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Experiment 15

The Sol–Gel Preparation of Silica Gel Sensors

Anne M. Buckley, Martha Greenblatt,
Peter G. Allen, and George C. Lisensky

Notes for Instructors

Purpose

To observe how cross-linking affects the physical properties of a silicate polymer containing an acid-base indicator, or other reagent appropriate for chemical sensing.

Method

Acid-catalyzed polymerization of $Si(OCH_2CH_3)_4$ gives linear molecules that are occasionally cross-linked and tangle to form additional branching and gelation. Base-catalyzed polymerization gives more highly branched polymers and discrete structures linked by gelation. Acid-base indicators or reagents for qualitative tests can be trapped in the gel for demonstrating the porosity of the structure.

Materials

Tetraethyl silicate, $Si(OCH_2CH_3)_4$ (Aldrich, tetraethylorthosilicate, 98%)

Absolute ethanol

2725-X/93/0463$06.00/1

Hydrochloric acid (conc)

Aqueous ammonia (conc)

Bromthymol blue, sodium salt (Prepared indicator solutions are less desirable, because they will change the amount of water in the reaction mixture.)

Potassium iodide

Potassium thiocyanate

Solutions of Fe^{3+}, Cu^{2+}, Ag^{+}, or Pb^{2+}

Sonicator (If magnetic stirring is used, the mixing requires 1–2 hours; with a sonicator only 20 minutes is needed.)

Graduated cylinder

Plastic or glass disposable pipettes

pH indicator paper

Drying oven set at 60 °C

Beakers, graduated cylinders, test tubes

Answers to Student Questions

1. Calculation of $Si(OCH_2CH_3)_4 : CH_3CH_2OH : H_2O$ mole ratio

   15.0 mL of $Si(OCH_2CH_3)_4$: 15.5 mL of CH_3CH_2OH : 19.0 mL of H_2O

   15.0 mL of $Si(OCH_2CH_3)_4 \; \frac{0.936\text{ g}}{\text{mL}} \; \frac{\text{mol}}{208.33\text{ g}} = 0.0674$ mol of $Si(OCH_2CH_3)_4$

   15.5 of mL $CH_3CH_2OH \; \frac{0.789\text{ g}}{\text{mL}} \frac{\text{mol}}{46.07\text{ g}} = 0.2655$ mol of CH_3CH_2OH

   19.0 mL of $H_2O \; \frac{1.00\text{ g}}{\text{mL}} \frac{\text{mol}}{18.0\text{ g}} = 1.056$ mol of H_2O

   or a mole ratio of 1 $Si(OCH_2CH_3)_4$: 4 CH_3CH_2OH : 16 H_2O

2. Balanced equation for complete hydrolysis of $Si(OCH_2CH_3)_4$

   $Si(OCH_2CH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3CH_2OH$

3. The approximate shrinkage between the wet and dried (in oven 7 days) alcogels is to one-fourth their original size. In the wet alcogel the SiO_2 network surrounds pores that are filled with CH_3CH_2OH and H_2O. The gel is left in a drying oven, so the solvent gradually evaporates and the gel ages by additional cross-linking of unreacted –OH and –OR groups. This cross-linking 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_2O. 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.)

4. Positive indicator tests for the oven-dried samples illustrate that the gel is still porous. (The pore structure is somewhat collapsed in the dried alcogel, relative to the wet alcogel, so the porosity of the wet alcogel is expected to be much greater. The porosity of the wet alcogel can be retained, before further shrinkage occurs in the oven, by the supercritical drying of the gel to form an aerogel.)

5. The acid-catalyzed xerogels have extremely fine microstructural features, and the low electron-density contrast in the xerogel suggests that the pores are extremely small and evenly spread. The individual silica particles cannot be resolved. The base-catalyzed xerogels are particulate, and the individual silica particles may be resolved (~10 nm) and are less densely packed than in the acid-catalyzed case.

