

## **Sol-Gel Preparation of Silica Gels**

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adapted from: Buckley, A.M.; Greenblatt, M. *J. Chem. Ed.* 1994, 71(7), 599.

### I. Objective

This laboratory examines preparation of silica gels by the sol-gel polymerization of tetraethylorthosilicate (TEOS) under hydrolytic conditions using either acid or base catalysis. The silica gels prepared in this experiment will be evaluated for surface area and porosity in a subsequent experiment.

### II. Introduction

Sol-gel polymerization of tetraalkoxysilanes,  $\text{Si}(\text{OEt})_4$  (TEOS) and  $\text{Si}(\text{OMe})_4$  (TMOS), is a mild and convenient method for the synthesis of amorphous silica gels. 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. At this transition, the solution becomes a rigid non-fluid mass. A specific example of a sol-gel process is the polymerization of TEOS in ethanol and water. Following addition of a catalyst this homogeneous solution undergoes a sol-gel transition to a rigid gel consisting of silica ( $\text{SiO}_2$ ) and solvent filled pores. The chemical steps involved in sol-gel polymerization, hydrolysis and condensation, result in formation of a network of Si-O-Si chemical linkages from the alkoxysilane (Figure 1). In a subsequent step, the gel is "processed" by drying. During this time the volume of the gel is reduced by approximately 80% resulting in a silica xerogel.

#### SOL GEL CHEMISTRY

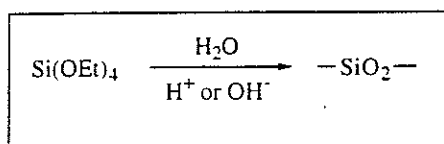
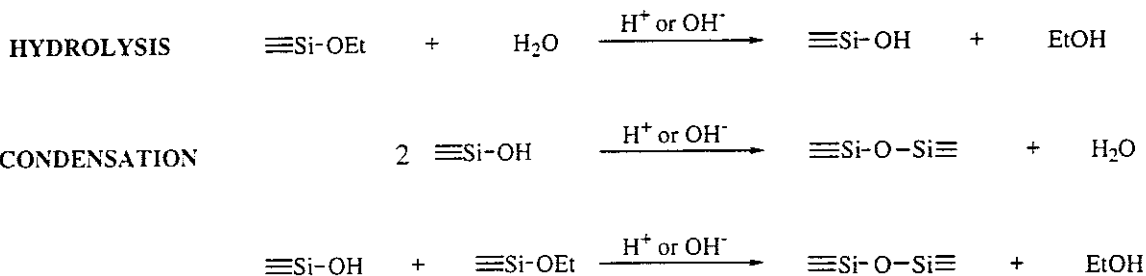


Figure 1. Summary of the key steps in sol-gel polymerization of ethoxysilanes.

The materials synthesized in this laboratory will be characterized by nitrogen porosimetry and  $\text{Si}^{29}$  solid state NMR.

Time table of events:

Week 2 - Synthesis of silica gels.

Week 4 - Work-up of silica gels.

Week 5 - Determination of surface area and porosity of sol-gel materials.

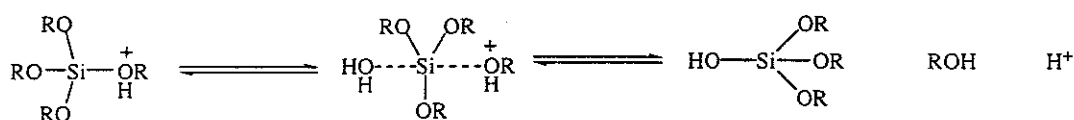
Week 6 - Solid state NMR analysis of silica gels.

This experiment will consist of a number of tasks that must be carefully planned and executed. The allotted time for this lab is 4 hours which includes preparation, reaction, and clean up time. You will only be able to complete the lab in the allotted time if you understand the tasks you need to perform **before** you come to the laboratory. Although the laboratory instructor should understand how to perform the lab you should not depend upon his or her advice to complete the lab; your own preparedness is the best insurance for successful completion of any experiments in this course This includes reading reference 1.

