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Formation of Highly Porous Opaque Gel from Alkoxysilane Solutions

Hiromitsu KOZUKA and Sumio SAKKA
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

Effects of kind of alkoxysilane, alcohol and acid on gelation of alkoxysilane solutions of high acid concentration and low water concentration have been studied in terms of the appearance of gel, the microstructure of gel and the gelling time to investigate the possibility of producing gels with high porosity and large pores, which are essential for obtaining large silica body without cracks and bloating. It has been found that tetramethoxysilane, methanol and hydrochloric acid have an effect of shortening the gelling time and make it possible to produce highly porous opaque gels.

Production of silica glass by the sol-gel method consists of gel formation through hydrolysis and polycondensation reaction of alkoxysilane, drying of wet gel and sintering of dried gel.[1,2] Problems often encountered in the production of large bulk glass by this method are generation of cracks in the gel and bloating of the gel in the drying and sintering processes. To overcome these problems, the gel structure has to be controlled, so that the gel would have a high porosity and large continuous pores. These conditions prevent crack generation and bloating, since the liquid phase left in the gel easily goes out of the gel without causing high mechanical stress in the gel.

Recently, it was found by us that a $Si(OCH_3)_4$ - H_2O - CH_3OH - HCl solution becomes opaque gel with large pores and large particles of about 5 μm diameter when the water content is small at $[H_2O]/[Si(OCH_3)_4]$ = 1.53 and the hydrochloric acid content is large at $[HCl]/[Si(OCH_3)_4]$ = 0.4 and that the particle size decreases as the amount of hydrochloric acid content decreases. Formation of opaque gels with large silica particles under such highly acidic condition is quite unique and interesting to us, since such gels might be one of the most important candidates for making large bulk glasses. In the present study, influence of the kind of alkoxysilane, solvent and acid on the formation of such porous gel was investigated.

Starting solutions prepared by mixing $Si(OR)_4$, H_2O, ROH, and HCl under vigorous stirring at room temperature were kept at 40 °C in a tight air-sealed beaker or flask.

The effect of the kind of $Si(OR)_4$ on the gelation was investigated using tetramethoxysilane $Si(OCH_3)_4$, tetraethoxysilane $Si(OC_2H_5)_4$, tetraisopropoxysilane $Si(i\text{-}OC_3H_7)_4$ and tetranormalbutoxysilane $Si(i\text{-}OC_4H_9)_4$.

Table 1. Effect of the kind of alkoxysilane on the gelation of $Si(OR)_4$ - H_2O - ROH - HCl solutions. The mole ratios $H_2O/Si(OR)_4$ and $HCl/Si(OR)_4$ are 1.5 and 0.4, respectively. $[Si(OR)_4]$ = 2 mol l^{-1}. The solutions were kept at 40 °C in a tight air-sealed flask.

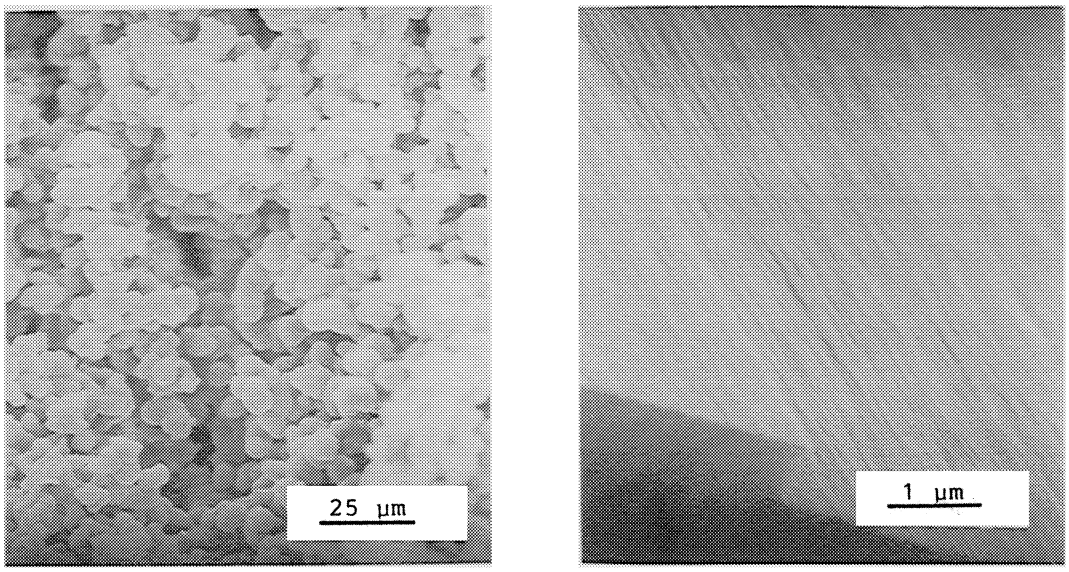
Alkoxysilane	Gelation
$Si(OCH_3)_4$	Opaque thin bulk gel was formed in 1 d
$Si(OC_2H_5)_4$	No gelation was found in 30 d
$Si(i\text{-}OC_3H_7)_4$	No gelation was found in 30 d
$Si(n\text{-}OC_4H_9)_4$	No gelation was found in 30 d

