Preparation of Colloidal Sols and Gels

Objective

This laboratory examines the preparation of silica suspensions and gels by the sol-gel processing of silicate solution under hydrolytic conditions using acid, base and a salt catalyst. The silica sols prepared in this experiment will be examined for sedimentation time and particle size. The silica gels prepared will be characterized for surface morphology and porosity.

Theory

Colloidal suspensions are used to generate polymers or particles from which ceramic materials can be made by the sol-gel process. The precursors for preparation of a colloidal suspension consist of a metal element surrounded by various ligands (attached groups not including another metal). For example, common precursors for sol-gel synthesis of aluminum oxide include inorganic salts such as $Al(NO_3)_3$ and organic compounds such as $Al(OC_4H_9)_3$. The latter is an alkoxide, the class of precursors most widely used in sol-gel research. Metal alkoxides are popular precursors in sol-gel because they react readily with water. The reaction is called hydrolysis, because a hydroxyl ion becomes attached to the metal atom as follows:

$$Si(OR)_4 + H_2O \rightarrow HO\text{-}Si(OR)_3 + ROH$$

where R represents a hydrogen ion or other ligand ((•OR is an alkoxy group if R is an alkyl), and ROH is an alcohol. Hydrolysis may go to completion depending on the amount of water and catalyst present, so that all of the OR groups are replaced by OH groups.

Two partially hydrolyzed molecules can link together in a condensation reaction such as:

$$(OR)_3Si\text{-}OH + HO\text{-}Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O$$

or

$$(OR)_3Si\text{-}OR + HO\text{-}Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + ROH$$

Condensation liberates a small molecule such as water or alcohol. This type of reaction can continue to build larger and larger metal containing molecules by the process of polymerization. A metal atom M with four ligands, $MR_2(OH)_2$ of which two are unreactive R groups and two are reactive hydroxyls; can polymerize into linear chains or rings.

