



## Characterization of Hydrophobic SiO<sub>2</sub> Powders Prepared by Surface Modification on Wet Gel

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**Abstract.** Hydrophobic porous silica has been prepared by surface modification of TEOS (tetraethylorthosilicate) wet gel with 6 and 12 vol.% of TMCS (trimethylchlorosilane). We characterized the products by using FT-IR, TGA, DTA, N<sub>2</sub> adsorption/desorption, contact angle and SEM. Surface silanol groups of the gel were widely replaced by  $-\text{Si}(\text{CH}_3)_3$  to result in a hydrophobic SiO<sub>2</sub> powder as confirmed by contact angle measurements with H<sub>2</sub>O, 1-butanol and ethanol. The modified dried gels had a surface area of 950–1000 m<sup>2</sup>/g (average pore size 120 Å), compared to the non-modified surface which had a surface area of 690 m<sup>2</sup>/g (average pore size 36 Å). The adsorption/desorption isotherm curves indicated they had similar pore characteristics as aerogels prepared by the supercritical drying process.

**Keywords:** SiO<sub>2</sub>, TMCS, hydrophobicity, TEOS, surface modification

### 1. Introduction

Highly porous ceramics with high surface areas have potential applications as dielectric materials, flat-panel displays, sensors, catalytic supports and filters for exhaust gases [1]. Aerogels are the most highly porous solids, and are normally prepared by the supercritical extraction of pore liquid from a wet gel [2–5]. However, there are important disadvantages; the first is the high processing cost which is incurred because of the need for high pressures in a large autoclave. The second is the fact that dried aerogels are highly sensitive to

water contact, which irreparably destroys their network structure [2].

Recently, Brinker et al. reported preparation of silica aerogel-like films at ambient pressure by chemical surface modification [6]. These aerogel films were prepared by adding surface groups to the inorganic gel, which make drying shrinkage reversible. The key chemistry for preserving the porous network is that the hydroxylated surface of the gel is modified with organosilanes making use of standard silylation chemistry [4]. One would perhaps anticipate that products of powder type exhibit surface properties which are attributable to the presence of hydrophobic groups. However, this has not been subjected to a comparison with

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conventional hydrophilic aerogels produced by the supercritical drying process. It is important that such a comparison be made to establish the merits of this newly developed process for its various applications.

In this study, we report upon our efforts to characterize aerogel-like SiO<sub>2</sub> powders prepared by surface modification of a wet gel at ambient pressure. The wetting behaviors and pore characteristics of the prepared powders were investigated by contact angle measurements for various liquids. N<sub>2</sub> adsorption/desorption behaviors were also determined.

## 2. Experimental

### 2.1. Specimen Preparation

Hydrophobic silicas were prepared by the acid/base catalyzed hydrolysis/condensation of TEOS (Tetraethylorthosilicate), based on Brinker's method with minor modification [6]. TEOS (Sigma-Aldrich, 98%), ethanol (Merck), H<sub>2</sub>O, HCl (Duksan Chem., 35%) were stirred in the molar ratio 1 : 39 : 3.6 : 0.07 for 5 h at room temperature [7]. 0.05 M NH<sub>4</sub>OH was added to bring the TEOS stock solution into a controlled pH range 5–7 to accelerate the condensation reaction, which was followed by heating at 50°C to induce gelation. The silica gel so prepared was placed in ethanol solvent at 50°C for 24 h to remove the unreacted compounds and water, and to strengthen the gel network by aging. Pore liquids in the wet gel were then exchanged with *n*-hexane at 50°C for 24 h in a shaker, which has a low surface tension (17.89 mN/m at 25°C). 6 vol.% and 12 vol.% TMCS (Trimethylchlorosilane, Fluka) was added to the mixture of hexane and wet gel, and the whole gently shaken at 50°C for 24 h. At this stage, it should be noted that water in the pore must be washed off in order to minimize the self-reactions between TMCS. After the reaction was complete, the modified gel was again washed with hexane, and dried at 60–80°C under ambient pressure for 2 days to obtain the powdery products. In this paper, the sample obtained without surface modification is referred to as 0-SiO<sub>2</sub>, the one modified with 6 vol.% TMCS as 6-SiO<sub>2</sub> and the sample modified with 12 vol.% TMCS as 12-SiO<sub>2</sub>.

