Pore structure evolution in silica gel during aging/drying. III. Effects of surface tension *

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A two-step acid/base-catalyzed silica gel has been aged in alcohol and water baths followed by various aprotic solvents with a wide range of surface tensions. Low temperature (CO_2) and high temperature (ethanol) aerogels were also prepared. The physical and chemical structures of gels dried from aprotic solvents were studied by a series of techniques (^{29}Si MAS-NMR, nitrogen adsorption, SAXS, elemental analysis, TGA). The aprotic solvents isolated the effects of pore fluid surface tension during drying since they do not participate in condensation and other reactions. For aprotic solvents, a linear decrease in xerogel surface area was observed with increasing surface tension. Pore volume and pore size distribution followed a similar trend. Depending upon whether the gel had been washed in ethanol or water prior to the aprotic solvent, the final pore volume was changed significantly for a given surface tension. This indicates that both surface area and pore volume may be independently controlled.

1. Introduction

Before drying, the structure and chemistry of a wet gel may be considerably altered by varying the aging conditions such as time, temperature, pH and pore fluid. In other papers in this series, Davis and co-workers used low field NMR and other characterization techniques to study the effects of time/temperature [1], pore fluid [2], and pore fluid pH [3] on the physical and chemical structure of wet gels and corresponding xerogels. They found that the wet gel surface area changed significantly with the pore fluid and the effect was partially preserved upon drying. However, the roles of surface tension, surface esterification/hydrolysis, and network polymerization/depolymerization were not separately determined.

At the gel point, the Si–O–Si network still contains many Si atoms with –OR and –OH groups bonded to them. After gelation, the structure and properties of a silica gel continue to change due to continuing condensation reactions involving the terminal sites, alcohol exchange, dissolution and reprecipitation, etc. These collective processes are called aging. A number of aging treatments may be used to tailor the gel structure and alter subsequent processing. One common approach is simply to place the wet gel in a solvent to exchange mother liquor from the pores prior to drying.

Davis et al. [2] have investigated the effect of exchanging water and ethanol with the initial pore fluid. Gels aged in and dried from water exhibit surface areas on the order of 1000 m^2/g immediately before drying and 500 m^2/g after drying, whereas those washed and aged in ethanol exhibit surface areas on the order of 2000 m^2/g prior to and 1000 m^2/g after drying. This effect was found to be reversible and the final pore

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fluid was the dominant factor in the xerogel surface area. This decrease in surface area upon drying may be the result of condensation during drying or surface tension induced collapse. If fully condensed silicons are assumed to be internal, hence not contributing to surface area, and silicons which contain –OH and/or –OR groups are assumed to be surface, increased condensation leads to a loss in surface area as a result of pore wall smoothing. In that work, the effect of surface tension on xerogel structure could not be isolated because of accompanying condensation reactions involving –OH and/or –OR groups.

In principle, various aprotic solvents may be used instead of alcohol/water mixtures to replace the pore fluid used to age the gel. These solvents do not participate in siloxane bond hydrolysis or alcoholysis so that the effects of surface tension and capillary stresses on the xerogel structure are more clearly elucidated. The availability of labile protons determines whether anions or cations are solvated more strongly through hydrogen bonding. Because hydrolysis is catalyzed either by hydroxyl or hydronium ions, solvent molecules that hydrogen bond to these ions reduce the catalytic activity under basic or acidic conditions, respectively. Therefore, aprotic solvents that do not hydrogen bond to hydroxyl ions have an effect on making the hydroxyl ions more nucleophilic [4].

The availability of labile protons also influences the extent of the reverse reaction, re-esterification. Aprotic solvents do not participate in reactions such as re-esterification or hydrolysis, because they lack sufficiently electrophilic protons and are unable to be deprotonated to form sufficiently strong nucleophiles necessary for these reactions [4]. Therefore aprotic solvents do not formally take part in sol–gel processing reactions and may be considered to be inert compared to water or ethanol.

The effect of surface tension, γ, during solvent exchange and drying is manifested in the form of capillary pressure, P_c. The force balance on the line of intersection in a solid–liquid–vapor system leads to Young's equation [4]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos(\theta), \tag{1}$$

where the contact angle, θ, is characteristic of the solid–liquid interface. Liquid rises in a capillary replacing solid–vapor interface with solid–liquid interface, thereby creating a net change in surface energy. The work done against gravity is proportional to capillary pressure, P_c, and capillary volume. Equating the work done with the change in surface energy, the contact angle is related to capillary pressure and pore radius, r_{pore}, as [5]

$$P_c = -\left(2\gamma_{LV} \cos(\theta)\right)/r_{pore}. \tag{2}$$

The negative sign indicates tension in the liquid. For small pores, the capillary pressure developed is very high. For the B2 silica gel, used in previous portions of this study [1–3], for which the average pore radius is about 10 nm, the capillary pressure developed would be around 140 atmospheres with water as the pore fluid, assuming complete wetting ($\theta = 0°$). Laplace [5] related the pressure difference across the vapor–liquid interface to the surface tension of liquid and the curvature of the interface as

$$\Delta P = \gamma_{LV}\left\{\frac{1}{r_1} + \frac{1}{r_2}\right\}, \tag{3}$$

where r_1 and r_2 are the principle radii of the vapor–liquid interface. For a cylindrical pore $r_1 = r_2$, and the pressure difference is simply P_c [5]. A comparison of eqs. (2) and (3) shows that the radius of curvature for a cylindrical pore is $-r_{pore}/\cos(\theta)$ (the negative sign indicates that the center of curvature is outside the liquid phase). For submicrometer capillaries, as in silica gels, the meniscus shape is affected by disjoining forces near the wall [4]. The importance of capillary pressure to the drying gels is its effect on the solid phase. The tension in the liquid is supported by the solid network, which in turn experiences compression. In gels where the pores are very small, very large stresses are developed during drying. The shrinkage depends on the maximum capillary stress generated [4]. Kingery and Francl [6] found a linear proportionality between surface tension and density of clay bodies mixed with various amounts of surfactant and then dried.

