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Pore structure evolution in silica gel during aging/drying II. Effect of pore fluids

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A two-step acid–base-catalyzed silica gel has been aged in a series of alcohol and water baths and some chemical and physical structures of the gel were measured using several techniques (low-field NMR, ^{29}Si and ^{13}C MAS-NMR, IR, Raman, nitrogen adsorption) on gels in wet and dry states. When the gel was placed in alcohol, the surface area increased as a result of esterification and depolymerization to 1500–2000 m^2/g in the wet state which then decreased to 1000 m^2/g after drying. In water, hydrolysis and condensation decreased surface area to 1000 m^2/g (wet) and 500 m^2/g (dry). This process was reversible. Alcohol-aging led to small pore size distributions (in much shorter times than previous studies of aging in the gel's mother liquor, ~ 90% ethanol, 10% H_2O). Surface areas calculated from ^{29}Si MAS-NMR-derived Q distributions were in good agreement with adsorption-derived values for the samples dried from alcohol but water-dried samples appeared to contain some surface area which was inaccessible to adsorbing nitrogen after drying. These results indicate that the pore structure of silica gels may be dramatically altered during the aging process and that their wet gel features may be preserved (at least partially) upon drying.

1. Introduction

After gelation but before complete drying, the chemistry and structure of a gel may be dramatically altered by varying the temperature, pH, and/or pore fluid composition in a process called aging. Most theories of growth, aging, and drying are based on chemical analysis and structural characterization of the dry gel. The previous paper in this series presented structural information obtained during aging of gels in their mother liquors (i.e., the ethanol/water/catalyst mixture in which the gel was made) via low-field NMR [1].

The microstructure of a xerogel (dry gel) is a consequence of successive gelation, aging, and drying steps. During drying the gel can initially shrink to accommodate loss of pore fluid maintaining the liquid–vapor interface at the exterior surface of the gel. At the final stage of drying, liquid–vapor menisci recede into the gel interior. The magnitude of the capillary pressure, p_c, exerted on the network depends on the surface tension of the liquid, γ, the contact angle, θ, and the pore size, r:

$$p_c = 2\gamma \cos(\theta)/r.$$

Because the pore size can be very small, the capillary pressure can be enormous (> 60 MPa [2]). This pressure causes the original gel network to collapse. Iler [3] states that the xerogel structure is a collapsed and distorted version of the structure that originally existed at the gel point.

Aging may be used to tailor the extent of collapse of the structure during drying. One common approach is to simply place the wet gel in a solvent or solution other than the mother liquor prior to drying. Basic solutions have been used to enhance dissolution/reprecipitation [2,3] that promote neck formation between particles and thus strengthen the gel matrix. This reduces

shrinkage during drying and results in a larger final pore size. Alternatively, the pore fluid may be exchanged with a neat solvent or solvent mixture. The use of pure water as an aging fluid has been used in a number of studies of base-catalyzed silica gels [4–7]. In each case a reduction in sample size is noted upon placing base-catalyzed silica gels in water or aqueous solutions. This reduction is attributed to syneresis, a process in which the gel shrinks through continued condensation reactions that increase the skeletal density, consequently forcing fluid out of the gel matrix. Scherer [4] has shown that the addition of water accelerates the macroscopic syneresis rate. Scherer [6] noted less shrinkage upon drying for gels aged in solutions of higher water contents than the mother liquor (1:9 water:ethanol by volume). These samples were believed to be strengthened by increased connectivity of the gel matrix resulting from both further condensation reactions that accompany syneresis and enhanced dissolution/reprecipitation, leading to 'neck' formation. This strengthening results in greater pore volumes for the dried gels despite the higher surface tension of water (which tends to compact the gel during drying). Aging gels in water also results in a decrease of surface areas for the xerogels. Boonstra and Bernards [7] found that increasing the amount of water in the preparation served to shorten the gel times for base-catalyzed silica gels and Scherer [4] found a higher degree of condensation for similarly prepared samples.

Mizuno et al. [5], interested in finding ways to reduce drying times needed to obtain monolithic xerogels, aged silica gels in various solutions including neutral water prior to drying. The goal was to strengthen the gel matrix prior to drying by hydrolysis of –OR groups and subsequent condensation to form siloxanes. Upon drying, pore walls are brought closer together and additional condensation reactions occur further strengthening the network. Both Mizuno et al. [5] and Scherer [6] noted an opacity of the gels when placed in water. Shrinkage upon placing gels in water was accompanied by an expulsion of a colorless oil found to be partially hydrolyzed and condensed TEOS [6]. The opacity is explained by Scherer as resulting from phase separation (and subsequent hydrolysis/condensation) of unhydrolyzed monomer on length scales large enough to scatter light.

