

THE INFLUENCE OF PARAMETERS IN SILICA SOL-GEL PROCESS

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Abstract: *The sol-gel process is an inorganic polymerization considered a promising route for the design of new materials for optical, electrical, (bio)-medical and solar energy applications. Special attention is focused on the design of silica-based material by of sol-gel process. The aim of the paper is to investigate, in order to understand, the role of some important parameters (precursors type, pH, catalysts, temperature etc.) in sol-gel routes. It is proved that the textural and structural material properties are strongly influenced by synthesis and processing parameters.*

Key words: *sol-gel process, silica, precursors, porosity, pH effects.*

1. Introduction

The sol-gel technique has been used for reproduce new porous nanomaterials, with well-defined structures and complex shapes. It is known that the sol-gel technology is relatively simple and allows the control of the distribution of the components in molecules, through a pre-orientation of the network. Thus, the potential applications of the materials synthesized by this method can be competitive (also in terms of production costs).

Sol-gel is a very flexible route for the synthesis of inorganic, organic-inorganic networks such as glasses, ceramics, films or powders. For a long time, sol-gel techniques have been used for manufacturing glasses and ceramics [6], [18]. More recent studies of this process have focused on optical and electrical applications [12], [25], [26], medical science [8], [27], protection coatings [22], [30] and solar energy applications [23].

The sol-gel process involves the formation of mineral phases starting from soluble

molecular precursors, following an inorganic polymerization reaction. The reaction is at room temperature, in water or organic solvents and in a wide range of pH/ionic strength conditions [8].

The transition from a liquid (solution or colloidal solution) into a solid (di- or multiphase gel) explains the name of the “sol-gel process”. The reaction is not restricted to an aqueous system, but the aqueous reaction has been known for a very long time. In 1842, the French chemist, J.J. Ebelmen reported the synthesis of uranium oxide by heating the corresponding hydroxide. In 1950, Roy and his co-workers make the sol-gel silicate powders quite popular in the market by changing the traditional sol-gel process into the synthesis of new ceramic oxides. In 1971, the production process of so-called low-bulk density silica, involving the hydrolysis of tetraethoxysilane (TEOS) in the presence of cationic surfactants was patented [30].

Basic principles of the sol-gel chemistry are therefore presented in the context of

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silica gel formation. Opposite to the common glass, which is a viscous fluid obtained by high temperature fusion of silica (SiO_2), sol-gel silica is an amorphous, porous material.

The first step in the sol-gel process of silica consists of hydrolyses of silicon alkoxides through condensation, forming the silica nanoparticles. Depending on the reaction conditions, these particles can further grow and form a sol that can be deposited on a substrate to form a film (e.g., by dip coating or spin coating), cast to obtain the desired shape (e.g., monolithic ceramics, glasses, fibres, membranes, aerogels), or used to synthesize powders (e.g., microspheres, nanospheres).

The nature of precursors, the molar ratios between the reactants, the nature of the solvent, the use of modifying agents, pH, the synthesis temperature, influence the microstructure and thus the properties of the resulting material [4], [10], [21], [29], [31].

This paper describes the influence of the most important parameters on the structural and textural properties of silica synthesized by sol-gel technique.

2. The Sol-Gel Chemistry of Silica

During the last two decades, the sol-gel process has become a large research field. Basically, the sol-gel process means the synthesis of an inorganic network by a chemical reaction produced in solution at low temperature.

The major advantage of the method - widely accepted - is that it offers the possibility to obtain hyaloids solids, which are very difficult to be obtained by conventional techniques [9], [14] of burning at high temperatures and offers the possibility to obtain materials with predetermined structure, depending on experimental conditions.

The advantages of the sol-gel process for material synthesis can be summarized as it

follows [26]:

- It provides high purity homogeneous materials;
- It offers an easy way for the introduction of trace elements;
- It allows the use of chemical techniques for the reaction control;
- It allows the formation of a “pre”-inorganic network in solution;
- It allows the densification to inorganic solids at comparatively low temperatures (due to the “pre”-inorganic network);
- It allows the introduction of permanent organic groups in solution (thus leading to inorganic-organic hybrid materials);
- It allows the synthesis of special materials such as films, reactive ceramic powders, fibres;
- It allows formation of new crystalline phases from the non-crystalline solids;
- It allows the preparation of new glass composition with superior properties determined by the specific properties of gel;
- Low processing temperatures allow energy saving, minimizes the evaporation losses, ensures purity by avoiding contamination with the containers during heat treatment, avoids undesirable separation and crystallization of microphases.

On the other hand, the disadvantages of the sol-gel process with respect to applications can be summarized as follows [26]:

- High cost of the precursors;
- Long process duration;
- Difficulties in the synthesis of monoliths;
- Difficulties in the process chemistry with respect to properties control and reproducibility.

