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The Sol-Gel Route to Nanocomposites

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1. Introduction

Nanocomposites are multiphase materials where one of the structural units, either organic or inorganic, is in a defined size range 1-100 nm. In order to prepare organic-inorganic nanocomposites either the particles or the polymers or both can be synthesized "in situ" or used in the final state. When dispersing the nanoparticles, the need of lowering the interface free energy would lead to their agglomeration. Alternatively interactions between inorganic particles and matrix polymer or between particles and an ultrathin layer of surrounding organic molecules must be set up. This is commonly indicated by saying that the inorganic nanoparticles must be compatibilized (Kickelbick 2007). When organic reactive groups are present at the surface of the nanoparticle allowing attachement of matrix polymer molecules, a firm polymer–particle interface can also be obtained. The proper nanoparticle surface engineering can give:

1. good dispersion of NP into polymer at high filler content
2. adjustment of rheology at high filler content
3. covalent bonds between filler and polymer and higher network density
4. Materials with improved mechanical properties (fatigue strength, toughness, scratch resistance…) and flame retardancy and coatings with barrier properties

Recently numerous synthesis methods were explored and successfully used to produce organic-inorganic hybrid nanoparticles with controlled defined shapes (core-shell, multinuclear, hairy-like raspberry …), nanoscale sizes, structure and composition. They have potential applications in a variety of domains, starting from their use as components of advanced both functional than structural nanocomposite materials, where, as reminded above, the engineering of the interface is critical to have good dispersion and for the tailoring of the final properties.

The paper will show that the Sol-Gel method is an outstanding route to the synthesis of hybrid nanoparticles and nanocomposites. Generally speaking it gives inorganic high purity materials at mild synthesis conditions (temperature and pH). An outstanding variation is the so called Stöber method allowing colloidal particles (with well-defined size and shape and with narrow size distribution) be produced through hydrolysis and polycondensation of silicon alcoxides in water /alcohol /ammonia mixtures. The sol gel method allows, also, easy functionalization of silica nanoparticles with specific organic groups. Many of the hybrid nanoparticles synthesis methods take advantage of all this. The sol gel method finds, however, applications in many other research fields. The aim of this paper is to give also, shortly, a contribution to the knowledge of the basic principles of the method, with

particular reference to the synthesis of functionalized silica nanoparticles through the Stöber method.

The paper is structured in six sections, the first one being the introduction. In the second a brief outline of the sol-gel process and the basic principles of the sol stability are reminded; the types of possible precursors are also shortly described. The third section is devoted to the silicates Sol-Gel chemistry, showing concepts that can be extrapolated to the other precursors. In the fourth section the Stöber method and its mechanism are treated. In the fifth the relevant applications to the synthesis of organic-inorganic hybrid nanoparticles and to nanocomposites are addressed.

2. Sol-gel method general remarks

2.1 Brief outline of sol-gel process

The sol-gel process is a synthesis route consisting in the preparation of a sol and successive gelation and solvent removal. The precursors, better described in the successive paragraph, consist of a metal or metalloid element surrounded by various ligands. Very popular are the metalorganic compounds used in the synthesis of silicates, like tetraethyl silicate (or tetraethoxy-silane) $Si(OC_2H_5)_4$, shortly indicated with the acronym TEOS. Very often organometallic compounds are used having some of the alcoxide groups substituted with other organics, having carbon directly bound to silicon, like methyltriethoxy-silane $CH_3Si(OC_2H_5)_4$.

The use of silicon metalorganic and organometallic compounds is reported in a great number of papers (Brinker 1990). The hydrolysis and polycondensation reactions are very useful to obtain both polymeric (containing no dense oxide particles larger than 1 nm) than particulate silicate sols:

$$\mathrm{Si}\left(\mathrm{OR}\right)_4 + \mathrm{n\,H_2O} \rightarrow \mathrm{Si}\left(\mathrm{OR}\right)_{4-\mathrm{n}}\left(\mathrm{OH}\right)_{\mathrm{n}} + \mathrm{n\,ROH} \tag{1}$$

$$\equiv \mathrm{Si-OH} + \mathrm{HOSi} \equiv \rightarrow \equiv \mathrm{Si-O-\ Si} \equiv + \mathrm{H_2O} \tag{2}$$

$$\equiv \mathrm{Si-OH} + \mathrm{ROSi} \equiv \rightarrow \equiv \mathrm{Si-O-\ Si} \equiv + \mathrm{ROH} \tag{3}$$

Polycondensation turns monomers into oligomers and, finally, polymers.

As long as the number of alcoxide groups, (therefore the number of bonds the monomer can form, that is the "functionality"), is greater than 2, complex random branching may occur finally leading to fractal structures. Euclidean objects ($m \propto r^3$, where m is the mass and r is the radius), instead, form in systems in which the particle is partially soluble in solvent: monomers can dissolve and reprecipitate until structures having minimal interfacial area form.

The fractal aggregates grow until they begin to impinge on one another and bonds form at random, linking them in a network and giving a gel. This is therefore a substance containing a continuous solid skeleton enclosing a continuous liquid phase. The "gel point" is reached when a "spanning cluster" appears extending throughout the sol. Initially it coexists with many smaller clusters present in the sol phase. However these progressively become attached to the network giving a monolith.

The gel "aging" involves important processes: condensation, dissolution and reprecipitation. Therefore it strongly affects the final structure and properties. Usually, at

first, syneresis occurs: contraction with expulsion of liquid from the pores. Drying by evaporation gives "xerogels" having a volume 5 to 10 times smaller of the original gel volume. Drying under supercritical conditions ("supercritical drying"), in autoclave, gives aerogel with relatively little shrinkage.
Successive thermal treatments give dense ceramics, both crystalline than amorphous.
In some experimental conditions stable sols are obtained and nanoparticles can be, therefore, produced as discussed at length in the following.
The sol-gel method is very versatile, allowing to easily obtain not only bulk samples and nanoparticles but also films and fibers.

