

The Sol-Gel Preparation of Silica Gels

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In this paper, we present the sol-gel preparation of silica from molecular precursors, which is an experiment appropriate for an introductory chemistry laboratory. Due to the increasing technological importance of the sol-gel process and the simplicity of this preparation, the sol-gel synthesis of silica provides an excellent illustration of materials chemistry in the introductory chemistry course. Also many fundamental chemical principles (including hydrolysis, homogeneous catalysis, condensation, inorganic polymerization) are involved.

The sol-gel process is the name given to any one of a number of processes in which solution or sol undergoes a sol-gel transition (1-3). At this transition, the solution becomes a rigid, porous mass. One particular example of a sol-gel process involves the system tetraethylorthosilicate (TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$, ethanol, and water. This is a one-phase solution that undergoes sol-gel transition to a rigid, two-phase system of solid silica (SiO_2) and solvent-filled pores.

Sols are dispersions of colloidal particles in a liquid. Colloidal particles are solid particles with diameters of 1-100 nm (10^{-9} m). A gel is an interconnected, rigid network with pores of submicrometer ($<10^{-6}$ m) dimensions and polymeric chains whose average length is greater than a micrometer (4).

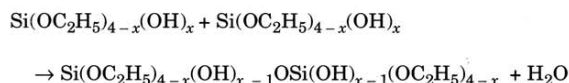
Preparation of Silica Gels

Silica gels may be prepared from the sol-gel polymerization of silicon alkoxides (e.g., $\text{Si}(\text{OC}_2\text{H}_5)_4$ or TEOS). Hydrolysis occurs when TEOS and water are mixed in a mutual solvent, generally ethanol.



The intermediates that exist as a result of partial hydrolysis include Si-OH groups, which are called silanols. Complete hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ to $\text{Si}(\text{OH})_4$ would give silicic acid, but this does not occur. Instead condensation may occur between either two silanols or a silanol and an ethoxy group to form a bridging oxygen or a siloxane group Si-O-Si. Water or an ethanol molecule is eliminated.

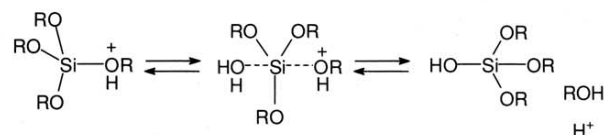
An example of the condensation between two silanols with the elimination of water is given below.



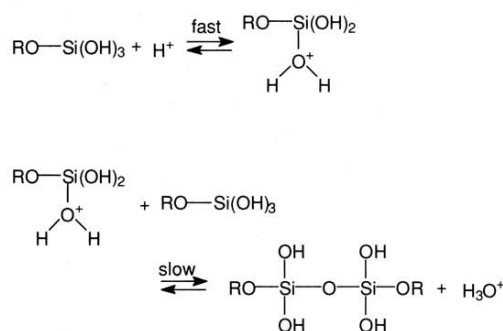
The hydrolysis and polycondensation reactions initiate at numerous sites within the TEOS and H_2O solution as mixing occurs. Both hydrolysis and condensation may occur by acid- or base-catalyzed bimolecular nucleophilic substitution reactions. The acid-catalyzed mechanisms are preceded by rapid deprotonation of the -OR or -OH substituents bonded to Si, whereas under basic conditions hydroxyl or silanolate anions attack Si directly. Mineral acids and ammonia are most generally used in sol-gel processing. The mechanisms are outlined in detail below (1).

The Mechanisms

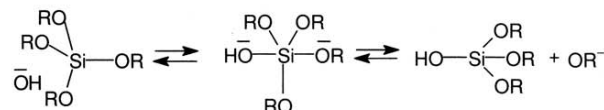
Acid-Catalyzed Hydrolysis



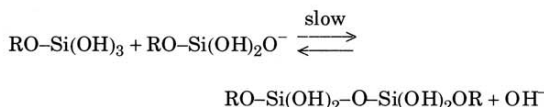
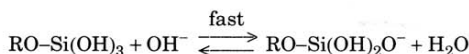
Acid-Catalyzed Condensation



Base-Catalyzed Hydrolysis



Base-Catalyzed Condensation



Formation of Colloidal Particles and Condensed Silica

At low pH levels, that is, acidic conditions (slow hydrolysis), the silica tends to form linear molecules that are occasionally cross-linked as shown in Figure 1. These molecular chains entangle and form additional branches resulting in gelation. Under basic conditions (faster hydrolysis) more highly branched clusters form that are not interpenetrable before drying and thus behave as discrete species. Gelation occurs by linking of the clusters (Fig. 2).

