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SURFACE STRUCTURE AND CHEMISTRY OF HIGH SURFACE AREA SILICA GELS

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Combined Raman and ^{29}Si NMR investigations of high surface area silica gels indicate that dehydroxylation of the a-SiO_2 surface results preferentially in the formation of cyclic trisiloxanes (3-membered rings). Estimates of the maximum experimentally observed concentration of 3-membered rings correspond to a surface coverage of about 28–58%. Two consequences of 3-membered rings on the a-SiO_2 surface are enhanced hydrolysis rates and increased skeletal densities.

1. Introduction

Silica gels prepared by the hydrolysis and condensation of metal alkoxide precursors followed by solvent evaporation (xerogels) or supercritical drying (aerogels) exhibit very high surface areas, typically 500–1000 m^2/g [1], over wide ranges of processing temperatures (room temperature to 1000 °C). In such high surface area silicates the percentage of surface silicons (Si_s) can easily exceed 50%. Therefore structural studies of bulk gels provide surface sensitive structural information. Correspondingly, the properties of bulk gels are dominated by the surface chemistry of the solid phase [2].

It has been stated that silica gels are 'special' [3], implying that structural information obtained from gels does not provide information pertinent to the surface structure of conventional amorphous silica (a-SiO_2). It can be argued that gel surfaces are less highly constrained than surfaces of a-SiO_2, allowing different configurations of terminating hydroxyl sites. However, Zhuravlev [4] recently determined the average OH coverage of over 100 amorphous silicates (prepared with Kr BET surface areas ranging from 9.5 to 950 m^2/g) to be 4.9 OH/nm^2 with all values falling between 4 and 6 OH/nm^2. The single measurement made on a gel prepared by the hydrolysis and condensation of a metal alkoxide (BET area = 500 m^2/g) resulted in an OH coverage value of 4.2 OH/nm^2. Considering the hydroxyl coverage to be a 'structural probe', Zhuravlev's results indicate that the silica gel surface is not so special. Therefore a thesis and a motivation of the present work is that information derived from our structural studies of bulk gels is relevant to the topic, 'Physics and Chemistry of Glass Surfaces'.

This paper first reviews Raman and NMR studies that relate the increasing relative intensity of the 608 cm^{-1} Raman 'defect' band with the formation of cyclic trisiloxanes (3-membered rings) during gel dehydroxylation above 200 °C and provides an estimate of the maximum surface concentration of 3-membered rings. Then, several structural models that accomodate 3-membered rings are discussed and the consequences of 3-membered rings on chemical and physical properties are commented on.

2. Experimental

Silica gels were prepared from $Si(OC_2H_5)_4$ using the two-step acid/base-catalyzed hydrolysis procedure described in ref. [5]. The gels were dried by evaporation at 50 °C to produce porous xerogels (BET surface area $\approx$ 1000 m^2/g). The xero-

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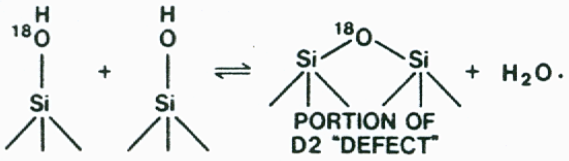
gels were dehydroxylated in oxygen or vacuum at temperatures ranging from 200–650 °C or fully consolidated to dense a-SiO_2 at 1100 °C. After heating, the porous specimens were cooled to room temperature and maintained under very dry conditions for the first set of Raman, solid-state ^{29}Si magic angle sample spinning (MASS) NMR, ^{1}H cross polarization (CP) MASS NMR and XPS experiments. In some cases, additional spectra were collected after exposure of the porous gels to water vapor. The instrumentation and experimental procedure for the Raman, NMR and XPS experiments are outlined in the authors' previous publications [6,7].