2.2 Types of precursors

Metal (Si, Ti, Zr, Al, B…) alkoxides precursors are largely used (Brinker 1990). The reactions are all similar to the ones above reported for silicon alkoxides. The mechanism are also similar to the ones described, in the following, for the silicon alkoxides, based on nucleophilic attack to the central atom.
Inorganic salts are, also, very often used (Brinker 1990, Livage 1988). Salts in water give, in fact, solvated cations. The charge transfer from the bonding orbitals of water molecules to empty d orbitals of transition metal makes the water molecule more acidic. Different complexes can form depending on the magnitude of electron transfer:

$$\underset{\text{aquo}-\text{ion},}{\left[M - OH_2\right]^{z+}} \rightarrow \underset{\text{hydroxo}-\text{ion}}{\left[M - OH\right]^{(z-1)+}} + H^+ \rightarrow \underset{\text{oxo}-\text{ion}}{\left[M - O\right]^{(z-2)+}} + 2H^+$$

When the water molecules number is N, also hydroxo-aquo and oxy-hydroxo ions may form. The general formula of the complex is:

$$\left[MO_N H_{2N-h}\right]^{(z-h)+}$$

Where aquo ions correspond to h=0, hydroxo ions to h=N, oxy ions to h=2N, hydroxo-aquo when $[1 \le h \le (N-1)]$, oxy-hydroxo when $[(N+1) \le h \le 2N-1]$
The nature of the complex depends on: charge, z; pH of the solution; coordination number, N; electronegativity, number of metal ions bridged by hydroxo or oxo ligands; number of H atoms in the ligand; number of OH coordinating M
The dependence on the charge and pH of the solution is roughly described by the diagram of Fig.1 giving the rough limits of existence of the various complexes
Condensation can occur by Nucleophilic substitution mechanism (SN) (when the preferred coordination is satisfied)

$$M_1 - OX + M_2OY \rightarrow M_1 - OX - M_2 + OY \quad (4)$$

Or through nucleophilic addition (AN) (when the preferred condensation is not satisfied):

$$M_1 - OX + M_2OY \rightarrow M_1 - OX - M_2OY \quad (5)$$

It is generally necessary to be in the hydroxo domain to generate condensed species. The exception is the case of coordinatevely unsaturated oxo-precursors. Changes of pH through addition of bases or acids, reduction of oxo-precursors or thermohydrolysis allow to move into the hydroxo domain.

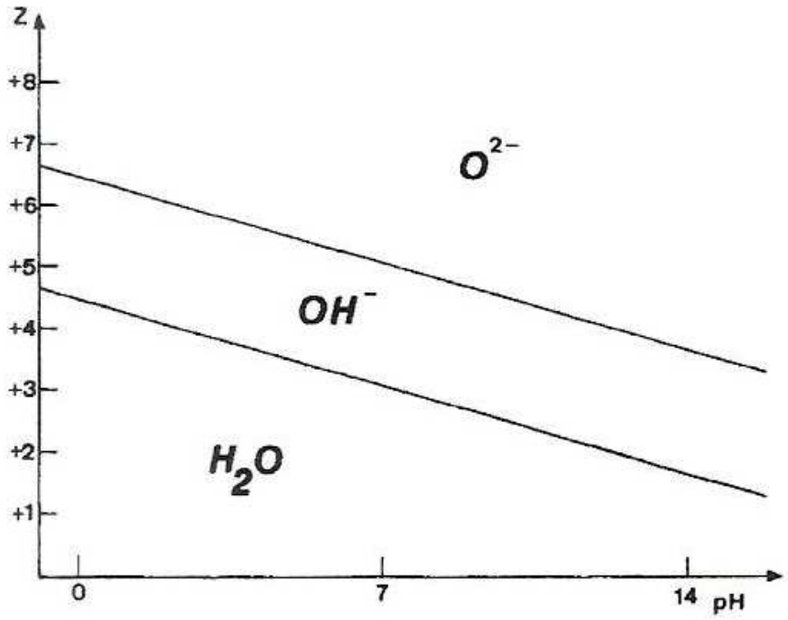


Fig. 1. The charge-pH diagram (from Livage 1988)

It's worth reminding that a predictive model for inorganic polymerization reactions was proposed (Livage 1988) based on the electronegativity concept introduced by L-Pauling as well on the principle of electronegativity equalization suggested by R.T.Sanderson (Sanderson 1951). The model works quite well (Brinker 1990, Livage 1988) to predict ionic and condensed species in the case the precursor is an inorganic salt so as the products of hydrolysis and condensation reactions of metalorganic precursors.

2.3 SOL stability

Nanoparticles are obtained, as previously reminded, when stable sols are formed during the hydrolysis and polycondensation of sol-gel precursors. Because of their very high specific surface area, nanoparticles have a themodynamic strong tendency to agglomerate to reduce surface energy.

The dispersion forces (Mahanty 1976) are the attractive ones responsible of flocculation. At atomic level the dispersion energy depends on the sixth power of the distance. Slower changes with the distance occur in the case of nanoparticles. Aggregation can be avoided through electrostatic and/or steric barriers due to electrostatic repulsion of surface charges and/or adsorption of organic molecules.

The DLVO theory (Parfitt 1981, Brinker 1990) successfully describes the stabilization due to electrostatic repulsion. The surface of oxide particles is positively or negatively charged because of the action of the "charge determining ions", H^+ and OH^-:

$$M-OH+H^+ \rightarrow M-OH_2^+ \tag{6}$$

$$M-OH+OH^- \rightarrow M-O^- + H_2O \tag{7}$$

A "Point of Zero Charge" (PZC) is defined as the pH at which the particle has no electric charge. Because of eq. 6 and 7 the particle is positively charged at pH<PZC and negatively

charged at pH>PZC respectively. PZC for silica is pH≈2; therefore, but in the case of very acid solutions, the surface has a negative charge due to reaction 7; this negative charge is greater the higher is the departure of pH from PZC. A surface potential, Φ_0, settles whose value also depends on the departure of pH from PZC. Counterions are, therefore, strongly attracted from the solution; altogether with water molecules they form the tightly bound "Stern layer" around the particle. The plane separating the "Stern layer" from the "Gouy layer", containing freely diffusing ions, is called Helmoltz plane. Another plane is individuated, the so called "slip plane": it separates, inside the Gouy layer, a inner part that moves with the particle during electrophoresis. The counterions screen the surface electrical charge, making the electrostatic potential to decrease; the decrease is linear inside the Stern layer but follows, in the Gouy layer, the law:

$$V_R \propto \exp\left[-k(h-H)\right] \tag{I}$$

Where h is the distance from the surface (H being the distance of the Helmoltz plane) and

$$k = \left(F^2 \sum\left(c_i z_i^2\right) / \varepsilon\varepsilon_0 R\,T\right)^{1/2} \tag{II}$$

where F and R are the Faraday and universal gas constants, ε and ε_0 are the dielectric constant of the solvent and the permittivity of vacuum, c_i and z_i are the charge and concentration of counterion of type i.