A number of interesting questions follow from these investigations of changing pore fluid: (1) are the chemical or physical effects of pore fluid reversible, (2) what is the role of unreacted or partially reacted reagents remaining in the pore fluid upon subsequent processing, and (3) are surface area decreases observed for gels aged in water a result of increased silica condensation or the higher surface tension of water. Answering these and related questions is the objective of this work.

2. Experimental procedure

Silica gels were prepared via a two-step acid–base-catalyzed procedure as described by Brinker et al. [8] and as used in our previous study [1]. In the first step tetraethylorthosilicate (TEOS), ethanol, water, and HCl (molar ratios 1:3:1:0.0007) were heated under constant reflux for 1.5 h at ~ 333 K. In the second step 1 ml of 0.05M NH_4OH was added to 10 ml of the TEOS stock solution. The resulting mixture was allowed to gel (2 h) in 5 mm diameter glass NMR tubes and then aged in the tubes at 303 K for 22 h.

To study the effect of monomer and pore fluid on aging, samples were prepared, as described above, and then aged in ethanol, water, various alcohols, or consecutive ethanol–water baths. After the initial 22 h aging period in the mother liquor, the 'wet' gels were forced out of the NMR tubes and placed in a large excess of the selected aging solvent/reagent. After the last aging step, each sample was placed in either a 5 or 7.5 mm NMR tube and allowed to thermally equilibrate at 303 K for at least 2 h. Pore structure was monitored during aging via low-field NMR spin–lattice relaxation measurements of the pore fluid as described previously [1,9–12].

After the NMR experiments were completed, samples were weighed and dried. The samples aged in pure ethanol were allowed to dry by placing a pin hole in the NMR tube caps and the caps were removed to dry samples aged in water

(to achieve approximately equal drying rates). The samples were dried at 298 K for 5 d and subsequently at 373 K for 3 h to complete the drying process. Duplicate samples for Raman analysis were dried over an extended time period (6 weeks) at 298 K followed by oven drying at 323 K overnight.

Nitrogen sorption at 77 K was used to obtain surface areas and pore volumes of the dry gels (xerogels). Samples were outgassed under vacuum at 373 K for at least 2 h prior to measurement. A five-point BET analysis ($0.05 < P/P_0 < 0.3$, N_2 molecular cross-sectional area of 0.162 nm^2) was conducted to obtain surface areas and a single condensation point ($P/P_0 = 0.995$) was used to determine the total pore volumes. IR spectra of wet gels were acquired using a Perkin–Elmer 683 dispersive spectrometer by placing a small amount of gel between AgCl windows in a sealed liquids cell. Raman spectra of wet and dried (323 K) gels prepared with either ethanol or water as the final pore fluid were acquired using the 514.5 nm excitation line of an Ar^+ laser.

Magic angle spining (MAS) ^{29}Si and ^{13}C spectra of dried gels were recorded at 39.6 and 50.2 MHz, respectively, on a Chemagnetics console interfaced to a General Electric 1280 data station and pulse programmer. ^{29}Si NMR experiments were not employed on wet gels because of the low ^{29}Si concentration and associated long experiment times as compared to aging times. A 7 mm diameter zirconia rotor was used to spin the sample at 5 to 6 kHz. High-power ^1H decoupling was applied during data acquisition. The RIDE pulse sequence [13] was used to reduce baseline roll. Pulse delay times of 240 s were used to accumulate 256 free induction decays for the ^{29}Si spectra. This time is at least a factor of 6 longer than the estimated spin–lattice relaxation times of 35 to 40 s. It was necessary to spin these samples with air because the paramagnetic oxygen in air provides an efficient relaxation mechanism. The ^{29}Si spin–lattice relaxation time increases to 120 s in a nitrogen atmosphere. This change in relaxation time was reversible with the reintroduction of air. The ^{13}C spectra were acquired with 1024 free induction decays and a pulse delay time of 4 s. This time is at least a factor of 6 longer than the ^{13}C spin–lattice relaxation times of approximately 0.6 s.

3. Results

3.1. Effect of pore fluid on pore structure

The effect of different pore fluids and/or aging times on gel structure is summarized in terms of the wet gel surface area (as determined via low-field NMR) and the xerogel BET surface area. To aid in the comparison between wet and dry surface areas, the NMR (wet) surface area is reported on a dry weight basis. The surface area of gels treated in alternating 24 h ethanol and water baths are presented in fig. 1. All gels were first aged for 22 h in their mother liquor. Figure 1 illustrates that the gel surface area (both wet and dry) is dramatically affected by whether the final pore fluid is water or ethanol. Gels aged in water exhibit surface areas on the order of 1000 m^2/g immediately before drying and 500 m^2/g after drying (in water). In contrast, gels washed in ethanol exhibit surface areas on the order of 2000 m^2/g before and 1000 m^2/g after drying. For a gel dried in mother liquor (water : ethanol ~ 1 : 9 [6]), the wet and dry surface areas were almost identical to gels that were dried with water in the pores even though the pore fluid is primarily ethanol (note: for NMR analysis of samples in mother liquor, the β surface-interaction parame-

