From (Sub)colloidal Growth to the Gel Structure

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Chapter 3

From (sub)colloidal growth to the gel structure

Abstract

An important consideration in the study of the sol-gel method is that there is no universal recipe for the preparation of a selected catalytic formulation. This means that it is not possible to provide a scheme for the preparation of a catalyst using the sol-gel process, as the synthesis route depends on the type of the selected approach. Furthermore, since its discovery, the sol-gel method has undergone continuous development and new synthesis routes have been designed.

Generally speaking, we can consider the following as starting materials: alkoxides and organic molecules (chelating agents, surfactants, esters, organic acids), inorganic salts (nitrates, chlorides), solvent - usually alcohol (methanol, ethanol)- water. Catalysts when it is necessary to increase the speed of hydrolysis or simply to change the particle growth mechanism.

The structure of the gel, responsible for the properties of the final material, is closely related to the hydrolysis and condensation pathway and the cluster growth mechanism. In 'colloidal' gels, the network consists of the agglomeration of dense colloidal particles, whereas in 'polymeric' gels, the particles have a polymeric substructure resulting from the aggregation of sub-colloidal chemical units. The latter are an entanglement of randomly branched polymer chains. Actually, it is not possible to predict which type of cluster will form in a specific case, due to the complexity of the system. However, if a particular synthesis protocol is followed exactly, the same cluster can be reliably synthesised in most cases, very often with high yields and in large quantities. This is one of the great advantages of this methodology.

Among the factors influencing hydrolysis and condensation reactions, water is a key parameter regulating the sol-to-gel transition and gelation time. In this chapter, we will see how it also affects the textural and structural properties of the synthesised material.

Keywords: Polymeric gel, Colloidal gel, gelation time, aging, synthesis parameters

3.1 Polymeric gel vs Colloidal gel

The transition from sol to gel and the pathway followed by the growing particles enclose most of the factors that define the final characteristics of the gel. For example, the textural properties in terms of surface area and average pore diameter are strongly dependent on the size and structure of the primary particles or polymers formed by condensation reactions, as well as the organisation of these structures. In order to tailor the catalyst using the sol-gel procedure, it is useful to delve into the mechanisms of particle growth revealing the key factors ruling the process.

As was mentioned in the previous chapter, small linear and cyclic oligomers are the first 'sol' forming products and serve as the building blocks for gel formation. This results in a broad spectrum of structures at different degrees of cross-linking, as evidenced by ^{29}Si NMR spectroscopy. Also contributing to the formation of these particles is the possible depolymerisation with the opening of ring structures and the resulting renewed availability of monomers [1]. The fate of the primary (nano)particles depends on the reaction conditions: clusters can condense with other clusters or clusters can grow by adding monomer [2].

Considering for silicon alkoxides the use of a catalyst to increase the reaction rates, it must be borne in mind which is the rate determining step in order to work out the path followed by the clusters. At acid pH, since hydrolysis is faster than condensation, small clusters are formed which condense together as the reaction proceeds. Reactions occurring on the terminal silicon atoms are favoured under these conditions, while the formation of Si-O-Si bonds can be considered irreversible. The result is the formation of small clusters that condense together, reminiscent of a classic organic polymerisation reaction. Gels formed under these conditions are typically microporous.

Unlike what happen in polymeric gels, the particles in colloidal gels interact via short-range forces with depolymerisation and re-polymerisation phenomena that allow the clusters to be reorganised towards more stable configurations. Under basic conditions, hydrolysis is the rate-determining step, and the clusters grow by adding monomer whose supply is ensured by the hydrolysis of siloxane bonds, Si-O-Si, more favoured at high pH. Highly branched clusters are so formed in this condition.

At high pH, an ammonia-catalysed hydrolysis of silicon alkoxides produces a uniform distribution of particles, known as Stöber silicas. In this case, the delicate balance between hydrolysis and condensation kinetics influences the amount of non-hydrolysed groups, which can alter the external morphology and affect the homogeneity in the internal structure of silica particles [3].