The potential on the sleep plane is called the ζ-potential, Φ_ζ, and the pH at which Φ_ζ=0 is the Isoelectric Point (IEP), often taken equal to PZC.

The reverse of k is called the Debye-Huckel screening length and is a measure of how much the repulsive potential extends far apart from the surface.

Following the DLVO theory, the potential energy near the surface of a particle is the sum of Van der Waals attractions and electrostatic repulsion potentials shown in Fig. 2 (from Parfitt).

Therefore it depends on the Debye-Huckel screening length as shown in Fig 3 (from Parfitt).

However it depends also on the radii of the two approaching particles, as shown by fig 4 (Parfitt).

The stability of the sol depends on the height of the maximum of the total potential energy. Therefore:

a. the sol stability decreases in the presence of salts (the more the higher the concentration).
b. Monodisperse particles are more stable than polydisperse ones.
c. The stability increases with the size of the particles.

Recently another attractive (Ping 2006) force was recognised to be active, the so called depletion force. A simple interpretation (M.Singh-Zocchi 1999) of the nature of these forces is based on the concept of osmotic pressure. It occurs when particles of radius R are dispersed in a liquid in the presence of a cosolute consisting of spherical polymeric particles of gyration radius r_p, that are not able to bind to the particles surface. When two or more particles come close enough to overlap the shells of thickness r_p, the polymeric particles are excluded from the space between them (the depletion zone). The osmotic pressure acting on the excluded volume gives rise to an attractive force and drives the particles closer.

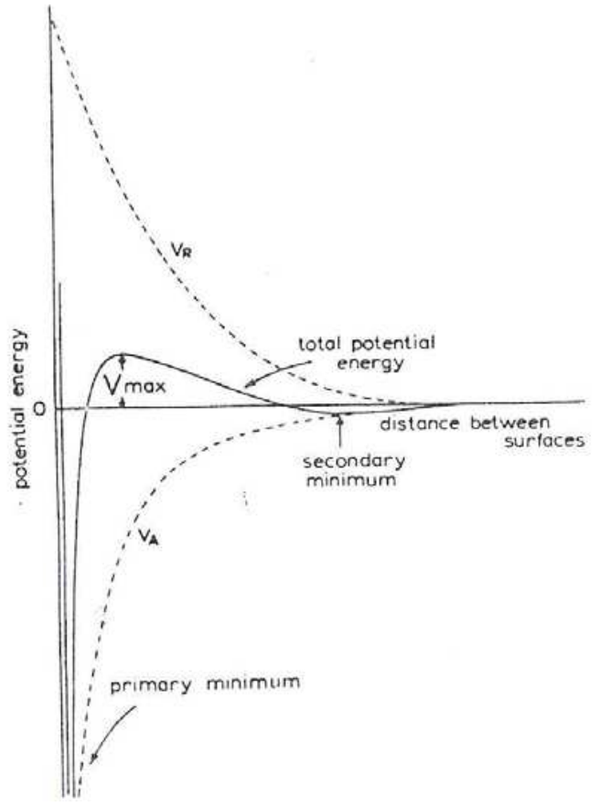


Fig. 2. DLVO potential representation: V_A: attractive Van der Waals potential; V_R repulsive electrostatic potential (from Parfitt 1981)

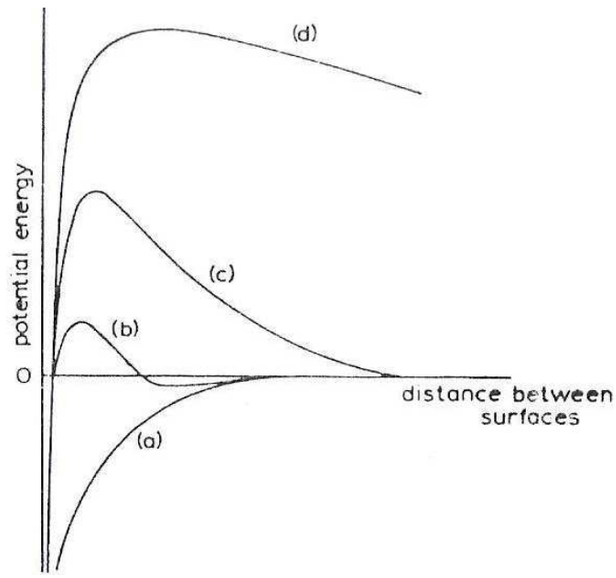


Fig. 3. Influence of electrolyte concentration on total potential energy of interaction of two spherical particles of radius 100 nm in aqueous media: a) $1/k = 10^{-7}$ cm; b) $1/k = 10^{-6}$ cm; c) $1/k = 10^{-5}$ cm; d) $1/k = 10^{-4}$ cm; (from Parfitt 1981)