3. Results and discussion

3.1. Evidence for 3-membered rings

Changes of the silicate framework structure resulting from dehydroxylation are evident from the series of Raman spectra shown in fig. 1. The most dramatic change attributable to framework vibrations is the behavior of the ~608 cm^{-1} band labeled D2: it is absent after drying at 50 °C; it appears at 200 °C, becomes quite intense at 600 °C, and is reduced in relative intensity in the fully consolidated gel to a level comparable to conventional a-SiO_2 (fused silica spectrum, fig. 1(e)). Previous Raman studies using isotopically labeled oxygen have shown that during dehydroxylation the relative intensity of the D2 band increases at the expense of the ~3740 and 980 cm^{-1} bands (assigned to SiO–H and Si–OH stretching, respectively) and that the D2 structure forms preferentially on the silica surface by condensation reactions involving isolated vicinal silanol groups [8]:



The inverse relationship between silanol coverage and the relative intensity of the D2 band is well-illustrated in fig. 2, which compares the Raman spectrum of a gel heated to 650 °C in oxygen (1 h)

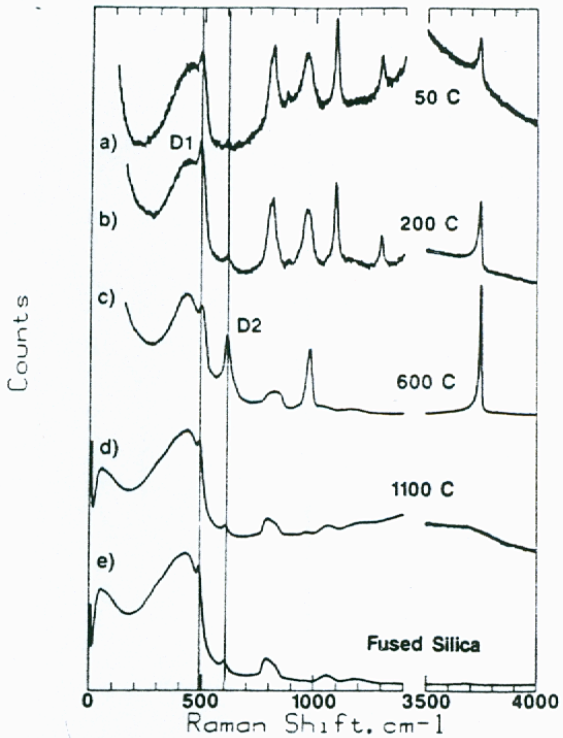


Fig. 1. Raman spectra of SiO_2 gels dried at 50 °C, heated to 200 or 600 °C, or fully consolidated at 1100 °C.

to the spectrum of a gel heated 1 h in oxygen followed by 24 h in vacuo (~ 7×10^{-8} Torr). Fig. 2 clearly shows that the relative intensity of the

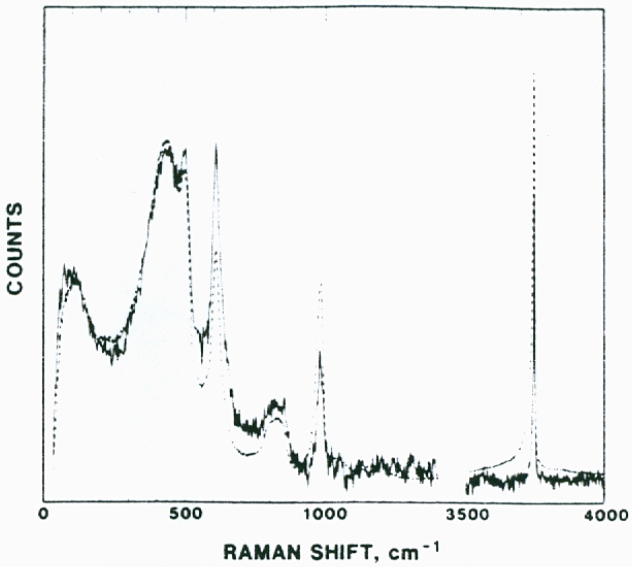


Fig. 2. Raman spectra of a silica gel heated to 650 °C in oxygen for 1 h (dashed line) or heated to 650 °C in oxygen for 1 h followed by 24 h at 650 °C in vacuo (7×10^{-8} Torr) (solid line).