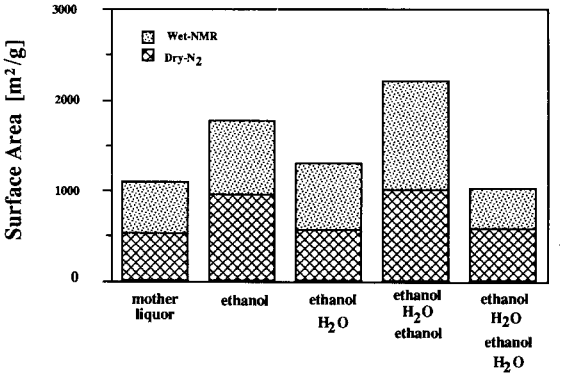

Fig. 1. Effect of pore fluid on wet and dry surface area.

ter corresponding to pure ethanol was assumed; there is only a 30% difference in β for silica–ethanol (2.83 nm/s) and for silica–water (1.98 nm/s) and β approximately varies linearly with composition between these values for mixtures). We should note that upon resaturation of the dried gels with either water or ethanol vapor (depending what fluid the gel was dried from), the NMR and BET/N2 surface areas are essentially equivalent.

In addition to the surface area reversibility with pore fluid, the xerogel pore volume also depends on the final pore fluid. Figure 2 shows that the pore volume is greater for samples dried from ethanol as compared to water. As the number of ethanol–water wash cycles is increased, we observe an increase in xerogel pore volume for samples dried in ethanol and a decrease in xerogel pore volume for samples dried in water.

To determine how the ethanol-to-water ratio in mixed alcohol–water pore fluids influenced the gel pore structure, a series of gels were aged in and dried from ethanol–water mixtures containing 0, 25, 50, 75, 85 or 100% ethanol by volume. Table 1 lists the xerogel surface area, pore volume and hydraulic radius (twice the pore volume to surface area ratio) for gels aged in an excess of ethanol for 24 h and then placed in the indicated ethanol/water mixture. For comparison the sample dried from mother liquor (no ethanol wash) is included in table 1. Mother liquor is approximately 90% ethanol; however, partially reacted TEOS [4] is also present and contributes to pore

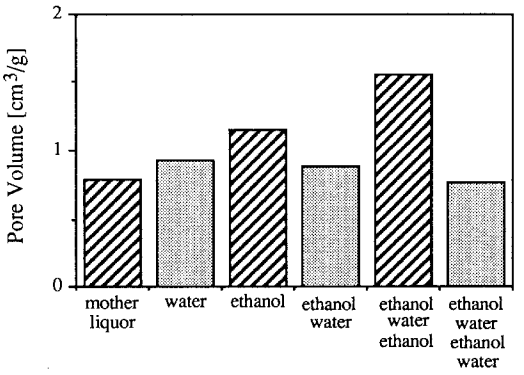

Fig. 2. Effect of pore fluid on xerogel pore volume.

Table 1
Xerogel surface areas and pore volumes as a function of pore fluid composition before drying

Ethanol (%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Radius (nm)
100	826	0.635	1.5
90 [a)]	512	0.793	3.1
85	551	0.321	1.2
75	572	0.331	1.2
50	470	0.269	1.1
25	607	0.393	1.3
0	605	0.474	1.6

[a)] Sample dried from mother liquor.

structure changes throughout drying. As the amount of water is increased, the surface area drops to a minimum at 50% ethanol and has a surface area similar to samples aged and dryed in water. For pore fluids containing less than 50% ethanol, surface area begins to increase. During drying, the composition of the pore fluid will change significantly as a result of the different vapor pressures of the two fluids; the analysis of this process is complicated by the presence of the ethanol–water azeotrope. From table 1, it appears that almost all samples on the water-rich side of the azeotrope (96% ethanol) act similar to pure water in terms of surface area but exhibit significant pore volume and mean pore radius differences.

The effect of unreacted or partially hydrolyzed TEOS (present at the gel point in the B2 gel [4]) was minimized by washing samples in an excess of ethanol for five consecutive 24 h periods. The 'washed' gels were then processed through a similar series of consecutive ethanol/water baths as those reported in fig. 1. (The reproducibility of the synthesis, processing, and measurements is illustrated via the duplicate samples which were washed five times with ethanol.) Again, a fluctuation of gel surface area (both wet and dry) is observed as pore fluids are switched (see fig. 3). The surface area differences for the xerogels are not as dramatic as for the unwashed samples (fig. 1) but are still significant. This may be attributed to the lack of TEOS in the pore fluid (which in the case of water washing could hydrolyze and reduce surface area upon drying) and the higher

