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SILICA AEROGELS PREPARED BY THE SUPERCRITICAL DRYING TECHNIQUE

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Résumé : Des aérogels de différentes densités ont été préparés par un préséchage suivi d'un séchage hypercritique à partir d'alcogels catalysés en milieu basique. Les effets du préséchage sur les propriétés des aérogels et sur leur comportement au frittage ont été étudiés.

Abstract : Some aerogels of different bulk density were synthesized by the combination of solvent evaporation and supercritical drying for a base-catalyzed gel prepared from the TEOS-EtOH-H₂O solution. The effects of shrinkage by solvent evaporation on properties and sintering behavior of the aerogels were examined.

1 - INTRODUCTION

In the sol-gel process of preparing SiO₂ glass from Si alkoxides, supercritical drying of gel is useful method to make monolithic glass /1,2,3/. Many studies for sintering behavior of aerogel obtained by the hypercritical drying have been done so far /4,5/. However, more detailed studies on aerogel are needed to understand the gel-to-glass transition.

Supercritical drying is also attractive method to evaluate porous structure of gel. Authors have examined the porous structure of aerogels converted from the partially dried gel by solvent evaporation and discussed their structural change through evaporation drying /6/. It was found that relatively large pores (more than 1000 Å in diameter) were collapsed selectively as the gel shrank and micropores (less than 150 Å in diameter) were formed at the last stage of drying.

In this article, the effect of evaporation drying on properties and sintering behavior of the gel is discussed. For the purpose, some aerogels of different bulk density were synthesized by the combination of solvent evaporation and supercritical drying for a base-catalyzed gel prepared from the TEOS-EtOH-H₂O solution and their physical and chemical changes during the gel-to-glass conversion were examined.

2 - EXPERIMENTAL

2.1 - Preparation of the gels

The hydrolysis reaction of Si(OC₂H₅)₄ (TEOS) was catalyzed by the addition of HCl and NH₃ water, using a two steps hydrolysis. TEOS/water/ethanol in the final solution was /1/4/1.6 (molar ratio). The detailed procedure is given with reference paper /7/.

100 ml of solution was poured into a poly-propylene container covered with plastic film, and converted to the gel at 65°C.

2.2 - Drying of the gels

After aging for 72 h at 65°C, the gel was dried. During the aging, the gel showed a linear shrinkage of about 2% by syneresis. The length of the gel just after the aging is defined as L₀.

The gel was partially dried slowly by solvent evaporation and then converted to the aerogel under the supercritical condition above the critical point of ethanol (270°C, 100 atm). The shrinkage by the supercritical drying was not found for the all gels. The dry gel which has fractional linear shrinkage ($\Delta L/L_0$) of 13, 26, 36, 38% was synthesized using this technique. Each of the aerogels is named A, B, C, D, respectively. And, the dry gel obtained without any shrinkage is called "aerogel". Here, the xerogel is defined as the gel which was desiccated by evaporating solvent through the all drying step. The fractional linear shrinkage of the xerogel was 40%. Each bulk density of the dry gels was evaluated by their weight and dimension. The bulk density of the aerogel was 0.21 g/cc. That of gel A-D was 0.31, 0.35, 0.58, 0.77 g/cc, respectively. The xerogel had bulk density of 0.77 g/cc.

2.3 - Heat treatment

The dry gels obtained were heated up to various temperature at the rate of 80°C/h to investigate the behavior during sintering. The heating atmosphere was N₂/O₂ up to 800°C and above that He gas was used to avoid bloating of the samples.

2.4 - Characterization

The chemical structure of the obtained aerogels and xerogel was studied by F.T.-I.R. spectroscopy of KBr pelletized method.

The physical and chemical change during heating was monitored by DTA-TGA dilatometric measurements. The changes in fractional linear shrinkage during sintering were evaluated from their dimensions of the heated gels.

BET surface area of the dry gels was evaluated from N₂ adsorption isotherm.

3 - RESULTS AND DISCUSSION

3.1 - Properties of aerogels

3.1.1 - Esterification

Infra-red transmission spectra for some dry gels are shown in figure 1. In the aerogels (Aerogel, Gel A, D) absorption bands between 2800 and 3000 cm⁻¹, i.e. the bands corresponding to the C-H stretching and C-H bending moles /8/, are clearly detected compared with the spectrum of the xerogel. These absorption bands probably result from the esterification induced by supercritical drying. Namely, the aerogels contain more remained organics than the xerogel.

