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Change of pore structure in freeze-dried silica gel during calcination

S. J. CHOI, H. C. PARK
School of Materials Science and Engineering, Pusan National University, Pusan 609-735, Korea
E-mail: hcpark1@pusan.ac.kr

R. STEVENS
Department of Applied Science and Engineering, Bath University, Bath BA2 9JT, UK

In the sol-gel route, both drying and calcining are essential steps in the process that determines the pore properties of resultant gels. Drying is generally applied to eliminate pore fluids in the gels while calcining is employed to remove residual organics, crystallize the amorphous phase and/or densify the matrix [1, 2]. Under subcritical drying conditions for xerogels, significant shrinkage in bulk volume and a reduction in the surface area, pore size and pore volume occur, possibly due to the surface tension induced pore collapse.

The capillary pressure (P_c) developed during drying is inversely proportional to the pore radius, as is shown in Laplace's equation [3]:

$$P_c = (2\gamma_{LV}\cos\theta)/a \tag{1}$$

where γ_{LV} is the surface tension, θ is the contact angle between the fluid meniscus and pore wall and a is the pore radius. Equation 1 shows that large stresses can arise during drying of highly microporous gels and that a significant fraction of the micropores can collapse. Freeze drying is accepted as a most useful technique to prepare highly homogeneous precursors for ceramic powder synthesis [4]. The resulting powders exhibit high reactivity because of their high specific surface area and small particle size. If no liquid phase exists during drying in the sol-gel process, the shrinkage of the gel network due to capillary forces may well be nullified, resulting in extremely porous materials. Consequently, a great deal of attention has recently been concentrated on the application of the freeze drying process to gels [5, 6]. Due to the importance of drying in the sol-gel process, most of the research has been focused on an examination of the relationship between drying condition and gel structure, for example pore fluid and surface tension [7, 8], supercritical drying [9, 10], hydroxyl groups and cracking of gels [11], pore structure of gel and pH [12], drying techniques and gel structure [13–15]. However, very little literature on the influence of calcination temperature on the microstructure of freeze-dried silica gel has been reported. In the present work, silica gel obtained by hydrolysis of ethyl silicate has been freeze-dried, and an investigation of the pore structure of the resultant gel during calcination above the crystallization temperature has been undertaken.

Tetraethyl orthosilicate $Si(OEt)_4$ (TEOS, 98%, Aldrich) was used as the starting alkoxide, ethanol EtOH (99.9%, Hayman) as the solvent, and aqueous ammonia NH_4OH (28%, Yakuri) as a catalyst. Distilled water was deionized just prior to use. The molar ratio of TEOS/water/alcohol/aqueous ammonia was 0.2/22/1.6/0.7. Colloidal silica with an average particle size of 31 nm was produced by the gelation of TEOS in the presence of NH_4OH. After gelation (35 °C, 2 h), the gel was aged for 6 h at room temperature. The aquagel thus obtained was frozen using liquid nitrogen and then dried in a laboratory freeze-drier (Labconco 77540, Western Medics). The freeze-dried gel was calcined at 400–1200 °C for 2 h in air, with a heating rate of 4 °C/min. The freeze-dried gel was examined using transmission electron microscopy (TEM, JEM-2010, Jeol) and a laser scattering technique (LS230, Coulter) to determine the particle morphology and agglomerate size distribution, respectively. Phase analysis was carried out using X-ray powder diffraction (XRD, *D*/max-IIA, Rigaku), and the crystallinity was measured by line broadening. The data on nitrogen adsorption isotherms at 77 K were calculated with the automatic program Gemini 2375 (Micromeritics) adopting the BJH method [16]. Because gas adsorption methods are usually used to evaluate micropores of up to 200 nm in diameter [17], macropore size distribution was examined using mercury porosimetry (Win9400-731, Micromeritics). The specific surface was calculated from the BET theory [18].

The freeze-dried gel (FD) of colloidal particles (6–150 nm) derived from TEOS hydrolysis consisted of a porous agglomerate with an average particle size of 37.6 μm (Fig. 1) and a surface specific area of 434.5 m^2/g. The XRD patterns of FD and two of the calcined materials are shown in Fig. 2. The noncrystalline FD began to crystallize at ∼1100 °C (FD11) and transformed wholly to cristobalite at 1200 °C (FD12). With increasing calcination temperature, the primary crystallite size, as determined by XRD line broadening, increased from ∼21 nm (FD) to 80 nm (FD12). When complete crystallization had occurred, the crystallite size then increased rapidly. The particle or crystallite size of crystalline FD12 was larger (117%) than that of the amorphous phase heated at 1000 °C (FD10). Sample FD12 existed as a lump due to sintering of the freeze-dried gel, and the existence of localized cavities in the microstructure was confirmed using SEM (Fig. 3). These probably resulted from differences in local shrinkage.

