

ABORATOIRE

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# Some basic rules for the preparation of aerogels

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#### In any case to obtain aerogels it is necessary to have gels !

### **Definition**

*Gelation* is a process that causes a solid phase to appear within a solution, which organizes itself to form a continuous three-dimensional network that will trap the solvent.



A gel is a thermodynamically stable solid-liquid biphasic system consisting of a continuous threedimensional double interpenetrating network, one solid and the second liquid.

Flory has proposed a classification of gels which applies to both organic and inorganic gels:

- Lamellar gels such as the mesophase and clay gels;
- Covalently bonded gels of the polymeric type;
- Particulate gels made up of particles of submicron size bound together to form a porous network.



An aerogel is a gel in which the solvent localized in the interstices of the solid parts has been replaced by air. The liquid network has been transformed into a pore network.

 $\rightarrow$  During this operation the solid part remains almost unchanged

### Definition

#### In any case to obtain aerogels it is necessary to have gels ! But this is not sufficient !!!

**Obtaining an aerogel** imposes constraints on the binding energies which ensure the cohesion of the solid network. They must be high enough to withstand supercritical drying treatments in the presence of a conventional solvent (ethanol, ether) or  $CO_2$ .

The principle of supercritical drying consists of subjecting the liquid to a variation in temperature and pressure bringing it into the domain of the supercritical fluid and then bypassing the critical point to transform the supercritical fluid into vapor.





But above all, we have to prepare inorganic or hybrid (organic-inorganic) gels.

The gels are the result of soft chemical reactions that take place in the liquid phase in the presence of an ionic or covalent precursor.

This precursor reacts in the presence of a reagent, catalysts or under the effect of temperature to form a colloidal or macromolecular solid species which will organize itself into a network.

The objective of this part is to describe the various modes of synthesis of these species and to give examples of operating conditions for obtaining gels intended for supercritical drying.



But above all, we have to prepare inorganic or hybrid (organic-inorganic) gels.

The gelation of metal oxide compounds is governed, in the majority of cases, by two main reactions which are hydrolysis and polycondensation.

Depending on the nature of the solvent, the catalyst and the precursors, their reaction mechanisms can be more or less complex.



#### But above all, we have to prepare inorganic or hybrid (organic-inorganic) gels.

Gels from ionic precursors: metallic cation and a counterion of the carbonate, nitrate, halide type...

They are soluble in water and react according to chemical mechanisms which involve their different acid-base forms ( $H^+$ ,  $H_2O$ ,  $OH^-$ ).

They lead to aquagels.

A cation (M<sup>z+</sup>) placed in solution undergoes solvation which leads to hydrolysis reactions defined below:

 $[M(OH_2)]^{z+} \leftrightarrow [M-OH]^{(z-1)+} + H^+ \leftrightarrow [MO]^{(z-2)+} + 2 H^+$ 

at the origin of the formation of the following species :



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• [MO<sub>N</sub>H<sub>2N</sub>]<sup>z+</sup> is called an "aquo-ion", with N corresponding to the number of water molecules solvating the metal cation. The bonds are of the aquo type M-(OH<sub>2</sub>).

• [M(OH)<sub>x</sub>(OH<sub>2</sub>)<sub>N-x</sub>]<sup>(z - x)+</sup> is called "hydroxo-aquo-ion", with N corresponding to the number of water molecules solvating the metal cation.

• [M(OH)<sub>N</sub>]<sup>(N - z)-</sup> is called "hydroxo-ion". The bonds are of the hydroxo type M-(OH).

•  $[MO_x(OH_2)_{N-x}]^{(N+x-z)-}$  is called "oxo-hydroxo-ion", with N corresponding to the number of water molecules solvating the metal cation.

•  $[MO_N]^{(2N-z)-}$  called "oxy-ion". The bonds are all of the oxo type M=O.