When sufficient interconnected Si-O-Si bonds are formed in a region, they respond cooperatively as colloidal particles or a sol. With time the colloidal particles and condensed silica species link to form a 3-dimensional network. At gelation the viscosity increases sharply, and the result is a solid object in the shape of the mold. The product of this process at the sol-gel transition is called an alcogel. After the sol-gel transition, the solvent phase is removed from the interconnected pore network. If it is removed by

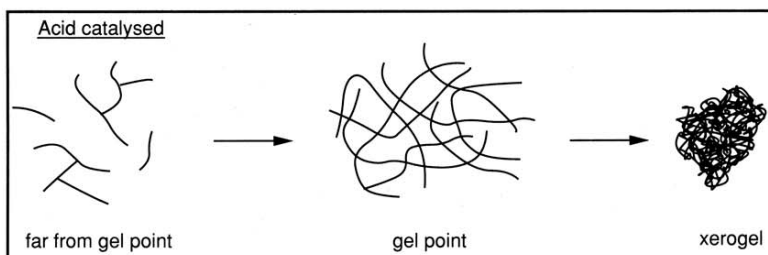


Figure 1. Acid-catalyzed hydrolysis.

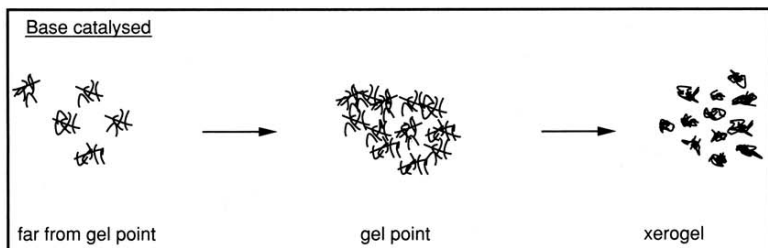


Figure 2. Base-catalyzed hydrolysis.

conventional drying, such as evaporation, xerogels result. If it is removed via supercritical evacuation, aerogels result (5). These processes are illustrated schematically in Figure 3.

Effect of Solvent Removal

Let us now consider what happens when the solvent is removed by evaporation to form xerogels. For polymer gels

dense gel structure. When hydrolysis is more rapid (base-catalyzed gels), polymers are larger and more highly cross-linked. On impingement the polymers will not deform as readily due to removal of solvent from within the polymer. The gel dries to a more or less randomly packed array of identifiable particles around which are large voids.

Properties of the Drygel

The method of removal of the solvent from the pores of the alcogel has a dramatic effect on the properties of the drygel. Aerogels have very low densities and very good thermal insulating properties when sandwiched between glass plates and evacuated (6). Xerogels are denser than aerogels, have high surface areas, and are often microporous. They can be used as catalyst supports (7), ionic conductors (8) (when appropriately doped), and precursors for a wide range of glasses, ceramics, coatings, films, and fibers, depending on the method of preparation.

There are also several commercialized processes of sol-gel technology, and an increasing amount of research is being carried out in this field. Advanced applications are now rapidly evolving, including synthesis of superconductors, coatings on optical memory disks, and large mirrors for laser weapons in space (9).

Experimental Procedure

- **Caution:** The following apparatus is assembled in the fume hood. The TEOS is added in the fumehood, and the sol-gel solution is stirred in the fume hood.

Preparation of Acid-Catalyzed Sols

A round-bottomed flask containing a magnetic stir bar is clamped by the neck above a magnetic stirrer, which is placed on a retort stand. (See Fig. 4.) The chemicals used were all reagent-grade and available from suppliers such as Fischer or Aldrich.