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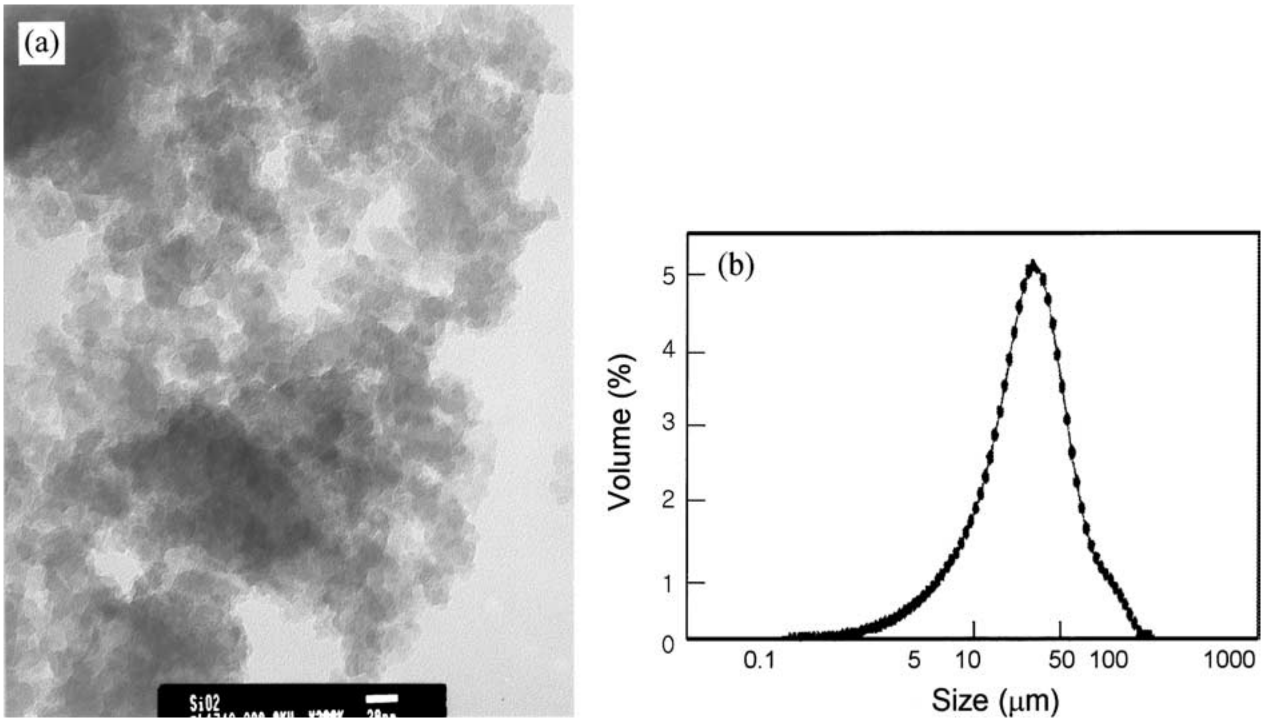

Figure 1 (a) TEM photograph and (b) particle size distribution of freeze dried gel.

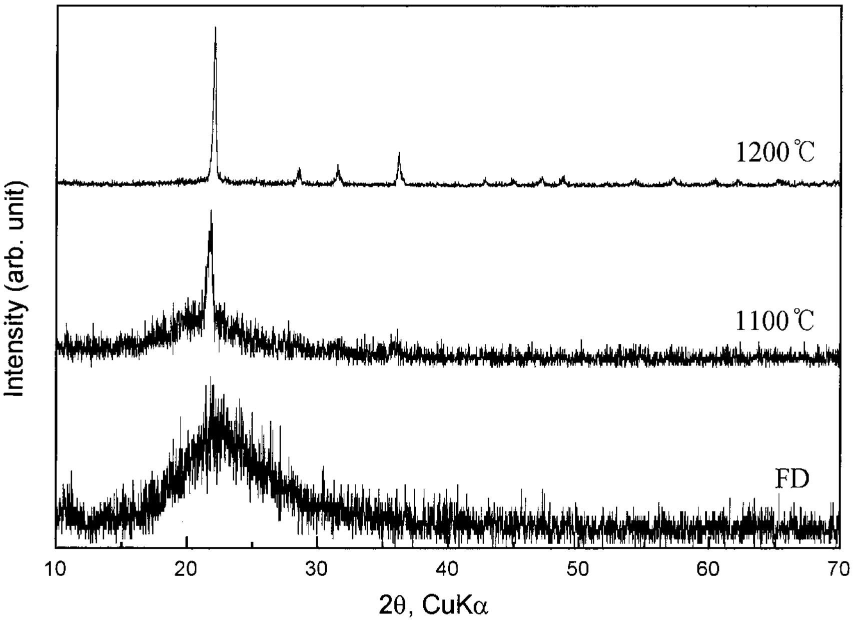

Figure 2 XRD patterns of freeze dried gel (FD) with calcination temperature.

