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Effect of Solution Composition, Aging and Exposure to Water Vapor on the Structure and Properties of Highly Porous Silica Gels

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The structure, properties and sintering behavior of silica gels derived from partially hydrolyzed tetramethoxysilane solutions containing large amounts of hydrochloric acid have been studied as functions of the HCl content of the starting solutions, the aging of the gel in the ambient atmosphere, and the exposure of the gel to a water-saturated atmosphere.

A higher amount of HCl results in the formation of monolithic gels with lower bulk densities and lower surface areas. Thermal shrinkage curves have shown that the nature of the gel changes from polymeric to colloidal as the HCl content increases. Aging of the gel in the ambient atmosphere reduces the number of unhydrolyzed species and decreases the specific surface area of the gel. The exposure of the gel to a water-saturated atmosphere also reduces the number of unhydrolyzed species, but does not change the structure of the gel and the porosity of the gel particles. A higher densification at a temperature region of 150–500°C and a lower sintering temperature at around 1200°C are found for the vapor-exposed gels.

1. INTRODUCTION

Preparation of silica glass through the sol-gel method is now attracting much attention in the field of glass technology, since this method allows the low temperature synthesis of silica glass.[1] This method consists of (1) hydrolysis and polycondensation of silicon alkoxides, (2) gelation of the silicon alkoxide solution, (3) drying of the silica gel and (4) sintering of the dried silica gel. The most serious problem encountered in the above process is the formation of cracks in the gel during the drying process. Because of the capillary forces generated in the gel during drying, gels are often fractured into small pieces. The general method for obtaining a crack-free gel monolith is to make a gel with large open pores, which prevent the occurrence of large stresses on drying. Rabinovich et al.[2] have prepared gels with a two-mode pore distribution, one maximum in the region of 1 to 8 μm and the other one in the region of 13 to 20 nm, by dispersing dense gels derived from commercial silica Cab-O-Sil in a high-shear device. Scherer and Loung[3] have prepared silica particles of 60 to 100 nm in diameter by flame oxidation of $SiCl_4$ and dispersed them in organic liquids with the additions of amines or ammonia. Prassas et al.[4] have prepared gels with a porous microstructure by heating sols in the autocalve prior to gelation. Adachi and Sakka[5] have used N, N-dimethylformamide as a DCCA (drying control chemical additive) in tetramethoxysilane solutions.

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Our previous studies[6-8] have shown that crack-free silica gel monoliths can be easily obtained from tetramethoxysilane solutions with a small amount of water which is less than that needed for hydrolyzing all the alkoxides and a large amount of hydrochloric acid. This method is unique in that the process is very simple and the silica particle size and accordingly the pore size in the gel can be controlled by changing the amount of hydrochloric acid.

The use of a small amount of water may leave some alkoxyl groups to be hydrolyzed on or in the gel particles. Therefore, it is expected that the aging of the gel in the air after gelation or exposure of the gel to humid atmosphere should greatly affect the properties or structure of the gel, which in turn influence the sintering behavior of the gel. In the present study, the effects of aging in the air and exposure to water-saturated atmosphere on the properties and structure of the gel have been investigated.

2. EXPERIMENTAL

2.1 Preparation of Silica Gels

Tetramethoxysilane $Si(OCH_3)_4$ (TMOS, Chisso Co. Ltd.), 99.6% methanol CH_3OH (Wako Pure Chemical Industries, Ltd.), 35% hydrochloric acid (Nakarai Chemicals, Ltd.) and ion-exchanged water were used as the starting materials. Alkoxide solutions having the mole ratio of $TMOS : H_2O : CH_3OH : HCl = 1 : 1.53 : 2 : x$ (x=0.05, 0.10, 0.15, 0.20, 0.25 and 0.40) were prepared by mixing the reagents at room temperature. 50 ml of the alkoxide solution was poured into a polypropylene container of 56 mm in diameter and 73 mm in height. A polypropylene cover having 5 holes of 2 mm in diameter was put on the container. For gelation and aging, the alkoxide solution or gel in the container was left in a 40°C oven.

Some of the dried gels were exposed to a water-saturated atmosphere by leaving them in the atmosphere saturated with water at 40°C for 2 days.