Approximately 30 mL of TEOS is poured into a 100-mL beaker (in the fume hood), and exactly 30 mL of TEOS from the beaker is measured out using a graduated cylinder. This quantity is then poured into the round-bottomed flask. Then 31 mL of ethanol is measured out in a graduated cylinder and added to the TEOS in the flask. The solution should be briskly agitated using the magnetic stir bar. Then 38 mL of distilled water is measured out using the graduated cylinder, and 3–4 drops of concentrated HCl is added to the water using a pipet. The acidic solution is poured into the TEOS solution in the flask, stirring all the time. The two solutions are initially immiscible but mix within a few minutes. The temperature of the solution is allowed to stabilize at

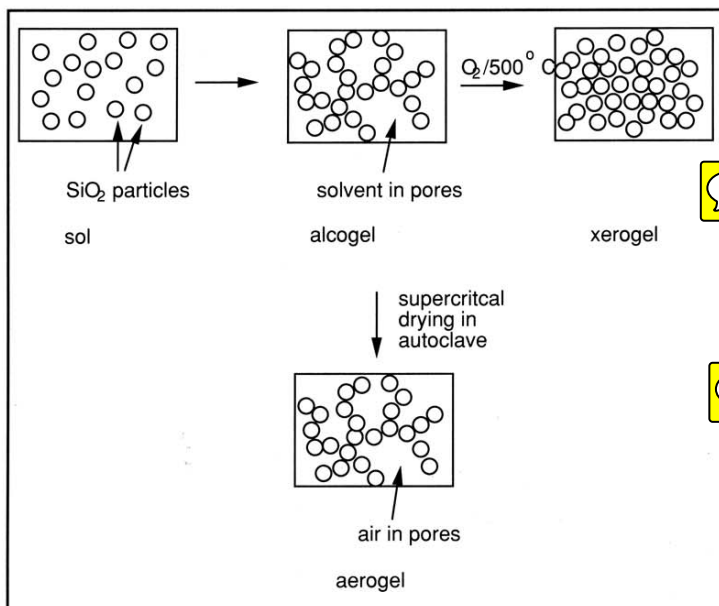


Figure 3. The sol-gel process.

such as these removal of solvent is expected to collapse the network, gradually resulting in additional cross-linking as unreacted -OH and -OR groups come into contact. The different structures of the slowly (acid-catalyzed) and rapidly (base-catalyzed) hydrolyzed gels respond differently to the removal of solvent during drying.

High-density low-pore-volume gels are formed in weakly cross-linked systems (acid-catalyzed gels). As the polymers impinge on one another they deform readily and form a

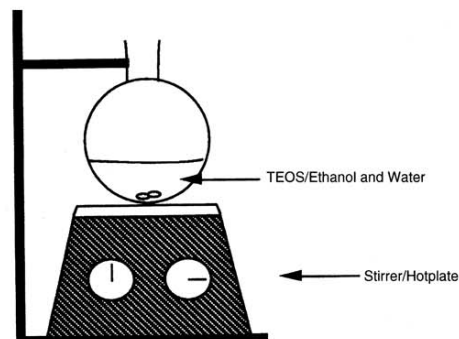


Figure 4. Experimental setup for the preparation of silica sols.

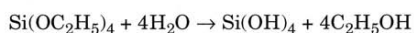


°C. The resulting pH of this acidic sol-gel solution should be about 3 and may be adjusted by adding more drops of acid as necessary.

The sol-gel solution is left stirring for 1.5 h in the fume hood. The change in pH is not significant during the course of the sol-gel process, and adjustment of the pH is not required. The molar ratio of TEOS:EtOH:H₂O is calculated to be 1:4:16 using the following data.

- mol wt TEOS = 208.33 g, density = 0.936 g/cm³
- mol wt ethanol = 46.07 g, density = 0.789 g/cm³

Because the balanced equation for the hydrolysis of TEOS is



4 mol of water are required for complete hydrolysis. However, excess water is used in this experiment to drive the reaction to the right. Previous experiments had shown that 16 mol of water allowed the sol-gel process to occur within a reasonable time period and produced monolithic gels.

The sol is poured into polythene tubes (about 5 or 6 tubes will be needed), and the lid is replaced tightly on one sample. The openings of the other samples are covered with clear plastic wrap, and each is secured with a rubber band. A few holes should be pierced in the wrap using a needle. Some samples are placed in the drying oven (60 °C), and one is left on the open bench.