### 2.2. Characterization

Sol-gel reaction and surface modification of the gel were confirmed by FT-IR (Genesis II, Matheson).

Densities of various samples were determined using weight measurements (Startorius, YDK 01) in ethanol, and the average of three measurements was used for the calculation. The wettability of the dried gels was determined by contact angle measurements on a pressed pellet using a Goniometer (RAME-HART, Inc.). Also the contact angles of powder packed in a capillary tube was determined with H<sub>2</sub>O, ethanol, 1-butanol and *n*-hexane by the Washburn equation [8] i.e.,

$$h^2 = \frac{tR\gamma \cos \theta}{2\eta}$$

*h* is liquid permeation height (cm), *t* is the time (sec) to reach that height, *R* is the effective radius (cm) of the capillary pore,  $\gamma$  is the liquid surface tension (mJ/m<sup>2</sup>) and  $\eta$  the liquid viscosity (cP). The thermal behavior of the dried gel was examined using TG (TGA2050, TA Instruments) and DTA (DTA-50, Shimadzu), and the morphology of the silica powder was determined using SEM (JEOL, JSM-840A). Pore characteristics were investigated by N<sub>2</sub> adsorption/desorption (ASAP2400 V3).

## 3. Results and Discussions

For the production of silica aerogel-like powders by the non-supercritical process, it is essential that hydroxyl groups on the wet gel are substituted by a silylating agent after a series of aging and washing processes. Figure 1 shows the FT-IR spectra of unmodified and modified gels.

In 0-SiO<sub>2</sub>, a strong —OH peak at 3500 cm<sup>-1</sup> indicates that a significant fraction of the Si atoms exist on the surface in a gel network as hydroxylated species. During the conventional drying process, these surface groups react to produce SiOSi bonds by condensation. It is known that the formation of SiOSi bonds collapses the pore network of the wet gel because of the high capillary pressures induced [4]. In the modified gels, 6-SiO<sub>2</sub> and 12-SiO<sub>2</sub> exhibited significantly reduced —OH peak intensities, while the —CH<sub>3</sub> peaks at 2965, 1256 and 850 cm<sup>-1</sup> were newly created. Surface reactions occurred homogeneously throughout the wet gel by diffusion along its open pore structure. That is, surfaces terminated with either hydroxyl (OH) or alkoxy (OR) groups converted to stable SiR groups which prevent further condensation reactions.

It is well known that the wettability of materials depends upon their surface chemistry. Table 1 shows