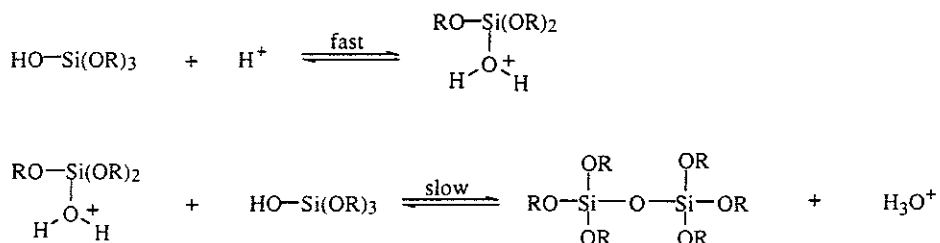
### Sol-Gel Polymerization of Tetraethylorthosilicate

Sol-gel polymerization of TEOS involves hydrolysis and condensation reactions. Hydrolysis occurs when TEOS and water are mixed in a mutual solvent, generally ethanol. The intermediates that are produced 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 ethanol is eliminated (Scheme 1).

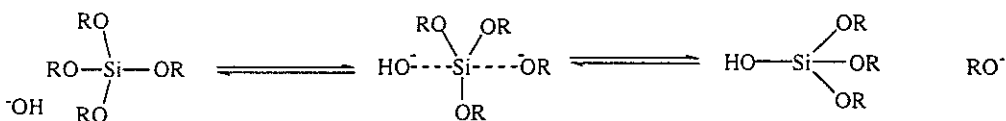
#### *Acid-Catalyzed Hydrolysis*



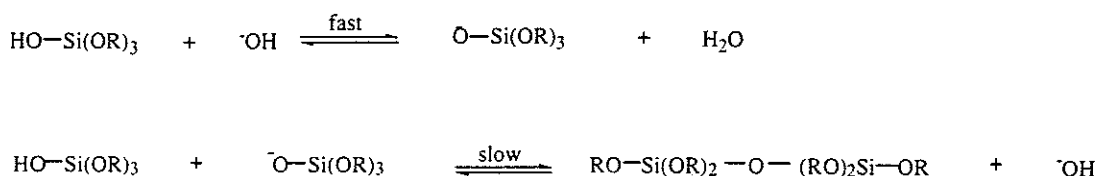
#### *Acid-Catalyzed Condensation*



#### *Base-Catalyzed Hydrolysis*



#### *Base-Catalyzed Condensation*



**Scheme 1.** Mechanism for hydrolysis and condensation of alkoxy silanes

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 3. These molecular chains entangle and form additional branches resulting in gelation. Under basic conditions (faster hydrolysis) more highly branched clusters form that are not interpenetratable before drying and thus behave as discrete species. Gelation occurs by linking of the clusters (Figure 4). 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 container. After the sol-gel transition, the solvent phase is removed from the interconnected pore network. If it is removed by conventional drying, such as evaporation, xerogels result. If it is removed via supercritical evacuation, aerogels result.