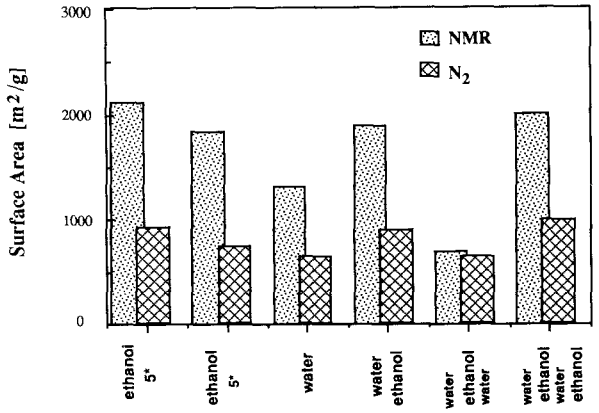

Fig. 3. Effect of pore fluid on wet and dry surface area after removal of monomer/reagents.

concentration of Si–OR groups which could inhibit condensation and therefore lead to greater collapse of the network.

Similar data are available for samples aged in one, two and five 24 h ethanol baths, then dried, and samples aged in zero, one, two and five 24 h ethanol baths and placed in water prior to drying. Figure 4 shows a slight decrease in xerogel surface area as the number of ethanol washings increases if the final pore fluid is ethanol. This surface area decrease is accompanied by a significant decrease in the final pore volume. In contrast, surface areas of gels dried from water increase as the number of prior ethanol washings increases (fig. 5). This surface area increase is followed by a large decrease in pore volume.

For a gel which has been placed directly in water after the mother liquor, the sample turns

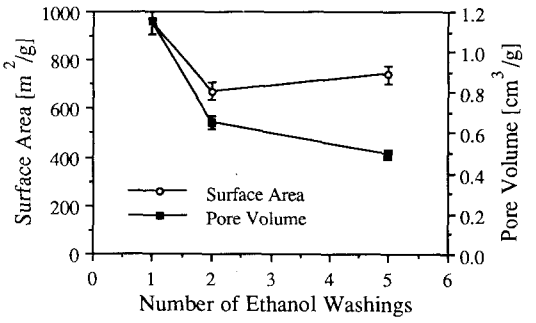

Fig. 4. Effect of repeated ethanol washings on the surface area and pore volume of xerogels.

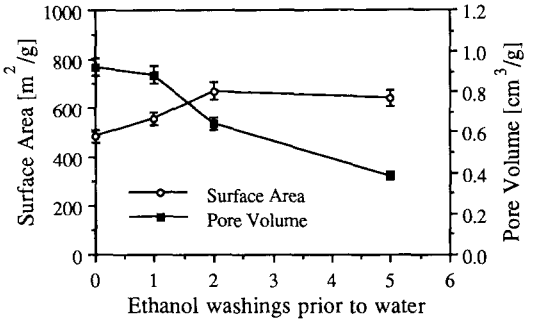

Fig. 5. Effect of repeated ethanol washings prior to introduction of water on the xerogel surface area and pore volume.

white and remains white even after drying at 373 K as has been previously observed [5,6]. Samples which are washed once with ethanol before being placed in water turn opaque and remain opaque after drying. In contrast, samples which are washed five times with ethanol before immersion in water remain translucent for the remainder of gel aging and drying. These findings support the idea [6] that opacity results from refractive-index differences that arise from silicate particles formed by hydrolysis and condensation of unreacted or partially reacted TEOS. Repeated washings with ethanol apparently serve to extract the unreacted or partially hydrolyzed TEOS prior to water addition. However, gravimetric measurements indicate that silica mass loss during the various washing steps was low ($< 3\%$) although it is difficult to quantify this number since the molecular composition of the gel network changes during washing.

In addition to ethanol, the effect of other alcohols (methanol, n-propanol, isopropanol) on surface area was assessed. Gels were first washed with ethanol and then washed (and dried) in the final alcohol. After drying, the xerogel surface area was found to increase with alcohol molecular weight. If one assumes that the silica surface is at least partially alcoxylated, the surface area may be changing as a result of a surface roughness effect rather than the creation of 'new' surface. If this is true, the change in surface area should be related to alcohol size. Assuming that the surface area occupied by each –OR group is that given by Stober et al. [14], we have plotted

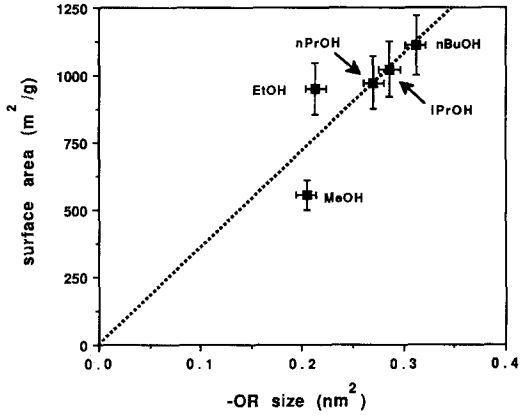

Fig. 6. Correlation between specific surface area and the surface area of the suspected surface group.

nitrogen surface area versus –OR area in fig. 6 and a general correlation is noted. We should note that the surface probably contains a mixture of SiOH, SiOEt, and SiOR groups and a direct correlation between surface area and surface group size would not be expected. If different size surface groups were appearing as small-scale surface roughness to adsorbed nitrogen, one would also expect to observe changes in the BET '*C*' parameter [15] and this was not observed.

