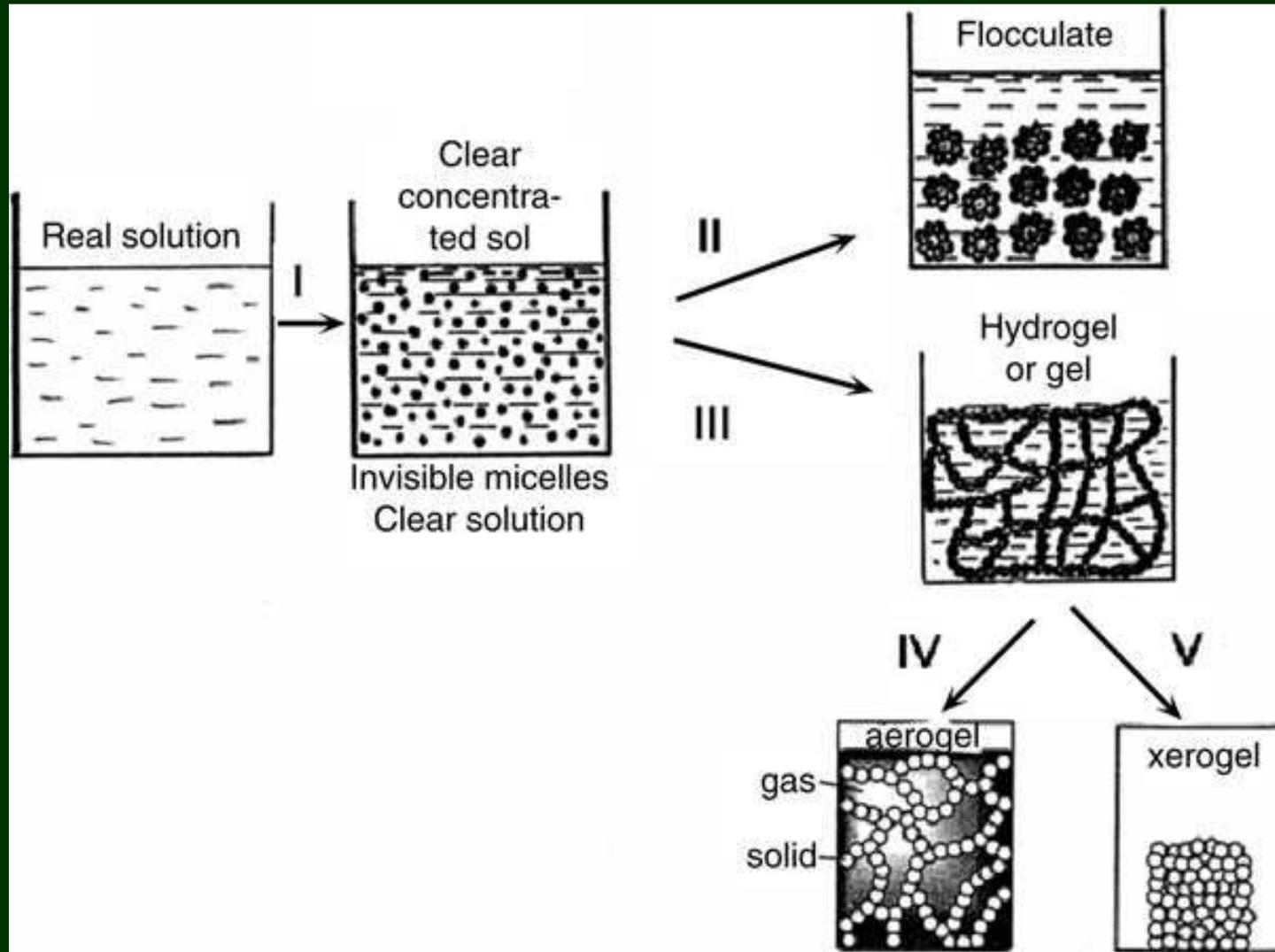
**Colloidal gels: network made by agglomeration of dense colloidal particles**

**Type of bonds:**

- covalent bonds → sol-gel process irreversible**
- van der Waals bonds, H-bonds → sol-gel process reversible**

# The physics of sols

## Sol gel process



## Aging of the gel, washing

# The physics of sols

What are the forces in a colloidal suspension?

- electrostatic repulsion between charged particles
- van der Waals attraction

Influence of pH on the surface hydroxyl groups M-OH (M = Al, Si, Zr, Ti, Fe...)

pH at which the particles are electrically neutral: PZC (Point of Zero Charge)

	SiO <sub>2</sub>	SnO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO
PZC	2.5	4.5	6.0	7.0-9.0	12

Formation of a double-layer on the surface → development of a surface potential

Ex.: positively charged surface

- rigid Stern layer containing water + counter ions → linear decrease of potential
- diffuse layer → exponential decrease of potential

- Helmholtz plane: between Stern layer and diffuse layer;

- slip plane: between diffuse layer and bulk;

potential  $\Phi_H$

Zeta potential  $\Phi_\zeta$

# The physics of sols

In an electric field, the particle move with the counter ions

The slip plane separates region of fluid that moves with the particles from bulk

pH for  $\Phi_\zeta = 0$

→ isoelectric point IEP

For stable colloidal suspensions

→  $\Phi_\zeta > 30 - 50$  mV

If  $\Phi_\zeta$  decreases (ionic strength increases)