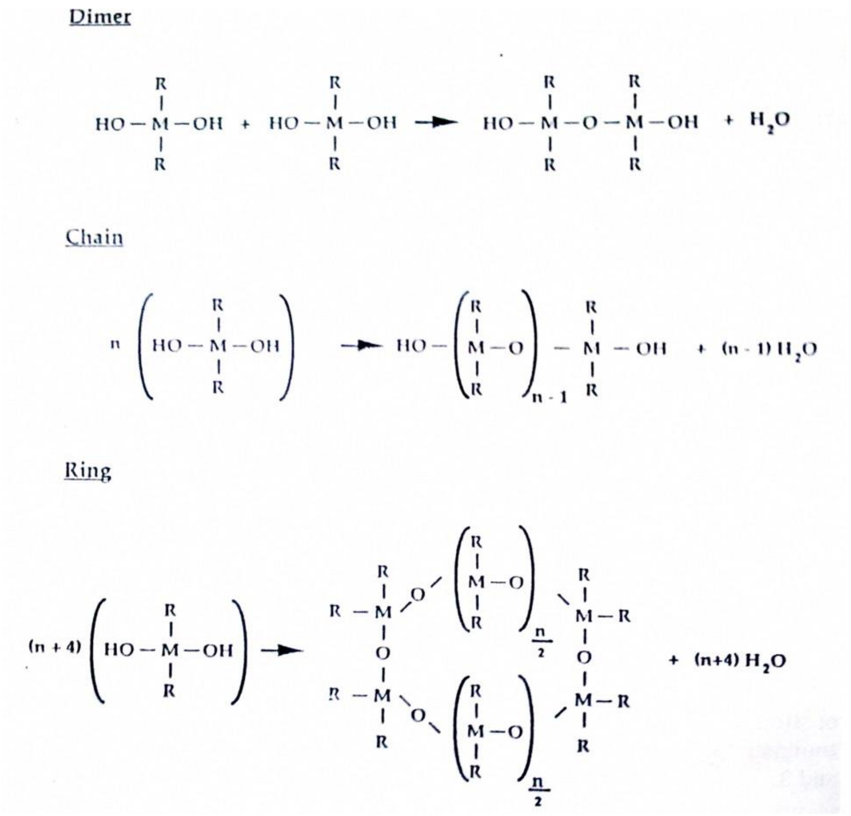


Figure 1. Types of polymerization reactions

The chains can be joined by crosslinks to form a three dimensional structure if a polyfunctional metal oxide unit with $f>2$ is present. Polymerization of a fully hydrolyzed monomer such as $Si(OH)_4$ can lead to complex branching of the polymer because of its tetrafunctionallity. On the other hand, fewer than four ligands will be capable of condensation in the case of low water concentration, so that relatively little branching will occur. When this three dimensional structure reaches microscopic dimensions so that it extends throughout the solution, the substance becomes a gel. Thus a gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. The continuity of the solid structure gives elasticity to the gel as in the gelatin desert. Particulate sols form gels when attractive dispersion forces cause particulates to stick in such a way as to form a three dimensional network. Particulate gels are established by van der Waals forces, polymeric gels are covalently linked and gelatin gels form by entanglement of chains. The bonds in the particulate gels are reversible so that they can often be redispersed by shaking. The polymeric gels have permanent, stable bonds.

The process of gel formation begins with the formation fractal aggregates that grow until they begin to contact each other. Near the gel point, bonds form at random between the nearly stationary clusters of polymers or aggregates of particles, linking them together in a network. The sol appears as a gel at that point when a single cluster extends throughout the sol and many small clusters coexisting in the sol gradually attach to the network. Since that giant cluster reaches across the vessel that contains it, the sol does not pour when the vessel is tipped. Bond formation does not stop at the gel point. The network is initially soft, so segments of the gel can still move close enough to allow further condensation.

Moreover, there is still a sol within the gel network where smaller polymers or particles continue to attach themselves to the network. The stiffness and viscosity of the gel increases as the remaining clusters progressively become connected to the network. The process of change in structure and properties after gelation is termed aging. Some gels exhibit spontaneous shrinkage as bond formation or attraction between particles induces contraction of the network and expulsion of liquid from the pores. Gels may also shrink during drying due to capillary pressures around pores if liquid evaporates rapidly. Xerogels and aerogels that are formed by different drying techniques are useful in the preparation of dense ceramic particles and porous monoliths due to their high porosity and surface area.