Aerogels may be prepared by supercritical extraction of the pore fluid [7]. This process avoids liquid–vapor menisci during drying, thus eliminating capillary pressure and essentially preserving the wet gel structure except for changes due to gel syneresis [8] and loss of microporosity [9]. The most common method of making aerogels involves directly removing pore fluid above its critical point (for ethanol T_c = 516 K, P_c = 63 bar) [7]. An alternate low temperature method [10] involves replacing pore fluid with liquid CO_2 and then removing CO_2 above its critical point (T_c = 304 K, P_c = 73 bar). During the high temperature process, significant chemical and physical changes in gel structure can occur as a result of the greatly accelerated rates of aging and changes in the equilibrium behavior of various reactions. The low temperature carbon dioxide exchange process better avoids structural changes but is limited to certain pore fluids that are miscible in liquid CO_2.

Here we use physical and chemical characterization of dried gels to study the effects of surface tension. Different aprotic solvents exhibiting a wide range of surface tension were used as the aging fluids to isolate partially the effects of surface tension without affecting the chemistry of the silica gel.

2. Experimental procedure

Silica gels were prepared via a two-step acid/base-catalyzed procedure as described by Brinker et al. [11], used in previous studies [1–3], and denoted as B2 gels. In the first step, tetraethylorthosilicate (TEOS), ethanol, water, and hydrochloric acid (molar ratios 1:3:1:0.0007) were heated under a constant reflux at 333 K for 1.5 h. In the second step, 1 ml of 0.05 M NH_4OH was added to 10 ml of the TEOS stock solution at room temperature. The resulting sol was allowed to gel (2 h) in 5 mm diameter glass NMR tubes and then aged in the tubes for 22 h at room temperature.

After the initial aging in the mother liquor, the 'wet' gels were forced out of the NMR tubes and placed in a large excess of ethanol. To remove

Table 1
Surface tension and boiling points of pore fluids employed [4,5,12–14]

Final pore fluid	Surface tension (dyn/cm)	Boiling point (K)
Supercritical	0	
Liquid CO_2 (283 K)	2	194.5
Liquid CO_2 (273 K)	4	194.5
Liquid CO_2 (268 K)	7	194.5
Ethanol	22.7	351.4
Tetrahydrofuran	23.1	338.5
Acetone	23.7	329.5
Cyclohexane	25.3	353.6
Acetonitrile	29.3	354.6
Nitromethane	32.7	374
1:4 Dioxane	33.6	373.5
Water	72	373

any unreacted monomer from the gel network [2], the gels were washed with pure ethanol in five 24 h steps, using fresh ethanol for each successive step. These gels were then washed in aprotic solvents with a range of surface tension. Exchange of the ethanol pore fluid was achieved by washing in an aprotic solvent for 48 h, with intermediate removal of excess solvent from the top of the container, followed by addition of fresh aprotic solvent. The various aprotic solvents employed are listed in table 1.

A similar series of samples was prepared by washing five times with ethanol and then once with water for 24 h prior to exchange with aprotic solvent (or water). Exchange of water pore fluid with aprotic solvents was achieved by washing as described above. Only aprotic solvents miscible with water were used in this set.

A similar drying scheme was followed for all the samples. The gels were dried in a dry air atmosphere at 323 K for 48 h and then at 383 K for 48 h. We should note that because of the different boiling points of the solvents employed (see table 1), the actual drying rates for the various samples varied significantly. Also, significant cracking was noted during drying and no attempt was made to correlate the degree of cracking with the pore fluid.

Two aerogel samples were prepared. The first was made by heating the gel, washed five times with ethanol, to over the critical point in an

autoclave and removing the supercritical ethanol while maintaining the temperature above the critical temperature. The second sample was prepared at low temperature by exchanging ethanol with liquid CO_2 and then removing CO_2 above its critical point. Additional samples were prepared by exchanging ethanol with liquid CO_2 but the CO_2 was removed below its critical point so that the surface tension experienced by the drying gel is that of liquid CO_2.

Nitrogen sorption measured with Autosorb-1 and ASAP-2000 automated volumetric analyzers at 77 K was used to obtain surface areas and pore volumes of the dried gels. Samples were outgassed under vacuum at 373 K for at least 2 h prior to measurement. A BET analysis (five points, $0.05 < P/P_0 < 0.3$, N_2 molecular cross-sectional area = 0.162 nm^2) was conducted to obtain surface areas and a single condensation point ($P/P_0 = 0.99$) was used to find the pore volume. Pore size distributions were calculated from the desorption isotherm. Because of the large upper pore size, only the surface area of the aerogels was obtained from nitrogen adsorption / condensation. The measurement of pore structure for aerogels using either nitrogen adsorption / condensation or mercury porosimetry is problematic because of possible changes in their fragile structure [7]. This can result from either the applied pressure of mercury porosimetry or the capillary pressure associated with condensing nitrogen (γ = 10 dyn/cm at 77 K). Therefore for some materials, the total pore volume was determined using the skeletal density found via helium displacement (1.97 g/cm^3) and the bulk density measured by mercury displacement at ambient pressure (0.27 g/cm^3). Nitrogen adsorption surface areas were repeated on the same samples and were similar within the limits of the experiment ($\pm 5\%$) indicating no collapse of small-scale structure as a result of capillary pressure from the nitrogen.