The small surface area of Stöber's silica limits its applications. The need to overcome this disadvantage has promoted intensive research to establish how to fine-tune the size, size distribution, internal structure and chemical characteristics of silica particles [3, 4]. The use of secondary alkanolamines (diethanolamine) and tertiary alkanolamines (triethanolamine) as catalysts instead of ammonia has proven to be a powerful means of altering the particle size and thus changing the textural properties [5].

In addition to pH, which has a strong impact on the mechanism of particle growth, cluster-monomer or cluster-cluster, and gel structure, there are other factors to consider, including solvent and temperature.

As mentioned in the previous chapter, a solvent is generally used to mix alkoxide and water because water and alkoxide are immiscible in all proportions and avoid nanoparticles precipitation. As the hydrolysis reaction proceeds, partially hydrolysed species are formed that are soluble in water. Alcohols are generally used as solvents, ethanol typically in the presence of TEOS. The choice of solvent is more critical in the case of metal alkoxides where alcohol-alkoxide exchange and the formation of oligomeric structures can affect the cluster structure [6].

Generally speaking, speed can be an insidious enemy in sol-gel preparations. Forcing the gelation could lead to a cloudy sol and a non-transparent gel. Excessive acceleration could then lead to the formation of precipitates. For these reasons, an ageing step is often added to the preparation.

The reaction temperature is crucial in regulating the chemical kinetics of the different reactions involved in nanoparticle formation and the assembly of nanoparticles into a gel network. It has been said that in the case of silicon alkoxides, gelation can take weeks or months; in this case, an increase in temperature can be beneficial, but if the temperature is too high, the reactions that assemble the nanoparticles into a gel network occur so quickly that clumps form (instead) and the solid precipitates from the liquid. It is therefore of utmost importance to be able to recognise what the product of a controlled gelation should be.

How can we recognise the gelation point? To answer this question, we must continue to distinguish between polymeric and colloidal routes. In the former, there is an unperceivable gradual increase in viscosity of the sol with the time. At the gelation point, the viscosity increases abruptly and a three-dimensionally continuous solid network is obtained. The gelation time (tg) is usually determined by the intercept between the two linear phases in Figure 3.1 [7, 8]. At the gelation point, no liquid escapes by turning the container upside down, because all the residual liquid is retained in the entire volume of the gel and cannot flow out of the becker, Figure 3.2.

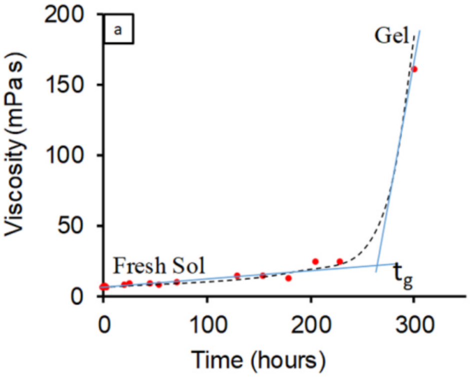

Figure 3.1 Evolution of viscosity versus time as reported in ref [7]

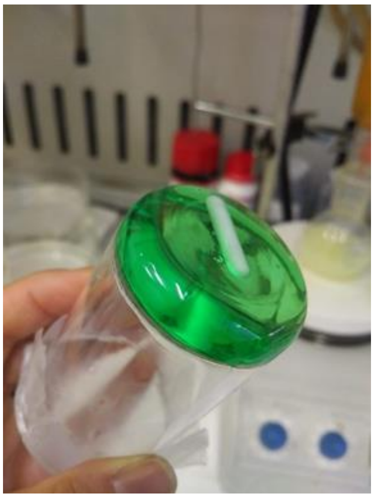

Figure 3.2 Wet gel by polymeric route

In the case of colloidal gels, for example those obtained by the Stöber method, there is first an increasing opalescence of the mixture in a time dependent on the concentration of the initial reagents. Finally, the solution takes on the appearance of a cloudy white suspension, indicating the formation of colloidal silica nanoparticles [9]. For stable colloidal particles, aggregation can be induced by removing the solvent. Alternatively, altering the pH, salinity or temperature can induce destabilisation of the particles.