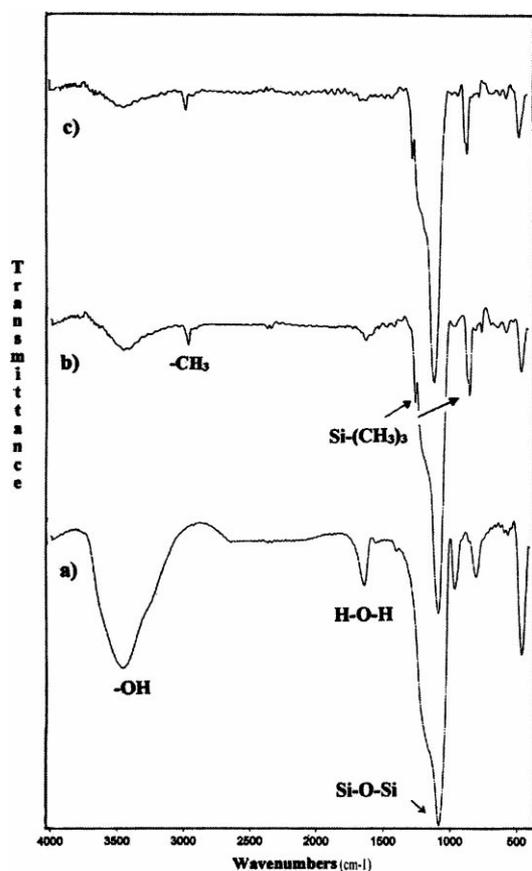


Figure 1. FT-IR spectra of (a) 0-SiO<sub>2</sub>, (b) 6-SiO<sub>2</sub> and (c) 12-SiO<sub>2</sub>.

contact angles of various solvents on pellets and powder products. Contact angles of water on SiO<sub>2</sub> pellets were near 0° for 0-SiO<sub>2</sub>, which quickly absorbed the water droplets due to the presence of -OH on the surface, but was about 150° for 6-SiO<sub>2</sub> and 12-SiO<sub>2</sub>, meaning low wettability, which had resulted from the

Table 1. Contact angles of 0-SiO<sub>2</sub>, 6-SiO<sub>2</sub> and 12-SiO<sub>2</sub> for various liquids.

Liquids	Samples		
	0-SiO <sub>2</sub>	6-SiO <sub>2</sub>	12-SiO <sub>2</sub>
H <sub>2</sub> O			
Pellet type	0-5°	156.9°	158.5°
Powder type	52°	90°	90°
Ethanol (powder type)	44°	46°	77°
Butanol (powder type)	-	68°	57°

Table 2. N<sub>2</sub> adsorption/desorption results of 0-SiO<sub>2</sub>, 6-SiO<sub>2</sub>, and 12-SiO<sub>2</sub>.

	Samples		
	0-SiO <sub>2</sub>	6-SiO <sub>2</sub>	12-SiO <sub>2</sub>
Average pore diameter <sup>a</sup> (Å)	36	122	125
Total pore volume <sup>b</sup> (cc/g)	0.63	2.98	2.97
Surface area <sup>c</sup> (m <sup>2</sup> /g)	693	979	949

<sup>a</sup>Calculated by  $4V/A$  ( $A$  = BET surface area).

<sup>b</sup>At  $P/P_0 = 0.99$ .

<sup>c</sup>By BET equation.

presence of organic groups. It has been reported that the contact angle on pellets is highly dependant upon the surface smoothness [9]. Therefore, the wetting behavior of powder itself was confirmed using the Washburn method. Generally speaking, as the polarity of applied liquids decreased, the contact angles of the surface modified specimens also decreased with a little ambiguity. For 12-SiO<sub>2</sub>, contact angle decreased from 90° to 57° for water and 1-butanol, respectively, which proved that the dried gel powders became hydrophobic compared to the original hydrophilic surface. This was achieved by a simple surface modification in the wet state before drying, although the technique only showed a slight difference between the two types of modified gels.

The density of 12-SiO<sub>2</sub>, 0.8 g/cm<sup>3</sup>, is much lower than 1.25 g/cm<sup>3</sup> of unmodified SiO<sub>2</sub> xerogel, but higher than the 0.3 g/cm<sup>3</sup> of supercritical aerogel [10]. As illustrated by Table 2, modified silica gels showed high surface areas, of approximately 1000 m<sup>2</sup>/g with a large pore size of 120 Å and high pore volume of 3 cc/g, while 0-SiO<sub>2</sub> showed the similar pore characteristics of xerogel. This indicates that the hydrophobic surface of the pore network reduced the capillary pressure by lowering the surface tension, and that this resulted in less shrinkage during the consequent aging/drying stages. It is also reported that the repulsion between -CH<sub>3</sub> groups, on the surface during the final stages of drying, also acted to expand the surface effecting a partial recovery of the wet gel structure [6]. In addition, it is expected that the surface area must be increased by annealing at over 300°C as reported [7]. However, the hydrophobicity must either be lost or much weaker after such a treatment, due to the oxidative removal of organics from the surface.

