

What is 'Inorganic Polymerization' or 'Sol Gel' technique for production of nanoscale materials?

Sol gel technique is a kind of colloidal precipitation technique that has shot into prominence over the last two decades. Its origin lies in the development of fabrication methods for ceramics and glass at lower temperature. It can also be looked upon as a polymerization technique for inorganic materials. The technique has attracted a great deal of research interest in the recent times owing to its following characteristics:

- Ability to make high purity inorganic nanoparticles
- High homogeneity of the nanostructures
- Wide applicability to variety of inorganic materials
- Control of particle size and shape of the structures
- Ability to make nanoporous phases
- Ability to make near monodisperse particles
- Control of crystallinity of the particles
- Relatively low temperature process
- Ability to make mixed metal oxide particles
- Ability to make organo-inorganic hybrid materials
- Good scalability to commercial levels

Sol-gel technique can be described as a process of synthesis of inorganic polymeric materials wherein molecular precursors dissolved in a liquid are first hydrolyzed to form solid-in-liquid dispersion (sol), immediately followed by their condensation to provide a solid network filled with the liquid (gel).

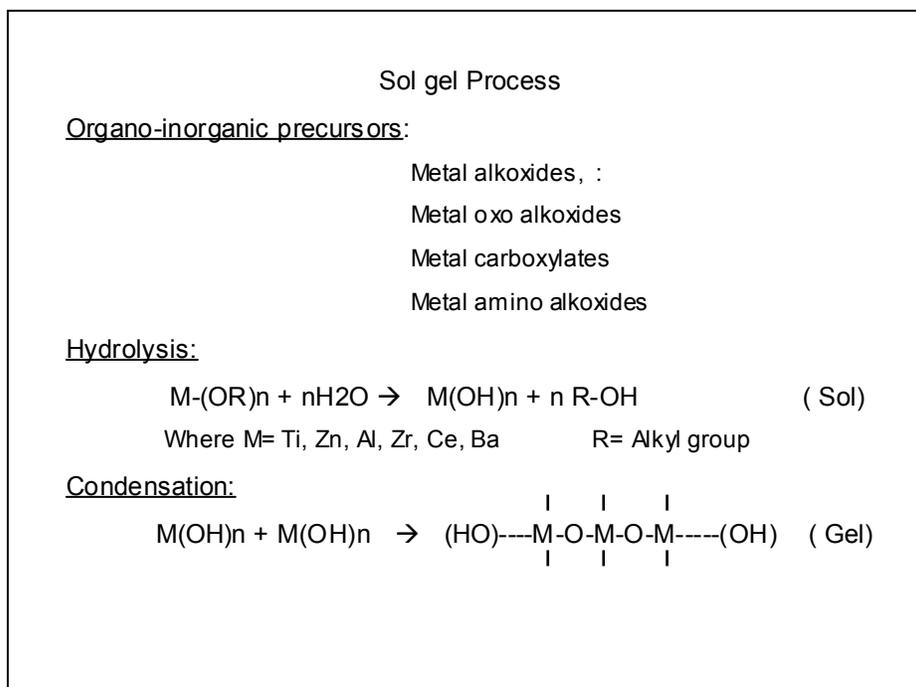


Figure: Sol gel Process

Precipitation of metal hydroxides from solutions of metal salts in water under alkaline conditions is a well known reaction. In this process, the rate of hydrolysis and condensation is so rapid that it is difficult to control the precipitation of coarse particles of metal hydroxides. Water adsorbed on the particles also impacts their properties. Hence for production of controlled sized nano structures, the reaction is carried out in organic solvents using metallic precursors.

The precursors for sol gel process can be inorganic salts or organo-metallic compounds which are stable and soluble in the liquid to be used. These are hydrolysable to produce reactive forms of hydrated oxides. Predominantly metal alkoxides are used as the precursors as these are available with high purity on commercial scale. The size and nature of the alkoxy group dictates its solubility and reactivity. Larger alkyl groups possess better solubility in the organic solvents and exhibit slower hydrolysability.

Typically, the solvents used are both protic as well as aprotic, depending on the nature of the precursors and the intended particle configuration. Solvents such as alcohols, ketones, dimethyl sulfoxide are common. Interaction between the solvent and the precursor such

as 'solvent exchange' needs to be taken into account while selecting the solvent.

Hydrolysis part of the process can be carried out employing water, alcohols, amines, inorganic acids or bases and other nucleophilic reagents. The metal hydroxyl particles so generated possess different degree of reactivity. This stage is a 'sol' form. This leads to the next step viz. Polycondensation. The hydroxyl groups associate with one another forming a network through oxygen linkages. The dimensionality of the network depends upon the valency of the metal and the rates of the hydrolysis and condensation reactions. This polymerization and cross-linking process is accompanied by release of water, alkyl ether, alcohol or carboxylic acid depending on the nature of the precursor and the hydrolyzing agent. The liquid medium fills up the voids in inorganic polymer network thereby producing 'Gel' state.

Morphology of the network is governed by the relative rates of hydrolysis and condensation. If the hydrolysis is slower than the condensation, the particles formed are finer and the network is highly branched. Alternatively, if the rate of condensation is slower, the particles are larger with weakly branched network. Both these processes are nucleophilic; and hence greater the electronegativity of the metal the slower reactions.

The size of the particles, the shape of the structure and the void volume is influenced not only by the nature of reactants and solvent chosen but also by the process factors like temperature, agitation and the pH.

There is one more effective tool available for control of the morphology which is called 'Templating'. This implies a directed self assembly of the gel structure guided by a surface active organic material which is generally of non ionic type such as ethylene oxide condensates. Inclusion of these templates materials during sol gel synthesis affords a great degree of control on the particle size, shape and porosity. The nature of the template also dictates the final drying process.

The gel so formed can be cast into films, fibers or nanostructures of various shapes by spraying, spinning and other such techniques. The liquid inside the gel structure can be removed in the following three ways:

- Low temperature expulsion employing supercritical drying with carbon dioxide: This method conserves the integrity of the structure as the forces due to surface tension are non-existent. The template materials are washed out thereby yielding nanostructures with high purity. The crystallinity and porosity of the structure is also preserved. These materials are called 'Aerogels' since the air is the dispersed phase in the continuous metal oxide phase.
- Moderate temperature drying (100~200 deg C): In this method, the liquid is driven off by evaporation leaving behind the nanostructure and the template material. There is a collapse of the nanostructure during solvent evaporation due to the strong surface tension forces as the solvent leaves the solid surface.
- High temperature drying: The liquid can also be removed by heating at higher temperatures (300~800 deg C). (these temperatures are still lower than conventional metal oxide melting or vapor phase processes) This method leads to the formation of pure nanoparticles powder devoid of any organic matter. The material thus produced may not possess monodisperse particle size as some amount of agglomeration can take place during the heat treatment process. These materials are called 'Xerogels' as the gel network is largely destroyed.

In summary, sol gel process offers an extremely flexible tool to tailor make nanostructured materials for various applications.