   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 prior to gelation. These clusters form relatively large polymers that grow at the expense of the smaller clusters. On drying by evaporation, the clusters impinge, but the polymers do not readily deform or shrink. Thus, the gel dries as a random packed array of identifiable particles. Consequently, silica xerogels prepared using base-catalyzed conditions are expected to be particulate. 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. This means that the gels prepared from acid hydrolysis have extremely fine microstructural features and are microporous.

The Sol–Gel Preparation of Silica Gel Sensors

Purpose

To observe how cross-linking affects the physical properties of a silicate polymer containing an acid-base indicator, or other reagent appropriate for chemical sensing.

Introduction

Sols are dispersions of colloidal particles (size 1–100 nm) in a liquid. A *gel* is an interconnected, rigid network with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micrometer.

The sol–gel process is the name given to any one of a number of processes that involve a solution or sol that undergoes a transition to a rigid, porous mass, a gel. One particular example of a sol–gel process is the reaction of $Si(OCH_2CH_3)_4$, ethanol, and water. These three reactants form a one-phase solution that goes through a sol–gel transition to a rigid, two-phase system of solid silica (SiO_2) and solvent-filled pores. In this lab experiment you will carry out a sol–gel preparation of silica gels.

The fundamental reaction of the sol–gel process is hydrolysis and polymerization of a silicon alkoxide. Hydrolysis occurs when $Si(OCH_2CH_3)_4$ and water are mixed in a mutual solvent, generally ethanol:

$$Si(OCH_2CH_3)_4 + H_2O \rightarrow Si(OCH_2CH_3)_3OH + CH_3CH_2OH.$$

The intermediates that exist as a result of partial hydrolysis include molecules with Si–OH groups, which are called silanols. Complete hydrolysis of $Si(OCH_2CH_3)_4$ to $Si(OH)_4$ would yield silicic acid, but complete hydrolysis 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 ($-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$), and a water or ethanol molecule is eliminated. An example of the condensation between two silanols with the elimination of water is

$$Si(OCH_2CH_3)_3OH + Si(OCH_2CH_3)_3OH \rightarrow (CH_3CH_2O)_3SiOSi(OCH_2CH_3)_3 + H_2O$$

NOTE: This experiment was written by Anne M. Buckley and Martha Greenblatt, Rutgers, The State University of New Jersey, Piscataway, NJ 08855; and Peter G. Allen and George C. Lisensky, Beloit College, Beloit, WI 53511.

Then hydrolysis of $(CH_3CH_2O)_3SiOSi(OCH_2CH_3)_3$ will produce, for example, $(CH_3CH_2O)_2Si(OH)OSi(OCH_2CH_3)_3$ that can undergo further polymerization.

The hydrolysis and polycondensation reactions are initiated at numerous sites within the $Si(OCH_2CH_3)_4$ and H_2O solution as mixing occurs. When a sufficient number of interconnected Si–O–Si bonds are formed in a region, they interact cooperatively to form colloidal particles or a sol. With time, the colloidal particles and condensed silica species link together to form a three-dimensional network. At gelation, the viscosity increases sharply, and a solid object in the shape of the mold results. The product of this process at the sol–gel transition is called an *alcogel*. Once through the sol–gel transition, the solvent phase can be removed. If it is removed by conventional drying, such as evaporation, *xerogels* result. If it is removed via supercritical (high-temperature) evacuation, *aerogels* result. *See* Figure 1.