The preparation of new materials by the sol-gel method consists of the following steps:

- Preparation of a gel from organic and/or inorganic sol-gel precursor;
- Gel aging (drying under strictly controlled conditions);
- Thermal treatment of dried gels.

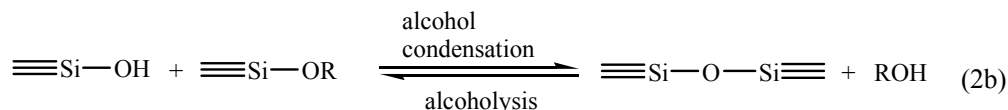
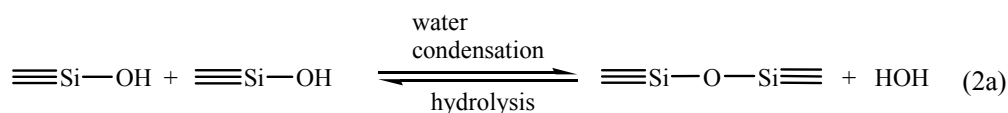
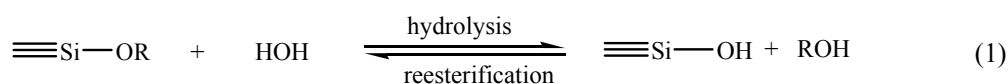
Theoretically, any precursor able to form reactive inorganic surface charges in order

to prevent the coagulation and the precipitation can be used in the sol-gel techniques. Most work in the sol-gel field was done by using metal alkoxides and metal chlorides as precursors that in most cases form monomers which are soluble in common organic solvents especially alcohols.

The development of silica sol-gel process in materials science starts with a solution of

silicon alkoxide precursor $\text{Si}(\text{OR})_n$ in an alcohol or other low-molecular weight organic solvent, where R is an alkyl group ($\text{C}_x\text{H}_{2x+1}$) [8], [30].

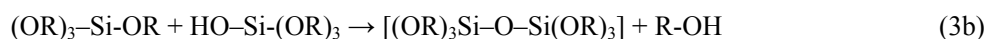
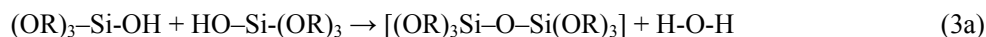
Compared with colloid chemistry, the alkoxide route can be more easily controlled by controlling hydrolysis (1) and condensation reactions (2a-water condensation, 2b-alcohol condensation):



Generally speaking, the hydrolysis reaction (1-4), consists in replacing of the alkoxide groups (-OR) with hydroxyl groups (-OH) and releasing of the corresponding ROH alcohol molecules. A complete hydrolysis (4) is obtained when the stoichiometric molar ratio water: $\text{Si}(\text{OR})_n$ is 4. Any intermediate species $[(\text{OR})_2\text{-Si}(\text{OH})_2]$ or $[(\text{OR})_3\text{-Si}(\text{OH})]$ would be considered the result of

partial hydrolysis (3a, 3b). A small amount of water leads to a slow hydrolysis due to the reduced reactant concentration. A large amount of water gives a slow hydrolysis due to the increased reactant dilution.

Subsequent condensation reactions involve the silanol groups (Si-OH), produce siloxane bonds (Si-O-Si) and as by-products water and alcohol:



Under most conditions, condensation can start before a complete hydrolysis. Conditions such as pH, $\text{H}_2\text{O}/\text{Si}$ molar ratio (R) and catalyst can force complete hydrolysis before condensation begins [16]. Due to the immiscibility of the alkoxide and water, a mutual solvent - an alcohol, is used as homogenizing agent to facilitate the hydrolysis process [24].

The condensation reaction is followed by an inorganic polymerization process with SiO_2 nanoparticles formation. This process is strongly pH dependent. Thus, acidic conditions lead to dense microporous (pore size < 2 nm) networks and in alkaline conditions mesoporous (2 nm < pore size < 50 nm) gels are obtained [8].

In the following sections, specific factors that influence the sol-gel reactions will be discussed.

3. Influence of Parameters in Sol-Gel Process

There are numerous parameters involved in the sol-gel technique with an important influence on textural and structural properties of the synthesized material. The process is basically affected by the initial reaction conditions, such as precursors, pH, and temperature, molar ratios (R) of reactants, solvent composition and by the aging and drying conditions.

3.1. The Precursors

There are two general requirements for sol-gel precursors as follows [26]:

- They have to be soluble in the reaction media;
- They have to be reactive enough to participate at the gel formation.

The most common precursors that can be used belong to one of the following categories [26]: salts, oxides, hydroxides, complexes, alkoxides, acylates, amines.