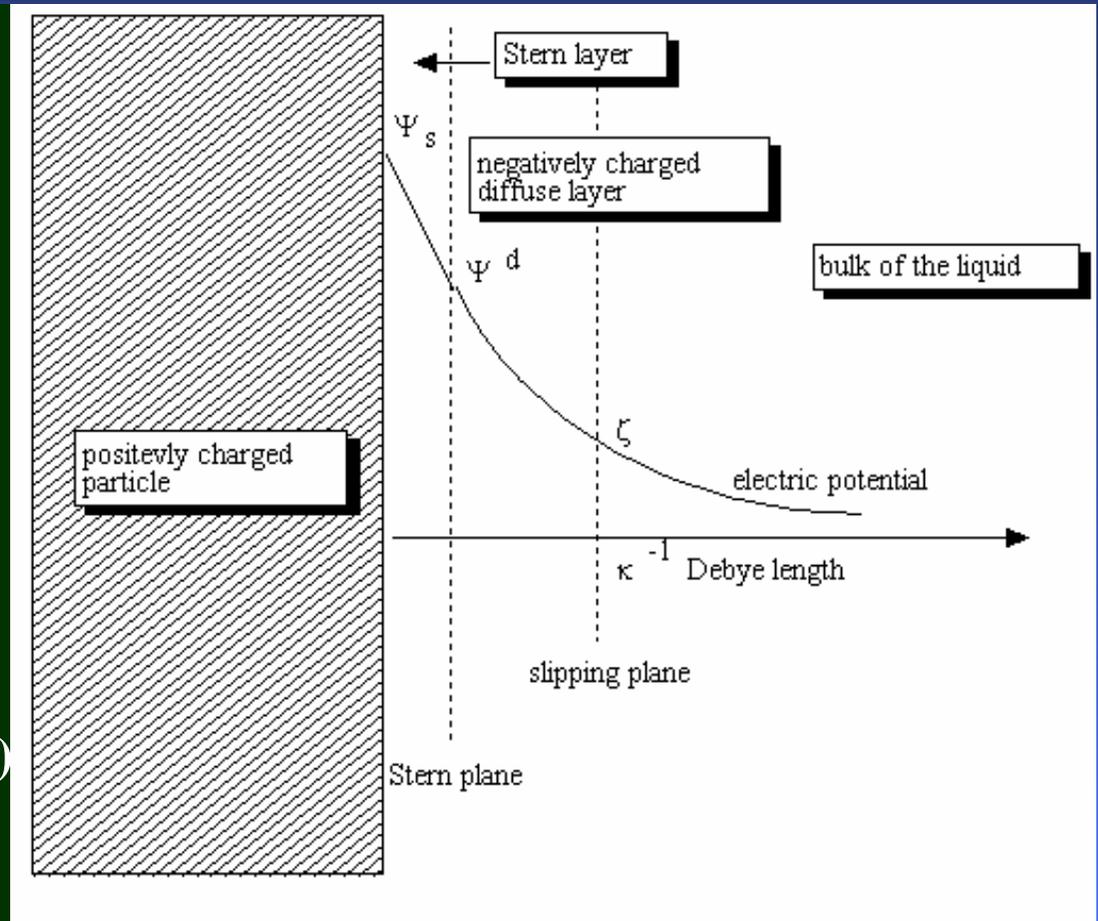
→ double layer is compressed

→ coagulation

Coagulated colloid can be redispersed → peptization

→ remove counter ions by washing

→ videos of gel formation



## Sol-gel chemistry processing

1) The physics of sols

 2) Sol-gel processing of silicate materials

3) Sol-gel chemistry of metal oxides

4) Aerogels

## Sol-gel processing of silicate materials



Tetraethoxysilane	$\text{Si(OC}_2\text{H}_5)_4$	TEOS
Tetramethoxysilane	$\text{Si(OCH}_3)_4$	TMOS

→ The gelation can be initiated by pH change

Reactions occurring: → see scheme

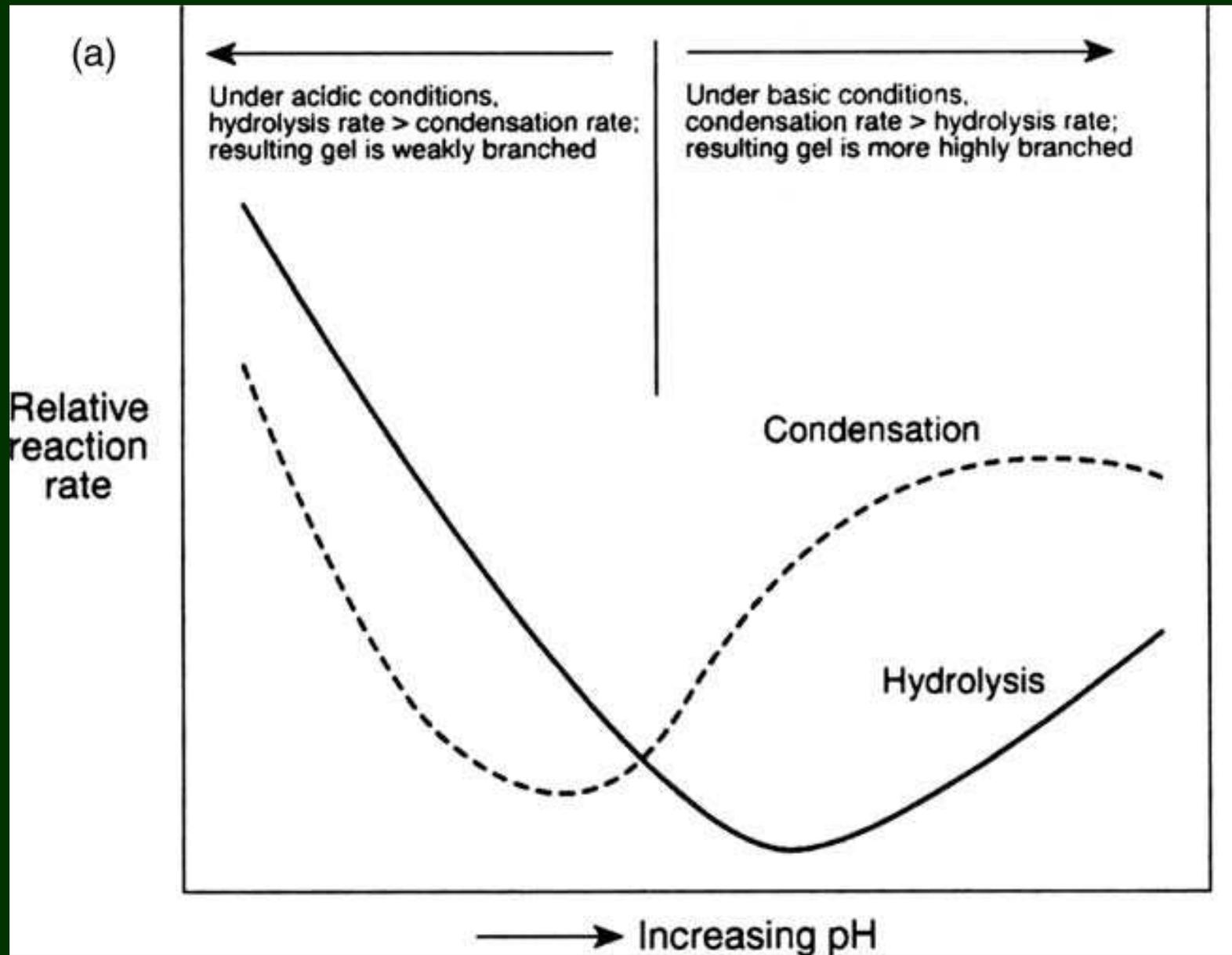
→ competition between hydrolysis reactions and condensation reactions