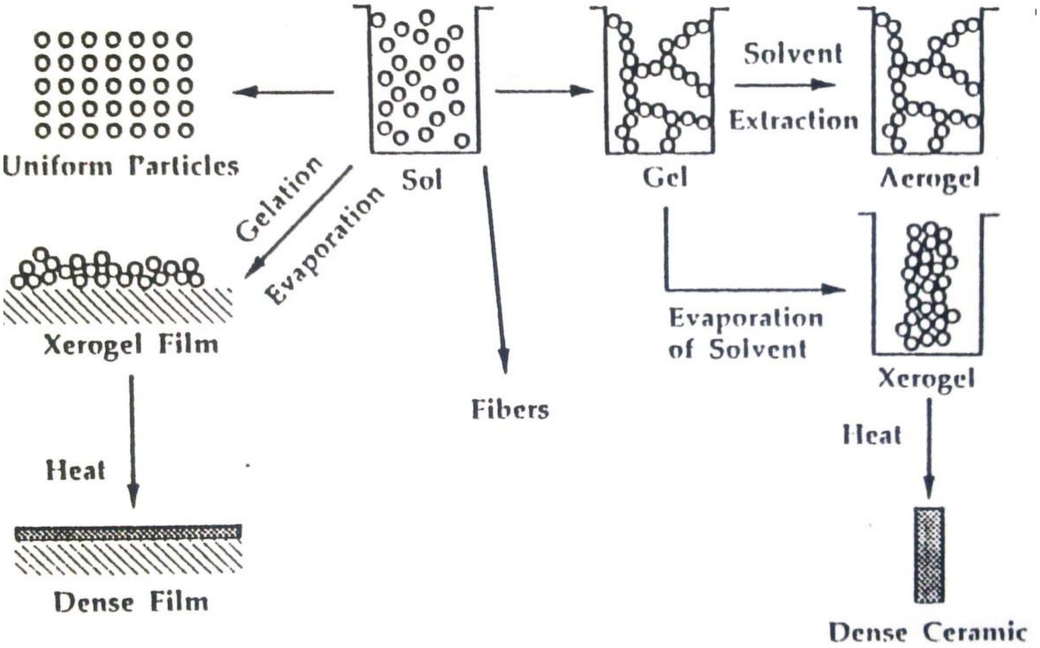


Figure 2. Particle Sol-gel processing scheme

The structure of a gel made from colloidal particles depends on the size distribution of the particles and the strength of the attractive forces between them. The sol may develop an ordered crystal-like structure if the particles are spherical and monodisperse; and the repulsive barrier is reduced gradually as seen in Figure 3. This sort of structure develops when the repulsive barrier around a colloid is sufficient to allow the particles to slip around each other into a dense packing. Disordered structures with high porosity result when the attractive potential is too great. This principle is illustrated in Fig X. Gelled colloids were separated from the solution by centrifugal force. The density of the centrifuged sediment increases as the repulsive potential of the sol increases from A to C. It is found that gels made from aggregated sols are about 70% porous when dried and so not sinter to full density when fired. On the other hand gels from unaggregated, monodisperse sols are about 40% porous and densify readily at relatively low temperatures.

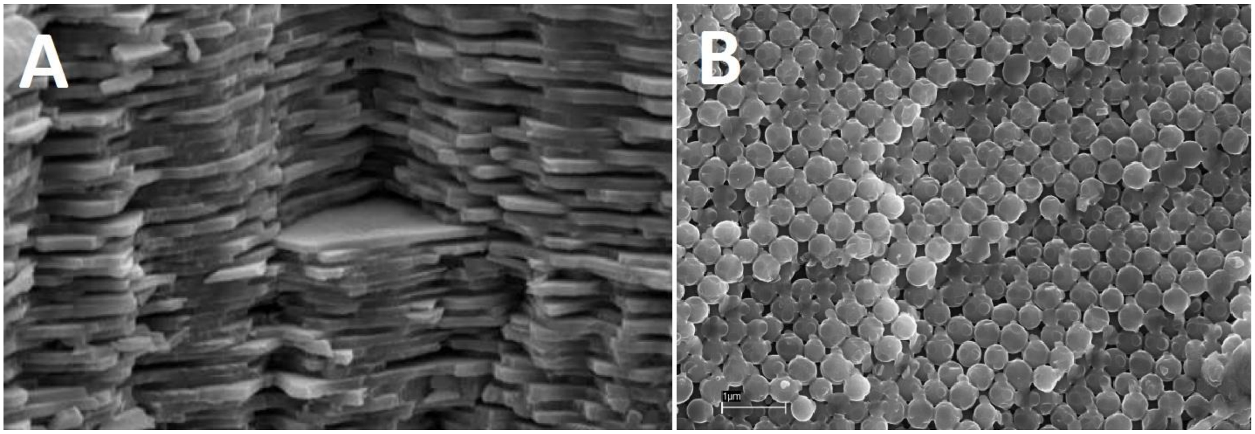


Figure 3. Electron micrograph of gelled silica particles that is obtained by centrifugal separation from the sol: (A) side view, (B) top view