Among these, the alkoxides are the most common used. Metal alkoxides of titanium, zirconium or aluminum are much more reactive towards water than alkoxisilanes due to the lower electronegativity and higher Lewis acidity [30].

The reaction between alkoxisilanes and water is quite gentle avoiding phase separation and leading to good homogeneity. That makes the SiO₂ formation the most investigated system in the sol-gel literature.

Some of the most used alkoxysilane precursors for sol-gel technique are [15], [30]:

- Tetraethyl orthosilicate (TEOS),
- Tetramethyl orthosilicate (TMOS),

- Methyl triethoxysilane (MTES),
- Methyl trimethoxysilane (MTMS),
- Vinyl trimethoxysilane (VTMS),
- 3-aminopropyl trimethoxysilane (APS),
- γ -metacryloxypropyl trimethoxysilane (γ -MAPTS).

The concentration and the type of silicon alkoxides influences the rates of the both hydrolysis and condensation, and thus reactive monomers are produced at different rates.

The synthesis of SiO₂ nanomaterials is usually based on TEOS as precursor. An increase in the TEOS concentration leads to an increase in the solution's viscosity but also in the polymer's concentration, without significant variations in their size or shape [1].

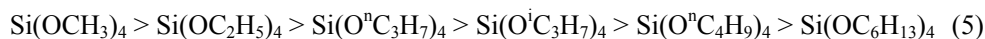
In practice, different complications can appear when using alkoxides with low boiling points due to evaporation of volatile compounds during the sol-gel reaction [26] (e.g. boron during the synthesis of borosilicate glasses).

A loss in the precursor's solution, especially at neutral pH, can also appear when a slowly reacting compound such as Si(OR)₄ is involved [26].

Higher alkyls networks such as Si(OHex)₄ leads on un-reacted or not completely reacted monomers which remain in the system and evaporate during drying and heating. Branching and increasing of the chain length of precursor substituent decreases the hydrolysis rate (5).

The alkoxide concentration has no impact on the density of the final material and no significant effects on the mechanical properties were observed [1].

Another recent study in sol-gel chemistry is based on aqueous precursors of silica such as silicates, which are low cost, non-toxic species, but are more difficult to control than alkoxides due to their reactivity [13]:



3.2. pH/Catalysts

The microstructure of the metal oxide obtained by sol-gel process depends on the hydrolysis and condensation reactions that are generally controlled by the solution's pH. Under acid-catalyzed conditions, the hydrolysis kinetic is favoured instead of the condensation, which generally starts when hydrolysis is completed [5], [17], [29]. In alkali-catalyzed reactions, condensation is faster than hydrolysis, resulting in a highly condensed species that may agglomerate into fine particles [5].

Compared to the transition metal alkoxides, TEOS is known to be less sensitive to hydrolysis, due to Si which is less electropositive [2]. Thus, in the case of silicon alkoxides, a change of surface charge can be easily carried out by changing pH using acid or alkaline catalysts to enhance the hydrolysis and condensation reactions.

For stabilizing the sols, the pH value can be maintained in a range aside from the point of zero charge (pH 2.2 isoelectric point of silica). The resulting surface charges reduce the particle-to-particle interaction and no aggregation or agglomeration takes place. By pH change or if the particle-to-particle distance is reduced by solvent evaporation, the surface charges are decreased and the gelation takes place. But, if particles grow too large, precipitation takes place. In the case of sol-gel systems based on oxides, the particle-to-particle interactions are strong (based on oxide bridges accompanied by hydrogen bridges) so that, especially after drying, the agglomeration is irreversible [26].

A number of papers have been published on the effects of catalysts on hydrolysis, condensation, gelation and properties of silica gels [1], [2], [11], [13], [20-21], [26], [29].

For example, some authors [11] report the influence of catalysts, usually with low amounts of water ($R = 4$, the molar ratio of water to TEOS), as one of the most

important parameters in sol-gel processing of porous silica films.

The rate of silicon alkoxides hydrolysis exhibits a minimum at $\text{pH} = 7$ and increases exponentially at both lower and higher pH. That is in contrast with the rate of condensation, which exhibits a minimum at $\text{pH} = 2$ and a maximum around $\text{pH} = 7$. This effect was observed by Coltrain et al. [7]. They conclude that under acidic conditions, the condensation of TEOS, with $R = 4$, was minimized at $\text{pH} = 2$ and maximized at intermediate pH values for various types of acid. They also observed that varying the catalyst, numerous effects on gelation time, porosity, density and volume shrinkage on drying process can be obtained.

Silicon alkoxides generally react slowly with water, but the reaction process can be speed up by the use of acid or base catalysts [11]. For example, gelation of TEOS dissolved in ethanol, was reduced from 1000 hours to 92 hours when HCl was employed in [2].