Although several valid attempts to define a gel can be found in the literature, there is still the difficulty of giving a definition that can encompass the different types of structures that a gel can assume. For this reason, it may be worth relying on Nijenhuis's more philosophical definition: 'A gel is a gel until it can be proved that it is not a gel' [10].

3.2 Aging

The gelation point could be read as a rapid solidification, but it is actually more properly described as a freezing of a particular polymeric structure. This three-dimensional structure, which occupies the entire volume previously occupied by the liquid, consists of the polymeric lattice that incorporates within its condensable particles, by-products and possibly monomers. Freezing is due to the high viscosity value, but the flexibility of the system allows reactions to continue over time. This time-consuming step is called aging and although it could be seen as a disadvantage of the sol-gel method, it is a very important phase in the preparation of the catalyst because it allows the porosity and structure of the gel to be altered. Ageing encompasses a wide range of processes, including the further formation of a cross-linked structure, associated shrinkage and hardening of the gel. Syneresis is one of the processes observed during ageing and consists of the expulsion of liquid from the pores, causing further shrinkage.

Coarsening is another age-related effect that strengthens the gel by changing the size and shape of the pores. It consists of the dissolution of the mass from thermodynamically unstable regions and re-condensation into thermodynamically more stable regions. Like the previous steps in the sol-gel process, it depends on temperature and pH, pressure and solvent type.

Many oxides used as catalysts or supports for catalysts exist in two or more polymorphic forms. Although they are isochemical, these crystal forms have distinct crystal structures and thus different physical properties. Anatase, rutile and brookite are the three main crystalline polymorphs of titania, an oxide with a great number of important technological applications and probably the most studied photocatalyst.

An extensive literature shows that titania activity is closely related to the presence of a crystalline phase or mixed crystalline phases and the degree of crystallinity. Beyond the type of sol-gel route followed to prepare titanium oxide, the aging phase can decisively affect the crystallinity of the sample [11-13].

3.3 Water can be a strategic parameter

Tuning the porosity features of the substrate is an essential task in the design of functional catalysts. The effect of water on the porous structure of the xerogel has long been debated, as it depends on the structure of the particles growing out of the sol. Although the simplest and most immediate conclusion that can be reached is the formation of more hydrolysed species as the water content increases, the effect of dilution must also be considered. Early studies conducted by Brinker, considered the pioneer of sol-gel science and the synthesis of materials from soluble molecular precursors, reported that the dilution effect for water to alkoxide ratio (Rw) > 5 changes the rate of hydrolysis and condensation in the direction that leads to longer gelation times [14-16].

Back to considering the hydrolysis and condensation reactions. According to reaction 1 of Figure 3.3, the stoichiometric ratio of water to alkoxide (Rw) is 4, which implies that the hydrolysis of a tetravalent alkoxide $M(OR)_4$, such as the tetraethylorthosilicate (TEOS), $Si(OC_2H_5)_4$, requires four water molecules to be completed. However, if one considers the condensation reaction that occurs between two hydroxyl groups, reaction 2 of Figure 3.3, water is produced as a result of the formation of a Si-O-Si bond. This suggests that it is possible to work with a under-stoichiometric addition of water as indicated by reaction 3 of Figure 3.3