2.2 Measurements

Specific surface area of the gels was measured by BET method using a Micromeritics Company model AccuSorb 2100E physical absorption analyzer. Pore size distribution of the gels was calculated on the basis of Cranston-Inkley cylinder model.[9] Gel powders of 75–106 μm in size were degassed by heating at 150°C for 18 h in vacuum before the BET measurement.

Differential thermal analysis (DTA) was performed for the gel powders of 75–106 μm in size using Shimadzu Thermal Analyzer DT-30. A heating rate of 10°C/min was used.

Linear thermal shrinkage of the gels was measured using Shimadzu Thermal Mechanical Analyzer TMA-30 under a heating rate of 5°C/min. The gel samples of 2 mm in thickness were used for measurement.

Infrared absorption spectra of the gels heated to various temperatures were measured by Nujol method using JASCO Fourier Transform Infrared Spectrophotometer Type FT/IR-5. Gel samples of 2 mm in thickness were heated at a rate of

5°C/min to various temperatures, quenched to room temperature, and then crushed into powder.

3. RESULTS

3.1 Formation of Dried Gels

All the alkoxide solutions gelled within 1 day. Figure 1 shows the weight change of the gel with time during drying. All the gels prepared with different amounts of HCl have nearly the same rate of decrease in weight, and the weight of the gel becomes constant after about 15 days.
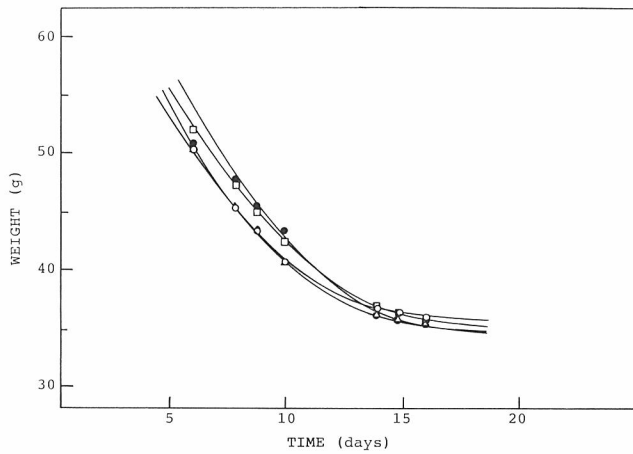
Figure 2 shows the appearance of the dried gels prepared with different amount

Fig. 1. Weight change of the gels with time during drying. The weight of the container, 20 g, is included. [HCl]/[TMOS]=0.05 (—○—), 0.10 (—□—), 0.25 (—△—) and 0.40 (—●—).
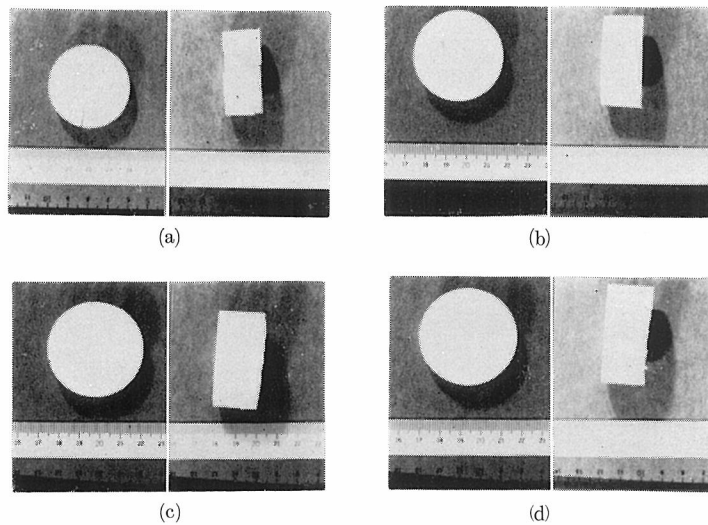

(a)

(b)

(c)

(d)

Fig. 2. Appearance of the dried gels. [HCl]/[TMOS]=0.05 (a), 0.10 (b), 0.25 (c) and 0.40 (d).

of HCl. The photographs show that monolithity of the gel increases with increasing amount of HCl added for hydrolysis. Cracks in the gels were formed after 10 days. No crack formation was found for the gels prepared with HCl amounts of larger than 0.1 in the [HCl]/[TMOS] ratio.