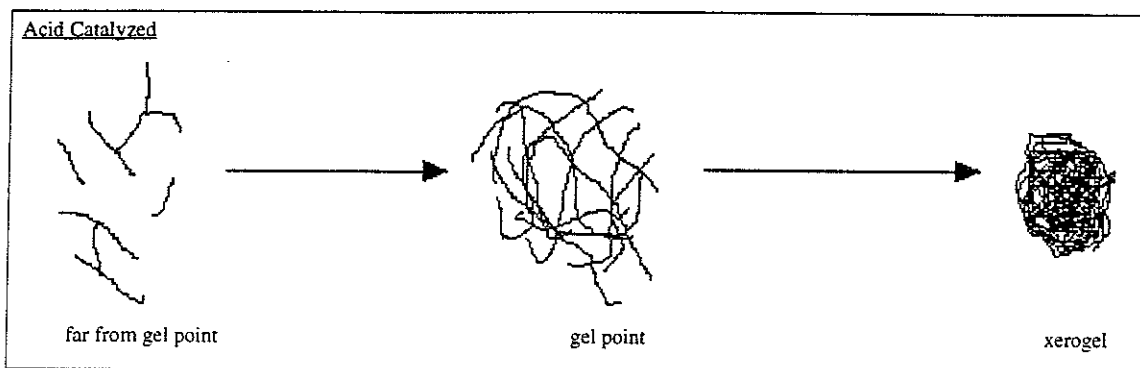


Figure 3. Acid catalyzed hydrolysis

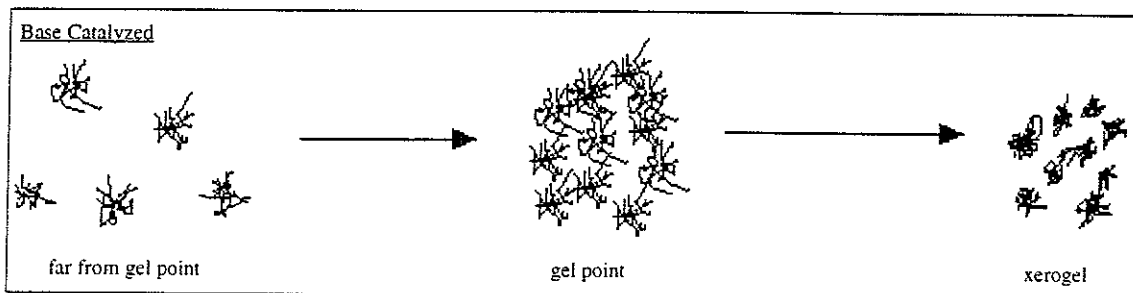


Figure 4. Base catalyzed hydrolysis

### III. References

1. Buckley, A.M.; Greenblatt, M. *J. Chem. Ed.* **1994**, 71(7), 599. see references there in.
2. Brinker, C.J.; Scherer, G.W. *Sol-Gel Science*; Academic, 1990.

#### IV. Precautions

All work should be done in the hood. TEOS is an irritant and highly water sensitive. The polymerization will require the use of concentrated acid and base solutions (HCl and  $\text{NH}_4\text{OH}$ ). Inhalation and contact with these chemicals should be avoided. Ethanol is a flammable liquid and should be treated with appropriate precautions.

#### V. Experimental Procedure

##### Preparation of Acid-Catalyzed Sols

Measure TEOS (30 mL) using a graduated cylinder and place into 250 mL roundbottom flask equipped with a reflux condenser and magnetic stir bar. Measure ethanol (31 mL) using a graduated cylinder and add to the TEOS in the flask. Stir the solution. In a graduated cylinder, add distilled water (38 mL) and 3-4 drops of concentrated HCl together. Pour this acidic solution into the TEOS solution in the flask under constant stirring. The two solutions are initially immiscible but mix after a few minutes. Heat the solution to  $60^\circ\text{C}$  and stir for 1.5 hours. The molar ratio of TEOS:EtOH: $\text{H}_2\text{O}$  is calculated to be 1:4:16. After the heating, cool the reaction mixture to room temperature and place the solution in a polyethylene bottle. Place the polyethylene bottle containing the sol-gel solutions in an drying oven ( $60^\circ\text{C}$ ) until the next lab period.

##### Preparation of Base-Catalyzed Sols

The base-catalyzed sols are prepared using the same procedure mentioned above with the exception that a few drops of conc.  $\text{NH}_4\text{OH}$  is used instead of HCl.

##### Work-up for Acid-Catalyzed and Base-Catalyzed Gels

Remove the gels from the drying oven and cut the polyethylene bottle to remove the gel. Place the gel into a 500 mL beaker and crush into small pieces using a spatula. To the beaker, add ethanol (200 mL) and allow the gel to soak in the solvent for 30 minutes to remove any residual catalyst from the material. Recover the gel by vacuum filtration. Place the gels back into the dry oven ( $60^\circ\text{C}$ ) for 1 hour. After drying, grind the gel into a fine powder and dry further under high vacuum at  $100^\circ\text{C}$  overnight. Store the materials in glass vials for future analysis.

#### VI. Equipment & Chemical list

##### Equipment:

- 2 \* 250 mL roundbottom flask
- 2 \* 250 mL sand bath
- 2 reflux condensers
- 2 \* 25 mL graduated cylinders
- 2 stir bars
- 2 filter flasks
- 2 filter funnels
- 2 \* 25 mL polyethylene bottles
- 2 \* 500 mL beakers

##### Chemicals: (amount for a group of 4 people)

- 80 mL TEOS (tetraethylorthosilicate)
- 500 mL EtOH
- 100 mL distilled water
- 10 mL HCl(conc.)
- 10 mL  $\text{NH}_4\text{OH}$ (conc.)

# The Sol-Gel Preparation of Silica Gels

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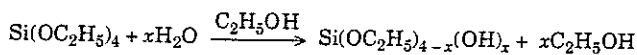
In this paper, we present the sol-gel preparation of silica from molecular precursors, which is an experiment appropriate for an introductory chemistry laboratory. Due to the increasing technological importance of the sol-gel process and the simplicity of this preparation, the sol-gel synthesis of silica 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 ( $\text{SiO}_2$ ) 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).