3.2. Mechanisms of surface area change

Based upon our observation that the increase in surface area with ethanol is obtained before drying and partially preserved during drying, we can postulate that the alcohol is either breaking Si–O–Si bonds to create new surface (depolymerization) or that the surface area change is simply a result of replacing surface hydroxyls with bulkier alcohol groups (re-esterification). To establish whether re-esterification is responsible for surface area change, the relative concentration of the respective surface groups must be determined. Although we plot surface area versus molecular area in fig. 6, we do not mean to imply that the surface is entirely covered with that particular group. In fact, Stober et al. [14] have shown that all surface silicons cannot be esterified with the larger alkoxy groups due to steric constraints.

IR spectra were obtained for five wet gels (unwashed, washed once in EtOH, washed five times in EtOH, washed once in EtOH and once in H_2O, and stored in EtOH for longer than 6 months). With increasing ethanol exposure, the Si–O–Et peak increased indicating esterification of the silica surface. The absence of Si–O–Et for the water-washed samples indicated that the hydrolysis is essentially complete under these conditions (24 h, 303 K). Comparison of Raman spectra for water–ethanol- and water–ethanol–water-prepared samples indicate that the ethoxide groups are nearly completely hydrolyzed in the wet water-containing gels and that hydrolysis is essentially complete after drying. A similar conclusion regarding gels prepared from tetramethylorthosilicate (TMOS) followed by water washing was reached by Zerda and Hoang [16]. Gels dried after washing with ethanol contain both surface silanol and surface ethoxide species (surface ethoxide species rather than merely adsorbed ethanol are confirmed by TGA/DTA experiments that show weight loss and an associated exotherm at 683 K during heating in air) [17]. ^{13}C MAS-NMR spectra of xerogels dried from ethanol all show peaks corresponding to surface ethoxide groups whereas gels dried from water have no organic peaks. Thus one important observation regarding the reversible changes in the wet and dry surface areas observed with aging is that ethanol washing is accompanied by partial esterification of silanol groups and water washing by essentially complete hydrolysis (and/or condensation) of ethoxide groups.

In order to assess if Si–O–Si bond alcoholysis (depolymerization) is responsible for creating new surface during ethanol washing and silanol condensation for surface area loss during water washing, ^{29}Si MAS-NMR experiments were performed on dry gels which were washed in ethanol, ethanol–water, and ethanol–water–ethanol. Figure 7 contains spectra for all three samples as well as the peak assignments for Q^2, Q^3 and Q^4 silicons [2]. When the gels are dried from ethanol, there is an increase in Q^3 as compared to Q^4 silicon. This effect is reversible and mimics the observed trend in surface area. In order to quantitatively assess the degree of depolymerization

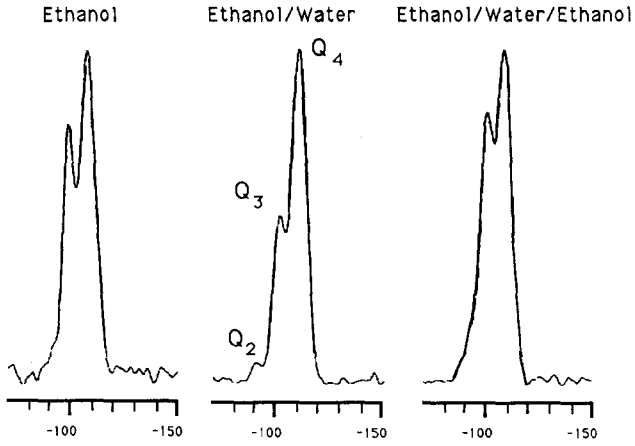

Fig. 7. ^{29}Si MAS NMR spectra for xerogels aged in ethanol, ethanol–water, and ethanol–water–ethanol.

that occurs upon placing the wet gels in ethanol, the spectra may be deconvoluted into separate components. The calculated Q distributions for a series of samples with different aging histories are given in table 2. For the ethanol–water sample, subsequent ethanol washing causes an increase in Q^3 at the expense of Q^4. The number of Si–O–Si bonds broken is essentially equal to the number which had been created during the water wash. (i.e., the alcohol–water–alcohol washing sequence reversibly depolymerizes–polymerizes–depolymerizes the gel matrix). For samples aged in ethanol and then aged in other alcohols (i.e., without a water wash), the Q distributions remain approximately the same. This might indicate that the observed increase in the xerogel surface area with increasing alcohol molecular weight is the result of different surface group size changing the 'roughness' of the pore surface as probed with adsorbed nitrogen. Alternatively, higher alcohols might cause the contact angle to increase, reducing the magnitude of the capillary pressure during drying.