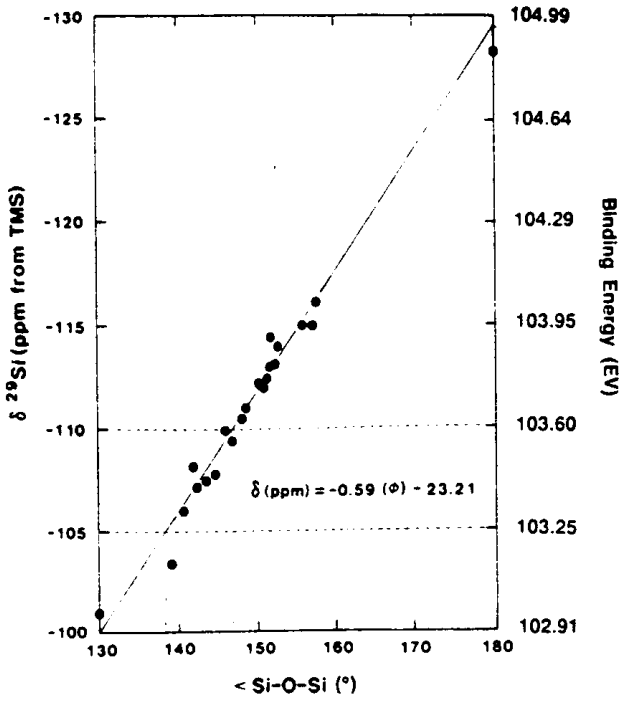


Fig. 3. ^{29}Si chemical shift δ and Si 2p binding energies versus Si–O–Si bond angle. Points are the measured δ ^{29}Si chemical shifts for crystalline silicates with known values of ϕ [9]. BE scale was established by Devine [24] for Si in $Si–Si_{4-m}O_m$ environments.

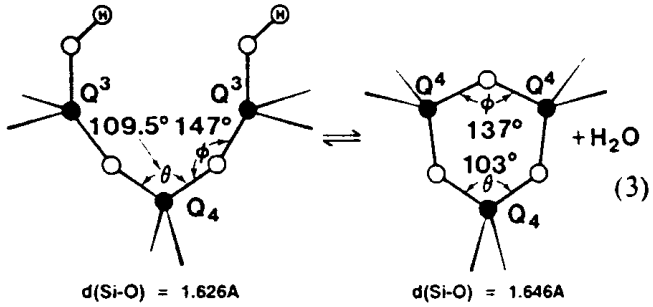
D2 band increases at the expense of the 980 and 3740 cm^{-1} bands, consistent with eq. (1).

^{29}Si MASS NMR studies [9] have associated the increased relative intensity of the D2 band with a reduction in the average Si–O–Si bond angle, ϕ, from the relationship between ϕ and the ^{29}Si chemical shift, δ, of Q^4 sites *:

$$\delta(\text{ppm}) = -0.59(\phi) - 23.21, \qquad (2)$$

(correlation coefficient = 0.982) where ϕ is the average of the four Si–O–Si angles per Q^4 site (see fig. 3). As shown in fig. 4, increasing the dehydroxylation temperature from 200 to 600 °C, which causes a dramatic increase in the relative intensity of the D2 band (fig. 1), causes a broadening of the envelope of silicon resonances and a shift of the Q^4 peak from about −110 to −107 ppm corresponding to a reduction in the average value of ϕ from about 148 to 142°, according to eq. (2). Statistically acceptable deconvolution of the 600 °C spectrum, using peak positions of −91 and −101 ppm for Q^2 and Q^3 sites can be performed with various combinations of numbers of peaks, peak intensities, and peak breadths. All of these deconvolutions, however, require a peak at about −105 ppm, which is evident from comparisons of the 200 and 600 °C CP MASS * spectra (fig. 4). Because Q^2 and Q^3 sites are not known to resonate in this chemical shift range, this additional peak must be due to a second Q^4 site with a small ϕ value: −105 ppm corresponds to ϕ = 137°. Exposure of the 600 °C sample to water vapor or consolidation of the gel at 1100 °C reduces the relative intensity of the D2 band to that of conventional a-SiO_2 (see, e.g., fig. 1(e)). In both cases, the reduced intensity of D2 is accompanied by a narrowing of the Q^4 resonance and a shift of the peak position back to its original value in the 200 °C sample (−110 ppm).