Alternate Procedure

The whole procedure may be repeated using a few drops of NH₄OH instead of HCl. The pH of the sol-gel solution should be about 9 in the alkaline case. The sol-gel solution may take longer to mix in the acid-catalyzed reaction. (Up to 2 h for reaction may be necessary.)

Obtaining the Alcogels

After 1 and 2 days the conditions of all the samples are reexamined. The samples in the oven should have gelled after 2 days (alcogels) and will move freely from the solution in the tubes. A proportion of these alcogel samples are removed from the oven, and their lids are tightly replaced. The remainder are left in the oven for up to 5 more days (7 days in total). Samples of acid- and base-catalyzed gels were placed in porcelain boat crucibles in a tube furnace

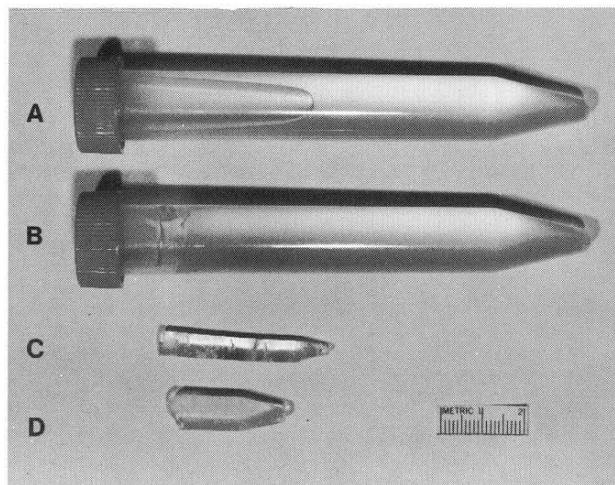


Figure 5. Physical appearance of (a) acid- or base-catalyzed sol, (b) acid-catalyzed alcogel after 2 days at 60 °C, (c) acid-catalyzed alcogel after 7 days at 60 °C, (d) base-catalyzed alcogel after 7 days at 60 °C.

and converted to xerogels by heating in a stream of oxygen gas for 5 h at 500 °C.

Results and Discussion

Physical Appearances

The physical appearances of the acid- and base-catalyzed xerogels are displayed in Figure 5. For both types of processing the sols contained in the tubes that were tightly sealed did not gel, nor did those that were covered with pierced plastic film and left at room temperature (Fig. 5a). However, if the acid- and base-catalyzed gels were covered with pierced plastic film and placed in an oven at 60 °C, alcogels were formed after 2 days (Fig. 5b) and had approximately the same volume as the original sols. After 7 days in the oven, the alcogels in both cases had shrunk to about 25% of their former volumes (Fig. 5c, d).

In the wet alcogel the SiO₂ network surrounds the pores that are filled with EtOH and H₂O. Because the gel is left in a drying oven, the solvent gradually evaporates, and the gel ages by additional cross-linking of unreacted -OH and -OR groups. This will cause the network to collapse somewhat and result in a reduction in volume. However, the dried alcogel still contains residual -OH and -OR species as well as ROH and H₂O. If these are to be removed completely to form a xerogel, the gel must be heated up to about 500 °C in an oxygen atmosphere.

Because the pore structure is somewhat collapsed in the dried alcogel relative to the wet alcogel, the porosity of the wet alcogel is expected to be much greater. The pore nature of the wet alcogel can be retained (before further shrinkage occurs in the oven) by supercritically drying the gel to form an aerogel.

Microstructural Features

Resolution of Particles

The acid-catalyzed alcogel (Fig. 5c) is transparent, whereas the base-catalyzed gel is opaque (Fig. 5d). The xerogels are similar in appearance to the alcogels but more shrunken. The physical appearances of the dried gels may be explained by their microstructures as obtained by transmission electron microscopy. Figures 6 and 7 show typical transmission electron microscope photographs of acid- and base-catalyzed xerogels.