Table 2
^{29}Si Q distributions for B2 xerogels aged and washed in different pore fluids

Washings	Q^2	Q^3	Q^4	BET surface area (m^2/g)
Mother liquor	2.6	38.3	59.1	510
Et–OH	2.5	38.0	59.0	958
Et–OH, H_2O	2.5	26.4	71.0	556
Et–OH, H_2O, Et–OH	5.5	41.2	53.3	993
Et–OH, Me–OH	4.5	39.1	56.4	952
Et–OH, nProp–OH	6.2	40.3	53.4	1109
Et–OH, H_2O, Me–OH	2.8	35.0	62.1	728
Et–OH, H_2O, nProp–OH	3.2	34.6	62.2	723

The Q distributions presented above provide the percentage of Q^2, Q^3 and Q^4 silicon species. In principle, one should be able to estimate the surface area knowing the surface coverage of these terminal groups and assuming that they reside on the pore surface. Q^2, Q^3 or Q^4 silicon have 2, 1 or 0 terminal groups respectively. We assume that the percentage of Q^0 and Q^1 is negligible in the xerogels (see fig. 7) and let x, y and z equal the mole fraction of Q^2, Q^3 and Q^4 ($x + y + z = 1$). For each Q^2 silicon there will be two bridging oxygens, for each Q^3 silicon, there are three bridging oxygens, each Q^4 silicon has four bridging oxygens, where each bridging oxygen is shared by two Si atoms. In order to calculate the surface area, the molecular structure must be determined, as is presented in table 3.

Using this approach with the Q distributions reported in table 2 and using literature values for the surface coverage [14], the surface area can be calculated. Figure 8 is a comparison of the surface areas calculated via this approach and the surface area obtained from BET analysis of nitrogen adsorption. Considering that the two meth-

Table 3
Molecular-structure specifications

The total amount of bridging oxygen is equal to $\frac{1}{2}(2x+3y+4z)$
Q^2 Si has two terminal groups, $2x$, (–OH, –OCH2CH3, ...)
Q^3 Si has one terminal group, y
Number of terminal Si groups is $2x+y$The total amount of oxygen, A, is the sum of the bridging and terminal:
$A=\frac{1}{2}(2x+3y+4z)+2x+y$
Total fraction of R(= H or C_xH_{2x+1}) is $B=2x+y$
The molecular structure is $Si_1O_AR_B$ from which the molecular weight (MW) is calculated, assuming for simplicity that the surface is either totally hydroxylated (water washed) or alcoxylated (alcohol washed). The number of terminal sites is found by multiplying B by Avogadro's number.
$SA(m^2/g)$ = (No. terminal sites) (SA/site)/MW

ods are completely independent, the level of agreement is encouraging. We observe that the 'Q' surface area is $\geqslant$ to the BET surface area. This is probably the result of surface area which is inaccessible to nitrogen at 77 K. The Q surface area measurement assumes that all terminal –OH or –OR groups reside on surfaces and thus does not distinguish between surface that is accessible or inaccessible to nitrogen. When the Q and BET surface areas agree, all the surface is accessible. When they do not agree, inaccessible surface exists, thus the Q surface area must be larger

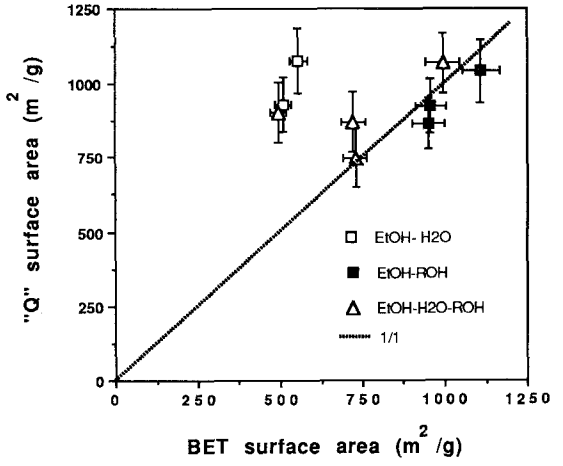

Fig. 8. Comparison of surface areas obtained from BET analysis (adsorption) and calculated from Q distributions (^{29}Si NMR).

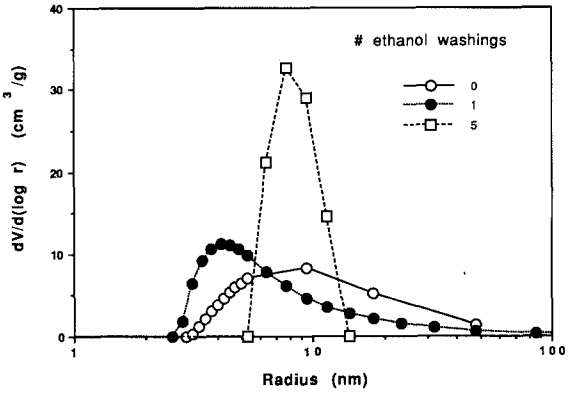

Fig. 9. Pore size distributions of gels washed in ethanol.

than the nitrogen surface area (as observed in fig. 8).