Small angle X-ray scattering (SAXS) data were collected using a Rigaku 12 kW rotating anode X-ray generator with Kratky U-slit optics and a position sensitive detector. The incident beam is Cu Kα radiation with a wavelength of 0.1542 nm. The data were then corrected for slit collimation in order to evaluate the radius of gyration and the fractal dimension by analysis of the Guinier and Porod regions, respectively.

To probe the quantity and nature of the surface groups (SiOH, SiOR), thermal and elemental analyses were performed. Thermal analysis (TGA, DTA) was conducted in air to 923 K at the rate of 10 K min^{-1} using an Omnitherm TGA/DTA. Carbon content was obtained using a Perkin–Elmer Elemental Analyzer. MAS ^{29}Si NMR spectra were recorded at 79.459 MHz using a Varian Unity 400 spectrometer. Samples were packed in a 5 mm diameter zirconia rotor and spun at approximately 3 kHz about the magic angle. Pulse delay times of 30 s were used to accumulate a minimum of 256 free induction decays for each.

3. Results

The effect of pore fluid surface tension on xerogel surface area (from N_2 adsorption) for samples washed five times in ethanol and exchanged with various aprotic solvents prior to drying is presented in fig. 1. The surface areas of low temperature and high temperature aerogels obtained by supercritical extraction are also presented. With the exception of the high temperature aerogel, the surface chemistry associated with all of the samples should be the same. Simply by changing the surface tension of the pore fluid, the surface area varied approximately linearly from ~ 700 to ~ 1200 m^2/g with decreasing surface tension. The high temperature aerogel surface area deviates from this general trend. This is a result of pressure and/or temperature enhanced esterification and condensation that accompanies this process.

Figure 2 shows xerogel surface areas for similar gels that received an intermediate water wash prior to exchange with an aprotic solvent and subsequent drying. The xerogel dried from water shows a surface area of 600–700 m^2/g which is consistent with earlier results for water washed B2 silica gel [2]. As above, increasing surface tension leads to lower surface area. However, the effect of surface tension was not as significant. Previously, water washing was found to have a
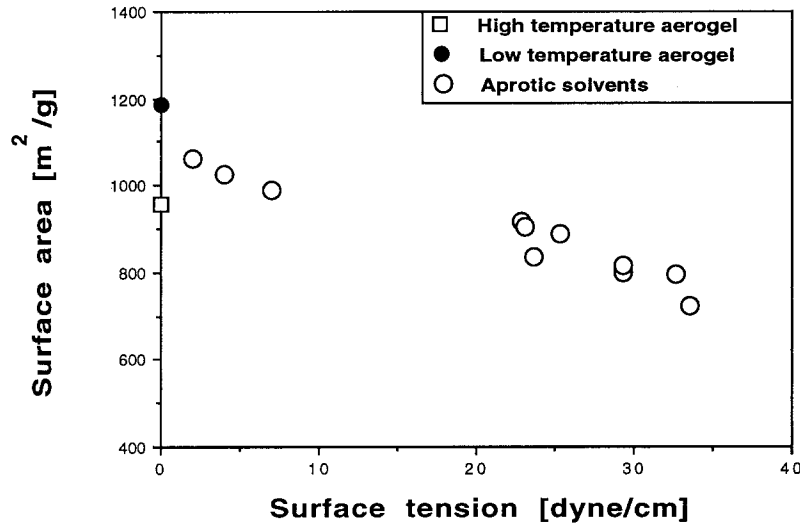
Fig. 1. Effect of pore fluid surface tension on surface area of xerogels washed in aprotic solvents.

large effect on the surface area of these same base-catalyzed silica gels in both the wet and dry states [2]. ^{29}Si MAS-NMR indicated that this was the result of depolymerization of the silica gel network when the pore fluid was ethanol, and condensation of surface groups to form additional Si-O-Si bonds when the pore fluid was water. In that study, it was assumed that this was primarily a chemical effect (the water leading to increased condensation) and not a direct result of increased condensation) and not a direct result of

the surface tension difference between the two pore fluids.