→ See next figure

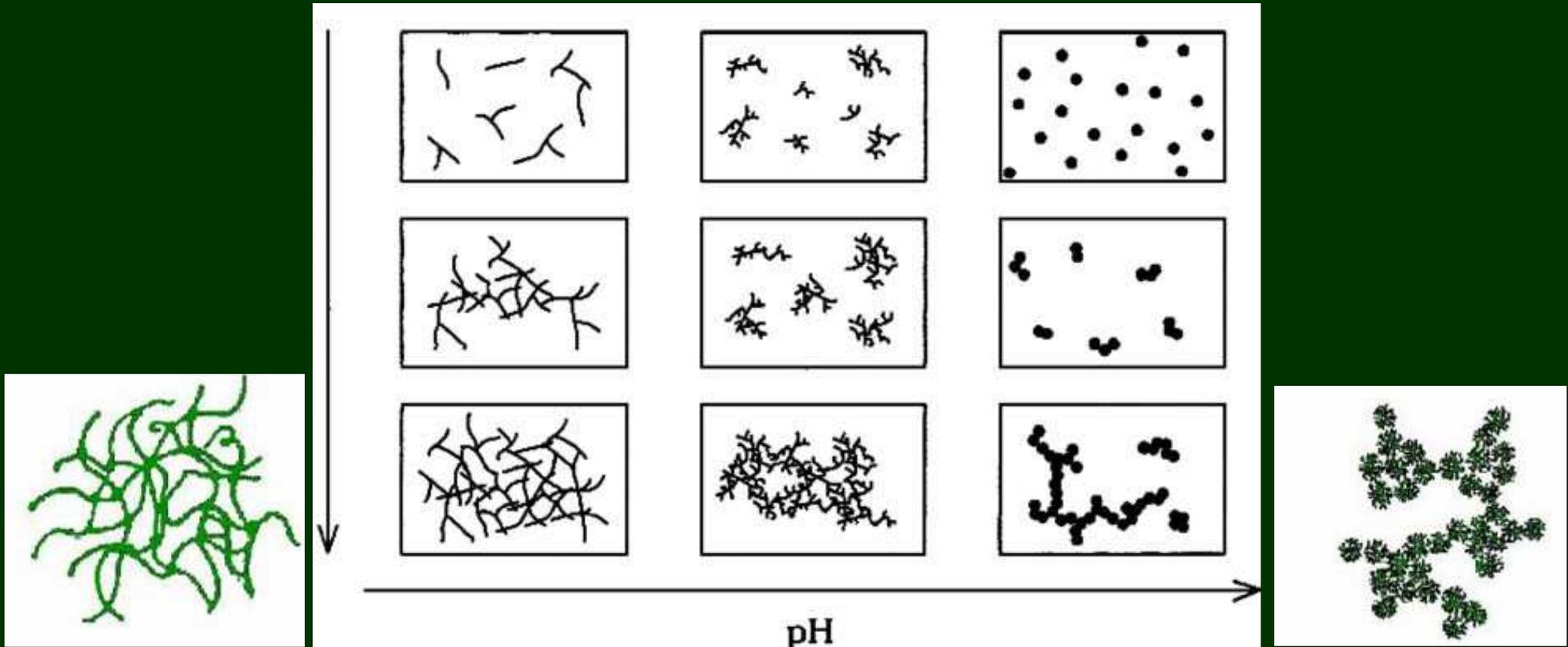
# Sol-gel processing of silicate materials



slow rate in water



# Sol-gel processing of silicate materials



Cross-linked linear chains

branched clusters

How to explain these differences?

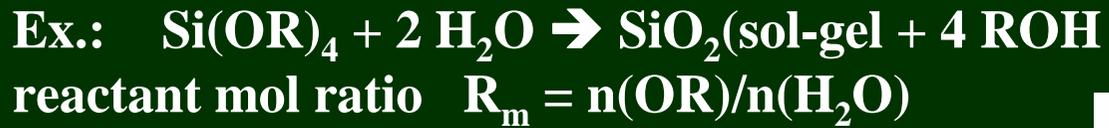
→ different relative rates

→ need of a simple model

Parameters:

- temperature
- catalyst
- reactant mol ratio  $R_m = n(OR)/n(H_2O)$
- pH
- nature of alkoxy group

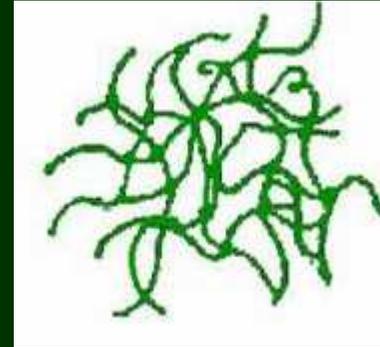
# Sol-gel processing of silicate materials



slow rate in water

Stoichiometry  $R_m = 2$

$R_m < 2$  (excess water)  $\rightarrow$  hydrolysis  
 $R_m > 2$  (excess silane)  $\rightarrow$  condensation



sol-gel transition

- $\rightarrow$  formation of a continuous network
- $\rightarrow$  viscosity increases strongly
- $\rightarrow$  gelification time:



# Sol-gel processing of silicate materials

Model: percolation theory

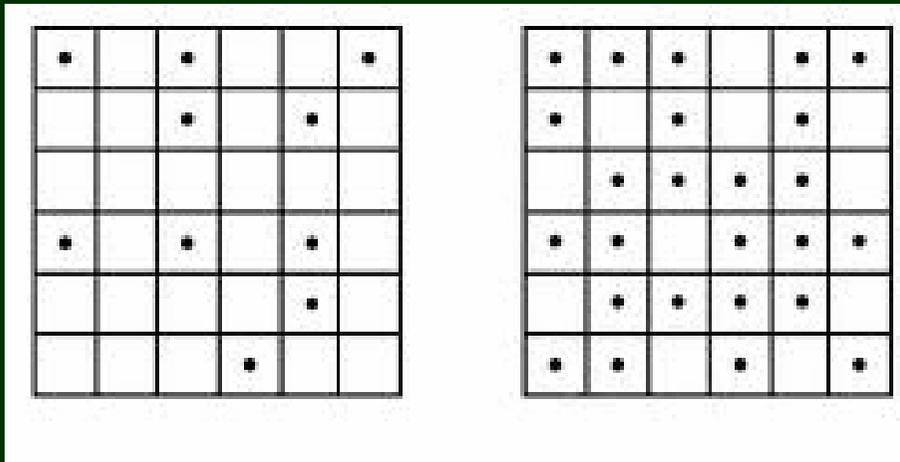
→ formation of clusters of particles

See figure

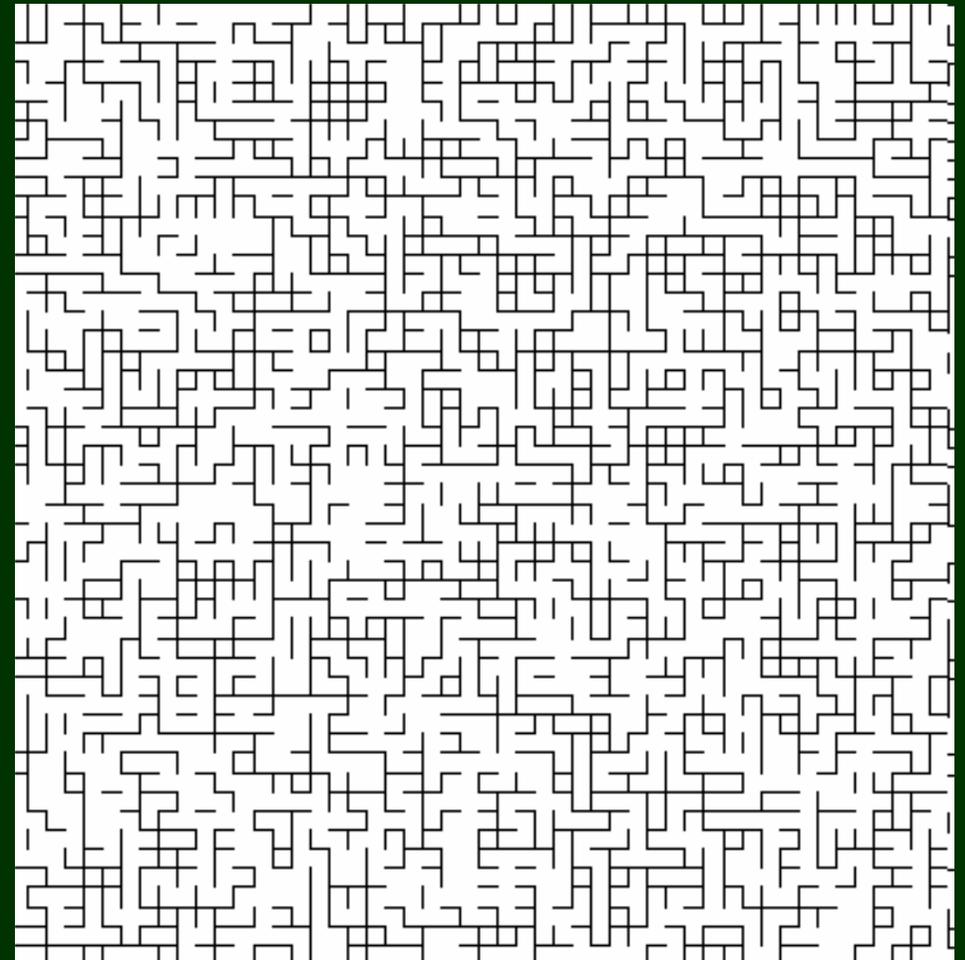
$p$ : fraction or probability of randomly filled sites (sol particles)

2 neighboring filled sites can form a bond → cluster of size  $s$

Detail of a bond percolation on the square lattice in two dimensions with percolation probability  $p = 0.51$



Site percolation on a square lattice  
left low fraction right high fraction



# Sol-gel processing of silicate materials

Model: percolation theory → formation of clusters of particles

See figure

$p$ : fraction of randomly filled sites (sol particles)

2 neighboring filled sites can form a bond → cluster of size  $s$

One important parameter →  $p_c$  = percolation threshold → gel point

At the gel point the network is formed, but unbounded clusters are still present

→ importance for aging process after reaching the gel point

This model → site percolation

Another model → bond percolation

Values of  $p_c$

	site percolation	bond percolation
2-D square	0.5927	0.5000
3-D cubic	0.3116	0.2488
3-D fcc	0.1992	0.1202

Aging: gelification reactions continue due to the presence of isolated clusters

# Sol-gel processing of silicate materials

## Drying step

- at 1 bar pressure → formation of xerogels,
  - shrinkage of the gel due to interface forces (liquid-vapor capillary forces)
  - network destroyed, formation of a powder
  - formation of films, coating layers after thermal treatments
- under supercritical conditions → formation of aerogels
  - volume of the gel is preserved
  - control of shrinkage

# Outline

## Sol-gel chemistry processing

1) The physics of sols

2) Sol-gel processing of silicate materials

 3) Sol-gel chemistry of metal oxides

4) Aerogels

# Sol-gel chemistry of metal oxides

Ex.:  $[\text{Al}(\text{OH}_2)_6]^{3+}$       stable for  $\text{pH} < 3$

Formation of alumina gel by increasing the pH

Acid-base equilibrium



Olation reaction



Oxolation reaction

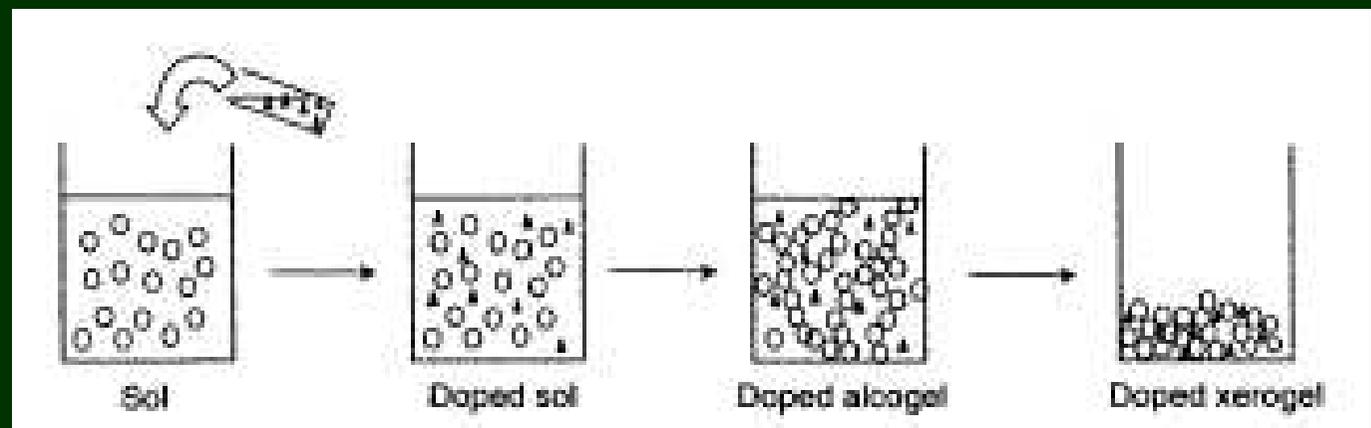


Difference between  $\text{Si}^{4+}$  and  $\text{M}$  ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zr}^{4+}$  ...)?

$\text{Si}$  coordination number 4, tetrahedral geometry (point group  $T_d$ )

$\text{M}$  coordination number 6, octahedral geometry (point group  $O_h$ )

Preparation of a supported catalyst



## Sol-gel chemistry processing

1) The physics of sols

2) Sol-gel processing of silicate materials

3) Sol-gel chemistry of metal oxides

 4) Aerogels

- supercritical drying
- drying at ambient temperature
- properties and applications

