

Preparation of a gel from metal alkoxide and its properties as a precursor of oxide glass

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Basic research on the formation of monolithic gel as the precursor of oxide glass has been done concerning the hydrolysis and gelling of silicon tetramethoxide and the properties of dry gel. Disks of dried gel were prepared without fracture by adding the necessary amount of water for hydrolysis into a methanol solution of silicon tetramethoxide, followed by drying the formed gel while keeping the vapour pressure of the methanol under control. The dried gel was porous with micropores ranging from 15 to 100 Å in diameter. It had a specific surface area of more than $300 \text{ m}^2 \text{ g}^{-1}$ and about 30% porosity. Monolithic gel was also prepared by using dilute ammonia water for hydrolysis. The time taken to gel became shorter with increasing ammonium ion concentration, but resulted in a gel of coarser structure. Dehydration polymerization of 60 to 75% occurred at room temperature. The polymerization was more pronounced in gels made with higher ammonium concentrations, but the amount of unreacted ethoxy group was also larger in these gels.

1. Introduction

Oxide glasses can be prepared by the hydrolysis of metal alkoxides, followed by heating the gel which is produced up to a temperature near the glass transition point [1-5]. This method of glass preparation without melting is of great interest because of the uniqueness of the method; glass is formed starting from liquid. The purification of raw materials, or mixing for homogenization, are much more easily performed for liquid than for solid. Fabrication into a special shape, such as thin film formation [3], or fibre drawing [4] can be carried out at room temperature without sophisticated processes.

Unfortunately, there is a very little reported on the reactions that occur in this interesting method. Because of the complexity of the reaction the hydrolysis product, a gel, usually fractures into small pieces. Only glass of a particulate form is

obtained, unless the powdered glass is hot-pressed. [5].

In order to fully utilize the advantages of this unique method in preparing glasses of high quality, it is necessary to find out the conditions governing the direct conversion of gel to monolithic oxide glass without complicated hot-pressing, which often reduces the optical quality of the glass [6].

Although Yoldas [7] succeeded quite recently in preparing monolithic glass of high silica content from a gel after pyrolysis up to 500°C , there are still many problems to be solved. There has been very little published on the best method of preparation of monolithic gel, for example, or how to correlate properties of a gel with the conditions of its preparation, except for the work by Yoldas [8-10] on alumina gel.

Silicon alkoxides are used yield silica, a typical glass former, but are quick to hydrolyse compared

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with most other alkoxides. Because of this there is need for basic research concerning the gel formation and properties of formed gel, as well as the reactions during pyrolysis of a gel, to establish the conditions for preparing monolithic glass of the desired form.

The present study was carried out to obtain more information about gel formation and the properties of gels, particularly in relation to the conditions of hydrolysis of silicon methoxide. The reason why silicon-tetramethoxide was chosen was that it is the easiest to hydrolyse among the silicon alkoxides, and that the investigations on the precursor of silica glass are essential for low temperature preparation of an oxide glass.

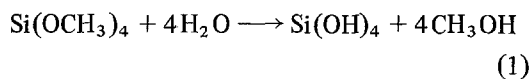
2. Experimental

2.1. Gelling of silicon-tetramethoxide by hydrolysis.

2.1.1. Preparation of the solution

The hydrolysis of metal alkoxide diluted with alcohol is usually carried out using the moisture in ambient atmosphere [1-5]. Using this method, however, the gelling of the solution starts from the surface and gradually develops into the bulk. The onset of the fracture before complete solidification of the gel is almost inevitable, due to the difference in the rate of contraction at the surface and the bottom of the gel.