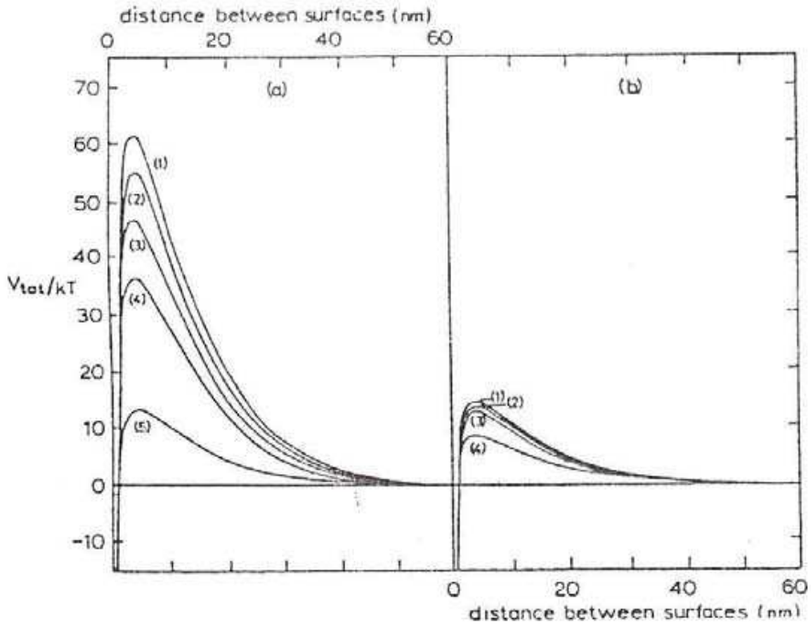


Fig. 4. Theoretical curves of total potential energy against distance of separation of two spherical particles of radii a_1 and a_2 and equal surface potential (35.86 mV); $1/k = 10^{-6}$ cm (from Parfitt 1981)

a): a_1=125 nm and a_2= 125 nm (1), 100nm (2), 75 nm (3), 50 nm (4) 12.5 nm (5)

b): a_1=12,5 nm and a_2= 125 nm (1), 100nm (2), 75 nm (3), 12.5 nm (4)

Steric barrier occurs, instead, when a thick layer of organic molecules is adsorbed (Sato 1980, Napper 1983). The need of the following conditions is recognised (Tadros 1982) for an effective steric barrier:

a. the particle surface should be completely covered
b. the polymer should be firmly anchored to the surface
c. the layer must be thick enough to have the particles at a distance where the Van der Waals attractions are weak
d. the nonanchored polymer segment must be well solvated

When the particles possess an electric charge or the polymers are polyelectrolytes an electrosteric barrier settles (Napper 1983).

Recently it was claimed (Gao 2009, Branda 2010) that in some cases polymer coated inorganic nanoparticles, a few nm in diameter, could form stable nanometric clusters of the kind represented in Fig. 5

The observed need of an optimal polymer/nanoparticle mass ratio for the long term stability can be explained (Branda 2010) by admitting that both steric than electrostatic stabilization occurs. In this case the polymer is expected to play a double role: at level of cluster formation and successive cluster aggregation. The polymer content increase makes, of course, the steric hindrance to increase thus improving stability. However just for the same reason, as illustrated in Fig.5, the number of silica particles per unit volume in the cluster is expected to decrease, by this way reducing the electrostatic hindrance among clusters and improving the tendency to cluster aggregation. Therefore the need for the stabilization of an optimal polymer/nanoparticle mass ratio was justified.

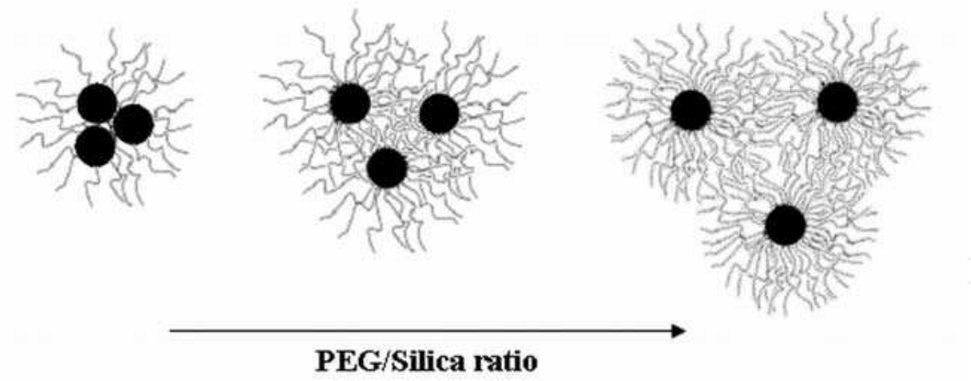


Fig. 5. Schematic representation of silica/PEG nanoparticles (from Branda 2010)

3. Silicates sol-gel chemistry

3.1 Aqueous silicate chemistry

Although 4+ is the only silicon important oxidation state and 4 is its most important coordination number, aqueous silicate chemistry is very complex.

When dissolving silicates in acidic solutions the formation of silicic acid would be expected:

$$Na_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2Na^+ + 2Cl^-$$

It was early observed that (Freundlich 1926) the silicic acid solutions slowly thicken and finally give a gel. This was explained by Iler (Iler 1979) through a polymerization mechanism in three steps: formation of particles from the monomers, successive growth of them and establishment of links giving chains and networks extending throughout the liquid medium.

^{29}Si NMR (Harris1982, Knight 1988)) allowed, effectively, to identify numerous silicate species (from dimers to prismatic hexamers) present in aqueous silicate solutions. Rings appear to easily form as a result of a tendency to maximise the number of siloxane Si-O-Si bonds and minimise the number of terminal hydroxyl groups. Nanosized particles are, by this way, easily formed. The successive fate (Iler 1979) depends on the synthesis conditions:

1. sols when working at pH=7-10 in the absence of salts
2. three dimensional gel networks when working at pH<7 or at pH=7-10 in the presence of salts.

This is illustrated in Fig. 6 that shows schematically the overall sol stability and gel time dependence on the pH (Iler 1979).

Two important pH values appear to be: a) the point of zero charge, where the electrical surface charge is zero (changing in the pH range 1-3); b) the pH≈7 where both silica solubility and dissolution rate begin to be important.