3.2 Size and Density of the Dried Gel

Table 1 shows the sizes and bulk densities of the dried gels. It can be seen that the weight is the same for the dried gels prepared with different amounts of HCl, corresponding to about 125% of the weight of SiO_2 calculated from the amount of TMOS, but the size of the gels increases with increasing amount of HCl. This indicates that the bulk density decreases with increasing amount of HCl. The bulk density of the gels ranges from 0.47 to 0.79 g/cm³ as shown in the table.

Table 1   Size and density of the dried gels.

[HCl]/[TMOS]	Aging time in a 40°C oven (days)	Size		Weight (g)	Bulk density (g/cm)
		Diameter (mm)	Hight (mm)		
0.05	21	37.5	16.9	14.72	0.79
0.10	21	40.0	18.5	14.41	0.62
0.25	21	43.3	18.5	14.20	0.52
0.40	21	44.6	19.1	14.20	0.47
0.25	120	41.5	15.0	13.23	0.65

Longer aging times allow the gel to shrink in diameter and height, as can be seen from the data of the gels prepared with [HCl]/[TMOS]=0.25 and aged for 21 and 120 days. Thus, longer aging times give larger bulk densities of the gels.

3.3 Specific Surface Area and Pore Size Distribution

Specific surface areas were measured for the gels (1) aged for 50 days in a 40°C oven, (2) exposed to water-saturated atmosphere at 40°C for 2 days after 50 days aging or (3) aged for 120 days in a 40°C oven. As shown in Table 2, smaller specific surface areas are found for the gels prepared with a larger amount of HCl. Almost no effect of exposure to water-saturated atmosphere on the specific surface area is found. Longer aging times greatly decrease the specific surface areas of the gels.

Table 2   Specific surface area of the gels.

[HCl]/[TMOS]	Specific surface area (m²/g)		
	Aged for 50 days	Exposed to humid atmosphere after aging for 50 days	Aged for 120 days
0.05	—	—	306
0.10	516	—	268
0.15	387	—	—
0.25	367	354	67
0.40	—	—	32

The dried gels obtained here are opaque in appearance as shown in Fig. 2, and the scanning electron micrographs of the gels have shown that the gels have micron- or submicron-sized voids among the gel particles.[8] The present authors were in- terested in whether the gel particles themselves have pores or not. Figure 3 shows the pore size distribution curves of the gels aged for 30 days at 40°C. It should be remembered that the pore radii shown here are limited to those smaller than 100 A. It can be seen from the figure that the gel particles themselves have small pores of
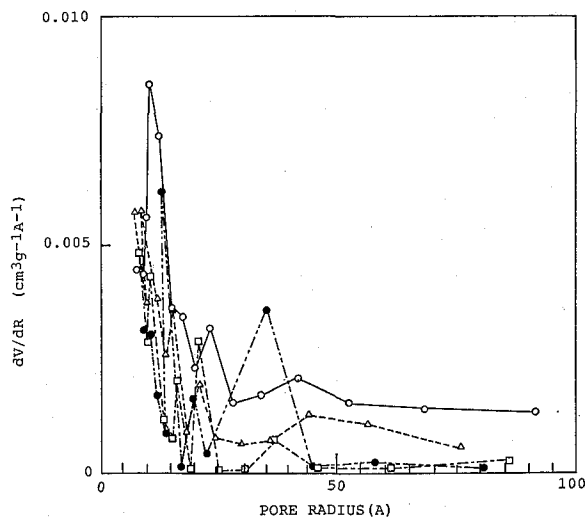
Fig. 3.   Pore size distribution curves of the gels aged for 30 days at
40°C.   [HCl]/[TMOS]=0.10 (—○—), 0.15 (---△---),
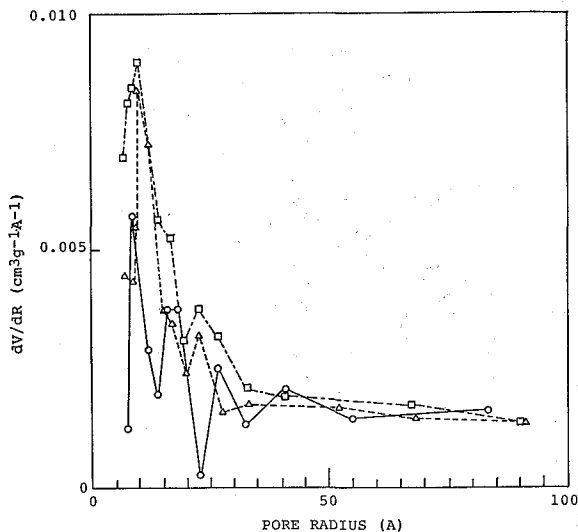0.20 (---□---) and 0.25 (----(●)----).