The final pore volume of the dried gels is a result of competing effects including capillary pressure induced collapse, which will tend to lower pore volume, and condensation/polymerization and dissolution/reprecipitation reactions which tend to stiffen the matrix leading to larger pore volumes. In previous work, these separate effects were not isolated [2]. Figures 3 and 4
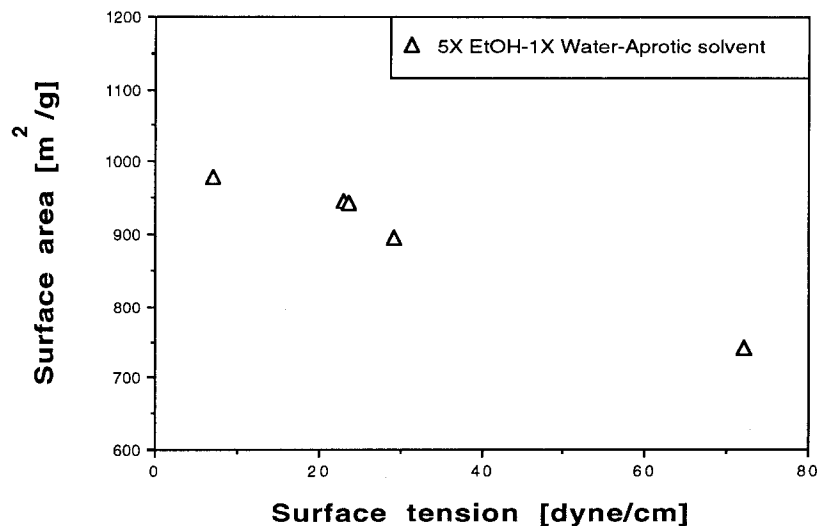
Fig. 2. Effect of pore fluid surface tension on surface area of xerogels washed in water followed by an aprotic solvent wash.
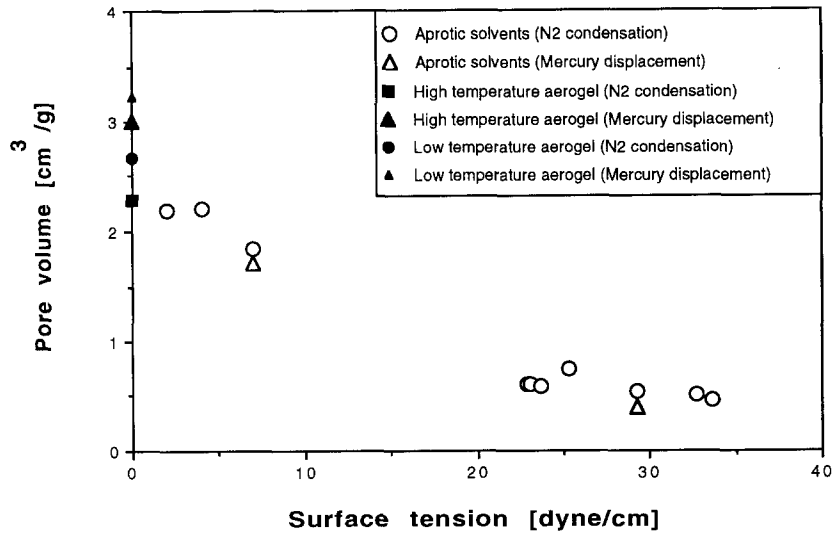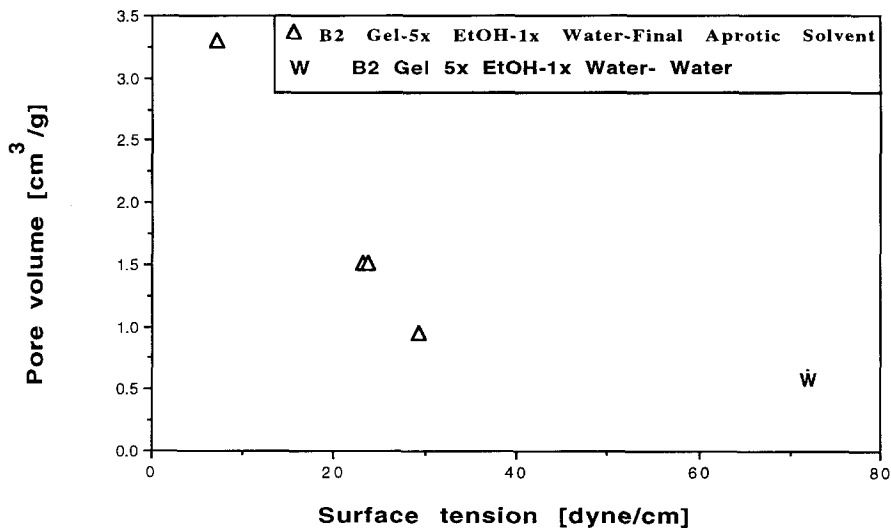
Fig. 3. Effect of pore fluid surface tension on pore volume of xerogels washed in aprotic solvents.

illustrate the effect of surface tension on the pore volume of xerogels prepared without and with an intermediate water wash prior to final solvent exchange, respectively. As a result of questions arising from the use of nitrogen condensation (i.e., nitrogen surface tension-induced pore collapse and incomplete filling of large pores), some pore volumes were determined from both nitrogen condensation and the difference between he-

lium and mercury displacement densities. For the samples without a water wash, the pore volume changes by over a factor of four for the surface tension range studied and the pore volume is inversely related to surface tension. For the samples dried from liquid carbon dioxide, the porosities are over 80% and approach those obtained for aerogels [4]. The effect of surface tension on pore volume is essentially linear and similar to

