

Structural Change of Gels Prepared from Highly Acidic  
Tetramethoxysilane Solutions in the Drying Process

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### Introduction

Sol-gel reaction of tetramethoxysilane (TMOS) under highly acidic conditions with a limited amount of water provides highly porous monolithic silica gels composed of micrometer-sized particles<sup>1-3</sup>). Because of the continuous large pores and particles, these gels and heated derivatives may be suitable for porous materials which can be used as filters or supports for catalysts and enzymes. For these uses, surface characteristics of the gels should be controlled. Since the amount of water for hydrolyzing TMOS in the starting solutions is limited, some of alkoxy groups may be left to be hydrolyzed at the time of gelation and water in the atmosphere may affect the nature of surfaces of the large particles of the gels during drying. In the present study, the surface properties of the gels have been investigated by BET analysis and electron microscopic observation as a function of drying time.

### Experimental

Silicon alkoxide solutions having the mole ratio of TMOS : H<sub>2</sub>O : CH<sub>3</sub>OH : HCl = 1 : 1.53 : 2 : 0.40 were prepared by mixing the reagents at room temperature. 50 ml of the alkoxide solution was poured into a polypropylene container and gelled at

40 °C in the oven. Gelation took place in a very short time of about 1.3 h. The resultant wet gels were dried in the same container and at the same temperature of 40 °C for 2, 5, 7 or 13 days.

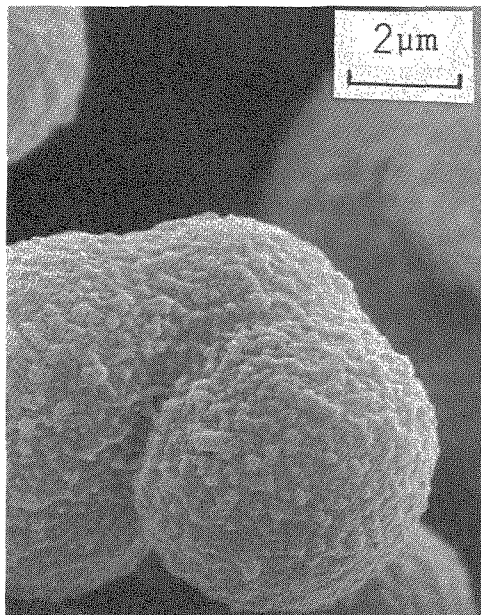
The specific surface area of the gels was measured by BET method using nitrogen gas and the pore size distribution of the gels was calculated on the basis of Cranston-Inkley model<sup>4</sup>). Gel powders of 75-106  $\mu\text{m}$  in size were degassed at room temperature for 24 h and at 75 °C for 18 h before the BET measurement.

#### Results and Discussin

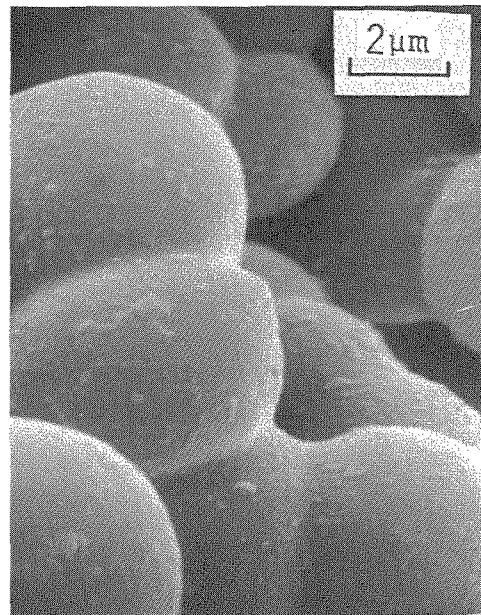
Figure 1 shows the scanning electron micrographs of the gels dried for 2 days (Fig.1(a)) and dried for 13 days (Fig.1(b)). As seen in Fig.1(a), the surface of the large particles are very rough and composed of smaller particles, indicating that the micrometer-sized large particles are secondary particles. It is seen in Fig.1(b), however, that further drying reduces the roughness of the surface.

Figure 2 shows the pore size distribution curves of the gels. It can be seen from the figure that the micrometer-sized particles have small pores of the radii less than 20 Å. These pores are regarded as voids among the primary particles. It is also seen that the number of detected pores decreases with drying time.

Figure 3 shows the specific surface area of the gels. The data points for each drying time have been obtained by repeating the surface measurement with the same sample. For the drying



(a)



(b)

Fig. 1 Scanning electron micrographs of the gels. (a) Dried for 2 days and (b) dried for 13 days in 40 °C oven.

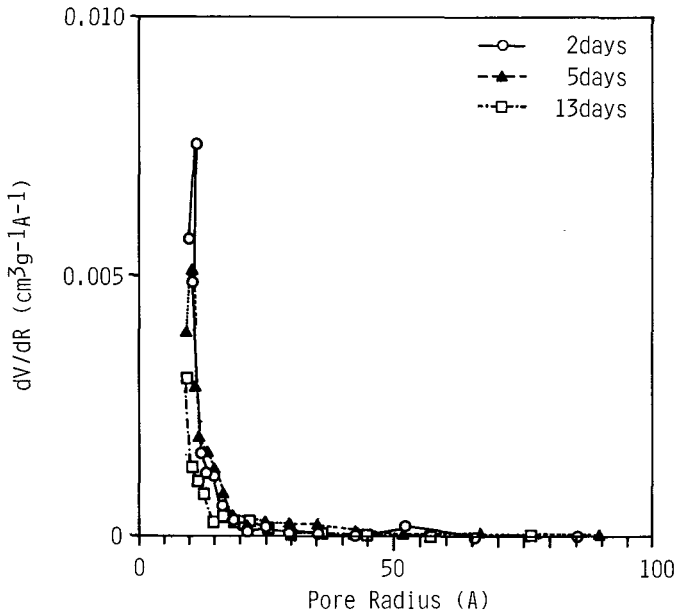


Fig. 2 Pore size distribution curves of the gels dried for 2 days (—○—), 5 days (—▲—), 13 days (---□---).