**Preparation of aerogel****Critical points:**

water:  $T_c = 374\text{ }^\circ\text{C}$   
 $P_c = 220\text{ bar}$

$\text{CO}_2$ :  $T_c = 31\text{ }^\circ\text{C}$   
 $P_c = 74\text{ bar}$

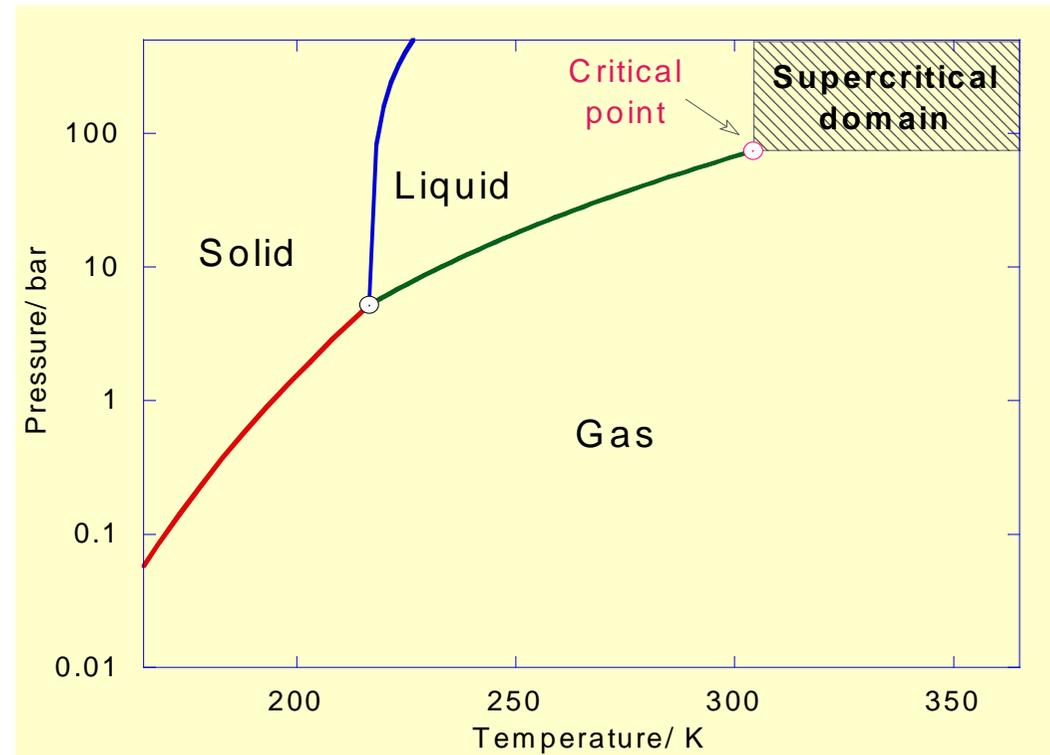
**Aerogel synthesis:**

**Gel**  $\xrightarrow{1}$  **acetogel**  $\xrightarrow{2}$  **carbogel**  $\xrightarrow{3}$  **aerogel**

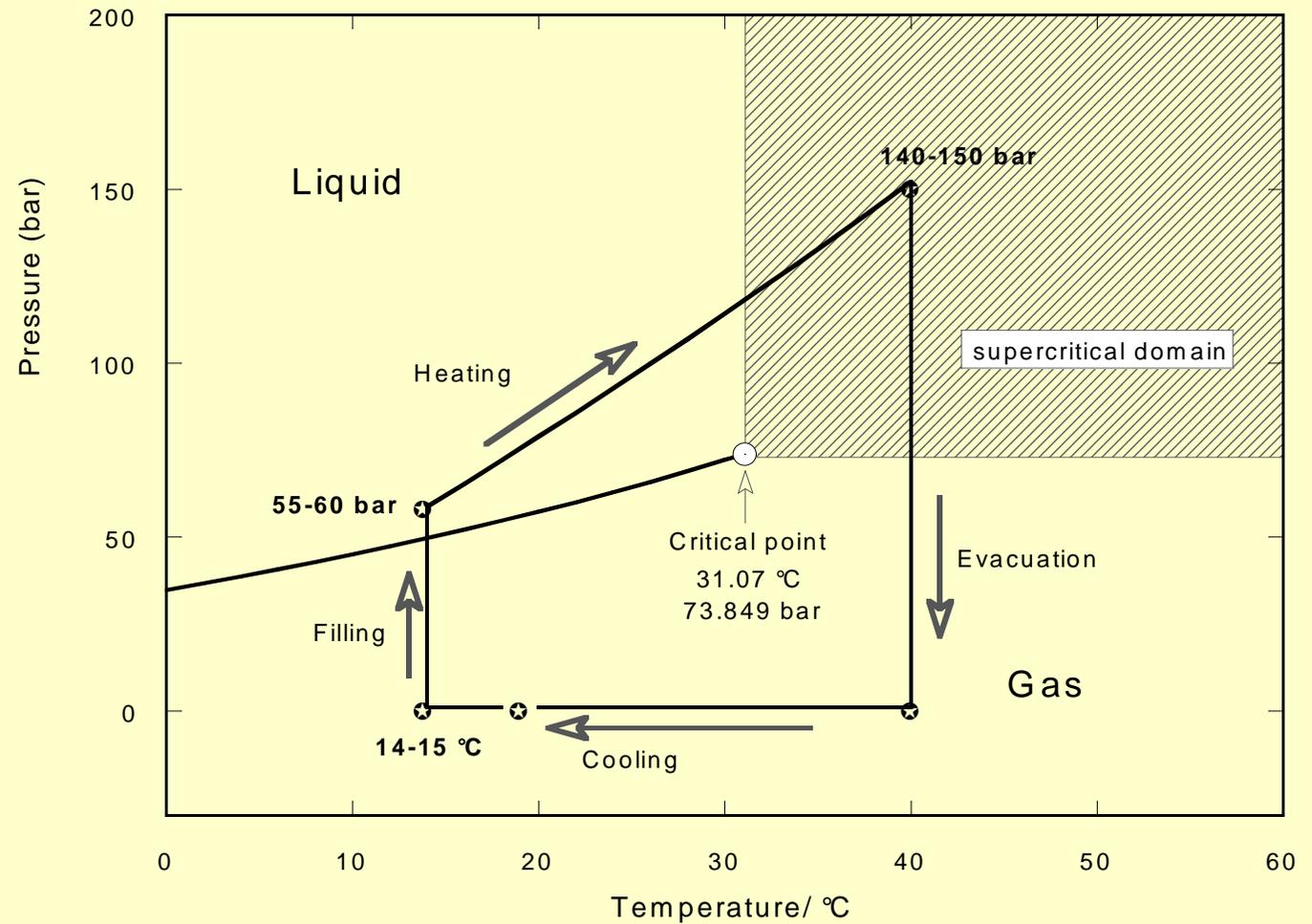
1: water/acetone exchange

2: acetone/ $\text{CO}_2$  exchange

3: supercritical drying



### Reactor for supercritical drying



How to reduce the capillary forces but avoiding the supercritical conditions?