Fig. 4. Effect of pore fluid surface tension on pore volume of xerogels washed in water followed by an aprotic solvent wash.
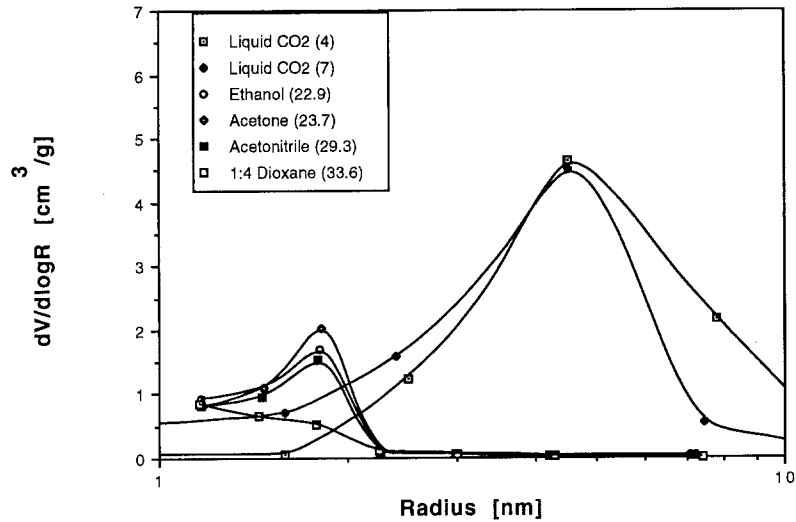
Fig. 5. Pore size distributions for xerogels washed in aprotic solvents. Lines are drawn through the data symbols as a guide for the eyes.

the surface area results, the effect of a water wash significantly increases the pore volume (by a factor of ~ 1.5).

Additional information about the xerogel structure can be extracted from the pore size distribution and average pore radius. Figure 5 presents a comparison between pore size distributions for ethanol-washed xerogels dried from various aprotic solvents. Pore size distributions were calculated from the desorption branch of the nitrogen adsorption isotherm. For acetone ($\gamma = 23.7$ dyn/cm), the pore size distribution was similar to that of the sample dried from ethanol ($\gamma = 22.9$ dyn/cm). However, for the remaining two solvents with higher surface tensions, considerable decreases in peak height and shifts to-
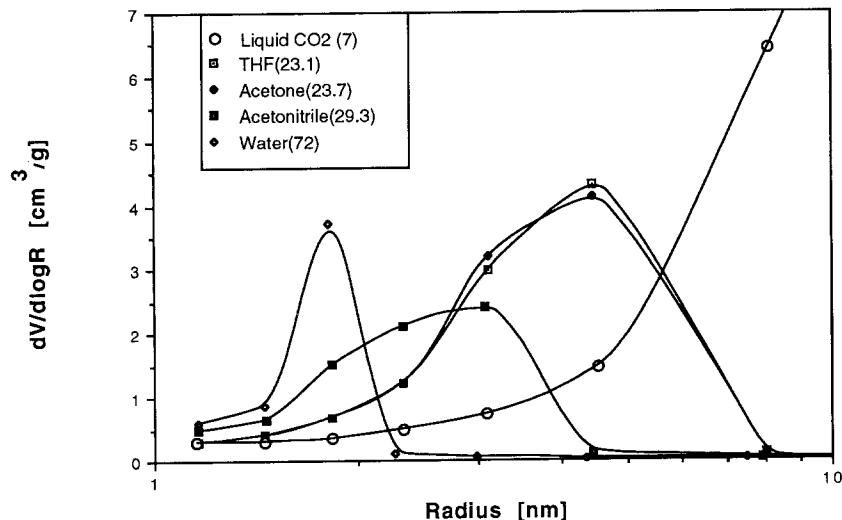

Fig. 6. Pore size distributions for xerogels washed in water followed by an aprotic solvent wash. Lines are drawn through the data symbols as a guide for the eyes.
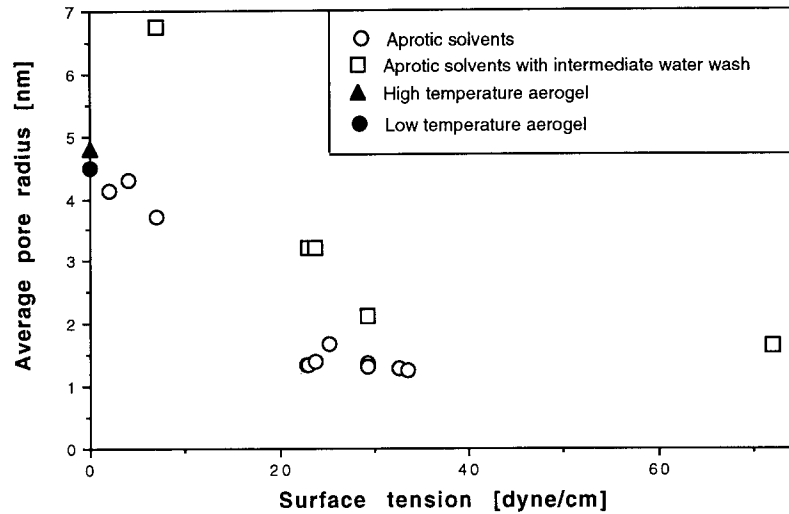
Fig. 7. Effect of pore fluid surface tension on xerogel average pore radius.

wards smaller pore radii were observed. For the xerogels dried from liquid CO_2 ($\gamma = 4$ and 7 dyn/cm), the pore size distribution was broader with significantly larger average pore radius (~ 4 nm) as compared with that of the other aprotic solvents (~ 1.5 nm). Figure 6 shows pore size distributions for xerogels with an intermediate water wash followed by drying from an aprotic solvent (or water). A broader pore size distribution and a considerable shift toward larger average pore size was observed with decreasing surface tension of the final pore fluid. Figure 7 presents the effect of surface tension on average pore radius (defined as the ratio of twice the pore volume to surface area) for both xerogels with and without water wash prior to drying from an aprotic solvent. For samples without an intermediate water wash, the average pore radius varied by a factor of four over the surface tension range studied. The use of a water wash increased the average pore radius by a factor of approximately two for the same pore fluid surface tension.