After freeze-drying (FD) followed by calcination at 600° (FD6), 800° (FD8) and 1000 °C (FD10) the surface and pore structure were examined by capillary adsorption of nitrogen at 77 K. The results of the mathematical analysis and isotherm plots are shown in Table I and Fig. 4, respectively. It is apparent that the hysteresis loops in Fig. 4 are related to capillary condensation occuring in mesopores, and the initial parts of the isotherms are due to monolayer-multilayer adsorption, mainly taking place in nonporous or macropore structures [19]. The samples consisted of mesopores of various sizes but mainly in the range 4–6 nm (Fig. 5). With increasing calcination temperature, the pore area and size of the mesopores generally decreased. During calcination of the freeze-dried gel derived from TEOS hydrolysis, additional mesopores can be formed due to the evaporation (temp <200 °C) of residual adsorbed water and solvent, or as a resulted of the thermal decomposition of residual organics (temp <600 °C) [15].

TABLE I Surface properties of freeze dried and calcined silica gels

Sample	FD	FD 6	FD 8	FD 10
BET surface area (m^2/g)	434.64	427.92	312.50	1.94
Pore area of micropores (m^2/g)	68.13	96.39	67.30	0.44
Pore area of mesopores (m^2/g)	443.30	385.88	297.48	1.65
Specific volume of micropores (cc/g)	0.0300	0.0451	0.0300	0.0002
Specific volume of mesopores (cc/g)	0.4202	0.3531	0.2646	0.0016

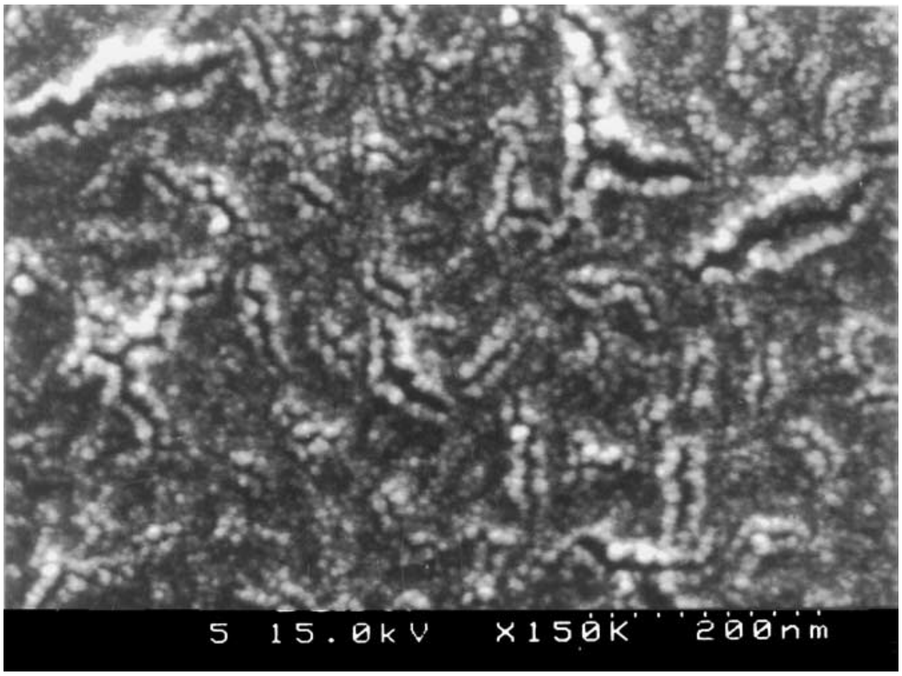

Figure 3 SEM photograph of freeze dried silica gel after calcining at 1200 °C.