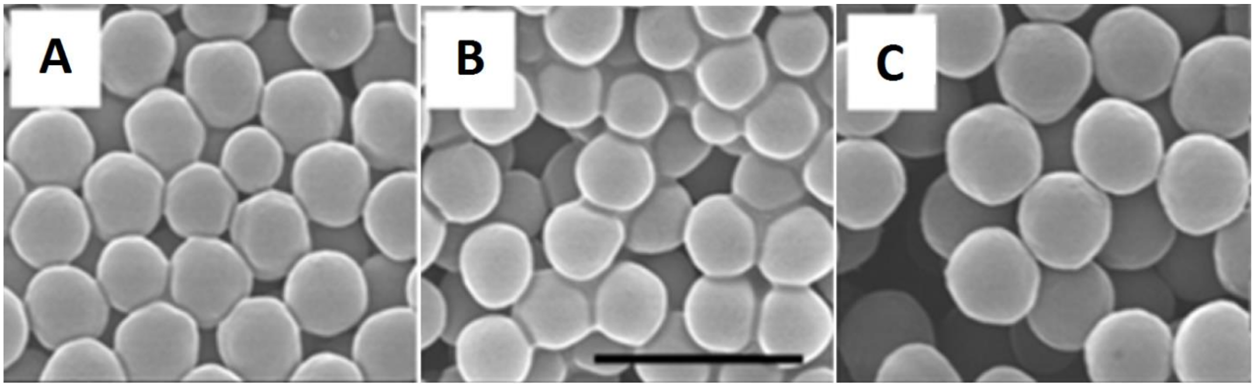


Figure 4. Electron micrograph of particle domains formed centrifugal sedimentation of silica microspheres in aqueous solution with (A) zeta potential = 110 mV, (B) zeta potential = 68 mV, (C) zeta potential = 0 mV

Gelation can occur after a sol is cast into a mold, in which case it is possible to make objects of a desired shape. The object is called a monolith if the smallest dimension of the gel is greater than a few millimeters. Alternatively film coatings can be prepared by rapid evaporation of the solvent on a substrate. Most gels are amorphous after drying and crystallize when heated. It is necessary to sinter the gel at a high enough temperature if the objective of the processing is to produce a dense ceramic. A gel forgets its structure if it is heated above its glass-transition temperature and acquires the equilibrium structure dictated by thermodynamics.

Sol-gel derived ceramics have wide application areas depending on their various shapes obtained directly from the gel state and their compositional and microstructural properties which are varied by many processing parameters. Monoliths, films, fibers and monosized powders with varying porosity and chemical composition are tailored by control on process conditions. The advantages and disadvantages of sol-gel processing over other conventional ceramic processing methods that lead to its utilization in synthesis of advanced ceramics are listed below. Among many applications of sol-gel derived materials, the most successful ones are those utilize the potential advantages of sol-gel processing such as purity, homogeneity, controlled porosity and the ability to form low-cost, precision shaped objects at low temperatures. For these reasons, dense or porous thin films or membranes, fine abrasive grains, corrosion resistant fibers and near-net-shape optics are the best applications.

Table 1. Sol-gel processing compared to other ceramic processing methods

Advantages	Disadvantages
Low temperature, environmental process	High cost of raw materials
Improved homogeneity	Large shrinkage during processing
Improved purity from raw materials	Residual fine pores
Ability to produce new noncrystalline solids	Residual impurities
Improved glass products	Health hazards of organic solutions
Special products such as films	Long processing times

Thin films and coatings

Films and coatings represent the earliest commercial application of sol-gel technology. Thin films less than 1 micrometer in thickness are formed by dipping the substrate in or deposition on a spinning substrate. Little raw material is used compared to advanced coating techniques and coatings are processed quickly without cracking, overcoming most of the disadvantages of sol-gel processing. It is possible to uniformly coat both sides of planar and axially symmetric substrates such as pipes, tubes, rods and fibers that are not easily handles by other coating processes The main applications of sol-gel films are optical coatings, electronic, protective, membrane and sensor applications.

Monoliths

Monoliths are bulk gels cast to shape and processed without cracking. These are popular materials because complex shapes may be formed at room temperature and they are consolidated at low temperatures without melting. The main application area of monolithic gels is optical. Fiber optic preforms, lenses, graded refractive index glasses and transparent aerogel foams are commercial products processed using sol-gel.