The gel time maximum at PZC can be explained taking into account the mechanisms of condensation:

1. above PZC:

$$\equiv Si - OH + OH^- \rightarrow \equiv Si - O^- + H_2O \quad (8)$$

$$\equiv Si - O^- + HO - Si \rightarrow \equiv Si - O - Si \equiv + OH^- \quad (9)$$

2. below PZC

$$\equiv Si - OH + H_3O^+ \rightarrow \equiv Si^+ + 2H_2O \quad (10)$$

$$\equiv Si^+ + HO - Si \equiv \rightarrow \equiv Si - O - Si \equiv + H^+ \quad (11)$$

As a consequence, according to Fig.6, the condensation rate is expected to increase with pH above PZC and with the H_3O^+ concentration (decreasing pH values) below PZC; therefore a maximum is expected at PZC. Owing to inductive effects, the most acidic silanols are the ones linked to the more highly condensed species; therefore we expect condensation to occur, preferentially, between more highly and less highly condensed species. Highly branched structures are, by this way, expected to form.

However at higher pH other effects become important. In fact (because of reaction 8) the higher is the pH the greater the ionization of the condensed species and, therefore, the negative charge making them mutually repulsive. It's worth reminding, also, that (section II 1) the "spanning cluster" forms as the result of the impingement of the fractal aggregates on one another and formation of bonds at random. Therefore the increase of the gel time above pH=7 can be explained, so as the effect of salts. In fact salts reduce stability furnishing ions screening the surface charge of the particles (see section II 3). The gel time is expected, therefore, to increase above pH 7 the less the higher the concentration of salts. This is in good agreement with Fig.6.

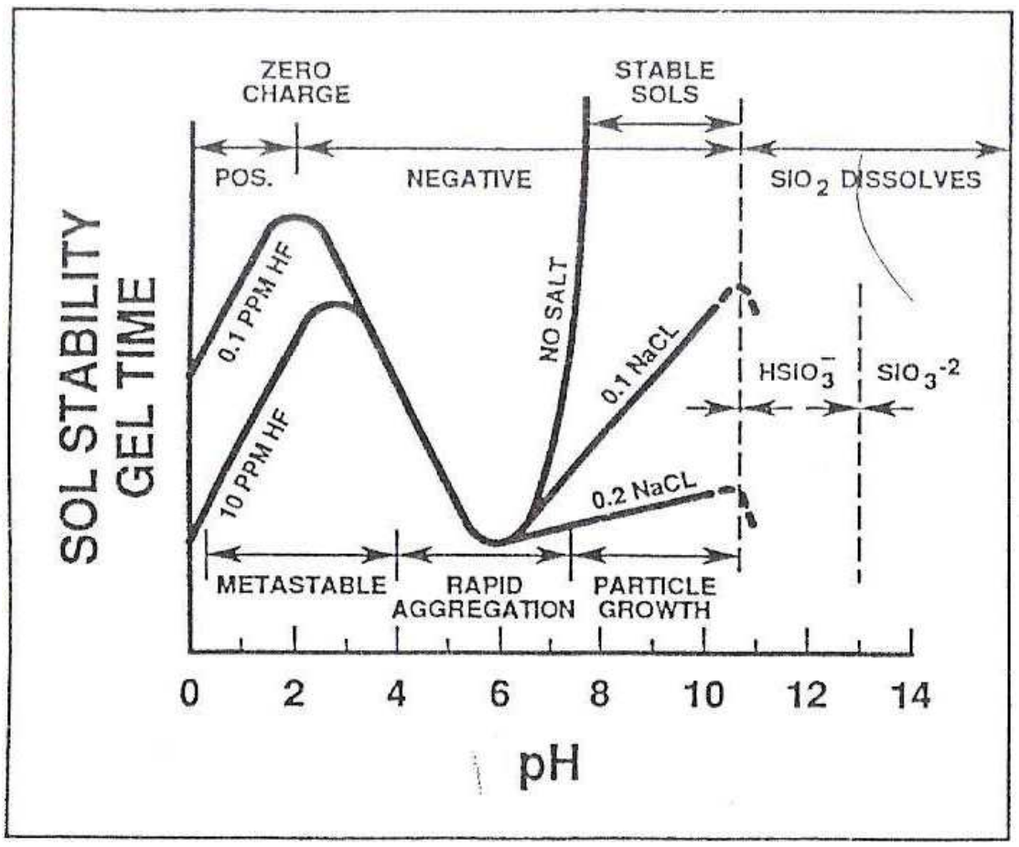


Fig. 6. Effects of pH in the colloidal silica-water system (from Iler 1979)

Moreover, in the pH range 7-10, both solubility and dissolution rate increase. Another growth mechanism is expected to take place. In fact, as solubility decreases when the radius of curvature increases, bigger particles may grow at the expense of the smaller ones (Ostwald ripening mechanism).
Above pH=10 the solubility is too high to allow gel or particles formation.

3.2 Silicates from alcoxides

Silicate gels are usually obtained from alkoxysilanes (eq.1-3). Owing to miscibility problems of water and alkoxysilanes, a mutual solvent must be used; the alcohol corresponding to the alkoxide group of the precursor is usually chosen. A water/silicon ratio (in the following indicated as r) equal to 2 would be required by the stoichiometry of the overall reaction:

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4\ ROH$$

However r values spanning from 1 to more than 50 have been used (Brinker 1982) in reaction media frequently acid or basic. Early works showed that, depending on the experimental conditions (alkoxide concentration, water/silicon ratio and concentration of acid or base), monoliths, films, fibers or monodisperse spheres can be easily obtained (Nogami 1980, Brinker 1982, Stöber 1968, Sakka 1984). A general trend was observed (Brinker 1982): acid catalysed hydrolysis with low r value produces weakly branched "polymeric sols" whereas base catalysed hydrolysis with larger r values produces highly condensed "particulate" sols.