3.3. Effect of pore fluid on pore size distribution

In addition to wet gel surface area, low-field NMR can also be used to obtain pore size distributions of wet gels [9]. Figure 9 illustrates the pore size distribution as a function of the number of ethanol washings. The average pore radius is fairly constant, $\cong$ 7 nm; however, the width of the distribution decreases significantly as the number of washings increases. The large pore size for these extremely high surface area gels is a result of the high solvent content (i.e. wet pore volume) since the hydraulic radius (which we measure with NMR [10–12]) is equal to twice the pore volume–surface area ratio. Figure 10 illustrates the pore size distribution for samples aged in different numbers of ethanol baths before a final water bath. Similar to ethanol washing, an increased number of washes results in a significant narrowing of the pore size distribution but in addition, a change of the average pore size. The number of distribution points that were calculated varied from sample to sample depending upon the number of magnetization measurements performed.

The narrowing of the pore size distribution (PSD) may depend on aging time, pore fluid composition or both. Previously, we presented the NMR-derived PSD of a gel aged in its mother liquor (90% ethanol, 10% water) for different

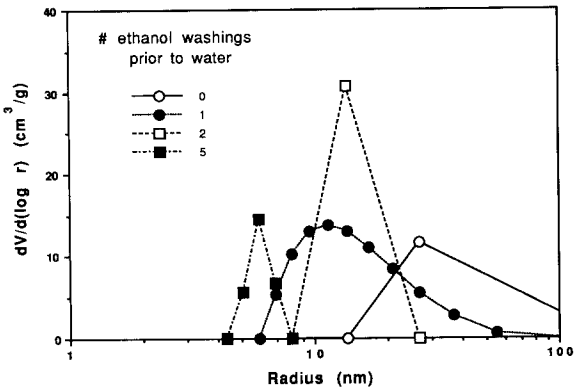

Fig. 10. Pore size distributions of gels placed in water after various numbers of ethanol washes.

time periods at 303 K. A narrowing of the PSD was observed over 3 weeks time [1]. However, this temporal aging, if considered separately, would be negligible on the timescale of these experiments. Thus the narrowing of the pore size distribution with ethanol washing is probably a result of the depolymerization and esterification reactions discussed previously.

Changes in the wet gel pore size distribution as it is placed in alternating 24 h ethanol and water baths are illustrated in fig. 11. Wet gels in ethanol typically have pore sizes in the range of 3 to 50 nm but when placed in water, the pore size increases to the 6 to 100 nm size range. As with the surface area results (for wet and dried gels) presented earlier, the trend is reversible between the ethanol and water baths and only seems to depend upon the final pore fluid.

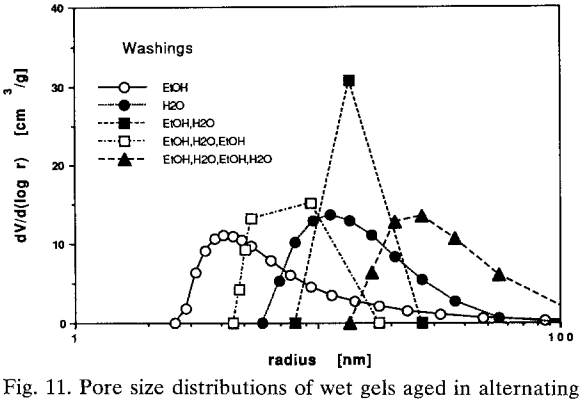

Fig. 11. Pore size distributions of wet gels aged in alternating water and ethanol baths.

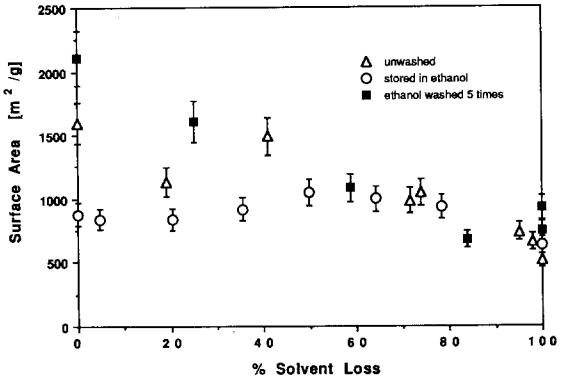

Fig. 12. Surface area evolution during drying.