Fig. 4.   Pore size distribution curves of the gels ([HCl]/[TMOS]=
0.10) aged for different times at 40°C.   Aged for 30 days
(---□---), 45 days (---△---) and 120 days (—○—).

(72)

the radii less than 100 A. Thus the gels have small pores less than 100 A in radius other than micron- or submicron-sized voids among the particles. It can also be pointed out that larger numbers of these small pores can be seen in the gels prepared with a smaller amount of HCl.

Decrease in the number of these small pores by aging at 40°C can be seen in the pore size distribution curves shown in Fig. 4. No effective change in the number of pores is observed in the gels exposed to water-saturated atmosphere, as seen in Fig. 5.

3.4 Differential Thermal Analysis

Figure 6 shows the DTA curves for the gels aged at 40°C for 30 days. Broad

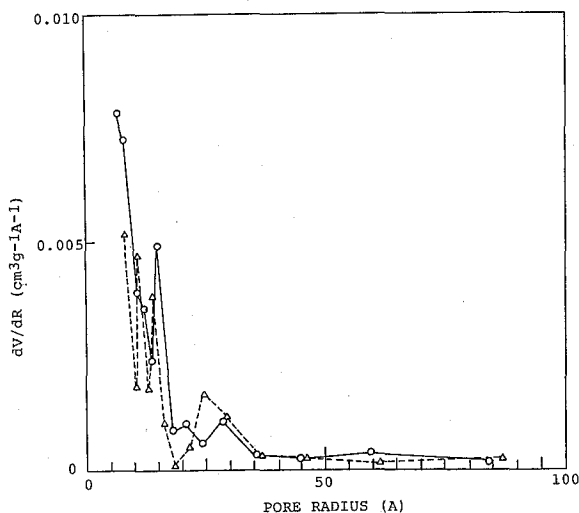Fig. 5. Pore size distribution curves of the gels ([HCl]/[TMOS]= 0.25) aged for 50 days at 40°C with (---△---) or without (—○—) exposure to water-saturated atmosphere for 2 days at 40°C.
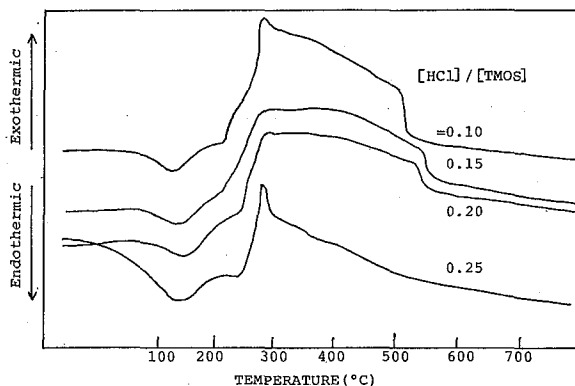