The NMR and Raman data unambiguously associate the formation of the species responsible for the D2 band with the presence of Q^4 silicon sites, which have reduced values of ϕ, and conversely the elimination of this species with an increase in ϕ. These observations are consistent with Galeener's assignment of the D2 band to the oxygen ring-breathing vibrational mode of cyclic trisiloxanes (3-membered rings) in conventional a-SiO_2 [10]. In silica gels and other high surface area silicates formed in solution, 3-membered rings are absent after drying at low temperatures. They form at intermediate temperatures (about 200–800 °C), predominantly on the silica surface, by condensation of isolated vicinal silanol groups located on unstrained precursors via the following reaction [6]:



(3)

* In Q terminology the superscript (0–4) is the number of bridging oxygens surrounding the central silicon nucleus.

* In the ^1H CP MASS spectra, the resonances of silicon species in close proximity to H (Q^2 and Q^3 species) are increased in relative intensity compared to Q^4 resonances.

MO calculations of the optimized 3-membered ring structure (right side eq. (3)) indicate that the reduction in the Si–O–Si bond angle, ϕ, is accompanied by a reduction in the tetrahedral angle, θ (from 109.5 to 103°), and an increase in the Si–O bond length, d (from 1.626 to 1.646 Å) [11]. The broadening of the envelope of Q^4 resonances toward more negative chemical shift values in the 600°C MASS and ^1H CP MASS spectra (fig. 4) suggests that, due to connectivity constraints of the 4–2 network, the formation of 3-membered rings may require an increase in the average values of ϕ for some of the remaining larger rings.

3.2. Surface coverage of 3-membered rings

We reasoned that a determination of the maximum coverage of 3-membered rings on the silica surface should provide insight into surface structure and reactivity. Various decompositions of the MASS spectrum of the vacuum annealed 650°C sample * (which exhibited the largest experimentally observed D2 band, fig. 2) required a second Q^4 resonance at −105 ppm whose area corresponded to about 19–39% of the total silicons ($Si_{c3}/Si = 0.19–0.39$). By assuming that all of the 3-membered rings are located on the silica surface (measured BET surface area = 840 m^2/g), the surface coverage of 3-membered rings is calculated as follows:

$$[0.19–0.39\ Si_{c3}/Si] \times [6.02 \times 10^{23} Si/60.084\ g\ SiO_2] \times [1\ g\ SiO_2/840 \times 10^{18}\ nm^2] = 2.2–4.5\ Si_{c3}/nm^2.$$

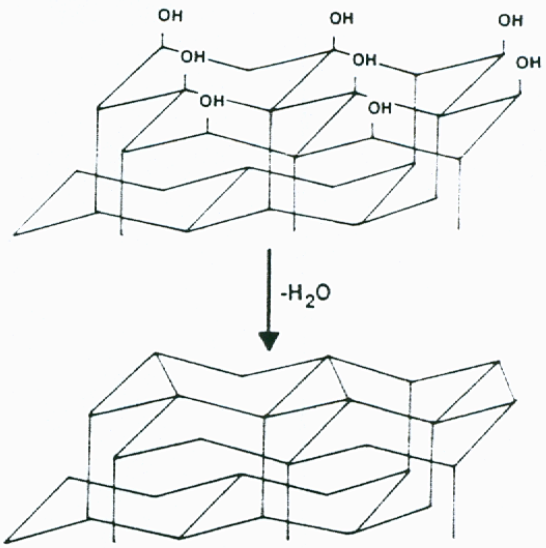
* Due to the overlap of the Q^3 and Q^4 peaks in the 650°C spectrum, spectral decomposition requires some assumptions regarding the peak positions, peak intensities (areas), and peak widths. By fixing the Q^2, Q^3, and Q^4 peak positions at −91, −101, and −110 ppm and FWHM at 10 ppm, the area of the −105 ppm peak equalled 0.19, but the Q^3 area was unrealistic (0.39). By fixing the area of the $Q^2 + Q^3$ peaks at 0.17 corresponding to ~75% dehydroxylation of the surface [2] (assuming OH to reside exclusively on the surface) and increasing FWHM to 15 ppm to account for the broader envelope of ^{29}Si NMR resonances, the area of the −105 ppm peak increased to 0.39 with an equally good fit to the data.

Since there are 7.8 silicons/nm^2 of a-SiO_2 surface [2], approximately 28–58% of the surface silicons are contained in 3-membered rings.