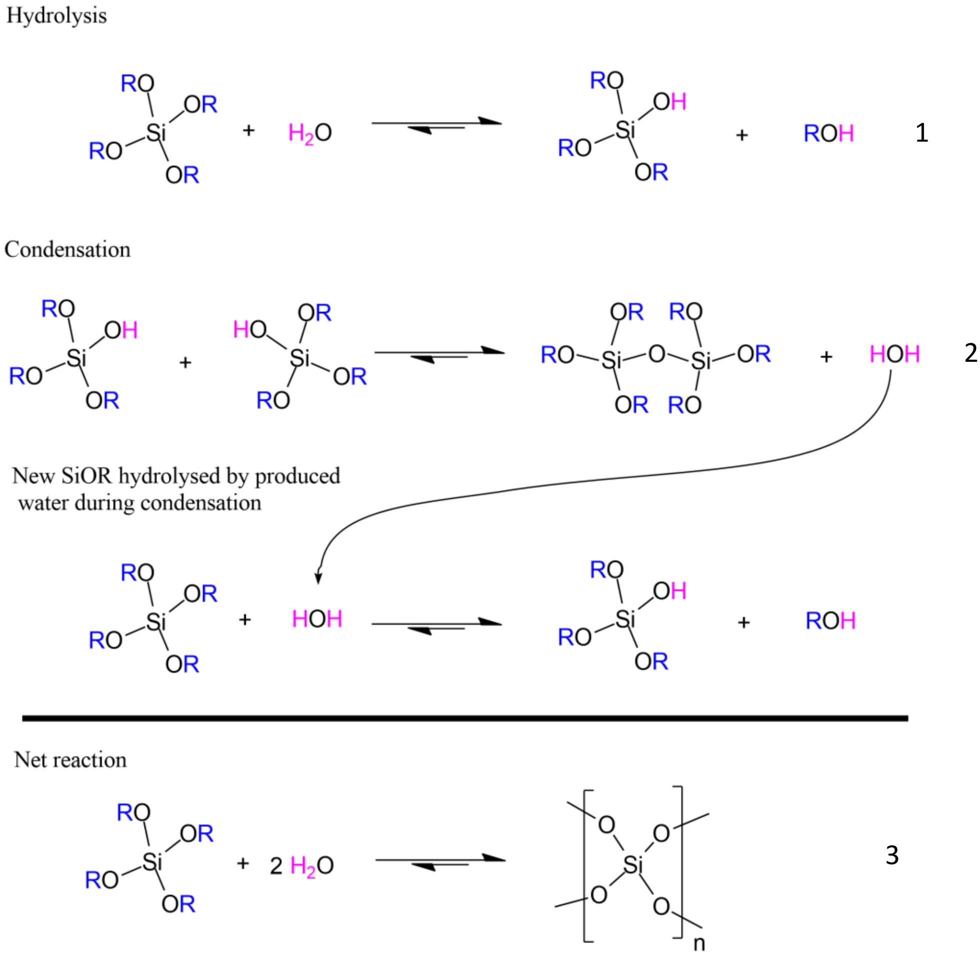

Figure 3.3 Hydrolysis of tetraalkoxysilane with under-stoichiometric addition of water.

The effect of the ratio of water to alkoxide in the acid catalysed hydrolysis is generally discussed by considering three ranges.

For an under-stoichiometric addition of water, the reaction product consists of linear chains with residual alkoxide groups. The explanation can be sought in the steric factors as the monomers are more easily hydrolysed than the dimers or end groups of the chains, which in turn are more easily hydrolysed than the intermediate groups of the chains. Moreover, the presence of alkoxy groups on the polymer chain could cause a low packing density [16].

At an intermediate water content, Rw>4, hydrolysis of the alkoxide is more pronounced given the excess water in the solutions. The growth of silicon-containing species again leads to the formation of linear chains, but the higher concentration of the latter favours intramolecular reactions. Strawbridge et al. [16], in agreement with the results of Brinker et al. [14] report that gelling occurs through the entanglement of linear species to give rise to very small overlapping clusters. These clusters then aggregate to give rise to a dense gel.

In this respect, Yoldas reports that a certain residual of alkoxide groups is always possible even in cases of high-water content [16, 17].

With a Rw above 25, the extent of hydrolysis could strongly influence subsequent condensation reactions. Strawbridge et al. [16] hypothesise that after an initial development of linear chains, high dilution in water favours intramolecular reactions, leading to the formation of cycles. Gelation then occurs from the nuclei formed as a result of the rearrangement of these cyclic species. The different growth mechanism at high water contents may introduce a different type of porosity from previous situations.