Fig. 6. DTA curves for the gels aged at 40°C for 30 days. Gel powders of the size 75–106 μm were used for the measurement. A heating rate of 10°C/min was used.
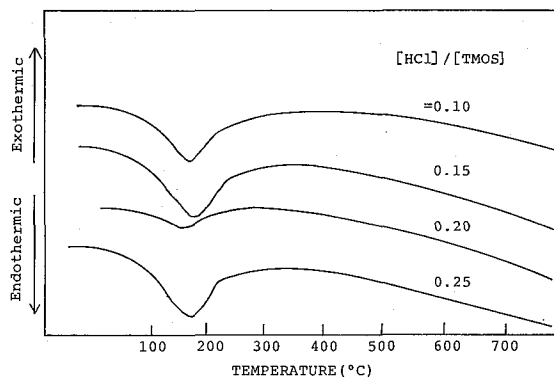
Fig. 7.   DTA curves for the gels aged at 40°C for 120 days.   Gel powders of 75–106 μm were used for the measurement.   A heating rate of 10°C/min was used.
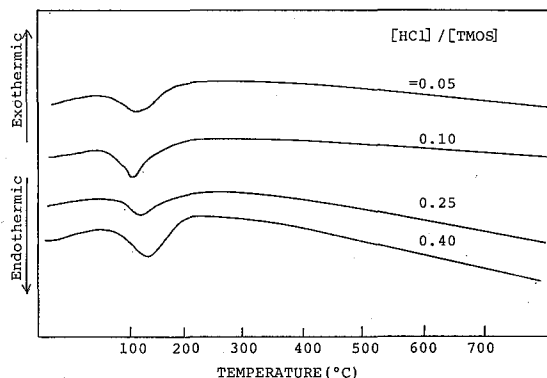

Fig. 8.   DTA curves for the gel powders exposed to water-saturated atmosphere at 40°C for 2 days after being aged at 40°C for 30 days.   The gels were crushed to powders of 75–106 μm in size before exposure to water-saturated atmosphere.   A heating rate of 10°C/min was used.

exothermic peaks attributed to burning of organics can be seen in the temperature range of 250°–550°C.   Larger exothermic peaks are observed for the gels prepared with smaller HCl contents.

Figure 7 and 8 show the DTA curves for the gels aged at 40°C for 120 days and for the gels aged at 40°C for 30 days and then exposed to water-saturated atmosphere at 40°C for 2 days, respectively.   Exothermic peaks disappear in these curves, indicating that both the longer aging treatment and the vapor-exposure treatment have effects for removing unhydrolyzed alkoxyl groups.

3.5   Sintering Behavior of the Gel

Figure 9 shows the linear thermal shrinkage curves for the gels.   A small abrupt shrinkage and a drastic shrinkage are observed respectively, at about 300°C and at around 1200°C.   The extent of the shrinkage around 300°C is larger in the gels prepared with smaller amounts of HCl.   It is to be pointed out that the shrinkage
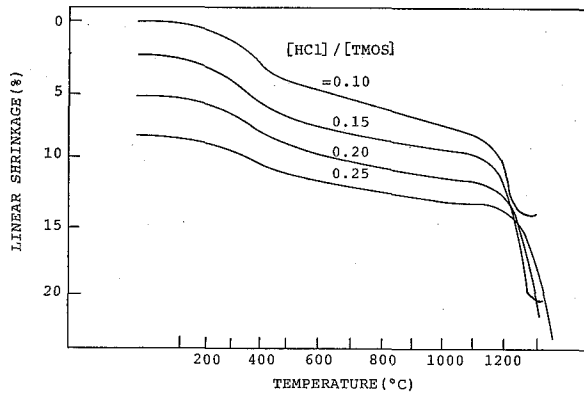
Fig. 9. Linear thermal shrinkage curves of the gels prepared with different amount of HCl. The gels aged at 40°C for 30 days and then left in a desiccator for 30 days at room temperature were used for measurement. A heating rate of 5°C/min was used.
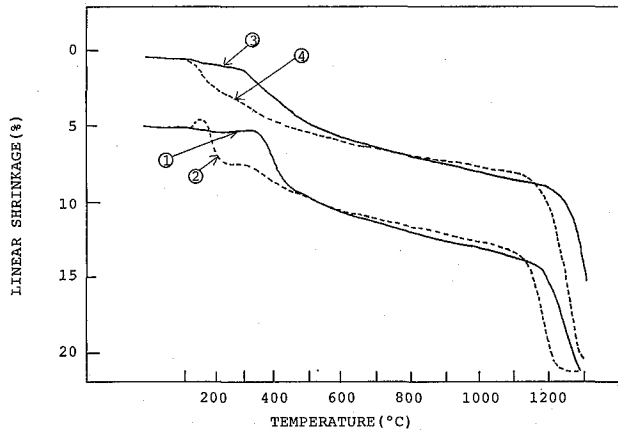

Fig. 10. Linear thermal shrinkage curves of the gels ([HCl]/[TMOS] =0.25) treated under various conditions after being aged at 40°C for 30 days. Left in a desiccator at room temperature for 30 days (curve 1) and then exposed to water-saturated atmosphere at 40°C for 2 days (curve 2). Left in a desiccator for 60 days (curve 3) and then exposed to water-saturated atmosphere (curve 4).

at around 1200°C begins at higher temperatures for the gels prepared with larger amounts of HCl.