Mechanisms

Both hydrolysis than condensation mechanisms proceed through nucleophile attack to the silicon, catalysed by acid or base.
In the case of acid catalysed hydrolysis it is thought (Pohl 1985, Keefer 1984, Uhlmann 1984) that protonation of an alkoxide group makes it a better leaving group allowing substitution with water:

$$H_2O + Si\ (OR)_3(OHR)^+ \rightarrow (H2O)^{\delta+} ..... Si(OR)_3 .....(\ OHR)^{\delta+} \quad (12)$$

$$(H2O)^{\delta+} ..... Si(OR)_3 .....(\ OHR)^{\delta+} \rightarrow Si(OR)_3OH + ROH + H^+ \quad (13)$$

The nucleophile attack may occur on the "opposite side" of the leaving group, as usually in the SN_2 mechanisms, or on the "flank side" involving no inversion of the silicon tetrahedron.
The base catalysed hydrolysis, instead, starts with the nucleophile attack (Iler 1979, Keefer 1984, Pohl 1985) of OH^-; this causes the displacement of alkoxide group (better leaving group than OH^-). The transition state is, in this case, negatively charged.
The acid catalysed condensation mechanism (Pohl 1985), as described by eq. 10 and 11, involves protonation of a silanol allowing successive nucleophilic attack. The base catalysed condensation mechanism (Pohl 1985, Voronkov 1978), described by eq. 8 and 9, occurs through the nucleophilic attack of deprotonated silanol
Steric effects. According to the mechanism, the hydrolisis and condensation rates strongly decrease as the chain length or degree of branching of the alkoxy or alkyl groups present in the precursor molecule increase (Voronkov 1978).
Inductive effects. The inductive effect can be easily understood if we take into account that hydrolisis and condensation involve the progressive substitution of -OR groups with –OH

and –OSi ones and occur through mechanisms involving transition states, positively charged in the case of acidic conditions and negatively charged in the case of basic conditions. We must, moreover, take into account that the substituent groups (including also the alkyl ones present in organometallic precursors) have different electron providing (or electron withdrawing) effect and, therefore, affect in a different manner the reactions in acidic or basic medium. The electron providing ability and the stability of transition states change in the sequence:

$$-\mathrm{OSi},\ -\mathrm{OH},\ -\mathrm{OR},\ \mathrm{R}.$$
$$\rightarrow$$
$$\text{increasing electron providing ability}$$
$$(\text{increasing stability of positively charged transition states})$$
$$(\text{decreasing stability of negatively charged transition states})$$

As a consequence collected experimental results (Schmidt 1984) can be interpreted:

- Under acidic conditions the hydrolisis rate would decrease with each subsequent hydrolisis step
- Under basic conditions each subsequent hydrolisis step would occur more quickly as hydrolisis and condensation proceeds
- Under acidic conditions the hydrolysis rate of organometallic precursors (RO)4-nSiR'n increases with n
- Under basic conditions the hydrolysis rate of organometallic precursors (RO)4-nSiR'n decreases with n

The silica (SiO_2) isoelectric point (IEP), usually taken equal to the point of zero charge (PZC), is about 2. It is clear that its value is influenced by the presence of electron-providing alkyl groups (reducing the acidity of silanols and therefore increasing the isoelectric point) or electron withdrawing OH or OSi groups (increasing silanols acidity and therefore reducing the IEP). As acid catalysed and basic catalysed condensation mechanisms involve protonated and deprotonated silanols, the base catalysed condensation occurs when the pH is greater than the IEP. In general base catalysed condensation is referred to as occurring starting from pH=2.

The observation that base catalysed condensation occurs preferentially between more highly condensed species and less highly ones can, therefore, be explained. In fact

- Replacement of more electron providing OR groups with progressively more electron-withdrawing OH and OSi groups reduces the nucleophile character
- Replacement of more electron providing OR groups with progressively more electron-withdrawing OH and OSi groups increases the ability to suffer nucleophile attack.

H_2O/Si ratio

The H_2O/Si ratio has a complex effect on the overall process. Of course hydrolisis accelerates as H_2O/Si ratio increases. Moreover the higher value of the ratio causes more complete hydrolisis of the monomers before significant condensation occurs. Two effects on the condensation reactions are easily recognised:

a. At low ratios the alcohol producing condensation reactions are favoured (reaction 3) while the water producing ones are favoured at high H_2O/Si ratios (reaction 2).
b. large values of the ratio promote siloxane bond hydrolysis (reverse of condensation reaction 2).

Solvent effect

Protic solvents (water, methanol, ethanol, 2-ethoxyethanol, formamide, etc.) so as aprotic solvents (dimethylformamide, tetrahydrofuran, dioxane 1,4 etc.) have been largely used having very different dipole moments (Brinker, 1982). Both protic and polar character of the solvent molecules affect the hydrolysis and condensation reactions (Brinker 1982).
The solvent dipole moment affects the elctrostatic stabilization and the distance over which a charged catalytic species, i.e. the oxydril nucleophile or hydronium electrophile ions, are attracted to or repelled from potential reaction sites.
Aprotic solvents do not hydrogen bond, therefore do not affect the nucleophile or electrophile character of the nucleophile and electrophile agents involved in hydrolisis and condensation reactions.
Usually the alcohol corresponding to the alkoxyde group of the metalorganic compound is used; this allows to avoid transesterification reactions:

$$R'OH + Si(OR)_4 \rightarrow Si(OR)_3 OR' + ROH \tag{14}$$

Some experimental results (Yamane 1984) would indicate that transesterification proceeds much further under acidic conditions than under basic conditions

4. Silica nanoparticles sinthesys

4.1 The Stöber method

Many methods (Brinker 1990) allow to prepare particles from solution or from vapour phase. One of the most popular is the so called Stöber method (Stöber 1968) allowing to prepare monodisperse silica spheres from less than 0.05 μm to 2 μm. The method is based on the hydrolysis and polycondensation of alkyl silicates in basic (ammonia) alcoholic solutions, therefore on the sol-gel method reactions 1-3. The particles size strongly depended on the water and ammonia concentration (Stöber 1968), but also on the nature of the alcohol used as a solvent. When using alcohols of higher molecular weigh the reaction was slowed down and both median particle size than the spread of the size distribution increased simultaneously.
The work was extended by Bogush et al. (Bogush 1988). A correlation was found allowing to predict quite well the final particles size, d, over concentrations of 0.1-0.5M TEOS, 0.5-17.0M H_2O, 0.5-3M NH_3:

$$d = A[H_2O]^2 \exp\left(-B[H_2O]^{1/2}\right)$$

Where

$$A = [TEOS]^{1/2}\left(82 - 151\,[NH_3] + 1200\,[NH_3]^2 - 366\,[NH_3]^3\right)$$

$$B = 1.05 + 0.523\,[NH_3] - 0.128\,[NH_3]^2$$

The correlation failed particularly at small particle size and high TEOS concentration. The effect of changing the temperature, in the range 9-55°C, was also studied. The final particle size was found to decrease monotonically as temperature increases with progressively narrower sizes distributions. The particles were found to have a porosity of 10-15%.