→ change the solvent: water → alcohol → water free solvent

→ transform the surface silanol groups Si-OH into hydrophobic groups



→ Gel shrinks, then expands again to a volume close to original size

# Aerogels

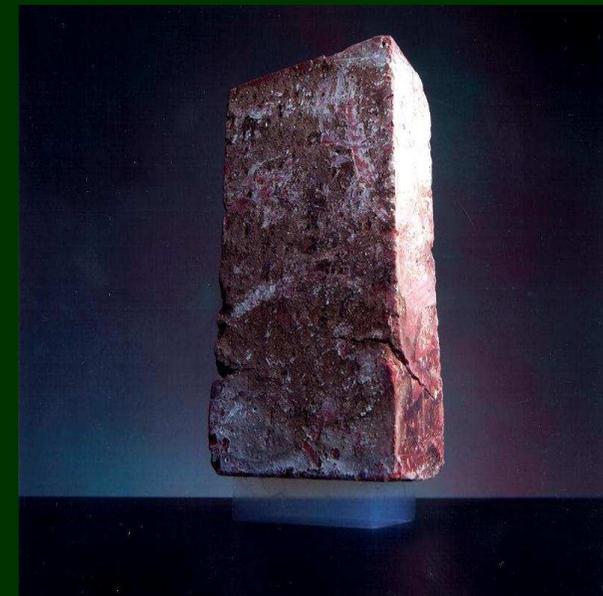
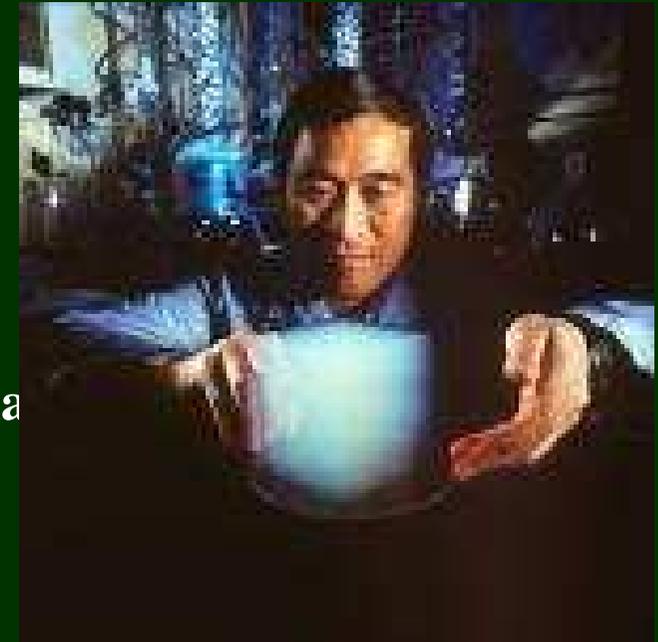
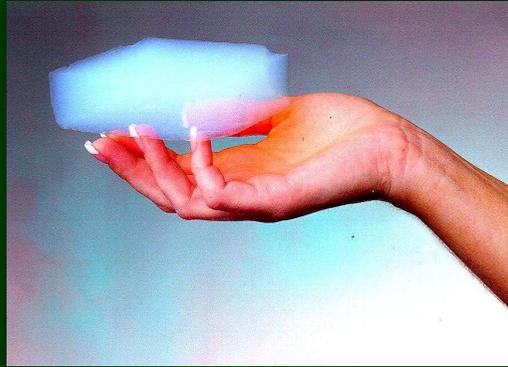
## c) Properties and applications

### Characteristics of aerogels

- very high porosity
- very low density

### SiO<sub>2</sub> aerogels

- most studied and used
- transparent
- very low thermal conductivity → very good thermal insulation



One famous example: Stardust NASA interplanetary mission

Website: <http://stardust.jpl.nasa.gov/tech/aerogel.html>

→ First mission to collect cosmic dust and return the sample to Earth.

Launched February 1999, travelled nearly  $5 \cdot 10^9$  km, returned to earth January 2006

Main challenges → slowing down the particles from their high velocity with minimal heating or other effects that would cause their physical alteration.

To collect the particles without damaging them, a silicon-based solid with a porous, sponge-like structure is used in which 99.8 percent of the volume is empty space.

Aerogel is 1,000 times less dense than glass.

When a particle hits the aerogel, it buries itself in the material, creating a carrot-shaped track up to 200 times its own length, as it slows down and comes to a stop.

Since aerogel is transparent, scientists use these tracks to find the tiny particles.

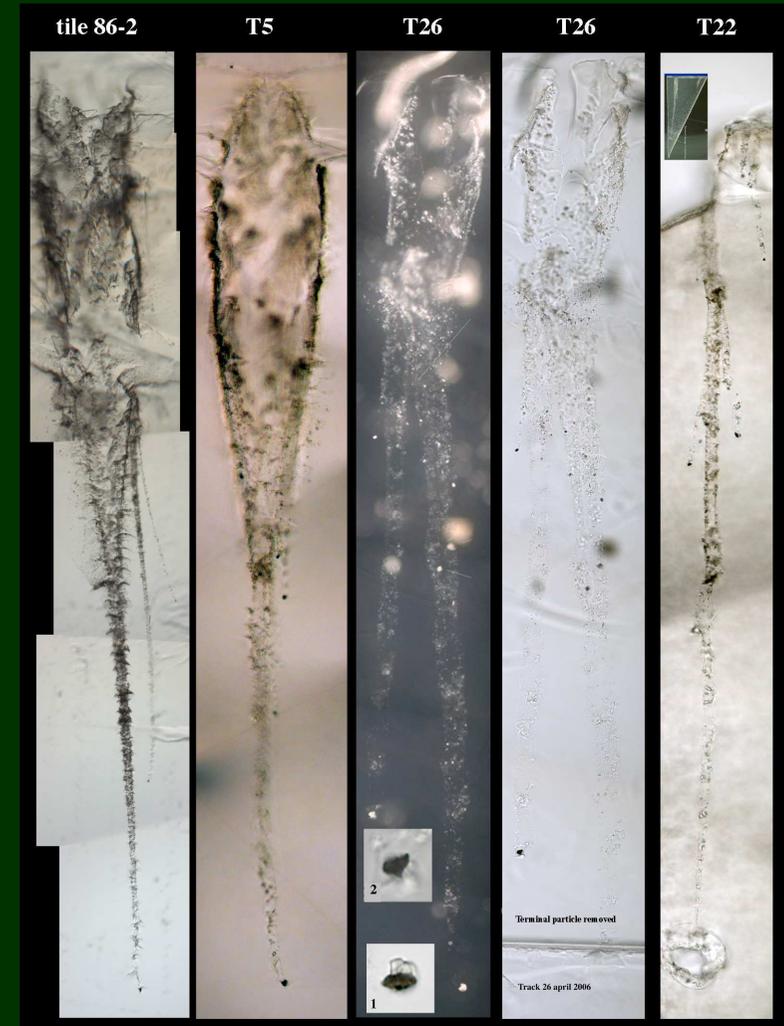
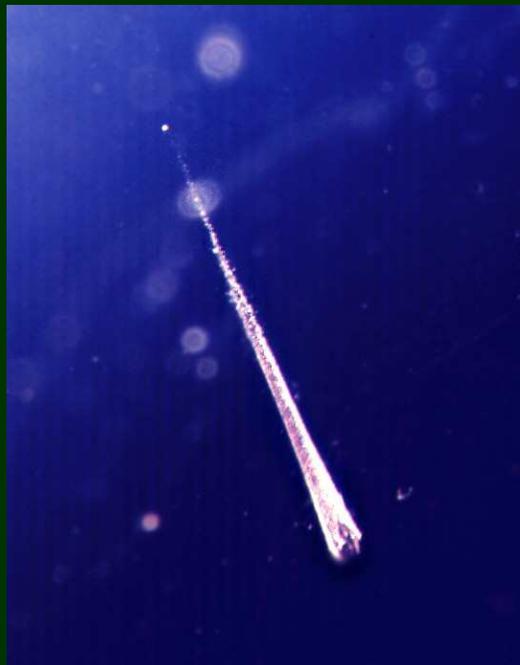
# Aerogels