Powders and spheres

Powders are the starting raw material for most polycrystalline ceramic forming processes. Ceramic powders are also used as catalysts, pigments, abrasives and fillers. Ceramic spheres are used in nuclear fuels, porous beads are used in chromatography and hollow spheres are used in fusion. Potential applications for sol-gel derived powders in high-tech products are extensive due to their homogenous size and composition.

Fibers

Sol-gel methods of fiber formation are drawing fibers directly from viscous sols at room temperature, unidirectional freezing of gels and high temperature fiber formation from sol-gel derived preforms. Chemically durable, strong and thermal shock resistant fibers can be formed at room temperature by sol-gel process. Their application areas are reinforcement in concrete, superconducting, electrolysis and optical.

Composites

Sol-gel processing can be used to form the matrix phase, the fiber or particle reinforcement phases, or both in ceramic-ceramic composites. High performance ceramic-ceramic composites such as SiC-reinforced alumina are used in turbine blades as well as highly efficient ceramic diesel engines. Sol-gel processing enables feasible production of such materials because low viscosity sols be cast to shape around fibers contained in a precision mold, simplifying the set up and reducing abrasion. In addition, the high surface area and small pores size of the gel matrix may establish an effective sintering force that results in stronger ceramics than produced by hot-pressing. Types of high performance sol-gel derived composites include fiber-reinforced sol-gel matrix, ceramic-ceramic, ceramic-metal and ceramic-glass composites

Basic Definitions

Colloid – Nonpolymeric solid oxide particles in the 1-1000 nm size range

Particulate Sol – A colloidal suspension of solid particles in a liquid in which the dispersed phase is so small that gravitational forces are negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface charges

Polymeric Sol - A suspension of solid particles in a liquid in which the dispersed phase contains no dense oxide particles larger than 1nm

Aerosol – A colloidal suspension of particles in a gas (The suspension is a fog if the particles are liquid and smoke if the particles are solid)

Aeorogel – A gel formed in the absence of shrinkage by supercritical drying which contains volume fractions of solid as low as 1%

Xerogel – A gel subjected to shrinkage by drying under normal conditions which is reduced in volume by a factor of 5-10 compared to the original wet gel

Emulsion – A suspension of liquid droplets in another liquid

Alkane – A molecule containing only carbon and hydrogen linked exclusively by single bonds as in methane (CH_4) and ethane (C_2H_6)

Alkyl – A ligand formed by removing one hydrogen from an alkane molecule, as in methyl ($\bullet CH_3$) or ethyl (($\bullet C_2H_5$)

Alcohol – A molecule formed by adding a hydroxyl (OH) group to an alkyl or other molecule, as in methanol (CH_3OH) or ethanol (C_2H_5OH)

Alkoxy – A ligand formed by removing a hydrogen from the hydroxyl on an alcohol, as in methoxy ((•OCH_3) or ethanol ((•OC_2H_5)

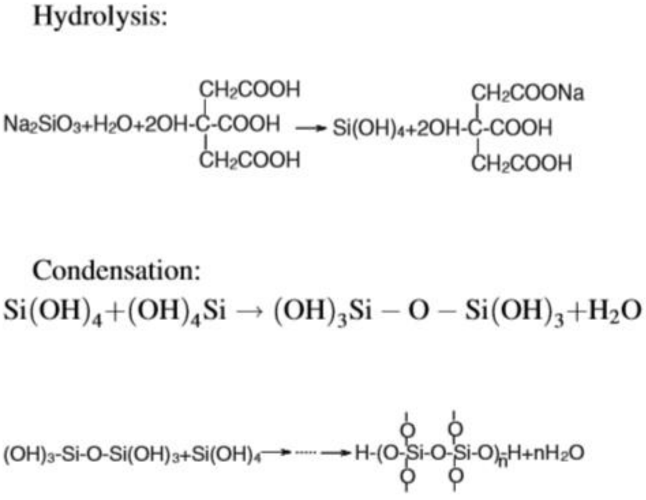
Polymer – A huge molecule or macromolecule that is formed by random branching of hundreds or thousands of units called monomers that are capable of forming at least two bonds.