The solids content achieves (Bogush 1988) a maximum value of 3% at a TEOS content of 0.5M. In order to obtain both larger particles than larger final mass fractions, a "seeded growth" process was proposed (Bogush 1988). In this case the particles obtained through the Stöber method act as seeds. When the Stöber synthesis goes to completion, proper amounts of TEOS and water (in a molar ratio 2) are added. The amounts must not exceed a critical value (depending on the initial particle size and number density and reaction temperature) for which a second population of stable colloidal particles may be formed. The process can be iterated several times. The final average diameter, d, is

$$d = d_0 \left(V / V_0 \right)^{1/3}$$

where d_0 is the initial average diameter and V and V_0 are respectively the total volume of alkoxide added and the volume of alkoxide used to produce the seed particles.

The method can be applied to alkoxide mixtures however a size effect of the partial substitution of alkoxides was observed (Branda 2007). Stable colloids were obtained when the pure alkoxides, tetraethoxysilane (TEOS) or 3-aminopropyltriethoxysilane (APTS), were used; a surprising particle size increase was observed when mixing TEOS and APTS at constant overall alkoxide content. This size effect was greater the closer was the TEOS/APTS concentration ratio to 1.

The "seeded growth" process and the use of alkoxides mixtures open the way to the ease production of functionalized nanoparticles. This is obtained through the use of organometallic precursors, having some alkoxide groups substituted with other organic groups bound through a direct Si-C bond which is not prone to hydrolysis. The use of APTS, for example, is the main route followed to have reactive amino groups present at the surface of the nanoparticles.

The Stöber method has been extended (Brinker 1982) to prepare nanoparticles of different composition, i.e TiO_2, ZrO2, ZnO, Ta2O5, SiO2 doped B2O3 etc.

4.2 The Stöber method mechanism

The factors affecting the sol stability (section II 3) play a central role in the Stöber method mechanism for which an aggregative growth model is nowadays universally accepted (Bogush 1991). Following this theory primary particles are formed through the sol-gel chemistry (section III) having a maximum diameter 1-10 nm. According to Flory-Huggins (Flory 1953) theory and Tanaka and co-workers (Tanaka 1977, Huchberg 1979) the primary particles size is smaller the poorer solvent is the suspending medium. The other assumption of the mechanism proposed by Bogush are:

1. particles grow solely by binary aggregation
2. aggregating particles coalesce to form a spherical particle of the mass of the aggregating pair
3. primary particles are formed in a constant size at a rate that can be related to the loss of soluble species from the solution and is independent of the amount of gel phase present. This stage is indicated as "nucleation"
4. aggregation rates are determined by typical colloidal interaction potentials

Size dependent aggregation rate constants are determined from estimates of particle properties and measures of particle surface potential. The model provides (Bogush 1991) good estimates of final particle size distribution parameters from silicon alcoxide reaction rates. The particle surface potential is considered to be governed by the sum of Van der

Waals, electrostatic and solvation interactions. These last are accounted for due to their importance in the flocculation of silica in aqueous dispersions (Allen, 1969, 1970, 1971). An interesting result of the calculations is that primary particles aggregate with larger ones more rapidly than they do with themselves; moreover larger particles aggregate slowly with particles of similar size. Primary particles production appears to be the rate limiting particle growth step.
The analysis was confirmed by other authors (Lee 1988). A narrow final size distribution can be obtained if the aggregation rate for large/large pairs is slower than for small/small or small/large pairs. The final particle size and density depends on the relative rate of nucleation and aggregation (Lee 1988).
SAXS results showed that (Boukari 1997 and 2000) the primary particles have the same size (Rg≈4nm in methanol and Rg≈10nm in ethanol) and low density structure independent of the ammonia and water concentrations. It was found (Green 2003) that ammonia and water concentrations control the balance between hydrolysis of TEOS and the condensation of its hydrolysed monomers. The first nanostructures appear at a hydrolysed monomer concentration around 0.1M (Green 2003), indicating that formation of the primary structures is thermodynamically controlled by supersaturation of the intermediate species. The differences in the particle size between methanol and ethanol were attributed (Green 2003) to differences in the interactions between the solvent and the hydrolized intermediates.
All this allowed to give an explanation (Branda 2007) to the reminded tricking size effect of mixing alcoxides (section IV 1). Nuclei of different size are expected to form when the alkoxides are mixed. The mixing appears to change the evolution of particle population favouring the establishment of a size distribution wherein the dominant aggregation event can be between the freshly generated nuclei and large aggregates, which is the faster aggregation event. The closer is the TEOS/APTS ratio to 1 the sooner particles size differentiation would occur and the fewer but greater particles would form, in short times.

5. Synthesis of nanocomposites

The sol-gel method allows to easily produce inorganic nanoparticles. However, as reminded in the Introduction section, their dispersion into a polymer matrix requires their functionalization (Kickelbick 2007). In fact, in a nanocomposite, the maximum interface free energy per volume of composite, $E_{v,max}$, is the sum of the free energy of the inorganic particles, γ_i, and the surface energy of the polymer, γ_p , in the vacuum. However γ_i is much higher than γ_p. In a nanocomposite the specific surface area of the particles is very high leading to very high values of $E_{v,max}$. This leads to a strong tendency to agglomeration of particles. This is a very great problem in the synthesis of nanocomposites. Alternatevely (Caseri 2007, Bourgeat-Lamy 2007) it can be decreased by interactions between particles and matrix polymer or between particles and an ultrathin layer of surrounding organic molecules. The tailoring of the interface is, otherwise, also relevant for the final properties of the composite. There is, therefore, a great interest in the synthesis of hybrid organic/inorganic nanoparticles. Many routes were followed to obtain this (Elodie Bourgeat Lamie 2007). In the greater part of them the sol-gel technique plays a central role. The topic was smartly revewed by Bourgeat-Lamie (Bourgeat-Lamy 2007) with a short and quite exhaustive description of examples. They are summarized in the following, where a phew interesting examples are indicated:

1. Self assembly of preformed organic and inorganic nanoparticles:
   a. heterocoagulation based on electrostatic interactions due to different surface charge of the organic and inorganic particles in colloidal solutions of properly selected pH (Marston 1998)
   b. layer by layer assembly consisting in the deposition of uniform polymer films onto mineral substrates by the sequential adsorption of polyanions and polycations (Decher 1997, Caruso 1998)
   c. molecular recognition assembly: the colloidal organization based on the presence of bifunctional mediating molecules bearing reactive groups on both ends capable of bonding particles together (Fleming 2001)
2. In situ polymerization in the presence of preformed mineral particles:
   a. grafting of organosilane and organotitanate coupling agents
   b. polymerization in multiphase systems. One strategy is the grafting of organometallic compounds (like methacrylate silane molecules (MPS)) that allows anchoring of the growing polymer chains on the mineral surface during the earlier stages of emulsion, dispersion or miniemulsion polymerization (Bourgeat-Lamie 1999 e 2006, Reculusa 2004).
   c. surface initiated polymerization, that is templating inorganic colloids with polymer brushes in solution (Advincula 2003, von Werne 2001). In the Graft-to technique a functional group of a preformed polymer is reacted with active sites on the inorganic surface. In the graft-from technique polymers are grown, through controlled radical polymerization (CRP), directly from the inorganic surface which has been functionalized with the appropriate initiator or catalyst. Owing to the narrow molecular weight polidisperity assured by CRP the grafted particles can self-organize into 2D arrays with controlled interparticle distances function of the degree of advancement of the reaction
3. In situ formation of minerals in the presence of polymer colloids
   a. sol-gel nanocoating (Imhof 2001) . In this case the polymer nanoparticles are the templates for the sol-gel polycondensation. The synthesis requires the use of appropriate compounds enhancing the coupling. These are either organometallic compounds (like MPS) containing groups capable to undergo a chemical reaction with the organic precursor or ionic molecules able to promote electrostatic attractions
   b. reaction of previously adsorbed metal salt precursors
   c. growth of inorganic nanoparticles within a swelling polymer matrix that plays the role of nanoreactor (Mayer 2000).
4. Hybrid nanoparticles (organic-inorganic interpenetrated networks (IPN)) through simultaneous reaction of organic monomers and mineral precursors. The rate of both reactions must be not too much different and a coupling agent must be used to link the inorganic network and the organic polymer. Very interesting hybrid colloids with interpenetrated networks (IPN) can be formed. Properties are expected significantly different than a simple combination of the two components ones, controlled by the functionality and connectivity of the molecular precursors

Although very short, the above reported description points out that all the reminded methods require a deep knowledge of the sol-gel chemistry. This is, in fact, fundamental to have nanoparticles with the desired size, structure, composition and right surface properties (electric charge and reactivity); it is also essential to plan and properly control grafting of molecules or the production of organic-inorganic interpenetrated networks.

6. Conclusions

The Sol-Gel route is a versatile method allowing to produce bulk materials, either crystalline or amorphous of controlled porosity, as well as fibers, films and nanoparticles. Also in the rapidly growing and very promising research field of nanocomposites it plays a central role; this is linked to the production of hybrid organic/inorganic nanoparticles. In fact the need to have a good dispersion of the nanophase into the matrix and the interest to proper tailoring of the final properties can be, just, satisfied through the synthesis of hybrid organic/inorganic nanoparticles.

The Stöber method allows to obtain inorganic monodisperse nanoparticles from less than 0.05 µm to 2 µm; the process involves a growth mechanism based on the aggregation of very fine primary particles; these are obtained through hydrolysis and polycondensation of the classical precursors of the sol-gel method. The sol-gel chemistry controls, therefore, the size, structure, composition and surface properties (electric charge and reactivity) of the Stöber nanoparticles. It is also important to plan and properly control grafting of molecules or the production of organic-inorganic interpenetrated networks. Its deep knowledge is, therefore, essential to plan and control the production of organic inorganic hybrid nanoparticles.

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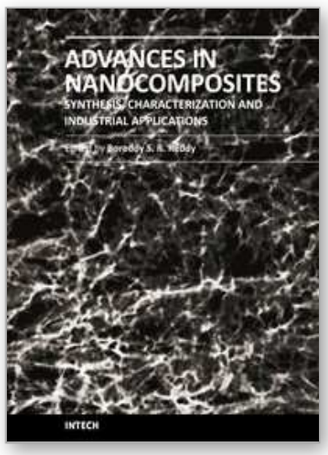
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Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications

Edited by Dr. Boreddy Reddy

ISBN 978-953-307-165-7
Hard cover, 966 pages
Publisher InTech
Published online 19, April, 2011
Published in print edition April, 2011

Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications was conceived as a comprehensive reference volume on various aspects of functional nanocomposites for engineering technologies. The term functional nanocomposites signifies a wide area of polymer/material science and engineering, involving the design, synthesis and study of nanocomposites of increasing structural sophistication and complexity useful for a wide range of chemical, physicochemical and biological/biomedical processes. "Emerging technologies" are also broadly understood to include new technological developments, beginning at the forefront of conventional industrial practices and extending into anticipated and speculative industries of the future. The scope of the present book on nanocomposites and applications extends far beyond emerging technologies. This book presents 40 chapters organized in four parts systematically providing a wealth of new ideas in design, synthesis and study of sophisticated nanocomposite structures.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Francesco Branda (2011). The Sol-Gel Route to Nanocomposites, Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications, Dr. Boreddy Reddy (Ed.), ISBN: 978-953-307-165-7, InTech, Available from: http://www.intechopen.com/books/advances-in-nanocomposites-synthesis-characterization-and-industrial-applications/the-sol-gel-route-to-nanocomposites

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