SAXS results support the nitrogen adsorption/ condensation observations. Scattering curves for ethanol washed gels dried from different surface tensions are shown in fig. 8. The top curve is the low temperature aerogel produced using supercritical CO_2 (surface tension $= 0$ dyn/cm) for comparison. As can be clearly seen,

the linear Porod region extends to smaller q when the surface tension decreases indicating an increase of the scattering length scale (pore size).
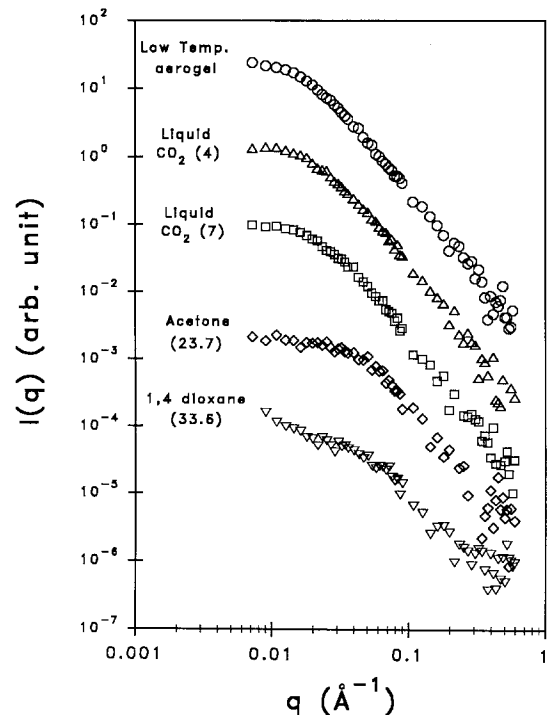

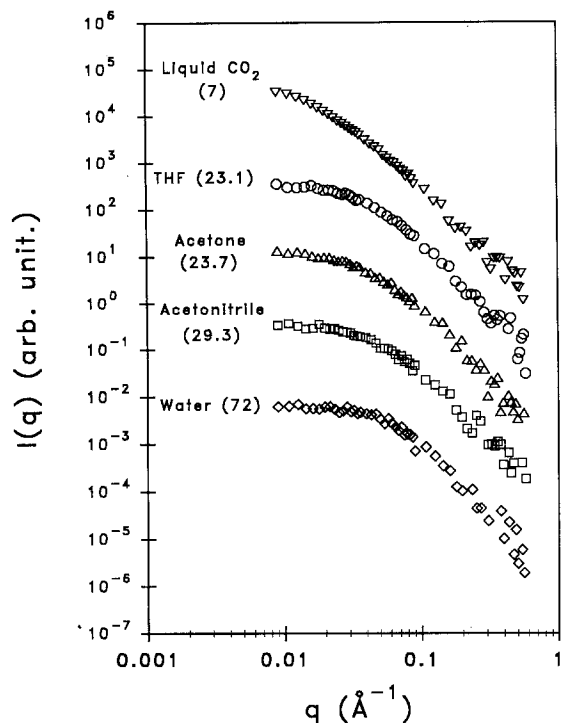Fig. 8. Small angle X-ray scattering (SAXS) curves for xerogels washed in aprotic solvents.

Fig. 9. Small angle X-ray scattering (SAXS) curves for xero-gels washed in water followed by an aprotic solvent wash.

Conversely when washed with higher surface tension solvents, the resulting gels have smaller feature sizes. Figure 9 shows the scattering curves for xerogels prepared with an intermediate water wash prior to solvent exchange and drying. The trend of the scattering behavior is the same as before: when surface tension increases, the feature size decreases.

The radius of gyration and limiting values of Porod slope evaluated at high q calculated from figs. 8 and 9 are shown in fig. 10. The radius of gyration closely parallels the adsorption/ condensation-derived average pore radius results presented in fig. 7. The SAXS results are 50% larger than the adsorption/condensation results which could arise from pore shape effects or pore roughness (i.e., the hydraulic radius, $2V_p/A_s$, decreases as a result of roughness but the radius of gyration does not). The Porod slopes (indicative of structure on intermediate length scales) show a significant difference between samples prepared with and without an intermediate water wash. For the ethanol-washed samples, a large decrease in slope from ~ 2.2 to ~ 2.7 is noted with increasing surface tension of final pore fluid indi-
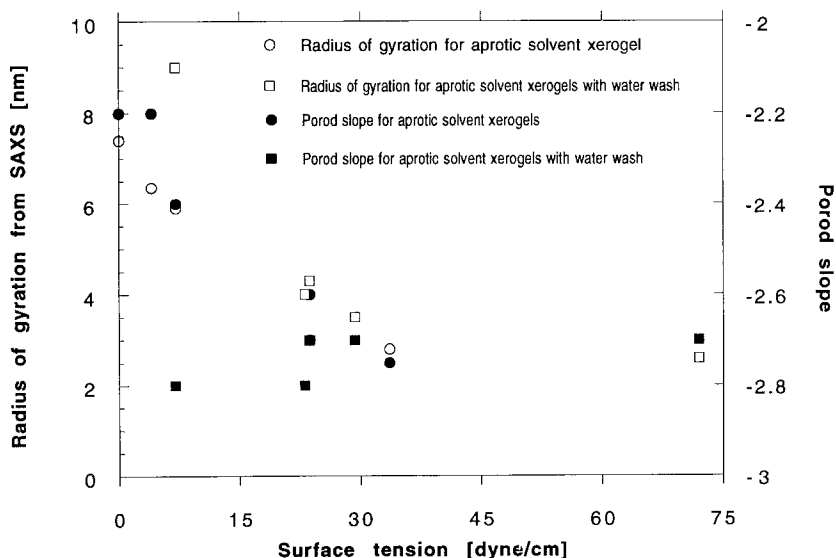