The pore characteristics are consistent with SEM observations in Fig. 2. 0-SiO<sub>2</sub> exhibited dense aggregates of spheres while the modified gel networks showed

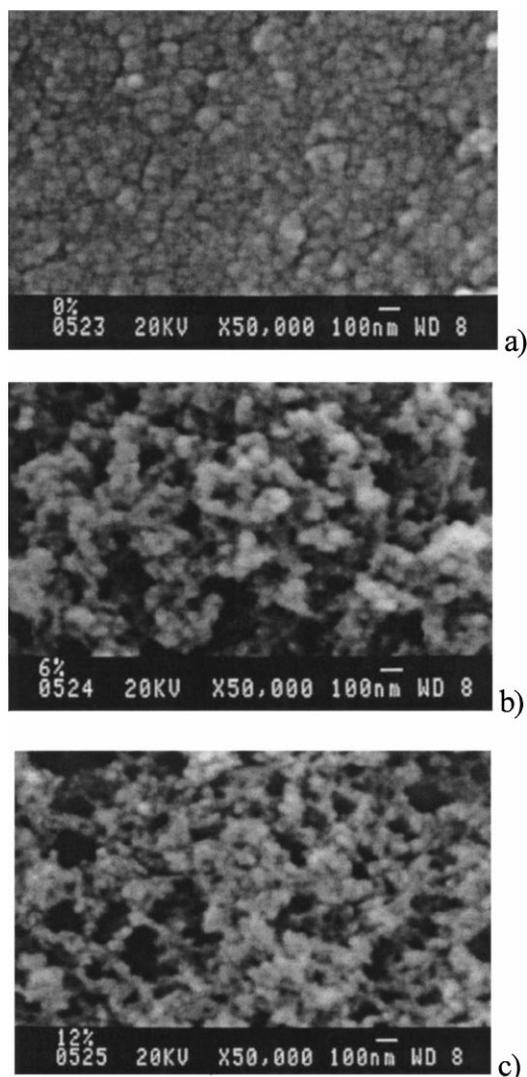


Figure 2. SEM micrographs of (a) 0-SiO<sub>2</sub>, (b) 6-SiO<sub>2</sub> and (c) 12-SiO<sub>2</sub> dried gel.

highly porous structures with average pore sizes of 120 Å in diameters, which is smaller than supercritical aerogel (186 Å).

Figure 3 illustrates TG/DTA curves of 0-SiO<sub>2</sub>, 6-SiO<sub>2</sub> and 12-SiO<sub>2</sub>. Unmodified SiO<sub>2</sub> showed a 15% weight loss in the temperature range 50°C–180°C and duplicated 5% at 300°C–450°C. Both weight losses are due to adsorbed solvents and the pyrolysis of residual organics, respectively. However, the two types of modified SiO<sub>2</sub> showed no weight loss up to 300°C, which was followed by a drastic weight loss between 350°C and 400°C. This corresponds exactly with a

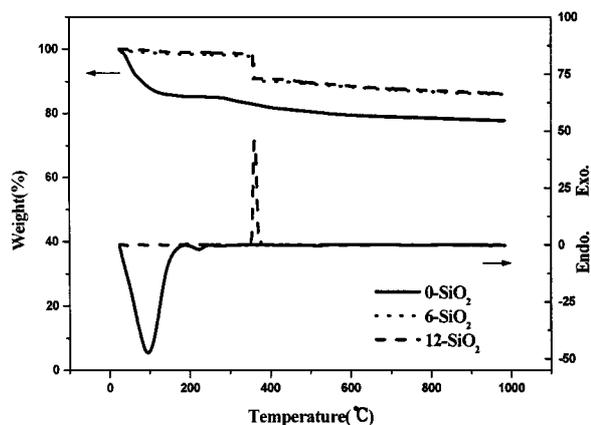


Figure 3. TG/DTA curves of 0-SiO<sub>2</sub>, 6-SiO<sub>2</sub> and 12-SiO<sub>2</sub>.