On the other hand, the xerogel seems to have relatively more H₂O or silanol groups because absorption bands of 3500, 1630, 960 cm⁻¹ are strongly observed /8/.

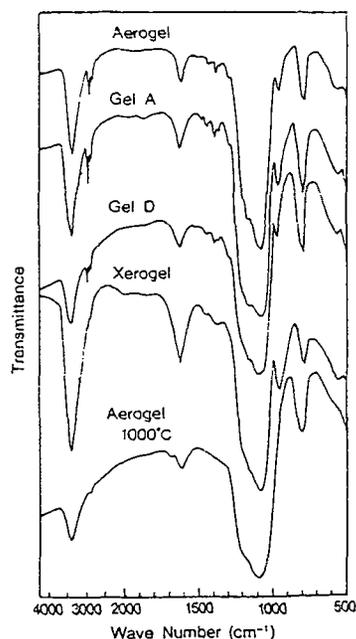


Figure 1 - F.T.-I.R. spectra for some dry gels and the aerogels heated to 1000°C.

3.1.2 - Combustion of remained organics

The results of DTA, TGA for the aerogels and xerogel are shown in figures 2,3.

The DTA curves for both aerogel and gel A derived from the initial region in the evaporation drying reveal very sharp exothermic peak which can be attributed to combustion of the residual organics,

accompanying the rapid loss of the weight.

However, in the case of gel C which was considerably shrunk by solvent evaporation, the tailing of the exothermic peak was noted. Further, the peak of gel D becomes broad and the exothermic combustion continues up to 400°C. It is considered as one of the reasons for these changes in the exothermic peak that removal of the residual organics becomes difficult with collapse of pores caused by evaporation. This is also reasonable from slow weight loss presented in gel C, D of figure 3.

Another reaction should be considered for the small exothermic peak around 400°C on the DTA curve of gel D. This peak is more clearly observed in the xerogel. This combustion seems to be related to another species of residual organic compounds, which is formed at the last stage in the solvent evaporation drying.

The TGA curve of the xerogel in figure 3 represents weight loss by the removal of physically adsorbed water at lower temperature. On the contrary, there is no weight loss less than 250°C for the aerogels. This hydrophobia is attributed to esterified surface and is consistent with the results of F.T.-I.R. spectroscopy (Fig. 1).

3.1.3 - Expansion and shrinkage of the aerogels

Figure 4 shows thermal expansion and shrinkage for the dry gels less than 300°C, in which ℓ_0 corresponds to the initial length of each dry gel before heating.

The aerogel starts to shrink rapidly after reaching the largest expansion. In gel A, C, D, derived from partially dried gels by solvent evaporation, the thermal expansion coefficient decreases and the transition from expansion to shrinkage becomes more smooth, in turn. However, the temperature range which shows the maximum expansion is almost same and slightly higher than that of the xerogel.

In figure 5, the curve (b) represents expansion and shrinkage examined for the aerogel once heated at 260°C. The thermal expansion coefficient is remarkably small and the rapid transition to shrinkage is disappeared. Therefore, it is considered that expansion of the aerogel is caused by remained organics in the gel. Further work should be done to study the influence of shrinkage by solvent evaporation on dilatometric behavior of the aerogels.

3.2 - Sintering behavior

3.2.1 - Contraction by heat treatment

The changes in fractional linear shrinkage when the dry gels were heated to various temperatures are shown in figure 6. Every dry gel contracts markedly above 800°C and completely sinters in the range between 1050 and 1200°C. The sintering temperature depends on the size of remained space in the dry gel. Namely, the larger the pore in the dry gel, the higher the sintering temperature is /6/.

The shrinkage curve in figure 7 is normalized on the basis of ℓ_0 which is the length of each dry gel before heating. The behavior of linear contraction with heating is identical. This means that each dry gel has the same microstructure which governs sintering behavior. Consequently, it is noted that the microstructure in the gel has not been affected by the shrinkage during solvent evaporation.

3.2.2 - Change in specific surface area

Specific surface area versus fractional linear shrinkage of each dry gel and sample heated at 1000°C is shown in figure 8.

The specific surface area increases in two stages as the gel contracts by solvent evaporation. The first rise is probably attributed to rearrangement of primary particles from the site at the initial stage on the solvent evaporation towards stable site to try to relax the deformation caused by the shrinkage. the second rise probably results from the formation of micropores by capillary force.