Fig. 10. Effect of surface tension on average pore radius and Porod slope obtained fron SAXS for xerogels washed in aprotic solvents and for xerogels washed in aprotic solvents followed by an intermediate water wash.

cating changing mass and surface fractal dimensions, whereas samples prepared with an intermediate water wash exhibit a Porod slope of ~ 2.8, independent of surface tension.

The C parameter in BET analysis is a function of the heat of adsorption (proportional to $e^{(-\Delta H_{ads}-\Delta H_{liq})}$), the chemical nature of the surface, and the surface roughness [15]. However for porous solids, this parameter also increases with a decrease in pore size because of proximity of the pore wall to the adsorbing molecule. This is illustrated in fig. 11. The C parameter was calculated over $0.1 < P/P_0 < 0.2$. Lowen and Broge [16] showed that the C parameter decreases with an increase in the concentration of terminal alkoxy groups on the surface of amorphous silica, thus explaining the differences between samples prepared with and without intermediate water wash. For the high temperature aerogel, which has a greater extent of surface esterification than the low temperature aerogel, the C parameter was significantly lower, in agreement with Lowen and Broge [16]. However for the other aprotic solvents, where surface tension-induced collapse and condensation of terminal $-OH$ groups leads to increased $-OR$ concentration on the surface, the C parameter showed an increase with increasing surface tension. The variation in the C parameter between 100 and 200 for samples with

a pore size of ~ 1.5 nm is a result of the changing roughness of these samples as shown previously in the SAXS results. This indicates that pore size effects have an important role in addition to the chemical nature of the surface in nitrogen adsorption.

To determine the contribution of condensation reactions to the loss of surface area with increasing surface tension, ^{29}Si MAS-NMR experiments were performed. Figure 12 shows a comparison between the aerogels and the aprotic solvent xerogels. The high temperature aerogel showed a significant amount of Q^2 (Q^n, $n = 0$ to 4 indicates the number of $-OSi$ bonds the reference silicon atom has) silicons as compared with the low temperature aerogel. This is probably due to the severe conditions employed to extract the pore fluid resulting in increased breakage of $Si-O-Si$ bonds. Surface areas calculated from ^{29}Si MAS-NMR Q distribution [2,3] did not show agreement with the nitrogen adsorption results. This could indicate that some terminal $-OR$ (and/or $-OH$) groups reside on surfaces that are inaccessible to nitrogen at 77 K as suggested by Vega and Scherer [17]. Alternatively the resolution of the deconvolution routine used to obtain the Q values might be insufficient to reveal the expected effects of the surface tension range employed. Qualitatively more Q^4 was observed for
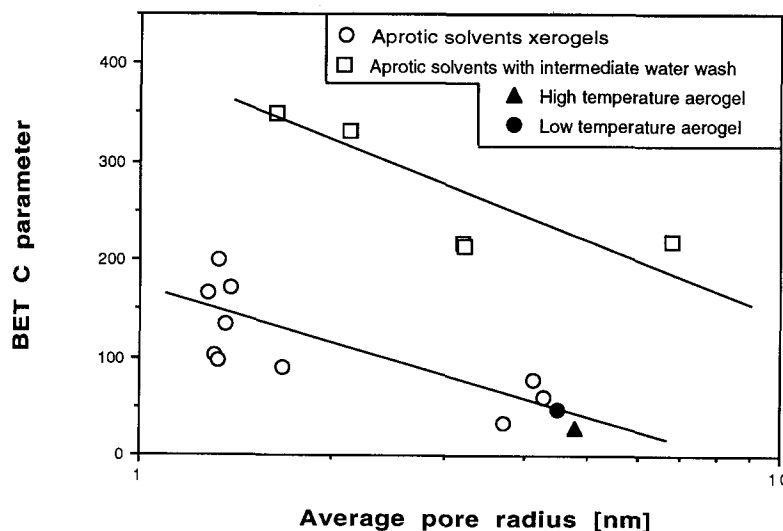

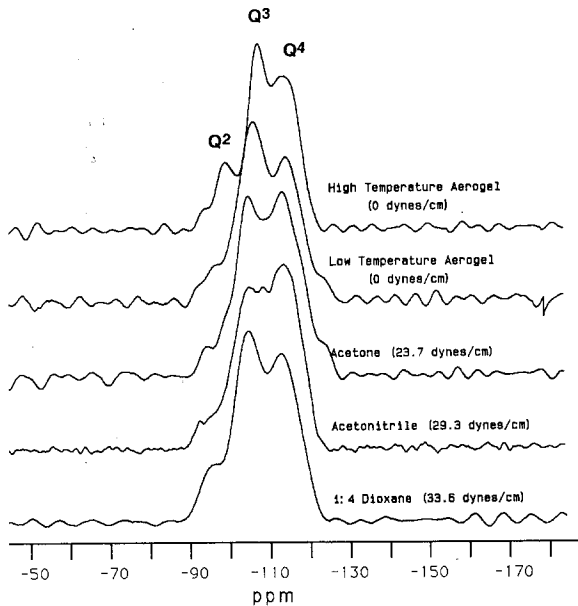Fig. 11. Effect of xerogel pore size on the BET C parameter. (Lines drawn for comparison purposes only.)