The pH also affects the dissolution and reprecipitation of silica [10]. At high pH values, where the particulates may have a high solubility in the sol, more porous structures are obtained. At low pH values fine pore networks and dense structure are obtained due to low dissolution-reprecipitation rate [28].

The investigation of Fardad [11] shows that the film thickness, shrinkage, porosity and optical quality depend on the type of catalyst used in the preparation of the precursor solution. In ethanol and below the stoichiometric water:TEOS molar ratio ($R = 2$), H_2SO_4 and H_3PO_4 increase the hydrolysis rate of the ethoxy groups (-OR) of TEOS, due to the formation, in the solution, of particles with high concentration of hydroxyl groups (-OH). This indicates the absence of ethoxy groups in the condensation reaction which lead to low porosity films. The poor quality of these films catalysed by H_2SO_4 and H_3PO_4

makes them less attractive for different applications. In the case of CH_3COOH and NH_4OH addition, large amounts of particles are precipitated and the formation of film from a stable suspension of oxide particles is not possible.

Therefore, the change in pH of the particulate silica sols is an easy tool in the design of the pore network for specific applications.

The main advantage of porous silica is the transparency, the chemical and thermal stability [10] but also the good mechanical strength [2].

3.3. The Water:TEOS Molar Ratio

As expected from Eqs. (1), (2a), (2b) the quantity of water in the sol-gel solution strongly influences the hydrolysis and condensation kinetics. At fixed TEOS concentration, an increase in water content leads to a corresponding increase in hydrolysis and condensation rate. According to McDonagh et al. [19] for obtaining SiO_2 films, $R = 2$ is insufficient for complete hydrolysis and higher R -values are required. It is also showed by Butler et al [3], that under low R -value, a matrix with a more open structure is produced due to incomplete hydrolysis and, consequently, less cross linking in the sol-gel material.

When involving $\text{Si}(\text{OR})_4$ as precursors it is preferable to use a water: alkoxide ratio of at least 4, with acid catalysis. A low water content or high dilution with alcohols (solvents) can lead to a high content of oligomers (soluble or volatile) and a decrease in the yield of SiO_2 . The presence of partially hydrolysed monomers and those different types of oligomers can affect the composition and the homogeneity of the final material [26]. Increasing of the water contents lead to a significant decrease in the quantity of organic species in the film.

The time of gelation and the pore size are influenced by the molar ratio of hydrolysis.

The time of gelation decreases for low water: TEOS molar ratio [26] and Musgo et al. [21] showed that pore size decreased with increasing ethanol: TEOS molar ratio and pH.

3.4. The Temperature, Aging and Drying

The role of chemistry for the steps after gelation may not look very important, but there are some interesting aspects especially with respect to homogeneity, purity and porosity of the silica gels.

Under atmospheric conditions, drying involves the loss of water, alcohol and other volatile components. This leads to gel shrinkage [10], and as consequence to high stresses in the structure [18]. If the strains cannot be stopped by relaxation, the monoliths obtaining will be difficult due to the cracks appearing [26]. This may create additional random porosity, deformation and breaking of the structures. In order to reduce this stress, drying additives, such as non-hydrolyzing organic groups (methyl or phenyl), can be used. They allow structural relaxation during the drying stage, decreasing the risk of cracking [26].

The addition of water to the alkoxide solution leads to the formation of polymeric species, whose size increases with aging time.

Because both hydrolysis and condensation are not completed after gel formation, reactive silanols are still in the system. Heating at relatively high temperatures (100-500 °C) is carried out to accelerate this phase, removes the organic species and leads to formation of covalent Si-O-Si bonds. Many of these Si-O-Si bonds are not stable at temperature below 450 °C and typically, temperatures higher than 1000 °C are needed to achieve bonding energy close to bulk fracture energy [1]. As Morpurgo et al [20] show, the aging at room temperature is a rather slow process.

Increasing thermal treatment temperature

leads to an increase in the porosity. As is presented in [12], the porosity of the xerogel film can reach 78% when the thermal temperature is 350 °C.

The addition of catalyst in the gelation mixture can be another method that may allow to speed up the aging process [20] and to obtain materials with stable properties compatible with practical uses.

4. Conclusions

The sol-gel process is a liquid-phase method of preparing glasses, ceramics, fibres, powders at ambient temperatures.

The advantages and disadvantages of this technique are pointed out.

The main advantage of this process is the easy way to obtain materials with targeted properties, by modifying the microstructure through the process parameters.

The process procedure is described taking as model, the well known silica sol-gel preparation.

The role of different synthesis and processing parameters onto the silica sol-gel process were presented and their influence on the structural and morphological properties was discussed from chemically but also economically point of view.

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