Table 2. Effect of the kind of alcohol on the gelation of $Si(OCH_3)_4$ - H_2O - ROH - HCl solutions. The compositions of the solutions are $Si(OCH_3)_4$: H_2O : ROH : HCl = 1 : 1.53 : 2 : 0.4 in mole. The solutions are kept at 40 °C in a tight air-sealed beaker.

Alcohol	Appearance of gel	Gelling time
CH_3OH	Opaque	0.5 h
$i\text{-}C_3H_7OH$	Slightly opalescent	1 d
$n\text{-}C_4H_9OH$	Slightly opalescent	1 d

The mole ratios $H_2O/Si(OR)_4$ and $HCl/Si(OR)_4$ were kept constant at 1.5 and 0.4, respectively and the concentration of $Si(OR)_4$ was kept at 2 mol l^{-1} by controlling the amount of alcohol. Alcohols corresponding to respective alkoxysilanes were used ; methyl alcohol, ethyl alcohol, isopropyl alcohol and normalbutyl alcohol were used as solvent for $Si(OCH_3)_4$, $Si(OC_2H_5)_4$, $Si(i\text{-}OC_3H_7)_4$ and $Si(n\text{-}OC_4H_9)_4$ solutions, respectively. Gelation behaviors of these solutions are summarized in Table 1. Opaque thin bulk gel was formed at the bottom of the solution within a day in $Si(OCH_3)_4$ solution, whereas no gelation occurred in $Si(OC_2H_5)_4$, $Si(i\text{-}OC_3H_7)_4$ and $Si(n\text{-}OC_4H_9)_4$ solutions. It is known that the rate of hydrolysis reaction decreases with increasing size of the ligand of alkoxysilane.[3] The highest rate of $Si(OCH_3)_4$ in the present series is expected and that may be the reason for gel formation only found in $Si(OCH_3)_4$ solution.

The effect of the kind of solvent was investigated in the system $Si(OCH_3)_4$ - H_2O - ROH - HCl, where ROH = CH_3OH, $i\text{-}C_3H_7OH$ and $n\text{-}C_4H_9OH$ and the mole ratios of the components were kept constant at $Si(OCH_3)_4$: H_2O : ROH : HCl = 1 : 1.53 : 2 : 0.4 (Table 2). Opaque gel was formed in the CH_3OH - containing solution, whereas only slightly opalescent gels were formed in the $i\text{-}C_3H_7OH$ - and $n\text{-}C_4H_9OH$ - containing solutions. Figure 1 shows the scanning electron micrographs of the dried gels prepared from the CH_3OH - and $n\text{-}C_4H_9OH$ - containing solutions. The dried gel prepared from the CH_3OH - containing solution was found to consist of large particles of about 5 μm diameter, whereas that from the $n\text{-}C_4H_9OH$ - containing solution has very fine texture. The differences in the appearnce of the gels reflect these differences in the



(a) (b)