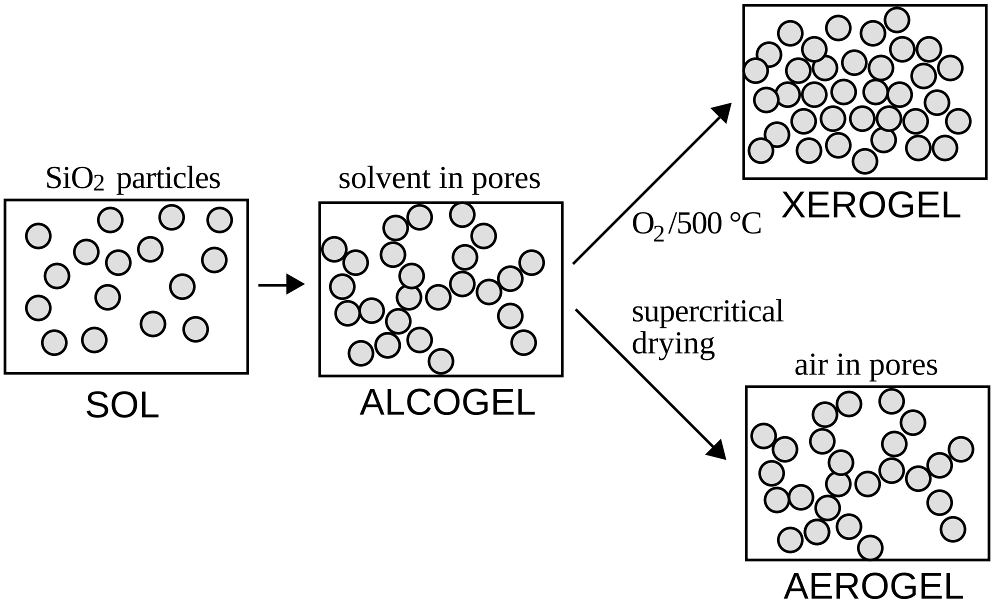


Figure 1. Formation of alcogels, xerogels, and aerogels.

If the solvent phase is removed via supercritical evacuation, the aerogel has a very low density. These aerogels have very good thermal insulating properties when sandwiched between glass plates and evacuated. Xerogels are denser than aerogels, have high surface areas and are often microporous. They can be used as catalyst supports, ionic conductors (when appropriately doped), and precursors for a wide range of glasses, ceramics, coatings, films, and fibers, depending upon the method of preparation. Also, several commercialized processes of sol–gel technology are in use, and an increasing amount of research is being carried out in this field. The hydrolysis and condensation reactions are not, of course, limited to silicon alkoxides, but can be applied to many metal alkoxide systems. Thus, the sol–gel processing of more complex ceramics is now rapidly evolving to include the synthesis of superconductors and coatings on optical memory disks.

Acid-Catalyzed Reaction

At low pH levels, that is, acidic conditions (slow hydrolysis), the silica tends to form linear molecules that are occasionally cross-linked. These entangle and form additional branches, resulting in gelation. *See* Figure 2.

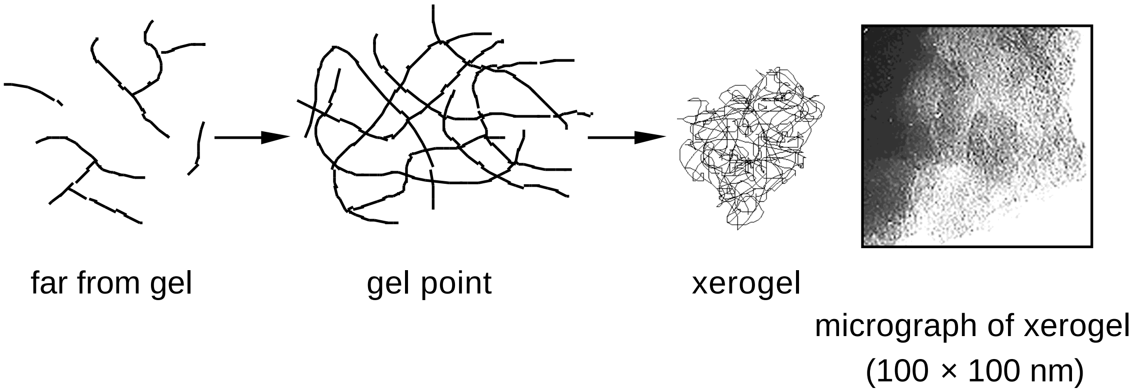


Figure 2. A representation of acid-catalyzed gelation.