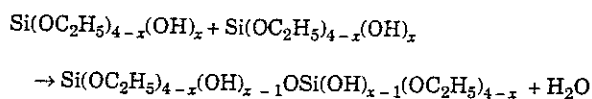
## Preparation of Silica Gels

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.

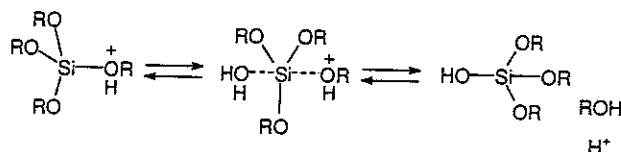
An example of the condensation between two silanols with the elimination of water is given below.



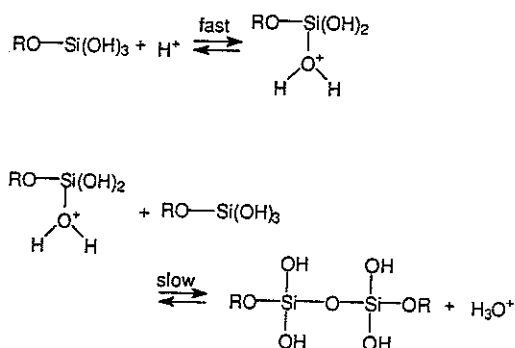
The hydrolysis and polycondensation reactions initiate at numerous sites within the TEOS and  $\text{H}_2\text{O}$  solution as mixing occurs. Both hydrolysis and condensation may occur by acid- or base-catalyzed bimolecular nucleophilic substitution reactions. The acid-catalyzed mechanisms are preceded 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

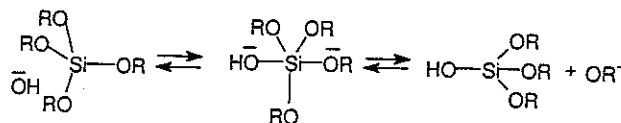
### Acid-Catalyzed Hydrolysis



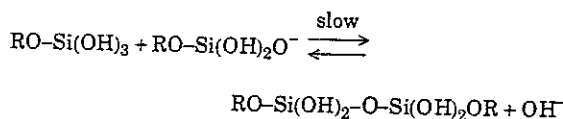
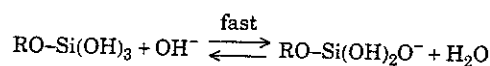
### Acid-Catalyzed Condensation



### 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

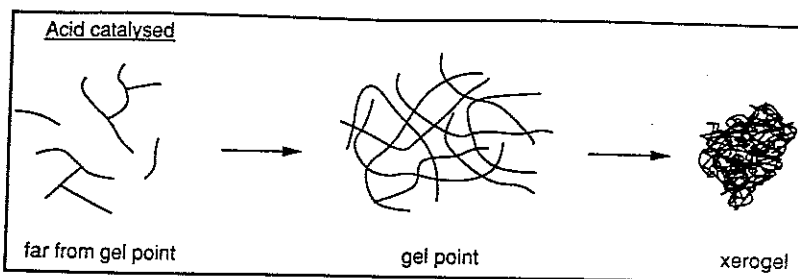


Figure 1. Acid-catalyzed hydrolysis.

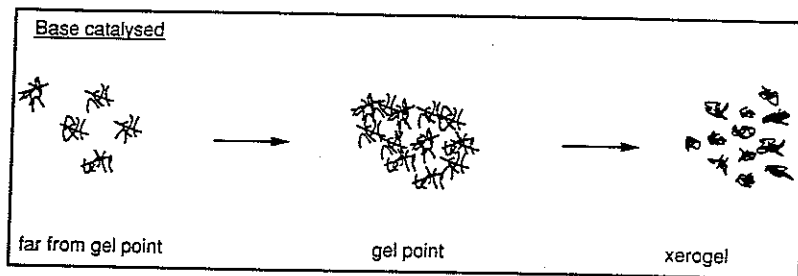


Figure 2. Base-catalyzed hydrolysis.