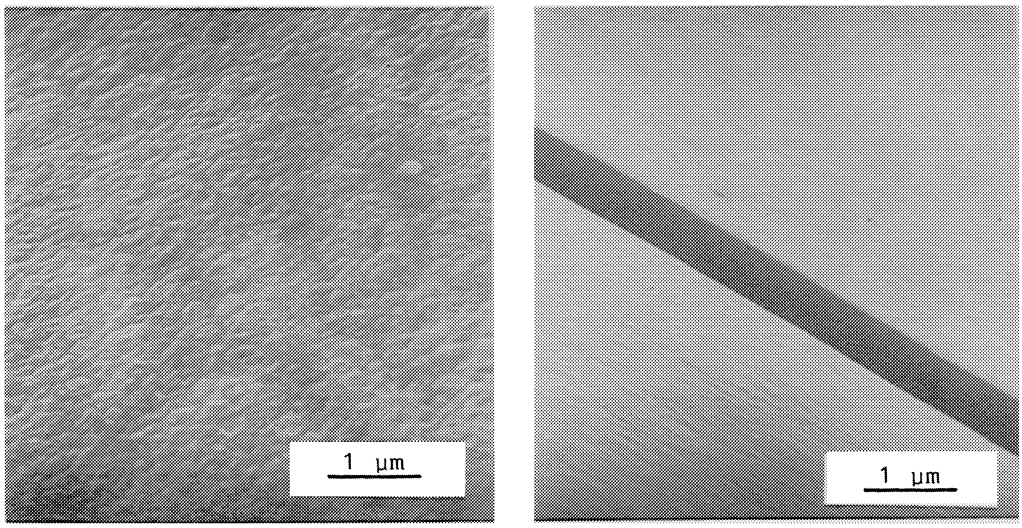
Fig. 1. Scanning electron micrographs of the dried gels prepared from the $Si(OCH_3)_4$ solutions of the compositions $Si(OCH_3)_4$: H_2O : ROH : HCl = 1 : 1.53 : 2 : 0.4 in mole. ROH = CH_3OH (a) and n-C_4H_9OH (b).

texture found in the electron micrographs. The CH_3OH - containing solution gelled in much shorter time than the i-C_3H_7OH - and n-C_4H_9OH - containing solutions. Ligand exchange is possible between $Si(OCH_3)_4$ and i-C_3H_7OH and n-C_4H_9OH[4,5] and alkoxysilanes with larger ligands and lower rate of hydrolysis than $Si(OCH_3)_4$ are expected to be formed in the solutions. That may be the reason why the CH_3OH - containing solution has a shorter gelling time than the other solutions.

Table 3 summarizes the gelation behavior of the solutions with various kinds of acids in the system $Si(OCH_3)_4$- H_2O - CH_3OH - acid. The compositions of the starting solutions are $Si(OCH_3)_4$: H_2O : CH_3OH : acid = 1 : 1.53 : 2 : 0.4 in mole. It was found that the transparency of the gels decreases as the pKa of the acid decreases, which indicates that the acid of lower pKa makes formation of gels with larger particles possible. This can also be seen in the electron

Table 3. Effect of the kind of acid on gelation of $Si(OCH_3)_4$ - H_2O - CH_3OH - acid solutions. The compositions of the solutions are $Si(OCH_3)_4$: H_2O : CH_3OH : acid = 1 : 1.53 : 2 : 0.4 in mole. The solutions are kept at 40 °C in a tight air-sealed beaker.

Acid	Initial pH	pKa of acid	Gelling time / h	Appearance at gelation
HCl	-1.1	-7	1.3	Opaque
$(H_2SO_4)_{0.5}$	-0.4	-3.2	3.8	Opalescent
HNO_3	-0.3	1.3	18	Opalescent
CH_3COOH	2.7	4.7	480	Transparent



(a) (b)

Fig. 2. Scanning electron micrographs of the dried gels prepared from the $Si(OCH_3)_4$ solutions of the compositions $Si(OCH_3)_4$: H_2O : CH_3OH : acid = 1 : 1.53 : 2 : 0.4 in mole. The acids used are $(H_2SO_4)_{0.5}$ (a) and CH_3COOH (b).

micrographs of the dried gels. Figure 2 shows the scanning electron micrographs of the dried gels prepared from the solutions with H_2SO_4 and CH_3COOH. The micrograph shown in Fig. 1 (a) corresponds to that of the dried gel prepared from the solution with HCl in these series. Comparing these three micrographs, it is found that the texture of the gels becomes finer as the pKa of the acid added in the solutions increases. The gelling time decreased with pKa of the acid decreasing. The initial pH of the solutions measured with a glass electrode at 35 ^{o}C was found to decrease with the pKa of the acid decreasing. Lower pH given by the addition of acid with lower pKa may promote gelation reaction.

In all series of the solutions studied, a relationship between the nature of gels and the gelling time was found to be present, that is, formation of the gels with larger particle size is possible in the solution of shorter gelling time. Reaction rate for gelation must be an important factor which affects the size of particles formed in the solutions.

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