In this study, water necessary for the hydrolysis was added into the solution, so that the gelling proceeded homogeneously in the bulk and crack formation could be avoided. 25 g of $\text{Si}(\text{OCH}_3)_4$ from Wako Chemicals was diluted with 30 ml of methanol of reagent grade, followed by adding distilled water necessary for hydrolysis (12 ml) while stirring vigorously, on the assumption that the reaction is as below;



Since the rate of hydrolysis, or gelling rate, is known to be influenced more by the pH value of the solution than by temperature of ageing or the degree of dilution [10, 11], dilute ammonia water of various concentrations, (0.00213%, 0.00427%, 0.00854%, or 0.068% weight) was also employed instead of distilled water for the purpose of promoting the reaction. It was hoped an optimum pH value could be found. It was known from preliminary studies that ageing at an elevated temperature (up to 60°C) was less ef-

fective than introducing ammonia with respect to promotion of gelling, and that the addition of acid (HCl), which was effective for alumina gel [10], made the gelling too slow for practical application in the case of silicon tetramethoxide (a few weeks to peptize and about a month to dry at room temperature for the solution of $\text{pH} \approx 2$).

2.1.2. Ageing of the solution.

The uniform mixture of $\text{Si}(\text{OCH}_3)_4$ and water gelatinizes and becomes viscous within a few to several tens hours at room temperature, followed by contraction by separation from the alcohol. The contraction of the gel proceeds with the vaporization of the alcohol until the gel is completely dry and solid.

In the experiment, the ageing of the solution was carried out at room temperature (25°C) in a cylindrical glass container 38 mm in diameter and 40 mm high. The top of the container was covered with aluminum foil fixed with tape, so that the vapour pressure of the alcohol in the container could be controlled. When the separation of alcohol due to the reaction in Equation 1 was observed, several pin-holes of about 1 mm in diameter were made on the aluminum foil to allow the alcohol to evaporate off gradually. The contraction of the gel was accelerated by increasing the number of pin-holes each day until the volume of the gel had been reduced to about one eighth of the initial volume. The gel was then transferred to a desiccator for complete drying.

2.2. Observations on the gelatinizing process

2.2.1. Values of pH of the mixture and gelatinizing time

Values of pH of the mixtures at their initial stage of the reaction were measured with a glass-electrode pH meter. The relation between the pH of the mixture and the gelling rate was investigated by measuring the time necessary for the solution to lose fluidity. This time, which we shall call gelation time, was determined from the observation of surface distortion when the container was gently tilted at certain time intervals.

2.2.2. Weight loss and volume change

In order to see the effect of ammonia concentration on the mechanism of condensation polymerization of the gel, which substantially determines the structure and properties of

solidified gel, the change in volume and weight of the gel throughout the contraction process was measured using a chemical balance and a travelling microscope.

2.3. Measurement of the properties of the gel

2.3.1. Apparent and true densities

Apparent and true densities of the completely dried gel (which we shall call dry gel) were measured from the weight and size of the disk of gel and by pycnometry. In this process, the fractured dry gel was subjected to evacuation before measurement to expel the water adhered on the surface.

2.3.2. Specific surface area and pore size distribution

The absorption isotherm of the dry gel was determined by a nitrogen adsorption technique to obtain the specific surface area and the pore size distribution. In the experiment, the pre-evacuation to expel the adhered water which is usually made at an elevated temperature, was carried out at room temperature overnight to avoid any change due to thermally accelerated dehydration polymerization.

2.3.3. Gas chromatography

The amount of hydrogen, carbon and nitrogen in the dry gel were measured by gas chromatography to find out the amount of $-OH$ group, residual $-OCH_3$ group and ammonium ion in the gel. The measurement was made by decomposing the powdered sample at $1200^\circ C$ and carrying the evolved gas with argon into a CHN coder made by Yanagimoto Manufacturing Co.