Base-Catalyzed Reaction

Under basic conditions (faster hydrolysis), more highly branched clusters form that do not interpenetrate prior to drying and thus behave as discrete species. Gelation occurs by linking of the clusters. *See* Figure 3.

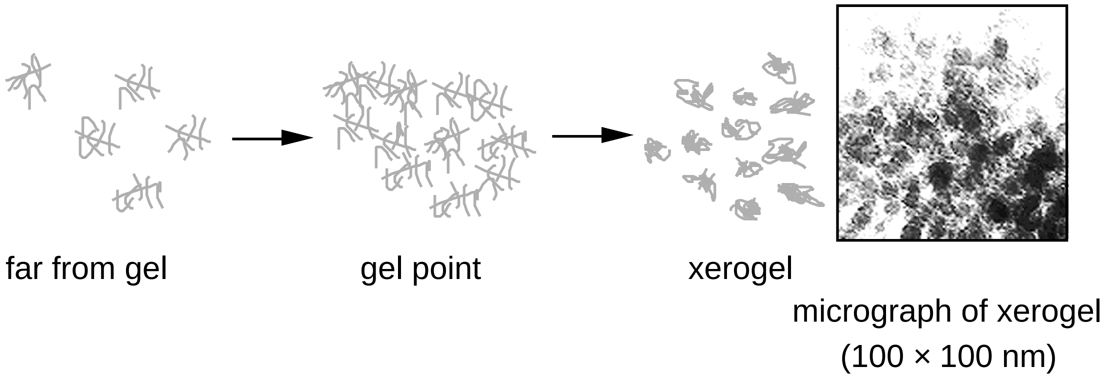


Figure 3. A representation of base-catalyzed gelation.

To understand how acid- and base-catalyzed sol–gel reactions lead to different microstructures in the gels, we now consider what happens when the solvent is removed by evaporation to form xerogels. For polymer gels such as these, removal of solvent is expected to collapse the network of pores, 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 larger and more highly cross-linked; on impingement the polymers will not deform as readily. The gel dries to a more or less randomly packed array of identifiable particles around which are large voids. Think of the two cases as the ability to further entangle a plate of spaghetti (acid-catalyzed) versus the inability to further entangle a plate of tumbleweeds (base-catalyzed).

Procedure

Wear eye protection.

CAUTION: $Si(OCH_2CH_3)_4$ is irritating to eyes, mucous membranes, and internal organs. Be sure to work in the fume hood as much as possible and wear gloves. Dispose of all waste in an organic waste solvent jug.

Measure 15.5 mL of absolute ethanol into each of two Erlenmeyer flasks. In a fume hood, pour about 30 mL of the liquid $Si(OCH_2CH_3)_4$ (tetraethyl silicate) into a small beaker and immediately recap the stock bottle. Use this $Si(OCH_2CH_3)_4$ to measure out and add exactly 15.0 mL of $Si(OCH_2CH_3)_4$ to each of the ethanol-containing flasks.

Acid-Catalyzed Hydrolysis

Measure out 19.0 mL of distilled water and mix in 2–3 drops of concentrated HCl. Pour this aqueous acid solution into the $Si(OCH_2CH_3)_4$–ethanol solution. Do any layers form? Test the pH of the water by dipping a glass rod into the solution and allowing a small drop to touch a piece of indicator paper. The pH should be about 3. Adjust the pH to this value by adding more drops of acid as necessary.

Base-Catalyzed Hydrolysis

Measure out 19.0 mL of distilled water and mix in 8–10 drops of concentrated aqueous ammonia. Pour this aqueous base solution into the $Si(OCH_2CH_3)_4$–ethanol solution. Do any layers form? Test the pH of the water by dipping a glass rod into the solution and allowing a small drop to touch a piece of indicator paper. The pH should be about 10. Adjust the pH to this value by adding more drops of base as necessary.