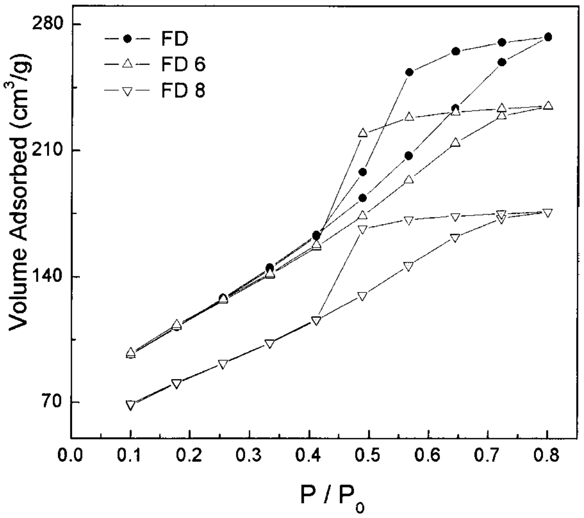

Figure 4 Adsorption-desorption isotherms of freeze dried and calcined silica powders.

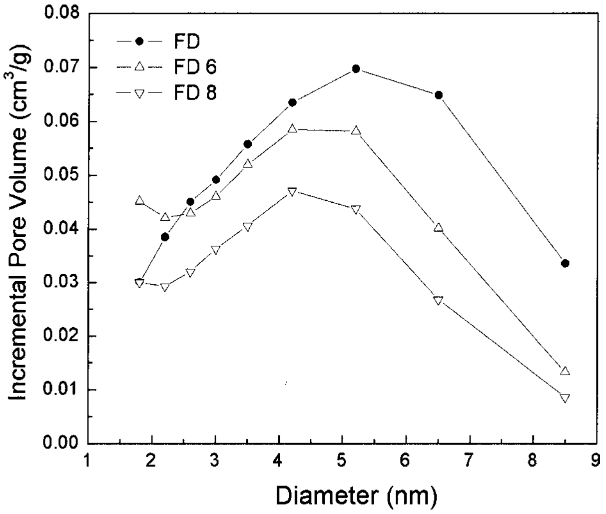

Figure 5 Pore size distributions of freeze dried and calcined silica powders, measured from N_2 adsorption-desorption.

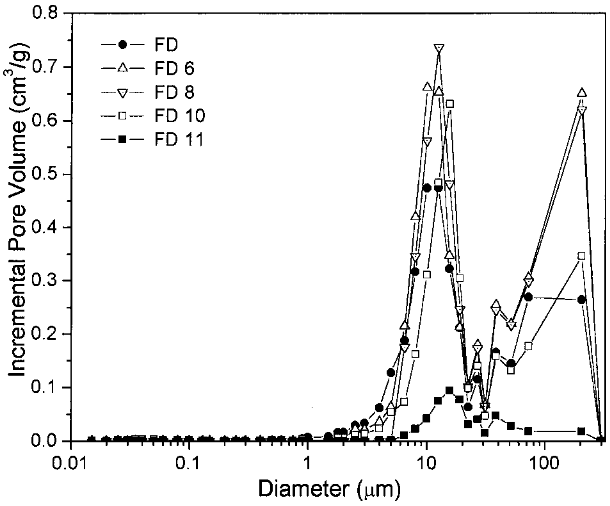

Figure 6 Pore size distribution of freeze dried and calcined silica powders, measured by mercury porosiometry.

However, it may be worthy of consideration that the shrinkage of the gel network on calcination at a relatively high temperature has a significant effect on mesopore structure. The properties and pore size distribution of macropores measured by injecting mercury into the pores are shown in Table II and Fig. 6. The macropores are made up of mainly 5–20 and 100–250 μm diameter

TABLE II Macropores of freeze dried and calcined silica gels measured by mercury porosiometry

Sample	Pore area of macropores (m^2/g)	Specific volume of macropores (cc/g)
FD	1.194	3.3690
FD 6	1.233	4.4517
FD 8	1.029	4.2733
FD 10	1.398	3.2056
FD 11	0.128	0.5297
FD 12	0.173	0.1527

porosity. The pore area and specific volume of macropores ($>10\ \mu$m) in the initial sintering stage generally increased with increasing calcinations temperature due to pore coherence, compared with freeze-dried gel ('FD') but they decreased remarkably at 1100 °C ('FD11') further shrinkage occurring by densification of the matrix.

In conclusion, the colloidal silica particles derived from TEOS hydrolysis, with an averge particle size of 31 nm, formed porous microsized (d_{50}: 28.56 μm) agglomerates with a high specific surface area (435 m^2/g) via the freeze drying route. The noncrystalline freeze-dried gel consisted mainly of mesopores (4–6 nm). Most mesopores and macropores were eliminated at temperatures $\geq$1000 °C.

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