To better understand the relevance of water content and bring this topic into an application scenario, the reader is presented with some important results obtained in the field of adsorption and drug delivery, where organic substances are trapped in sol-gel matrices and subsequently released. Although these examples deviate slightly from the catalysis, it is important to emphasise that the reported findings could be fruitful for the preparation of hybrid systems for biocatalysts, where tailored sol-gel materials are successfully used for trapping a wide variety of biomolecules. An important example is the trapping of enzymes in inorganic matrices.

The firs example concerns with the design of materials for the removal of pesticides from water [18-25]. For this specific application the textural properties of the material are particularly relevant.

An ideal sorbent should have high surface area (i.e., a large number of sorption sites), accessible pores and physical and chemical stability. The sorbents are often modified to enhance their adsorption efficiency to improve the affinity to a specific organic compound. Viewed from the perspective of matching all the requirements, the sol-gel method is a powerful platform.

The achievements of my research group concerning the preparation of porous silicas with acid catalysis will be discussed below.

Figure 3.4a shows a 'standard' procedure in which TEOS is added to ethyl alcohol in a molar ratio 1 : 4 and water, in a ratio lower than stoichiometric, is added for hydrolysis. The catalysis is acidic due to the addition of hydrochloric acid. This procedure is time-consuming as evidenced by the gelation time, tgel, of about 2 months.

In Figure 3.4b, a solvent-free route was explored in which TEOS is hydrolysed in water at 50 °C for 1h. The system is initially biphasic because TEOS and water are immiscible, but when the reactions start, alcohol is produced by condensation reactions with the partially hydrolysed species soluble in the hydroalcoholic medium. The Rw values explored are 5, 10 and 20 corresponding to SG-5, SG-10 and SG-20, respectively. This procedure in the first place allows a drastic reduction in the time required for gel formation toward tgel more useful for practical applications.

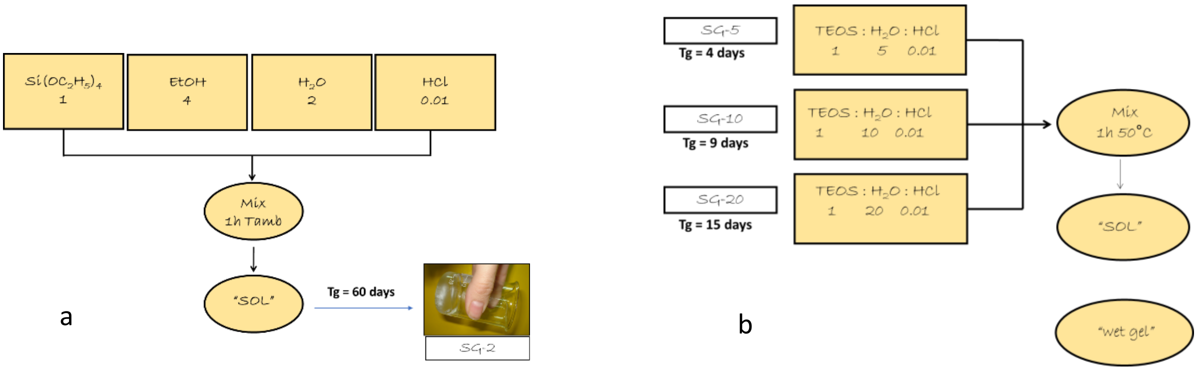

Figure 3.4 Flow chart of (a) silica gel preparation in acidic condition, Rw = 2 and (b) silica gel preparation at Rw = 5, 10 and 20.

The wet gels are dried and then heat-treated to remove all organic residues. The temperature of heat treatment is stabilized based on the results of the thermal analysis [26-28].

Based on the results obtained by the authors [26-28], the xerogels were heat treated at 400 ° C in order to burn all organic residues and give the material adequate mechanical properties.

The gelation time is not the only feature that differentiates the two sol-gel approaches. Textural properties undergo considerable change, which testifies the relevance of synthesis parameters in the rational design of a functional material. In particular, as evident from the adsorption/desorption isotherms shown in Figure 3.5, the porous texture changes strongly by increasing the water content in the series of samples prepared without alcohol.