The acid-catalyzed xerogels exhibit extremely fine microstructural features, and the low electron density contrast in the photograph of the xerogel sample suggests that

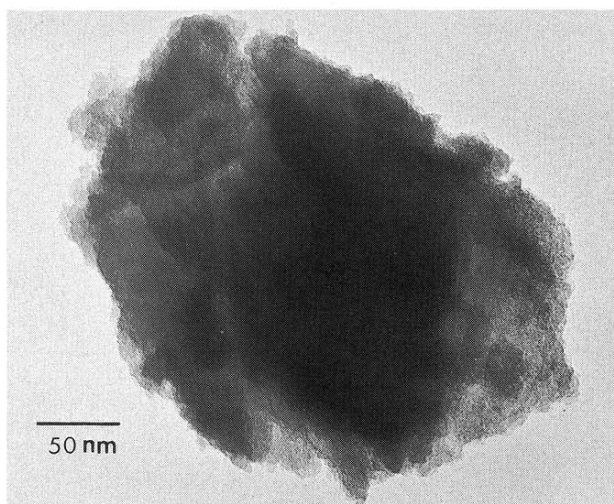


Figure 6. Typical microstructure of an acid-catalyzed xerogel.

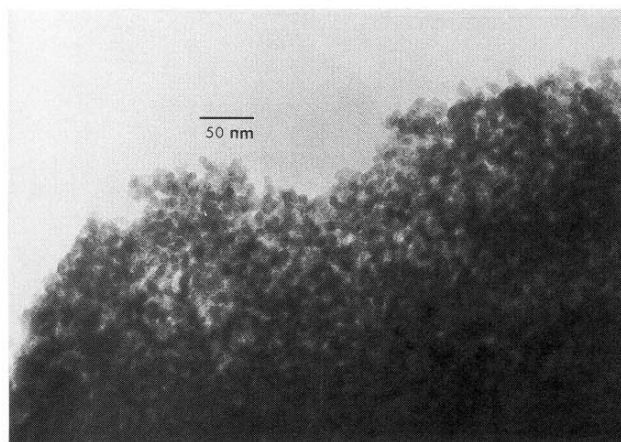


Figure 7. Typical microstructure of a base-catalyzed xerogel.

the pores are extremely small and evenly spread. The individual silica particles cannot be resolved. Hence, light incident on these gels is mostly transmitted through the solid, and the gels are observed to be transparent.

The base-catalyzed xerogels are particulate, and the individual silica particles may be resolved (~ 10 nm). They are also less tightly packed than in the acid-catalyzed example. Hence, light incident on the gels is reflected from the solid, and the gels appear more opaque.

Size and Complexity of Polymers

Base catalysis favors rapid hydrolysis of silicon alkoxides compared to condensation. These conditions favor the

formation of highly branched silica clusters that do not interconnect before gelation. These clusters form relatively large polymers that grow at the expense of the deform or shrink. Hence the gel dries as a random packed array of identifiable particles (Fig. 2), and silica xerogels prepared using base catalysis are expected to be particulate (Fig. 7).

However, acid catalysis favors a reduced rate of hydrolysis, causing relatively small polymers. When these are dried, strong surface tension forces are generated by the removal of solvent from the small regions between the polymers. As these weakly cross-linked polymers impinge, they readily deform and produce a dense gel structure (Fig. 1). Hence the gels prepared from acid hydrolysis have extremely fine microstructural features and are microporous (Fig. 6).

Acknowledgment

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Literature Cited

1. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic, 1990.
2. Klein, L. C. "Sol-Gel Processing of Silicates"; *Ann. Rev. Mater. Sci.* **1985**, 15, 227.
3. Hench, L. L.; West, J. K. "The Sol-Gel Process"; *Chem. Rev.* **1990**, 90, 33-72.
4. Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.
5. Teichner, S. J.; Nicolaon, G. A.; Vicarini, M. A.; Gardes, G. E. E. *Adv. Coll. Int. Sci.* **1976**, 5, 245.
6. Tewari, P. H.; Hund, A. J.; Lofftus, K. D. In *Proc. 1st Int. Symp. on Aerogels*; Fricke, J., Ed.; Springer Proc. Phys.; Springer: Heidelberg, 1986; Vol. 6, p 31.
7. Pommier, B.; Teichner, S. J. *Proc. Int. Congr. on Catalysis* **1988**, 2, 610.
8. Klein, L. C. *Solid State Ionics* **1989**, 32/33, 639.
9. Jones, R. W. *Fundamental Principles of Sol-Gel Technology*; Institute of Metals: London, 1989.