Scintillating Porous Architecture for RadioacTivE gas detection

#### But above all, we have to prepare inorganic or hybrid (organic-inorganic) gels.

Hydroxo-ions are the most likely to condense and therefore potentially form a gel. Two types of condensation reactions exist :

Olation: the bond between metal atoms is ensured by a hydroxyl group (OH).

$$M - \overset{\delta^{-}}{OH} + \overset{\delta^{+}}{M} - \overset{OH}{OH}_{2} \rightarrow M - \overset{OH}{OH} + \overset{H_{2}O}{H}_{2}$$

■ Oxolation: the bond between atoms is ensured by an oxo bridge (- O -).

$$M \xrightarrow{\delta^{-}} M \xrightarrow{\delta^{+}} M \xrightarrow{\delta^{-}} M \xrightarrow{\delta^{-}$$



#### But above all, we have to prepare inorganic or hybrid (organic-inorganic) gels.

Aquagels derived from metallic salts					
Metallic Precursor	1st stage	1st stage 2nd stage		Supercritical drying	
Sodium silicate	Formation of an aquagel in the presence of HCl		Water → Ethanol	Ethanol	
Sodium tungstate	Formation of an aquagel in the presence of HNO <sub>3</sub>		Water $\rightarrow$ Ethanol $\rightarrow$ Ether	Ether	
Aluminum acetate	Formation of a sol by dialysis	Gelation by sol destabilization in the presence of $SO_4^{2-}$	Water → Ethanol	Ethanol	
Iron III chloride	Formation of a sol in the presence of $CO_3(NH_4)_2$	Gelation by sol destabilization in the presence of K <sub>2</sub> SO <sub>4</sub> or Gelation at 100°C	Water $\rightarrow$ Ethanol $\rightarrow$ Ether $\rightarrow$ Petroleum ether $\rightarrow$ Propane	Propane	
Tin III chloride	Hydrolysis and peptization of the precipitate in the precipitate and the precipitate in the presence of ammonia	Sol gelation by slow solvent evaporation	Water $\rightarrow$ Ethanol $\rightarrow$ Ether	Ether	
multi-step processes → simplification by using the same precursors					

#### But above all, we have to prepare inorganic or hybrid (organic-inorganic) gels.

**Epoxide-Initiated Gelation :** Alkoxide-free, sol-gel synthesis technique for preparing various transition, main group, and rare earth metal oxides.

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Through the use of an organic epoxide that acts as a proton scavenger, solutions of common hydrated metal salts undergo hydrolysis and condensation reactions to form metal oxide gels.

Prepared oxides : Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, HfO<sub>2</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>...

Instead of ionic precursors...

### Different approaches to prepare gels

Metal oxide gels from molecular precursors : Compounds such as carboxylates,  $\beta$ -diketonates, alkoxides M(OR)<sub>n</sub> or oxoalkoxides MO(OR)<sub>n</sub> (M a generally metallic element and R an alkyl group) can constitute oxide precursors.

Alkoxides are the most used precursors thanks to the many advantages they present:

- Great diversity of accessible elements,
- Existence of heterometallic precursors,
- Possibility of using several different precursors during the same synthesis,
- High purity,
- High solubility...



#### н He Li Be В С Ν 0 F Ne Ρ S AI Si CI Na Mg Ar K Sc V Ca Ti Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr Y Zr Rb Sr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te 1 Xe Cs Ba La Hf Ta W Re Os Ir Pt Hg TI Pb Bi Po At Au Rn Fr Ra Ac La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Th Pa U Np Pu Cm Bk Cf Es Fm Md No Ac Am Lw 12

List of elements of the periodic table existing as alkoxides



The general reaction between a metal alkoxide and water, if it is total, can be written :



Examples of metal oxide gel syntheses from metal alkoxides					
Precursor	Solvent	Operating parameters	Gelation	Gel obtained	
$VO(OC_3H_7)_3$	Acetone	T=0°C	5 s < tg < 290 s	V <sub>2</sub> O <sub>5</sub> hydrated	
AI(OC <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Ethanol	Addition of an additive ethyl acetoacetate forming a complex with the precursor to moderate the reactions	Formation of a sol that gels at 60°C	Al <sub>2</sub> O <sub>3</sub>	
$Zr(OC_3H_7)_4$	Propanol	Addition of a moderator (acetic acid or nitric acid)	2 min < tg < 3 min	ZrO <sub>2</sub>	







Hydrolytic methods Vs non-hydrolytic methods...