sharp exothermic DTA peak. It is believed that the —CH<sub>3</sub> groups covering the silica were burned off by air diffusing through the highly open pore networks. Furthermore, the identical weight loss observed for 12-SiO<sub>2</sub> and 6-SiO<sub>2</sub> indicated that 6 vol.% of TMCS was probably sufficient to exchange the surface hydroxyl groups completely for alkyl groups.

Figure 4 displays the N<sub>2</sub> adsorption/desorption isotherms of 0-SiO<sub>2</sub> and 6-SiO<sub>2</sub>. Unmodified samples

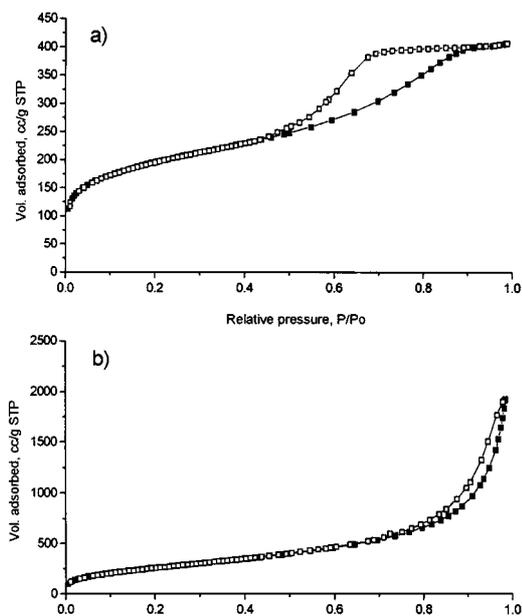


Figure 4. N<sub>2</sub> adsorption/desorption isotherms of (a) 0-SiO<sub>2</sub> and (b) 6-SiO<sub>2</sub>.

showed the typical adsorption/desorption curve of xerogels with hysteresis behavior, which indicates ink bottle shape of pores. On the contrary, the curve of the modified silica is very similar to that of the supercritical aerogels, although it has relatively low surface area and pore size [11].

Micropore analysis using *t*-Plot demonstrated that pore sizes under 15Å in the unmodified silica made up approximately 15% of the total volume, but this amounted to less than 1% for the modified silica.

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### References

1. M.J. Lee and J.Y. Kim, *Sci. Tech. of Ceram. Mater.* **7**(4), 429 (1992).
2. D.J. Kim and S.H. Hyun, *J. Kor. Ceram. Soc.* **33**(5), 485 (1996).
3. C.H. Shin, *Catalysis* **7**(2), 5 (1991).
4. C.J. Brinker and S.W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* (Academic Press, San Diego, 1990), p. 501.
5. D.G. Park, *Polym. Sci. & Tech.* **8**(3), 248 (1997).
6. S.S. Prakash, C.J. Brinker, and A.J. Hurd, *J. Non-Cryst. Solids* **190**, 264 (1995).
7. S.K. Kang and S.Y. Choi, *J. Kor. Ceram. Soc.* **33**(12), 1394 (1996).
8. Z. Bi, Z. Zhang, F. Xu, Y. Qian, and J. Yu, *J. Colloid Interface Sci.* **214**, 368 (1999).
9. F.M. Fowkes, *Contact Angle, Wettability, and Adhesion* (American Chemical Society, Washington, 1964), p. 58.
10. R. Deshpande, D.M. Smith, and C.J. Brinker, U.S. Patent, 5565142, 1996.
11. H.S. Yang, S.Y. Choi, S.H. Hyun, and H.H. Park, *J. Non-Cryst. Solids* **221**, 151 (1997).