Functionality of a monomer – The number of bonds that a monomer can form. Typical oxide monomers are bifunctional (*f*=2), trifunctional (*f*=3) or tetrafunctional (*f*=4)

Experimental Work

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 favored instead of the condensation, which generally starts when hydrolysis is completed. In base-catalyzed reactions, condensation is faster than hydrolysis, resulting in a highly condensed species that may agglomerate into fine particles

The hydrolysis and condensation reaction for the silica sol in the presence of citric acid are represented as follows:



Hydrolysis:

$$Na_2SiO_3+H_2O+2OH\text{-}\overset{\displaystyle CH_2COOH}{\underset{\displaystyle CH_2COOH}{C}}\text{-}COOH \rightarrow Si(OH)_4+2OH\text{-}\overset{\displaystyle CH_2COONa}{\underset{\displaystyle CH_2COOH}{C}}\text{-}COOH$$

Condensation:

$$Si(OH)_4+(OH)_4Si \rightarrow (OH)_3Si-O-Si(OH)_3+H_2O$$

$$(OH)_3\text{-}Si\text{-}O\text{-}Si(OH)_3+Si(OH)_4 \rightarrow \cdots \rightarrow H\text{-}(O\text{-}\overset{\displaystyle O}{\underset{\displaystyle O}{Si}}\text{-}O\text{-}\overset{\displaystyle O}{\underset{\displaystyle O}{Si}}\text{-}O)_nH+nH_2O$$

Silica sols will be prepared via hydrolysis of water glass in aqueous solutions with citric acid as the acid catalyst and NH_3 as the base catalyst. A second experimental parameter is the NaCl addition as metal oxides tend to coagulate in the presence of counter ions from salts. 4 sets of sols will be prepared using only citric acid, citric acid with NaCl, only NH_3 and NH_3 with NaCl according to the following steps:

- Add 50 mL of 4 wt% silica containing water glass solution at a rate of 12–13 mL/min to 50 mL aqueous solution of 10 wt% citric acid under moderate stirring. Stir the mixture for 30 min at 25 C to form a homogeneous silica sol.

- Add 50 mL of 4 wt% silica containing water glass solution at a rate of 12–13 mL/min to 50 mL aqueous solution of 10 wt% citric acid and 5 wt% NaCl under moderate stirring. Stir the mixture for 30 min at 25 C to form a homogeneous silica sol.
- Add 50 mL of 4 wt% silica containing water glass solution at a rate of 12–13 mL/min to 50 mL aqueous solution of 10 wt% NH_3 under moderate stirring. Stir the mixture for 30 min at 25 C to form a homogeneous silica sol.
- Add 50 mL of 4 wt% silica containing water glass solution at a rate of 12–13 mL/min to 50 mL aqueous solution of 4 wt% NH_3 and 5 wt% NaCl under moderate stirring. Stir the mixture for 30 min at 25 C to form a homogeneous silica sol.
- Reserve half of the sols for ageing to a gel
- Examine the sedimentation time of the sols
- Separate the silica colloids from the sol using filters
- Examine the particle size of the colloids

Experimental Apparatus:

8 250 ml beakers

1 L graduated cylinder

Magnetic stirrer

Timer

200 ml Distilled water

200 ml water glass solution

10 gr citric acid

10 gr NaCl

10 gr NH_3

100 ml 0.1 M HCl solution

100 ml 0.1 M NaOH solution

Suggested Reading

C. J. Brinker, G. W. Scherer, “Sol-gel science: the physics and chemistry of sol-gel processing”, 1990, Academic Press

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L. Jinyun,H. Wenqi, “Preparation of durable superhydrophobic surface by sol-gel method with water glass and citric acid”, Journal of Sol-Gel Science and Technology, 2011,58, P 18-23