3.4. *Surface area change during drying*

Since the gels undergo a large reduction in surface area from the wet state to the dry state, it is instructive to observe the change in surface area as a function of drying. Figure 12 illustrates the change in surface area for two samples dried from ethanol and one sample from mother liquor (labeled: unwashed). Figure 12 also includes the corresponding surface area of the fully dried xerogel as determined via N_2 adsorption/BET analysis (100% solvent loss). The unwashed sample and sample stored in ethanol are from previously reported work using the same gel but different aging times [9]. It is interesting to note that the unwashed sample and ethanol-stored sample indicate a maximum in surface area during drying in the vicinity of 50% solvent loss. This maximum was also observed in a previous study [9] using the same base-catalyzed gel. However, after five ethanol washes, the surface area exhibits a monotonic decrease during drying. For the first 50–75% of solvent loss, the gel remains saturated as it shrinks. The gel then stiffens and vapor–liquid menisci penetrate the gel leading to increased capillary forces.

4. Discussion

As a two-step acid–base-catalyzed silica gel is reversibly aged in either alcohol or water, the wet gel undergoes chemical and structural rearrange-

ments that influence the structure of the fully dried gel. The changes in wet surface area are apparently reversible and the final pore fluid is the dominant factor in establishing the wet and dry surface areas. Upon drying, much of this structure is preserved although a direct comparison is precluded by surface tension effects. The reason why the dry surface area is always lower may be the result of several factors. These include: (1) pore closure/collapse due to surface tension, (2) increased condensation reactions, and/or (3) the presence of low molecular-weight silica species in the pore fluid that condense on the silica surface during drying. However, from the deviations between the nitrogen and ^{29}Si NMR 'Q' surface areas, we conclude that water-dried samples have greater inaccessible surface area (possibly a result of the higher surface tension of water).

The larger pore volumes observed for gels dried from ethanol as compared to those dried from water are the result of several competing effects including (1) the lower surface tension of ethanol compared to water (which reduces capillary forces acting during drying, so less collapse of the network occurs), (2) changing wet gel pore size distribution, (3) changes in the contact angle as the nature of the pore surface changes, (4) the inability to maintain the same exact drying time–temperature profile for the different pore fluids, and (5) increased rates of syneresis and dissolution/reprecipitation in water which tend to stiffen the gel matrix retarding further shrinkage during drying.

We attribute the increase in surface area for the unwashed sample during drying at ~ 50% solvent loss to the continued reaction/condensation (and hence generation of surface area) of previously unreacted and partially reacted monomer contained in the pore fluid. This is consistent with our observation that unwashed gels turned opaque when immersed in water due to phase separation of monomer. Repeated ethanol washings prior to water immersion remove monomer and samples remain clear. Within the precision of the low-field NMR measurements, drying serves to continually reduce surface

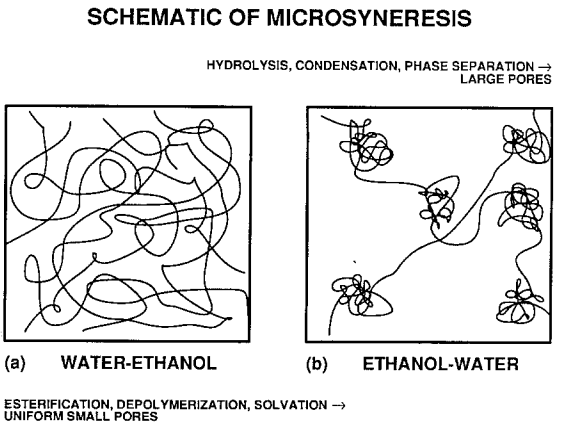

Fig. 13. Conceptual picture of gel structure changes when aged in either ethanol or water.

area, presumably by pore collapse and condensation of the gel network.

The observed changes in structure with pore fluid indicate that even at room temperature, alcohol can depolymerize the gel network in addition to simply esterifying surface SiOH groups. The overall alcohol–water aging process is illustrated in fig. 13. Aging in alcohol causes esterification and depolymerization of the network causing an increase in surface area. The less-highly condensed polymer can be solvated by ethanol resulting in a reduction in pore size and a narrowing of the pore size distribution. Aging in water has the reverse effect: hydrolysis of alkoxide groups is followed by condensation and phase separation, resulting in lower surface area, larger pores, and a broader pore size distribution. These processes occur reversibly in the wet state. Both the effect of pore fluid on phase separation and solvation, and the possibility of inaccessible surface are the subject of a current study using small-angle X-ray and neutron scattering (SAXS/SANS) [18].

5. Conclusions

Aging wet, base-catalyzed gels in alcohols causes significant structural rearrangement leading to larger surface area, smaller pore size, and

narrower pore size distribution as a result of both esterification of the pore surface and depolymerization of the gel matrix. These results are reversed when the gel is placed in water causing hydrolysis of surface alkoxy groups and polymerization. Upon drying, these effects of alcohol versus water aging are partially preserved. Surface areas calculated from ^{29}Si MAS-NMR present an upper bound on the total surface area and agrees well with nitrogen BET surface areas when all porosity is accessible.

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