Ionic and molecular precursors...

## Different approaches to prepare gels

Non-hydrolytic sol-gel approach. During the last 25 years, non-hydrolytic sol-gel techniques were found to be attractive and versatile methods for the preparation of metal oxide gels.

Sol-gel chemistry based on hydrolysis and condensation of metal alkoxides <u>is a powerful and well-established technique</u>. However it has some disadvantages :

- In many cases the hydrolysis rates of metal alkoxides differ significantly (Si(OR)<sub>4</sub> vs. Ti(OR)<sub>4</sub> or Si(OR)<sub>4</sub> vs. R'<sub>x</sub>Si(OR)<sub>4-x</sub>.
- This disparity in reaction rates can be an obstacle in the preparation of homogeneous mixed metal oxides.
- Phase separation can then occur.
- Water during the drying of the gels can exert significant capillary forces leading to pore collapse.

One possible improvement is to switch to non-aqueous conditions and use oxygen donors other than water.

For example the procedure may be based on the condensation of metal chlorides with metal alkoxides for the

synthesis of metal oxides:

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- Alkoxides are the oxygen donor, no water is used during the synthesis.
- Less problem of chemical reactivity with regard to condensation.
- Highly homogeneous dispersions of metal cations in mixed oxides are achieved.
- Volatile organic solvents are easily removed, drying is thus simplified.
- Simplicity  $\rightarrow$  But difficulty in handling certain precursors (in particular chlorides)



**Overview of some known condensation reactions:** 

- Alkyl halide elimination during the reaction between a metal chloride and a metal alkoxide.

 $\equiv$ M-Cl + R-O-M $\equiv$   $\rightarrow$   $\equiv$ M-O-M $\equiv$  + RCl

- Ester elimination in the reaction between metal alkoxides and acetates.

$$\equiv$$
M-O-R +  $\equiv$ M-OC(O)R'  $\rightarrow \equiv$ M-O-M $\equiv$  + RC(O)OR'

- Acetamide elimination route : reactions of acetoxysilanes with metal amides.

 $\equiv$  M-NR<sub>2</sub> +  $\equiv$  M-OC(O)R'  $\rightarrow \equiv$  M-O-M $\equiv$  + R'C(O)NR<sub>2</sub>







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amorphous Vs crystallized...

## Different approaches to prepare gels

Crystallized nanoparticles in solution are the building blocks of the solid part The destabilization of colloidal solutions can lead to the formation of gels



#### Sophisticated approach:

Oxide particles in aqueous solution  $\rightarrow$  Surface charge organization  $\rightarrow$  Electrical double layer  $\rightarrow$  electrostatic stabilization of colloids.



#### Sophisticated approach:

#### Partial removal of capping ligands



Highly concentrated CdS colloids (about 30 wt %) are prepared in acetone through the grafting of 4-fluorophenylthiol at their surface.

**Controlled thiol oxidation by an aqueous solution of hydrogen peroxide** leads to dithiol and fluorosulfonate species.



Aggregation of the particles can thus produce transparent gels.



<u>Selective removal of capping molecules by heat treatment of trizma functionalized anatase NPs.</u>

#### Trizma-functionalized TiO<sub>2</sub> NPs in water







Trizma-functionalized anatase nanoparticles are heated in water, the selective replacement of trizma from the {001} facets by water molecules promotes an oriented attachment process that leads to gelation

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### Now we have gels, but we have to remove the solvent by keeping the solid network unchanged !!!!