Figure 10 shows the linear thermal shrinkage curves for the gels ([HCl]/[TMOS] =0.25) left in a desiccator at room temperature for 1 or 2 months with or without the vapor-exposure treatment. Exposure to water-saturated atmosphere shifts the starting point of the thermal shrinkage from 350°C–400°C to 100°–150°C. The sharp thermal shrinkage around 1200°C also occurs at lower temperatures when the vapor-exposure treatment is made.

3.6 Infrared Absorption Spectra

Figure 11 shows the infrared absorption spectra of the gels, in which [HCl]/[TMOS]=0.25, heated to various temperatures with or without vapor-exposure treatment. Absorption peaks at 1370, 1460 and 2900 cm^{-1} are those of Nujol. The 1620 cm^{-1} peak is attributed to the molecular H_2O, and the 950 cm^{-1} and 3200–3800 cm^{-1} bands are assigned to silanol groups.[10-13] The 800 and 1100 cm^{-1} bands are attributed to Si-O-Si vibration.[10-13] It is seen that the 950 cm^{-1} peak assigned to silanol groups becomes a shoulder at 400°C for the vapor-exposed sample, whereas it is left as a distinct peak for the non-exposed sample.
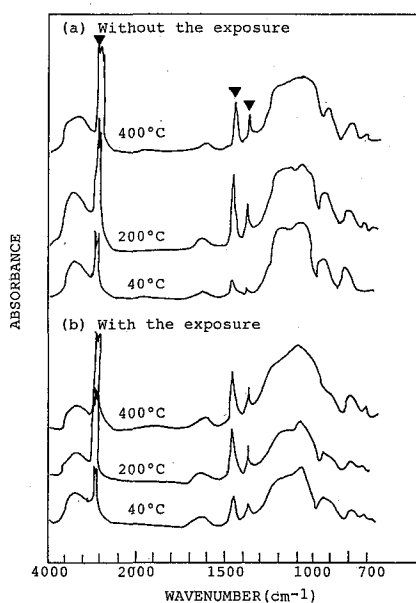

Fig. 11. Infrared absorption spectra of the gels and heated samples. The gel prepared with [HCl]/[TMOS]=0.25 was aged at 40°C for 30 days and left in a desiccator at room temperature for 30 days. The gel was heated at a rate of 5°C/min. Without (a) and with (b) exposure to water-saturated atmosphere before heat treatment.

4. DISCUSSION

4.1 Effect of the HCl content

Larger contents of HCl in the starting solutions give rise to the formation of larger particles[6,8] and gels with smaller specific surface areas (Table 2) and with lower bulk densities (Table 1). Smaller specific surface areas found in the gels prepared with the higher HCl content may reflect both larger gel particles observed in the scanning electron micrographs[8] and smaller number of pores in the gel particles. Less crack formation in the dried gels prepared with larger amounts of HCl can be attributed to larger open pores or voids of the gels in which lower capillary forces are generated in the drying process. Because of the larger open pores in the gels,

the alkoxyl groups are hydrolyzed by water vapor in the air to a greater extent during the aging treatment for the gels prepared with larger amounts of HCl. This results in generation of smaller exothermic peaks on the DTA curves (Fig. 6).

Densification curves shown in Fig. 9 can be divided into two regions: a lower temperature region at around 300°C and a higher temperature region at around 1200°C. The thermal shrinkage in the lower temperature region may occur as a result of skeletal densification by polymerization reaction and structural relaxation, as proposed by Brinker et al.[14] Polymerization reaction may occur through dehydration of silanol groups. Exothermic reactions can be seen on the DTA curves (Fig. 6) in the same temperature region, indicating that decomposition of unhydrolyzed alkoxyl groups gives new sites for condensation reactions. Collapse of small pores less than 100 A in radius also contributes to densification[14] at this temperature region. Collapse of such small pores is regarded as structural relaxation of the gel.[14] It can be thought that a larger number of small pores less than 100 A in radius (Fig. 7) may be responsible for a larger shrinkage of the gels prepared with smaller amounts of HCl.