## c) Properties and applications

One famous exemple: Stardust NASA interplanetary mission

Website: <http://stardust.jpl.nasa.gov/tech/aerogel.html>

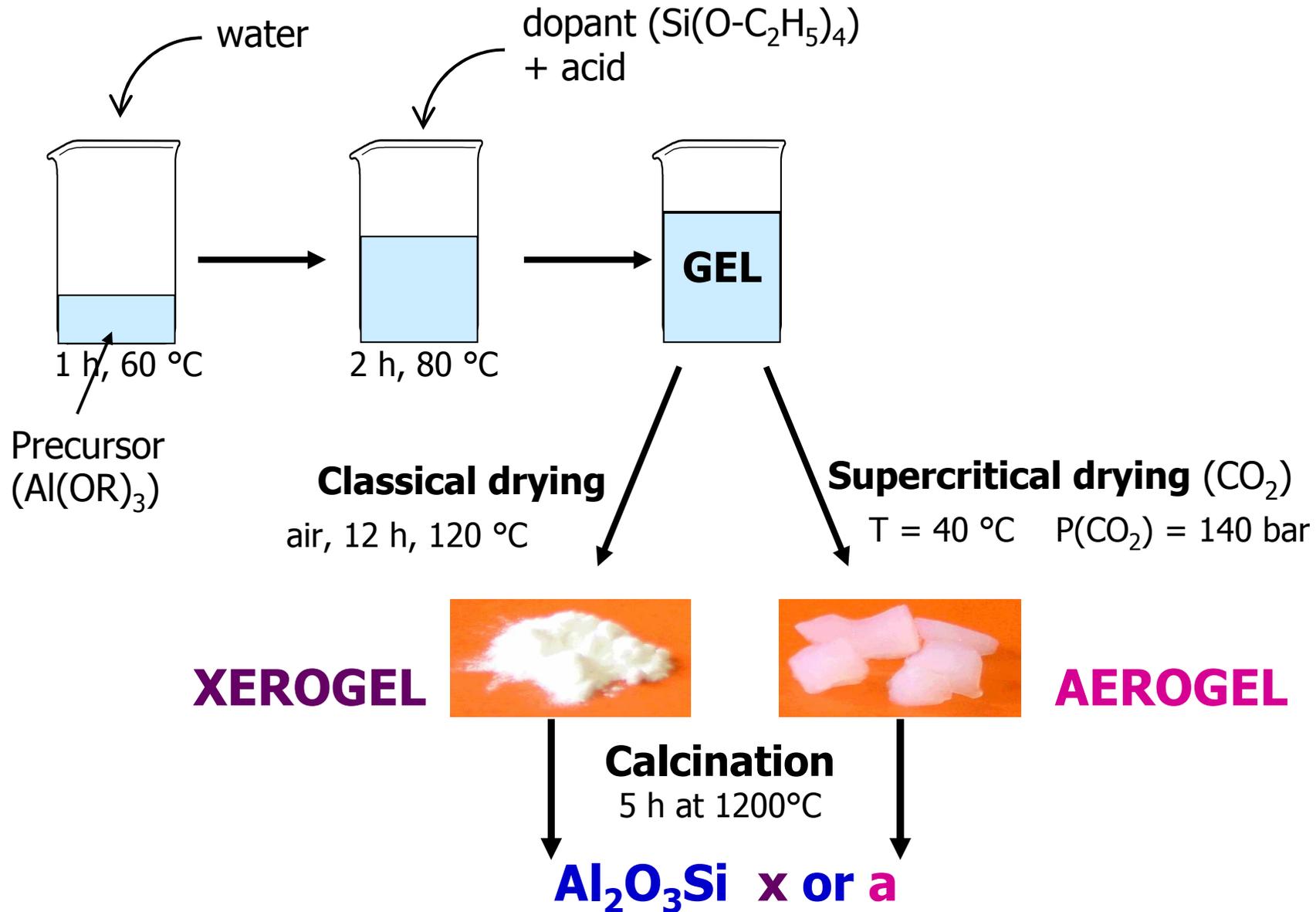
Traces of dust particles:



# Aerogels

## c) Properties and applications

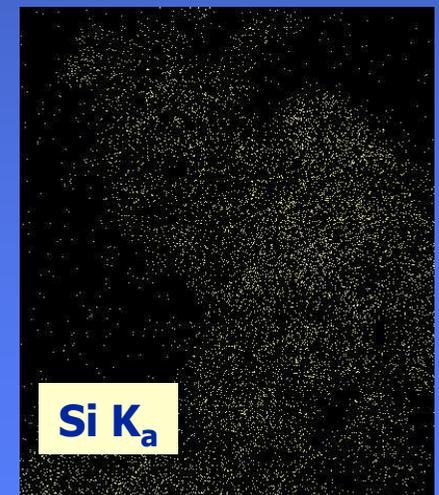
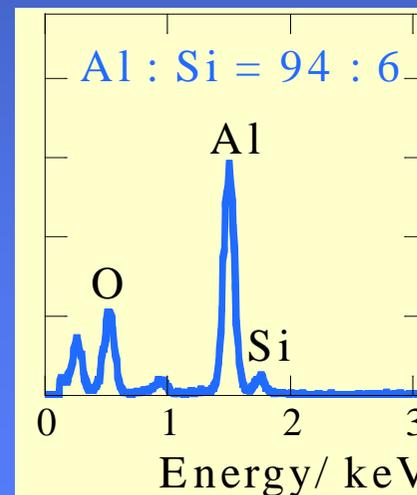
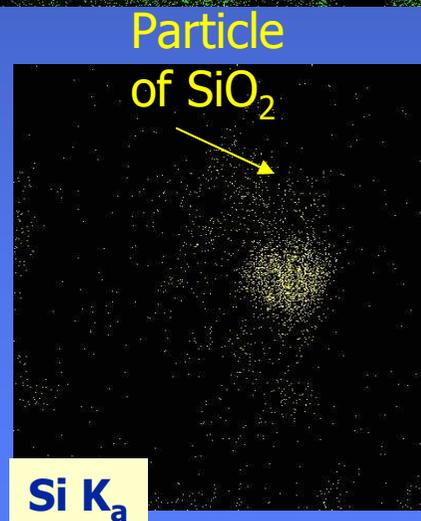
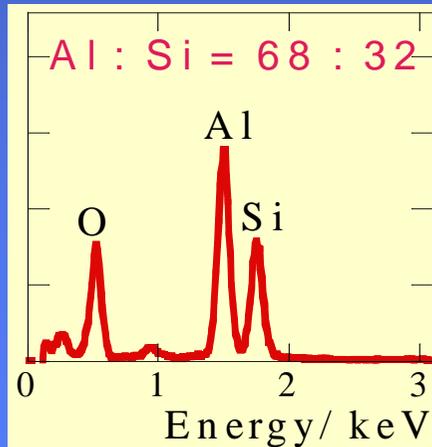
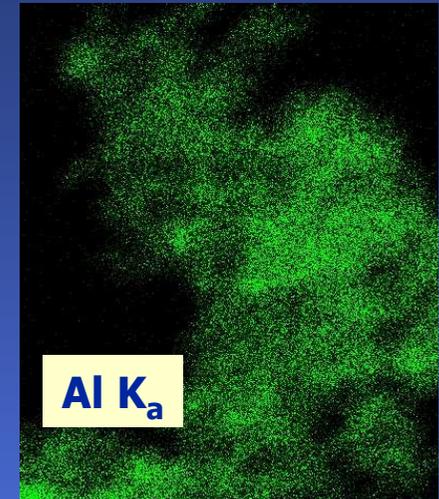
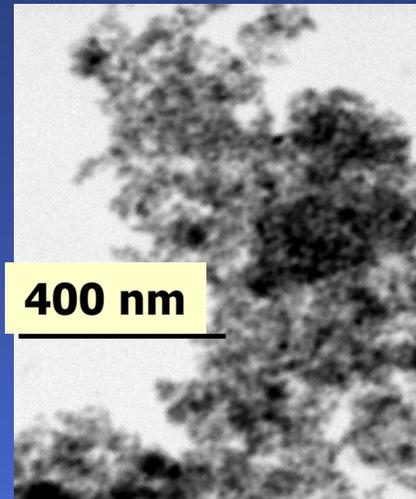
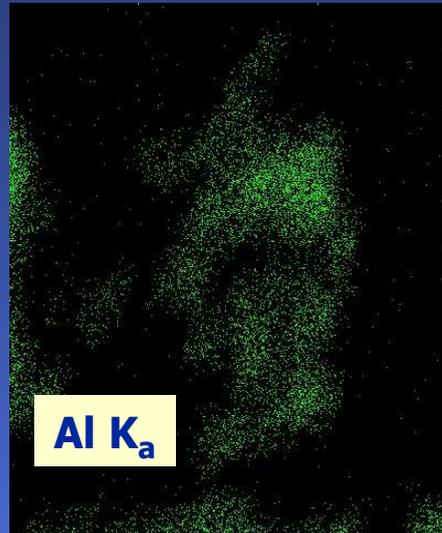
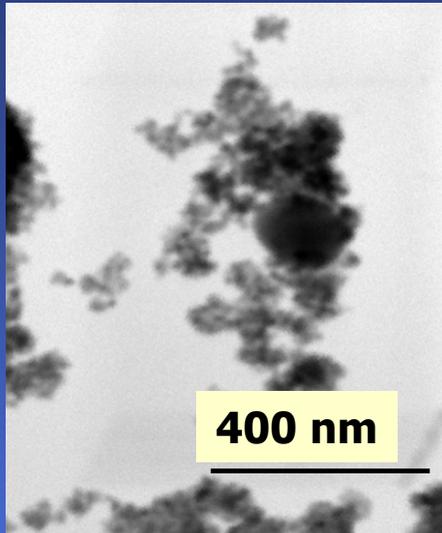
### Sol-gel synthesis: preparation of Si-doped alumina supports



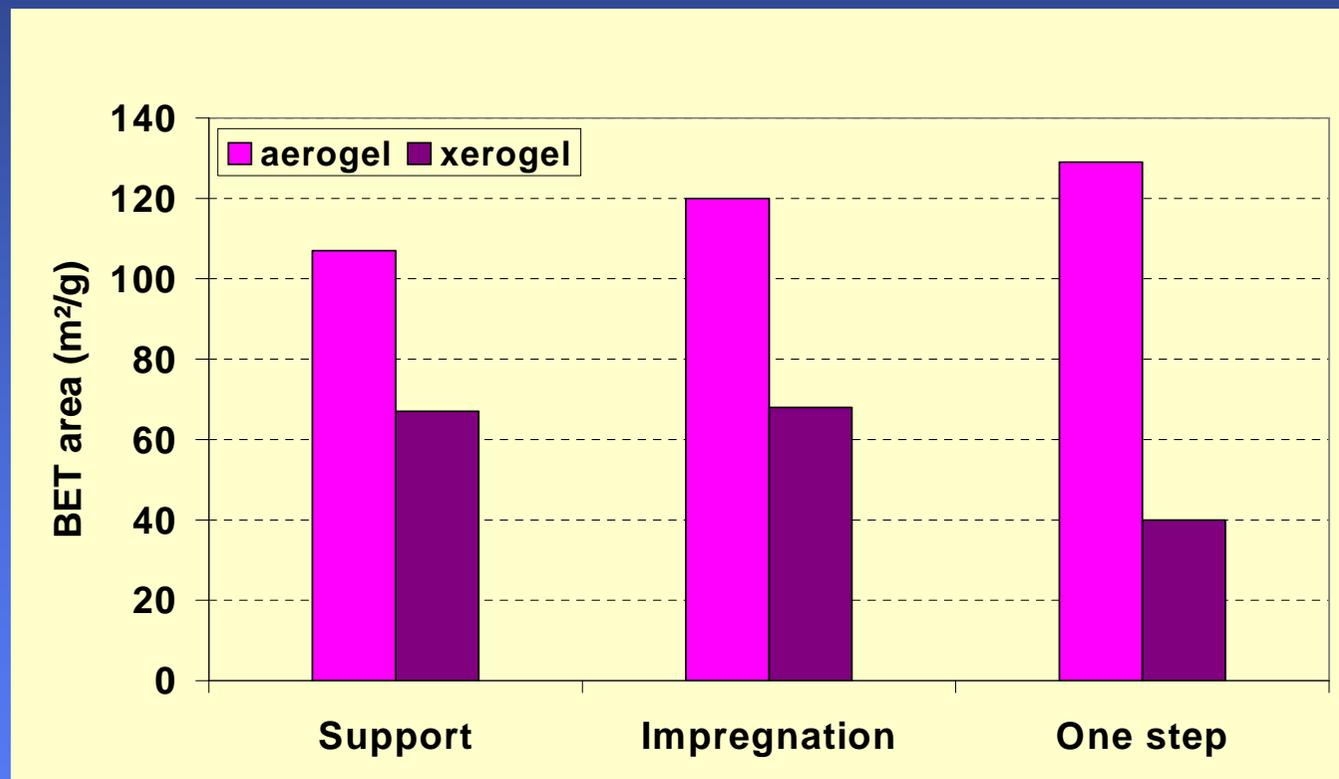
Xerogel

### Transmission electron microscopy

Aerogel



**Silicium is more homogeneously dispersed in aerogel**

**Characterization: support alone and Pt catalyst****Specific surface area (after calcination at 1200 °C)**

**Aerogel: better thermal stability**  
**Impregnation: smaller particles size**

# End of part 3