Fig. 12. ^{29}Si MAS-NMR spectra for xerogels washed in aprotic solvents.

xerogels dried from aprotic solvents than for the two types of aerogels.

Another approach to determine the extent of condensation is thermal analysis of the xerogels. TGA analysis of the xerogels dried from various

aprotic solvents and liquid CO_2 indicated that the weight loss after 423 K was proportional to the nitrogen (accessible) surface area. These results are presented in fig. 13. TGA and DTA analysis also established the increased esterification of the high temperature aerogel surface. The high temperature aerogel showed 14% weight loss with a sharp exotherm at around 513 K, which corresponds to terminal –OR groups. For the low temperature aerogel, this weight loss was only 8%. A second weight loss occurred at around 673 K. This loss was due to terminal –OH groups. For the high temperature aerogel, this loss was less than 2%, while for the low temperature aerogel it was about 5%.

4. Discussion

The linear proportionality between surface area and surface tension indicates that surface tension effects dominate the effect of pore fluid on surface area rather than the chemistry (among the aprotic solvents) of the pore fluid. One can postulate two mechanisms for the linear trend observed in surface area and pore volume of xerogels: (1) the higher surface tension causes
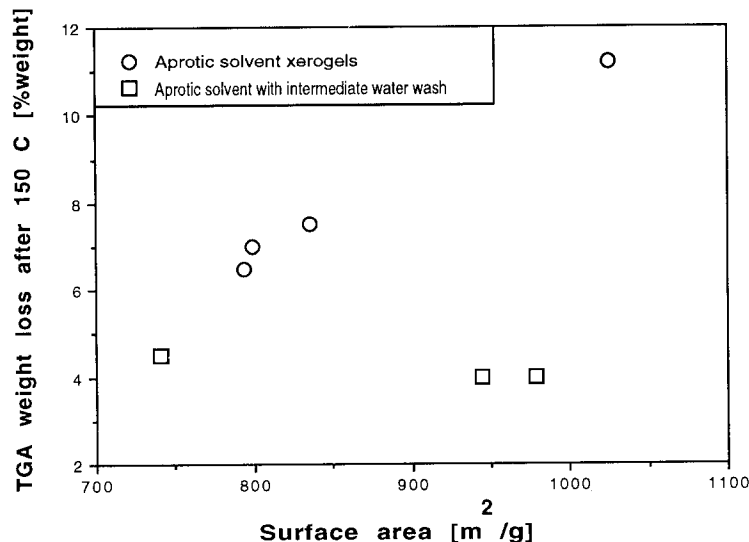

Fig. 13. Variation of TGA weight loss after 423 K versus surface area for xerogels washed in aprotic solvents and for xerogels washed in water followed by an aprotic solvent wash.

greater matrix collapse during the final stages of drying leading to an increasing portion of the internal pore surface being inaccessible to nitrogen; or (2) condensation reactions occur between adjacent surface Si–OH and Si–OH/Si–OR groups as the network is collapsed forming Si–O–Si bonds and leading to a decrease in the actual pore surface area. Since Si–OR groups will not react with other Si–OR groups, the magnitude of this effect will depend upon the surface hydroxyl coverage. The effect of surface tension for this mechanism must be related to forcing near neighbor groups into closer proximity and thus, the higher the surface tension, the greater the degree of condensation. The first mechanism would result in surface Si–OH and Si–OR concentrations which are independent of surface tension, whereas the second mechanism would result in a lower Si–OH concentration. Both the TGA and ^{29}Si NMR results indicate a decreasing concentration of surface groups with increasing surface tension which thus supports the second mechanism described above.

The trend in the pore size distributions of the xerogels further illustrates the action of capillary forces during drying, which tend to bring the pore walls closer and may be resulting in additional condensation of surface groups. Basically, SAXS results support those from the other techniques in this study. The higher the surface tension, the smaller the feature size. Further, the intermediate water washed xerogels have larger feature sizes. Under the same surface tension, this is reasonable since water washed xerogels should have more Si–OH groups on the surface and thus experience a greater degree of condensation. This results in more Si–O–Si bonds which should make the gel structure stronger than ethanol washed gels, therefore they withstand capillary forces better [4]. This may also explain the different surface roughness associated with the water washed samples.

5. Conclusions

Drying silica gels aged in various aprotic solvents results in a linear decrease in xerogel surface area with increasing solvent surface tension. Pore volume and pore size distribution follow a similar trend with surface tension. Condensation reactions occur between adjacent surface Si–OH and Si–OH/Si–OR groups as the network is collapsed forming Si–O–Si bonds and lead to a decrease in the actual pore surface area. Depending upon whether the gel had been washed in ethanol or water prior to the aprotic solvent, the volume changes significantly for a given surface tension. This result indicates that both surface area and pore volume may be independently controlled.

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