Brinker et al.[14] have proposed that the contribution of the skeletal densification to the shrinkage is the greatest in weakly crosslinked polymer gels and the smallest in colloidal gels. The larger shrinkage at this temperature region suggests that the gels prepared with a smaller amount of HCl may be polymeric rather than colloidal. This concept agrees well with the fact that spinnability is more likely to be found for the sols prepared with a smaller amount of HCl[6], their structure being polymeric.

The sharp densification at a higher temperature region is caused by viscous sintering of the gels.[14] Gels consisting of larger silica particles or smaller specific surface areas appear to begin to shrink at higher temperatures (Fig. 9) than those of smaller particles, indicating that the rate of sintering by viscous flow is lower for gels with a smaller specific surface areas. This is explained by the assumption that decrease in the surface area should be the driving force for the viscous sintering.[15]

4.2 Effect of Aging

Aging of the gels in the air reduces the amount of unhydrolyzed alkoxyl groups as shown in the DTA curves (Fig. 7). Water vapor in the air may hydrolyze the alkoxyl groups, producing silanol groups on the gel particles. The increased number of silanol groups gave rise to the subsequent condensation reactions, which cause collapse of small pores in the gel particles (Fig. 4) and decrease the specific surface areas (Table 2), increasing the bulk densities (Table 1) of the gels.

4.3 Effect of Exposure to Water Saturated Atmosphere

As seen in the DTA curves (Fig. 8), exposure of the gels to water-saturated atmosphere is effective in hydrolyzing the alkoxyl groups remaining on the gels. However, densification or collapse of small pores in the gel particles does not arise from the exposure treatment (see Table 2 and Fig. 5). Condensation reactions, which lead to densification and collapse of small pores, seem to proceed slowly and require longer times. In the aging process mentioned in 4.2, vaporization of water also

occurs, which may shift the equilibrium from non-condensed to condensed states, because water is a product of condensation reactions. This cannot be expected in the exposure treatment performed here, because the closed system is used in the treatment.

The exposure of the gels to water-saturated atmosphere greatly influences the densification and sintering behavior on heat treatment. A larger shrinkage occurs at a lower temperature region, 150–500°C, in the vapor-exposed gels (see Fig. 10). The infrared absorption spectra in Fig. 11 show a decrease in the amount of silanol groups on heat treatment up to 400°C in the vapor-exposed gel. The decrease in the number of silanol groups suggests the occurrence of condensation reactions on the heat treatment. A larger number of silanol groups produced by the exposure may give a larger chance for condensation, which leads to a larger shrinkage of the gel at this temperature range.

Viscous sintering at around 1200°C occurs at lower temperatures for the vapor-exposed gels (Fig. 11). Lowering of the sintering temperature by about 100°C is observed. Hydroxyl groups contained in the gel may reduce the viscosity of the SiO_2 matrix,[16] leading to a higher rate of viscous sintering.

5. CONCLUSIONS

The effects of the HCl content of the starting solutions, the aging time and the exposure to water-saturated atmosphere on the structure and properties of gels have been investigated for the silica gels derived from partially hydrolyzed TMOS solutions.

(1) Higher amounts of HCl in the starting solutions produced gels with lower bulk densities and lower specific surface areas. Gels prepared with smaller amounts of HCl were densified to a higher extent at around 300°C, because of a larger number of small pores in the gel particles and polymeric nature of the gels.

(2) Aging of the gels in the ambient atmosphere at 40°C reduced the number of unhydrolyzed alkoxyl groups, decreasing the specific surface areas of the gels and collapse small pores in the gel particles.

(3) Exposure of the gels to water-saturated atmosphere reduced the number of unhydrolyzed alkoxyl groups, without affecting the structure of the gels and the porosity of the gel particles. The vapor-exposure treatment gave rise to larger densification at the temperature region of 150°–500°C and lower viscous sintering temperatures of the gels.

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