3. Results and discussion

3.1. Gelling and the solidification to dry gel

3.1.1. Gelling of the solution

The initial values of pH of the uniformly mixed solution of $Si(OCH_3)_4$ and ammonia water of concentrations 0, 0.00213, 0.00427, 0.00854, and 0.068 wt % were 7.42, 8.18, 8.38, 8.48, and 8.54, respectively. The values of pH decreased with time to approach 7 at various rates depending on the initial value, i.e. the higher the initial value, the faster the decrease rate. The solution gellatinized uniformly to lose fluidity in a few hours. to several tens hours. The gelation time was

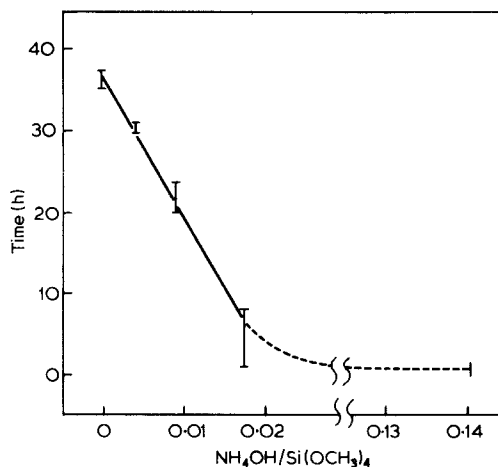


Figure 1 Effect of NH_4OH on gelation time.

dependent on the concentration of ammonium ions, as shown in Fig. 1.

3.1.2. Solidification to dry gel

The gelled solutions contracted uniformly without fracturing, except for one prepared from the solution with the highest ammonium ion concentration, and solidified to a disk about one eighth of the initial volume in two weeks. The appearance of the gels from various solutions are shown in Fig. 2.

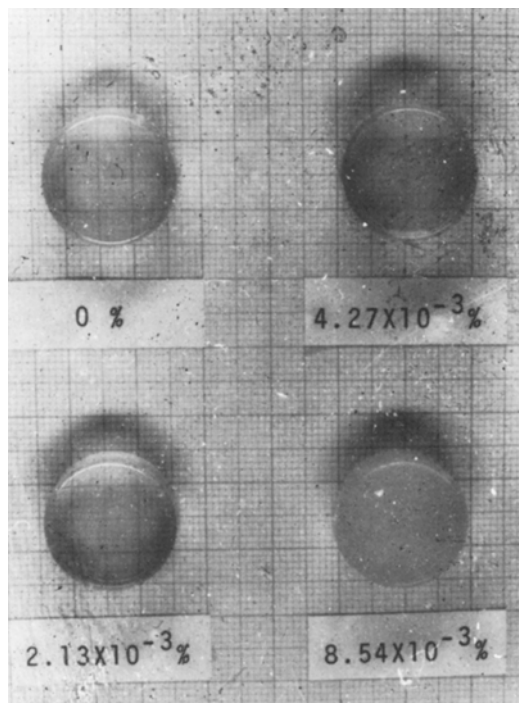


Figure 2 Dried gel prepared by the hydrolysis of $Si(OCH_3)_4$ with ammonia water of various concentrations.

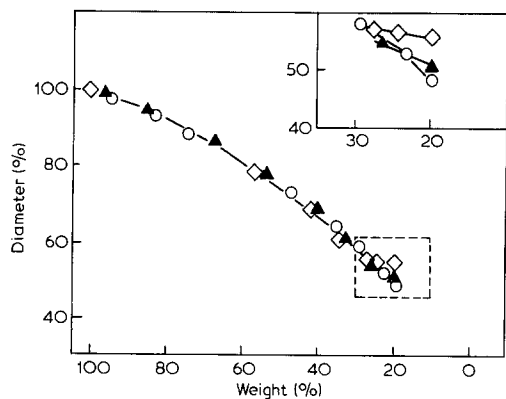


Figure 3 Weight-volume relationship in the contraction process of gel peptized from hydrolyzed $\text{Si}(\text{OCH}_3)_4$ with water containing (○), 0%; (▲), 2.13×10^{-3} %; (◇), 8.54×10^{-3} % NH_4OH .

The ratio of volume to weight of the gel, which should reflect the structural change during contraction, was somewhat different depending on the concentration of ammonium ions in the original solution, as shown in Fig. 3. Although the behaviour at the initial stage seemed independent of the ammonium ion concentration, in the later stage the behaviour was slightly different for each, and the final volume when the gel was completely dried in a desiccator was larger for those formed from the solution containing larger amounts of ammonium ions. This pattern is similar to the shrinkage of alumina gel [10] prepared from solutions of various electrolyte (e.g. HCl) concentrations.