Sol–Gel Formation

Place both flasks in a sonicator for 20 minutes (or mix with a magnetic stirrer for 1–2 hours if no sonicator is available). If multiple layers are still present, add a few more drops of concentrated HCl (acid-catalyzed) or concentrated aqueous ammonia (base-catalyzed) and mix them in the sonicator for another 10 minutes or stir for another hour. Continue until the layers are completely mixed.

Remove some of the sol from the *acid-catalyzed* reaction flask, and fill a Petri dish to a level of about 5 mm. Take the remainder of the sol and divide it among three small test tubes. Add a few crystals of the sodium salt of bromthymol blue to one of the tubes. In the second tube, add a few crystals of potassium iodide. Add a few crystals of potassium thiocyanate to the third tube. What is the color of the sols? Put the three labeled tubes in a drying oven at 60 °C. Let the contents of the Petri dish evaporate slowly at room temperature.

Remove some of the sol from the *base-catalyzed* reaction flask, and fill a Petri dish to a level of about 5 mm. Take the remainder of the sol and divide it among three small test tubes. Add a few crystals of the sodium salt of bromthymol blue to one of the tubes. In the second tube, add a few crystals of potassium iodide. Add a few crystals of potassium thiocyanate to the third tube. What is the color of the sols? Let the contents of the Petri dish evaporate slowly. Put the three labeled tubes in a drying oven at 60 °C.

After 1 week, take the tubes from the oven. Did any changes occur? Examine the contents of the Petri dishes. Record your observations.

Indicator Tests

Place some of the *acid-catalyzed* product that contains bromthymol blue in a covered beaker. Also place a small open container of concentrated aqueous ammonia in the beaker (a source of NH_3 gas). What happens? What does this tell you about the porosity of the product?

Place some of the *base-catalyzed* product that contains bromthymol blue in a covered beaker. Also place a small open container of concentrated HCl in the beaker (a source of HCl gas). What happens? What does this tell you about the porosity of the product?

Add some of a KI-containing product to a Ag^+ or Pb^{2+} solution. What happens? Why? Do the acid- and base-catalyzed products do the same thing?

Add some of a KSCN-containing product to a Fe^{3+} or Cu^{2+} solution. What happens? Why? Do the acid- and base-catalyzed products do the same thing?

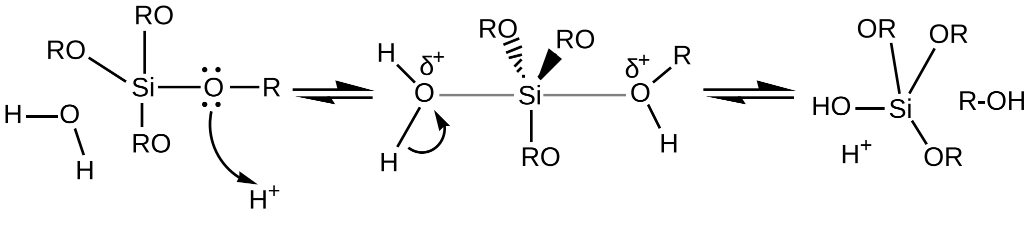
Questions

1. Calculate the mole ratio of $Si(OCH_2CH_3)_4$ to CH_3CH_2OH to H_2O used in the experiment (the density of $Si(OCH_2CH_3)_4$ is 0.936 g/mL; the density of ethanol is 0.789 g/mL).
2. What is the ratio of $Si(OCH_2CH_3)_4$ to H_2O required for complete hydrolysis to $Si(OH)_4$? (Hint: Write a balanced equation.)
3. Did you observe any changes in volume after mixing? After drying? Why does this happen?
4. What evidence do you have for the porosity of the gels?
5. Study the electron micrographs of the acid- and base-catalyzed xerogels. What are the differences in the microstructures of the two types of gels? Can you suggest a reason for the differences in the microstructures?