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

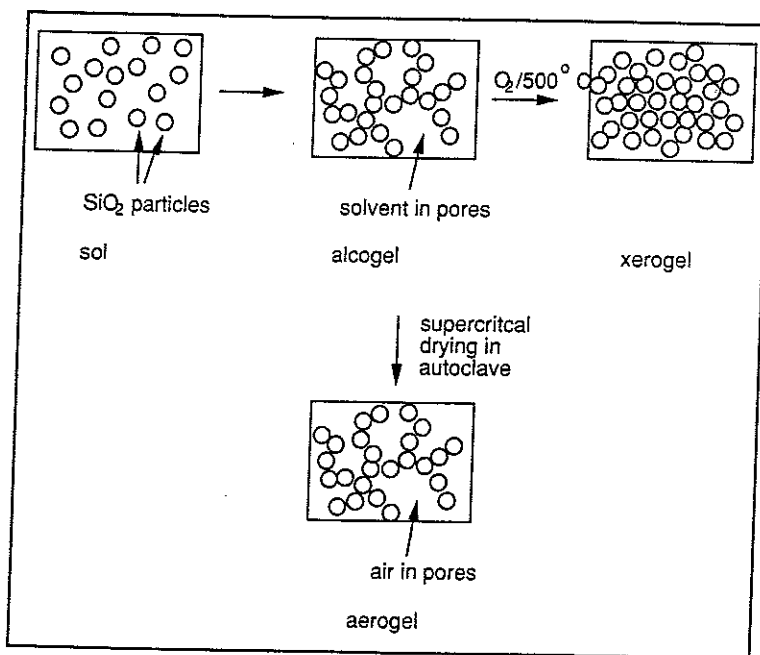


Figure 3. The sol-gel process.

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

dense gel structure. When hydrolysis is more rapid (base-catalyzed gels), polymers are large 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 fume hood, 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. This acidic solution is poured into the TEOS solution in the flask, stirring all the time. The two solutions are initially immiscible but mix after a few minutes. The temperature of the solution is allowed to stabilize at

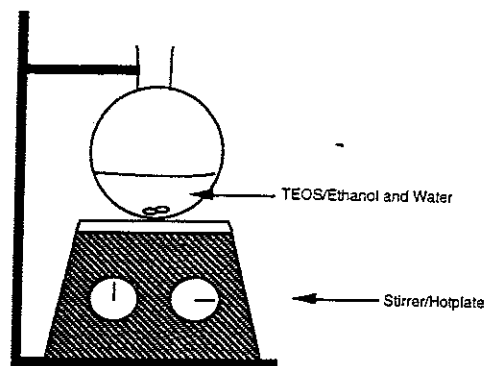


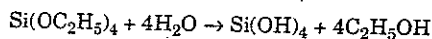
Figure 4. Experimental setup for the preparation of silica sols.

60 °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:H<sub>2</sub>O is calculated to be 1:4:16 using the following data.

- mol wt TEOS = 208.33 g, density = 0.936 g/cm<sup>3</sup>
- mol wt ethanol = 46.07 g, density = 0.789 g/cm<sup>3</sup>

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 NH<sub>4</sub>OH 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

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 SiO<sub>2</sub> network surrounds the pores that are filled with EtOH and H<sub>2</sub>O. 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 H<sub>2</sub>O. 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

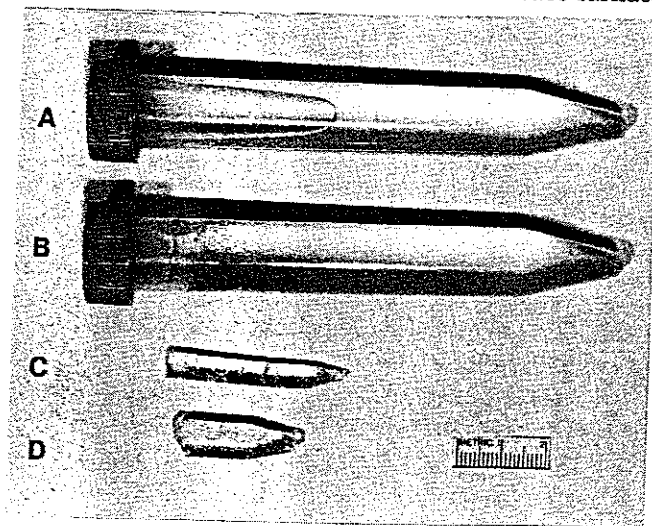


Figure 5. Physical appearance of (a) acid- or base-catalyzed sol, (b) acid-catalyzed alcogel after 2 days at 60 °C, (c) acid-catalyzed alcogel after 7 days at 60 °C, (d) base-catalyzed alcogel after 7 days at 60 °C.