#### **Conventional drying Vs supercritical drying**



TMU TMU TMU

TML

#### Ambient pressure drying $\rightarrow$ Xerogel

Upon drying in air alcogels or aquagels experience strong capillary forces, which cause a collapse of the delicate gel skeleton and considerable shrinkage.



To avoid capillary forces...

lating Porous Architectures

for RadioacTivE gas detection

### Different approaches to prepare aerogels

Supercritical drying → Aerogel (The principle of SCD was originally exposed by S.S. Kistler)

During SCD the solvent is submitted to a variation in temperature and pressure bringing it into the domain of the supercritical fluid and then bypassing the critical point to transform the supercritical fluid into vapor.



at the origin of the collapse of the structure of the gel.



Solvent	Tc (°C)	Pc (bars)
Methanol	239	81
Ethanol	243	65
<sup>1</sup> Propanol	264	52
<sup>2</sup> Propanol	235	48
<sup>1</sup> Butanol	290	44
Diethyl Ether	195	36
Acetone	235	47
Xenon	17	58
CO <sub>2</sub>	31	74 22

Supercritical drying using liquid  $CO_2 \rightarrow$  Aerogel In this case the porous structure must be filled with a solvent miscible with liquid  $CO_2$ . It is often necessary to carry out a solvent exchange, in particular for the drying of

			aquag	gels.		Acétal diéthylique	N,N-Diéthylformamide	
essure (bars)	Solid	Company iti and		<u>- \  \\</u> Q		Acétate d'éthyle	N,N-Diméthylacétamide	
		Supercritical			4000	Acétate de méthyle	N,N-Diméthylformamide	
						Acétone	<i>p</i> -Dioxanne	
	Liquid Critical				140- YO	Acétonitrile	<i>n</i> -Dodécane	
	+/	point		Water	880.8	Acétylbenzène	Éthane	
P <sub>triple</sub> (tBuOH)	point	•	Acetone			Acide acétique	Éthanol	
P <sub>triple</sub> (water)		Gas		$m \gamma c \gamma 2$	U Water	Acide caproïque	Éther éthylique	
6x10 <sup>-3</sup>						Acide formique	Éthylacétoacétate	
-				AND A A	00,000	Acrylonitrile	Furfural	
	0.01 T <sub>triple</sub> (tBuOH) 25.9	T <sub>c</sub> (CO <sub>2</sub> ) 31.1		<u>2012</u> 000	Seco	Aldéhyde acétique (acétaldéhyde)	<i>n</i> -Heptane	
Temperature (°C)					Benzaldéhyde	Hexanol		
		- ( -)		0,000		Benzène	Indène	
					800 Y	Bénzonitrile	Isopropanol	
					<u> </u>	<i>n</i> -Butane	Lactate d'éthyle	
				B X CCC	Acetone	sec-Butanol	Méthanol	
					2-Butanone	Méthoxybenzène		
						n-Butyléther	2-Méthyl-2-butanol	
						Carbonate d'éthyle	2-Octanone	
				CTD Y	2	Chloroforme	Paraldéhyde	
1800						Cyclohexane	Propane	
				Liquid CO		Cyclohexanone	Propioaldéhyde	
SP.	$\Delta RIF$					1-Décène	Propylène	
					Diacétonealcool	Tétrachlorure de carbone		
for Radioa	ng Porous Architecti acTivE gas detection	Auron Technologies Abirt	Solve	nts miscible with l	iquid CO <sub>2</sub> .	N,N-Diéthylacétamide	Toluène	23

**Freeze Drying :**  $\rightarrow$  Cryogel (the solvent is solidified and then sublimated, by bypassing the triple point )



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a

Solvent

substitution



Cryogel

► Vacuum











Preparation of nanowire aerogels by a typical ice templating method. Ag nanowire and  $TiO_2$  nanowire aerogels prepared by the ice templating method.

#### But we can use the ambient Pressure Drying to prepare aerogel !!!!



The goal is to reduce the action of capillary forces



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#### **Examples of aerogels COMPOSITES (Organic-Inorganic)**

Heat to

700°C

METALS