The isotherm related to this silica prepared with a conventional method, SG-2, is of type I, according to the IUPAC classification, and is characteristic of a microporous material with high quantities of N_2 adsorbed at low pressures and a large "plateau" at P/ 0> 0.1. The knee of the isotherms progressively shifts towards higher partial pressure values by increasing Rw, suggesting the presence of mesopores and thus a gradual deviation from an exclusively microporous structure. The surface area increases up to a remarkable value of 705 m^2g^{-1} with the highest water content, the average pore diameter increases and enters the mesopore range and the volume of the micropores becomes negligible compared to the total pore volume [26].

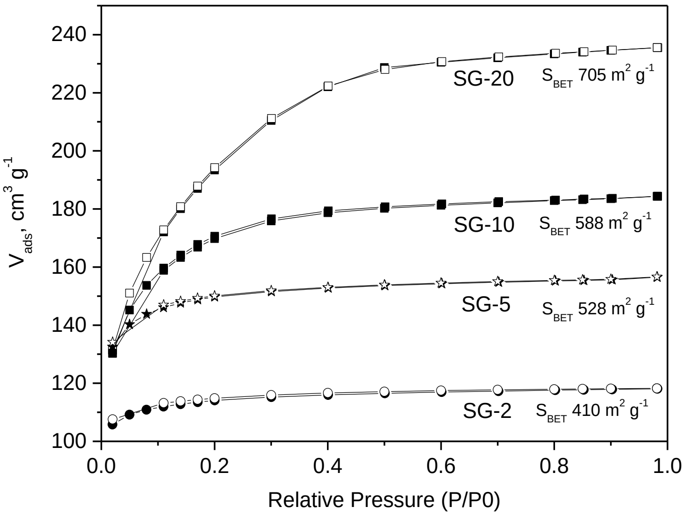

Figure 3.5 N_2 adsorption–desorption isotherms of SiO_2 prepared at different Rw values

These results suggest that in order to obtain a product with the desired characteristics, it is not always necessary to turn to complex synthesis procedures. We have shown how important it is to know the relationship between the synthesis parameters and the final properties of the final material. The H_2O/TEOS ratio is a simple strategy to change the textural properties of silica. By simply changing the value of Rw, a silica gel with a surface area comparable to that of some zeolites can be obtained, albeit with a disordered porous structure.

Silica samples were used as adsorbents for the removal of simazine (2-chloro-4,6- bis(ethylamino)-s-triazine), a common herbicide belonging to the s-triazine family. S-triazines are selective persistent herbicides that are widely studied for their still wide application in forestry and agricultural soils. Porous silica sample SG-20 showed a high affinity for simazine, making it potentially usable for practical applications in iterative removal experiments [18-25].

The water-alkoxide ratio is not only a critical parameter in the hydrolysis of silicon precursors but also in the case of metal alkoxides. Lópex et al. synthesised a sol-gel titania containing encapsulated the sodium salt of 5,5-diphenylhydantoin, an anti-epileptic drug commonly used to suppress abnormal brain activity during a seizure. The release profile of this drug delivery system is influenced by the physico-chemical and surface properties of the matrix. The authors demonstrated how the water/alkoxide ratio impacts on the type and strength of drug-matrix interactions of the phenytoin-titania complex, resulting in changes in short- and long-term release kinetics [29].

Titania is a material with great potential and is therefore widely used in numerous applications. In catalysis, titania is often used as a support for the catalytic active phase, often a transition metal. One of the key parameters for increasing catalytic performance is the degree of metal dispersion, which according to the authors T. Umegaki et al. can be improved by increasing the Rw ratio in the preparation of titania nickel nanocomposites. The authors report that textural properties are also changed, with an increase in specific surface area and an increase in pore diameter. All these changes result in a higher rate of hydrogen evolution from aqueous borane ammonia [30].

The role played by the sol-gel reaction conditions in the design of bulk and surface physico-chemical properties has also been reported in the case of sulphated zirconia obtained by a one-pot sol-gel approach. The water/alkoxide ratio plays no role in obtaining a specific crystalline phase, but is important for the development of a high surface area and in the retention of sulphur after the calcination step [31].

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