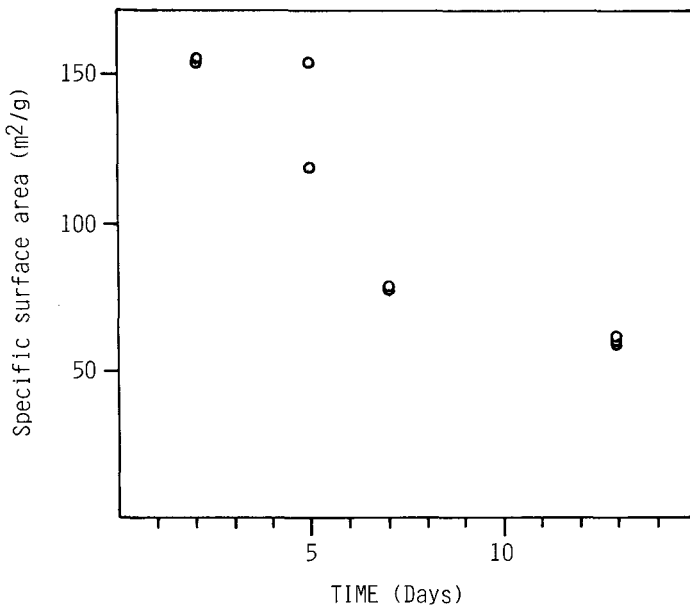


Fig. 3 Specific surface area of the gels as a function of drying time.

time of 2, 7 and 13 days, the repeated measurements give the similar values, indicating that almost no change occurs in the specific surface area during the measurement. A larger scatter of the data for the drying time of 5 days indicates that in this time periods, some change may occur during the treatment for the measurement. The specific surface area decreases drastically with drying time till 7 days, and then continues to decrease more slowly. It is seen that the specific surface area decreases down to about  $1/3$  ( $60 \text{ m}^2/\text{g}$ ) of the initial value after 13 days. It is assumed that this decrease in surface area reflects the collapse of a portion of voids among the primary particles within the secondary particles. Assuming that the gel consists of  $5 \text{ \AA}$  dense silica particles with smooth surface, the specific surface area of the gel is estimated to be  $0.5 \text{ m}^2/\text{g}$ . This value is much lower than the value of  $60 \text{ m}^2/\text{g}$  obtained by the BET method, indicating that there remain still some voids to be collapsed within the secondary particles even after drying in the air atmosphere.

The theoretical amount of water required for the complete hydrolysis and polycondensation is 2 moles per mole of TMOS. Taking into account that the amount of the water added to the starting solution is 1.53 mole per mole of TMOS, it is presumed that not all of the alkoxy groups may be hydrolyzed and some of the alkoxy groups may remain non-hydrolyzed when gelation takes place. These non-hydrolyzed alkoxy groups would be attacked by water vapor in the atmosphere during drying. Thus, the decrease in the specific surface area and the number of pores can be attributed to further hydrolysis and subsequent

polycondensation reaction leading to bonding of primary particles within a secondary large particles. The mechanism of formation of large micrometer-sized secondary particles, has been discussed elsewhere<sup>5</sup>).

### Conclusion

The change of the surface characteristics of the gels with micrometer-sized large particles prepared under highly acidic conditions with a limited amount of water during drying have been investigated. It has been found that the specific surface area and the number of pores decrease with drying time. It has been discussed that the micrometer-sized particles of the gels are densified by the collapse of voids among the primary particles due to water vapor in the drying atmosphere causing hydrolysis and polycondensation reactions.

### References

1. H. Kozuka and S. Sakka, "Formation of Highly Porous Opaque Gel from Alkoxysilane Solution," *Chem. Lett.*, 1987, 1791-1794 (1987).
2. S. Sakka and H. Kozuka, "Properties and Sintering of Gels Derived from Metal Alkoxide," *Sintering '87*, ed. by S. Somiya, M. Shimada, M. Yoshimura and R. Watanabe, Elsevier Applied Science, New York, 145-50 (1988).
3. H. Kozuka, J. Yamaguchi and S. Sakka, "Effect of Solution Composition, Aging and Exposure to Water Vapor on the Structure and Properties of Highly Porous Silica Gels," *Bull. Inst. Chem. Res., Kyoto Univ.*, 66, 68-79 (1988).

4. R. W. Cranston and F. A. Inkley, "Determination of Pore Structures from Nitrogen Adsorption Isotherms," Adv. in Catalysis, 9, 143-54 (1957).
5. H. Kozuka and S. Sakka, " Formation of Particulate Opaque Silica Gels from Highly Acidic Solutions of Tetramethoxysilane," submitted to Chemistry of Materials.