3.2. Properties of the dry gel

3.2.1. Apparent and true densities and specific surface area

The apparent and true densities of the dry gels are shown in Table I, as well as the porosities estimated from two densities, and specific surface area obtained by the nitrogen adsorption technique.

The true density is about 90% that of silica glass and tends to increase slightly with am-

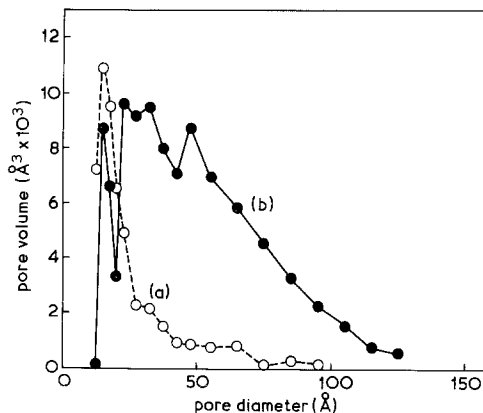


Figure 4 Pore size distribution in dry gel prepared by the hydrolysis of $\text{Si}(\text{OCH}_3)_4$ with (a) distilled water, (b) 8.54×10^{-3} % ammonia water.

monium ion concentration. The apparent density is greatly affected by ammonium ion concentration and is lower for those formed from higher concentrations. The value of specific surface area of the gel, which is larger for those formed from higher ammonium ion concentrations as well as porosity, is comparable with those of typical porous materials.

3.2.2. Pore size distribution in dry gel

Typical examples of pore-size distribution calculated from the adsorption isotherm using Cranston-Inkley's model are shown in Fig. 4. It is seen that most of the pores in the gel from the solution without ammonium ions are about 15 to 20 Å in diameter, while the gel from 0.00854% ammonia water has larger pores ranging up to about 100 Å in diameter. Although the results for the gels from ammonia water of other concentrations are not shown, this tendency of the increase in pore size with concentration of ammonium ions was also applicable.

3.2.3. Hydrogen, carbon and nitrogen content in the gel

The results for gas chromatography on the dry

TABLE I Apparent and true densities, porosity, and specific surface area of dry gel

Concentration of ammonia water (%)	True density (g cm^{-3})	Apparent density (g cm^{-3})	Porosity (%)	Specific surface area ($\text{m}^2 \text{g}^{-1}$)
0	1.98	1.47	25.8	379
2.13×10^{-3}	2.00	1.47	25.5	420
4.27×10^{-3}	2.02	1.29	36.1	552
8.54×10^{-3}	2.03	1.02	49.8	626
68.0×10^{-3}	2.06	1.12	45.6	626

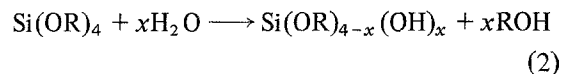
TABLE II Hydrogen, carbon and nitrogen content of dry gel

Concentration of ammonia water (%)	Hydrogen content (wt %)	Carbon content (wt %)	Nitrogen content (wt %)
0	2.04	0.21	trace
2.13×10^{-3}	1.68	0.38	trace
8.54×10^{-3}	1.54	0.58	trace

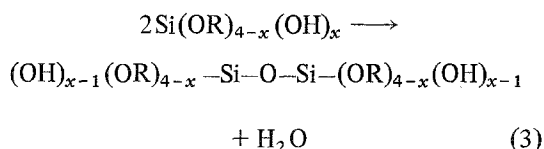
gel is shown in Table II. The amount of carbon present due to the residual $-\text{OCH}_3$ group is greater for the gels formed from higher ammonium concentrations, while the amount of hydrogen from $-\text{OH}$ group is correspondingly smaller.