The values of the specific surface area of samples heated at 1000°C, however, are almost the same, not depending on shrinkage size. The packing configuration evaluated by BET measurements seems to be reflected on the microstructure for sintering. Consequently, the similarity of the microstructure for sintering in the dry gels is also supported by the same values of BET surface area.

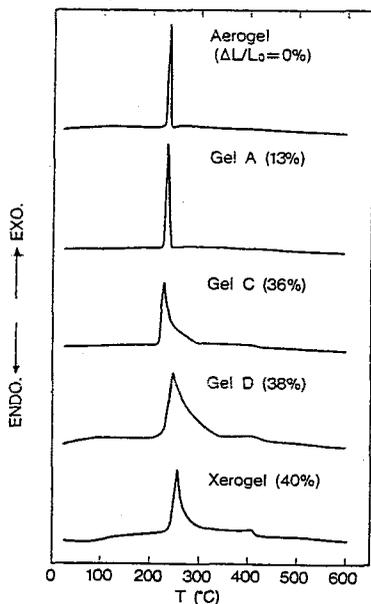


Figure 2 - DTA curves of the dry gels (at the rate of 10°C/min).

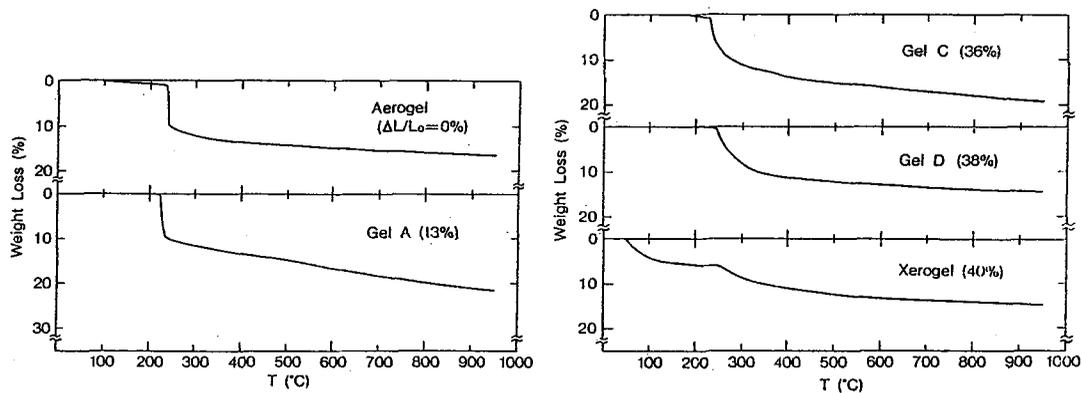


Figure 3 : TGA curves of the dry gels (at the rate of 10°C/min).

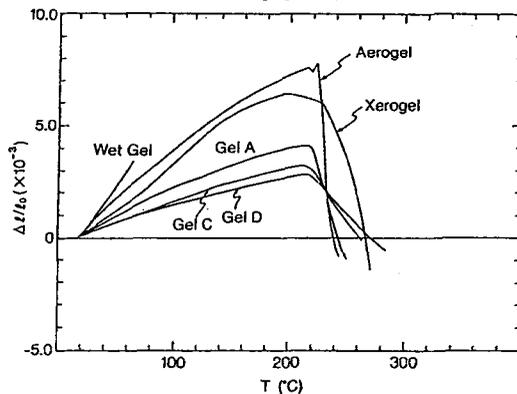


Figure 4 - Dilatometric curves of the dry gels (at the rate of 2.5°C/min).
(The curve of wet gel from ref./10/).

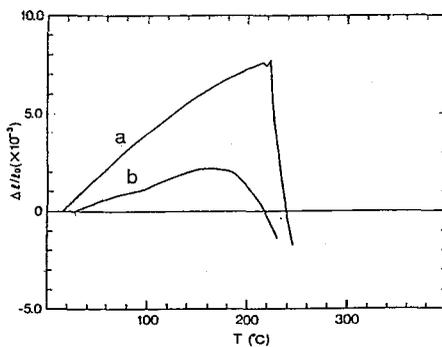


Figure 5 : Dilatometric curve of the aerogel, (a) after drying, (b) once heated at 260°C.

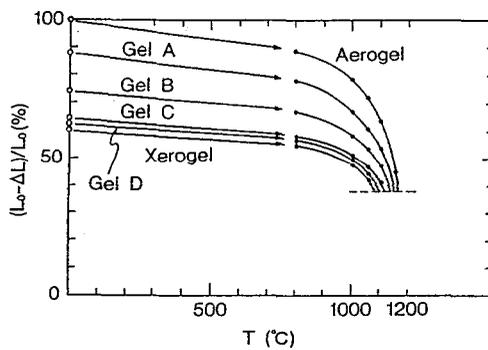


Figure 6 : Relative linear shrinkage versus temperature for the dry gels.