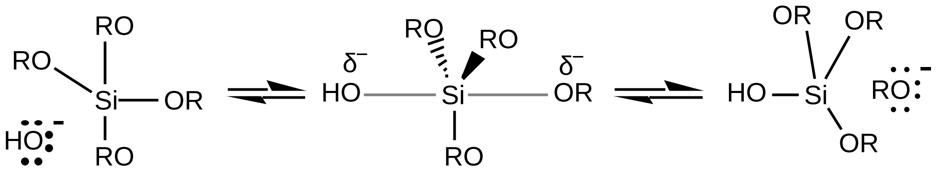
Appendix. Hydrolysis and Condensation Mechanisms

Both hydrolysis and condensation may occur by acid- or base-catalyzed bimolecular nucleophilic substitution reactions. The acid-catalyzed mechanisms are preceded by rapid protonation of the OR or OH substituents bonded to Si, whereas under basic conditions hydroxyl or silanolate anions attack Si directly. The mechanisms are outlined in more detail as follows.

Acid-Catalyzed Hydrolysis

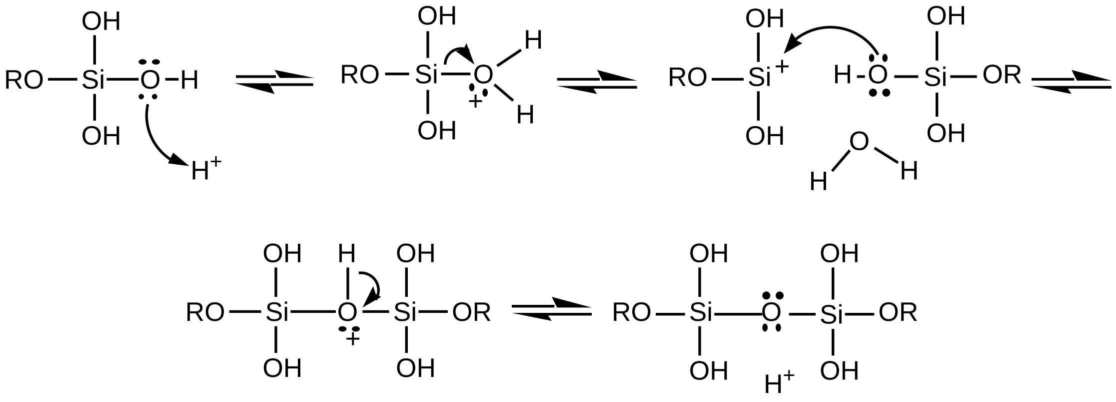


Base-Catalyzed Hydrolysis

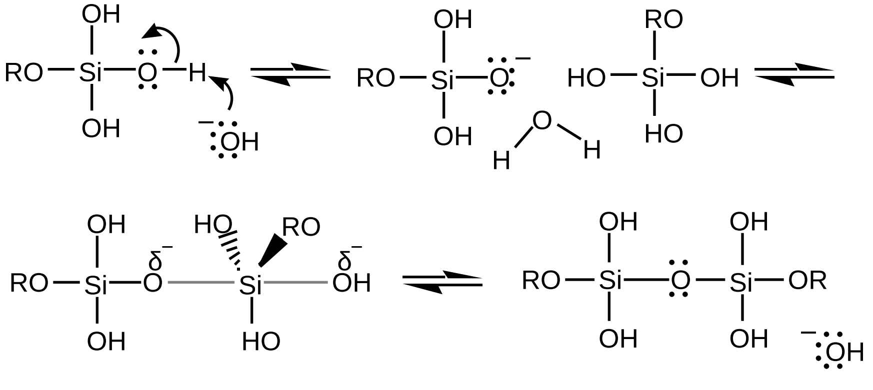


After one or more –OR groups has been replaced by –OH, a condensation reaction can occur.

Acid-Catalyzed Condensation



Base-Catalyzed Condensation



Further hydrolysis of the OR groups can occur, resulting in further condensation and eventual formation of a polymer.