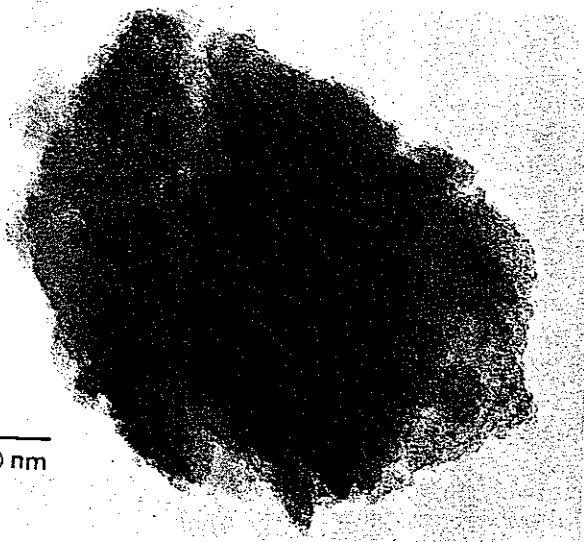


Figure 6. Typical microstructure of an acid-catalyzed xerogel.



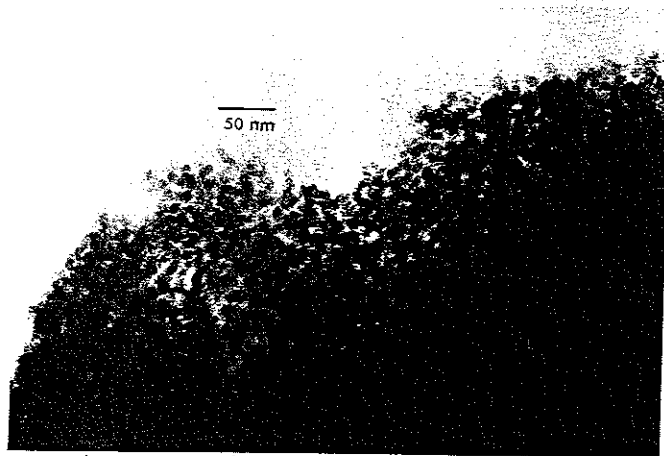


Figure 7. Typical microstructure of a base-catalyzed xerogel.

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

The authors would like to thank the Dreyfus Foundation and the National Science Foundation (Grant USE-9150484) for financial support.

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## Cyclic Voltammetry with Ultramicroelectrodes

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The development of ultramicroelectrode techniques is arguably the most important contribution to electroanalytical chemistry in the past 20 years. As their name implies, ultramicroelectrodes are extremely small, with dimensions on the order of micrometers or less. This small size, and the electrode characteristics that come with it, can be exploited in a number of unique applications. Indeed, ultramicroelectrodes provide access to cyclic voltammetry experiments previously considered impossible with conventionally-sized electrodes. New research includes measurements in highly resistive media (nonpolar solvents, polymers, gaseous interfaces, supercritical fluids), high-speed voltammetry (scan rates over one million volts per second), and analyses in small volumes or at microscopic locations (single brain cells, capillary chromatography detectors, electrochemical microscopes) (1-4).

This article presents a basic introduction to the theory and use of ultramicroelectrodes in cyclic voltammetry. Although numerous undergraduate-level experiments are available for cyclic voltammetry (5-15) none have addressed the topic of ultramicroelectrode techniques. The laboratory exercises and discussions provided here are designed to complement existing experiments on conventional cyclic voltammetry (6, 8-10).

#### Cyclic Voltammetry at Ultramicroelectrode Disks

In experiments with normal time scales, cyclic voltammograms (CVs) obtained with ultramicroelectrodes differ significantly from those obtained using electrodes of conventional size. This is due to differences in mass transport within the diffusion layer, the region adjacent to the electrode in which electrolysis takes place. The influence of the diffusion layer on the appearance of a CV is shown in Figure 1. At large electrodes, mass transport occurs mostly perpendicular to the surface (planar diffusion), Figure 1a. The result is a typical peak-shaped voltammogram. For a reversible redox process, the peak current follows the Randles-Sevcik relationship (16, 17), eq 1, in which  $i_p$  is peak current (A),  $n$  is electron stoichiometry,  $A$  is electrode area ( $\text{cm}^2$ ),  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $C^*$  is bulk concentration of electroactive substance, and  $v$  is scan rate (V/s).

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C^* v^{1/2} \quad (1)$$

By contrast, mass transport at ultramicroelectrodes takes on a hemispherical profile (radial diffusion), Figure 1b. This produces a sigmoidal, steady-state voltammogram (1-4). Unlike the situation for a standard size electrode, currents generated at ultramicroelectrodes are dependent on their geometry. For a disk-shaped electrode, the limiting plateau current from a CV is given by eq 2, in which  $i_{\text{lim}}$