3.3. Discussion of the gelation process and the role of ammonia

In the course of hydrolysis and gelling of silicon-tetramethoxide by the addition of water, the first reaction expected to occur is hydrolysis, as given below;



where, $-\text{OR}$, in the right hand side of the equation represents the unreacted methoxy group. The hydrolysis product, $\text{Si}(\text{OR})_{4-x}(\text{OH})_x$, being dispersed in solvent methanol. It then polymerizes either by hydrogen bonding or by dehydration [1] following the reaction;

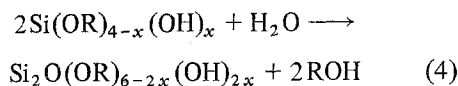


Since $\text{Si}-\text{O}-\text{Si}$ bonding formed by this reaction is very strong, the further dehydration polymerization after the monomer, $\text{Si}(\text{OR})_{4-x}(\text{OH})_x$, in the neighbourhood has been consumed, will be dependent on the progress of the separation and vaporization of methanol, which brings the polymers closer to each other. When dehydration polymerization has proceeded to some extent, the gel becomes too rigid for further contraction due either to the development of strong $\text{Si}-\text{O}-\text{Si}$ bonds or contact of the polymers at their non-reactive sites.

If the rate of dehydration polymerization is large compared to that of separation and vaporization of solvent alcohol, polymerization to form new bonding occurs as soon as the

hydroxides come close to each other. The gel attains its final volume while a certain amount of solvent is still left within it, resulting in a dry gel of large porosity. The large porosity and the levelling-off in weight-volume relation at the final stage of contraction of the gel from solutions of higher ammonium content, are the result of the high rate of dehydration polymerization, which is due to the catalytic nature of hydroxyl ions. If the rate of dehydration polymerization is small there is enough time for the solvent methanol to escape from the system while the size of the individual polymers is small, resulting in the formation of a denser gel.

As well as the dehydration polymerization, other processes occur to form polymers, such as polymerization accompanying hydrolysis, as given by;



This is possible at the initial stages of the polymerization reaction or when the hydrolysis by Equation 2 is far from complete. In the present study, where the water necessary for hydrolysis was initially introduced, the possibility of hydrolysis of this kind is small compared with that by Equation 2, particularly for the system in which the dehydration polymerization is slow to occur.

Thus, the composition, structure and properties of a dry gel are substantially determined by the rate of dehydration polymerization which occurs after hydrolysis of metal-alkoxides. The greater the rate of dehydration polymerization, the more unreacted $-\text{OR}$ group will be left in the dry gel, which will have greater porosity.

The results of the estimation of an average composition of a gel, $\text{SiO}_x(\text{OH})_y(\text{OCH}_3)_z$, based on the results of analysis in Table II, were $\text{SiO}_{1.26}(\text{OH})_{1.47}(\text{CH}_3)_{0.013}$, $\text{SiO}_{1.43}(\text{OH})_{1.12}(\text{OCH}_3)_{0.022}$ and $\text{SiO}_{1.50}(\text{OH})_{0.96}(\text{OCH}_3)_{0.033}$ for the gels from 0%, 0.00213% and 0.00854% ammonia water. These values, together with the gelation time shown in Fig. 1 and the properties given in Table I, clearly show the role of ammonium or hydroxyl ion concentration on the gel formation from silicon methoxide, to yield a more porous, more highly polymerized but less completely hydrolyzed gel.

Since the dry gel prepared in this study is

porous and contains residual $-\text{OCH}_3$ group and plenty of $-\text{(OH)}$ due to incomplete dehydration polymerization, at least three reaction processes are involved in the pyrolysis of the gel into a silica glass. Although we must wait for further experiments to investigate where and how these reactions, say, decomposition of $-\text{OCH}_3$, further dehydration polymerization and the collapse of micropores, progress during pyrolysis, the versatility of the preparation of a precursor is of practical importance. The above results of this study, together with the report of Yoldas [10] on alumina gel, are believed to be useful in determining the optimum conditions for the preparation of monolithic glass at low temperatures.

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