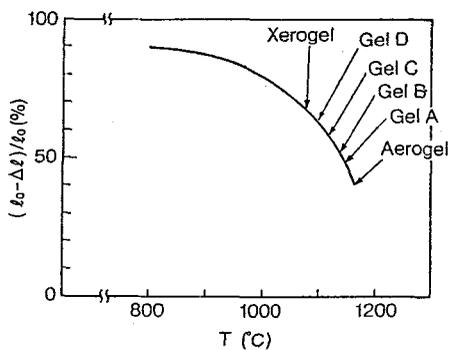


Figure 7 : Normalized relative linear shrinkage versus temperature for the dry gels. The arrow indicates the sintering temperature of each dry gel.

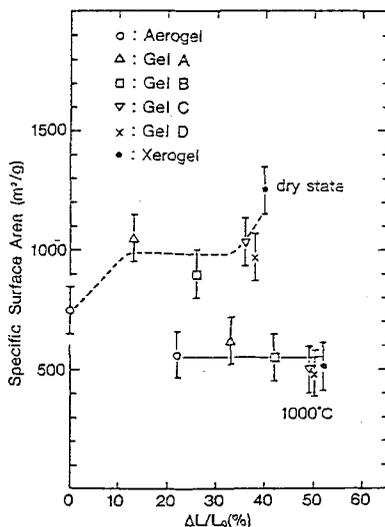


Figure 8 : Specific surface area (BET) of the dry gels and samples heated at 1000°C.

4 - CONCLUSION

Some aerogels were synthesized by the combination of solvent evaporation and supercritical drying for a base-catalyzed gel prepared from the TEOS-EtOH-H₂O solution. The effects of shrinkage by solvent evaporation on properties and sintering behavior of the aerogels were examined and compared.

The all aerogels seemed to have esterified surface by supercritical drying. However, the difference between the aerogels was observed on the exothermic peak with weight loss around 250°C and on the dilatometric curve less than 300°C. The aerogels of differing chemical and physical properties could be obtained in this study.

Bulk densities of the aerogels become higher with increasing of shrinkage size by solvent evaporation. The sintering temperature depended on the size of remained space in the dry gel. Namely, the larger the pore in the dry gel, the higher the sintering temperature was.

On the other hand, the behavior of linear contraction above 800°C was identical between the dry gels. The similarity of the microstructure which governs sintering behavior was reflected on the same values of BET surface area of the dry gels heated at 1000°C. The thermal contraction behavior was not affected by the shrinkage during solvent evaporation and was independent of chemical and physical properties of the dry gels.

REFERENCES

- /1/ WOIGNIER, T., PHALIPPOU, J., ZARZYCKI, J., J. Non-Cryst. Solids, **63** (1984) 117.
- /2/ PRASSAS, M., PHALIPPOU, J., ZARZYCKI, J., J. Material Science, **19** (1984) 1656.
- /3/ VAN LIEROP, J.G., HUIZING, A., MEERMAN, W.C.P.M., MULDER, C.A.M., J. Non-Cryst. Solids, **82** (1986) 265.
- /4/ PHALIPPOU, J., WOIGNIER, T., ZARZYCKI, J., p.70 in "Ultrastructure Processing of Ceramics, Glasses and Composites" eds. Hench, L.L. and Ulrich, D.R., John Wiley & Sons, NY (1984).
- /5/ MULDER, C.A.M., VAN LIEROP, J.g., FRENS, G., J. Non-Cryst. Solids, **80** (1986) 92.
- /6/ IURA, J., HISHIKURA, H., KAMIKATANO, M., KAWAGUCHI, T., J. Non-Cryst. Solids, **100** (1988) 241.
- /7/ KAWAGUCHI, T., HISHIKURA, H., IURA, J., KOKUBU, Y., J. Non-Cryst. Solids, **63** (1984) 61.
- /8/ BERTOLUZZA, A., FAGNANO, C., MORELLI, M.A., GOTTARDI, V., GUGLIELMI, M., J. Non-Cryst. Solids, **48** (1982) 117.
- /9/ KAWAGUCHI, T., IURA, J., TANEDA, N., HISHIKURA, H., KOKUBU, Y., J. Non-Cryst. Solids, **82** (1984) 61.