3.3. Structural models

In order to reconcile the large surface coverage of Si_{c3}, it is useful to consider several 'crystalline' models of the a-SiO_2 surface involving 6-membered rings. Based on the close correspondence of the OH coverage of the ⟨111⟩ face of β-cristobalite (4.55 OH/nm^2) with that of a-SiO_2(4.9 OH/nm^2) and their similar bulk densities, viz. 2.2 g/cm^3, β-cristobalite has often been used as a structural model of the a-SiO_2 surface. DeBoer and Vleeskins [12] and Hockey [13] proposed models involving the ⟨111⟩ face. Sindorf and Maciel [14] have proposed a mixed-surface model comprising regions of ⟨111⟩ and ⟨100⟩ faces to account for the presence of both Q^3 and Q^2 silanols.

Dehydroxylation of the β-cristobalite ⟨111⟩ face results in equal numbers of 3-, 5-, and 6-membered rings according to the following scheme:



The precursor structure (top) is unstrained, and the 3-membered rings formed by dehydroxylation are composed exclusively of Q^4 silicon species, consistent with experiment. Two OH groups are consumed per 3-membered ring; therefore the maximum coverage of Si_{c3} resulting from dehy-

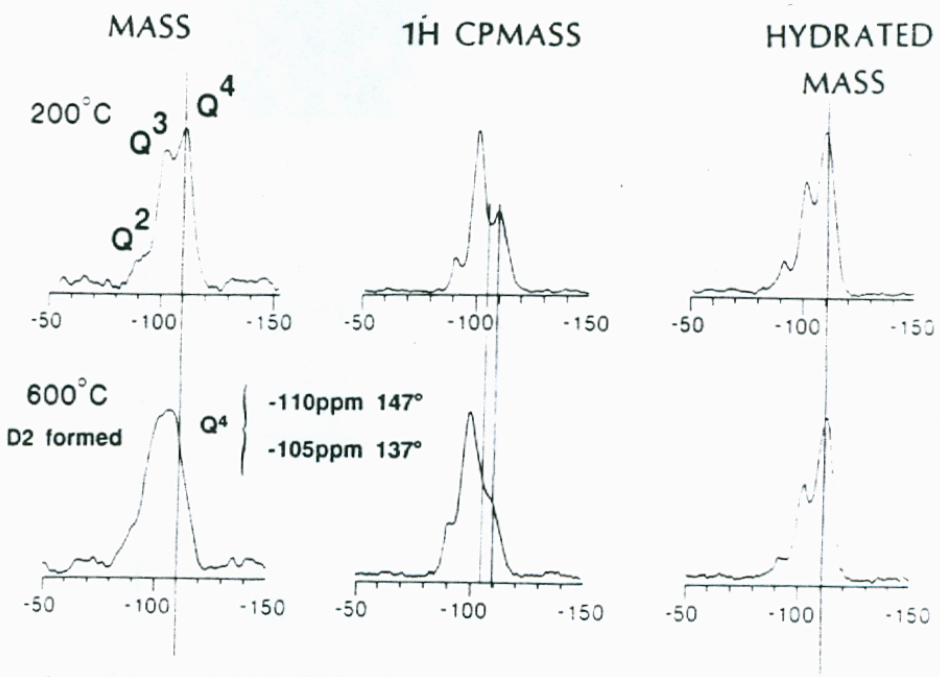


Fig. 4. ^{29}Si MASS and ^{1}H CP MASS spectra of gels dehydroxylated at 200 or 600 °C (as in fig. 1) and ^{29}Si MASS spectra of the heated and rehydrated gels (24 h exposure to 100% RH water vapor).

droxylation of the β-cristobalite $\langle 111 \rangle$ face is [4.55/2 3-membered rings/nm^2] × [3 Si_{c3}/3-membered ring] = 6.9 Si_{c3}/nm^2, exceeding the range of values observed experimentally at 650 °C (2.2–4.5 Si_{c3}/nm^2) by a factor of 1.5–3. Since the extent of dehydroxylation of the silica gel surface at 650 °C is estimated to be $\geq 75\%$ [4], complete dehydroxylation of the silica gel should result in a maximum surface coverage ≤ 6 Si_{c3}/nm^2 (4.5 Si_{c3}/nm^2 × 4/3). Thus it is not necessary to invoke a pure $\langle 111 \rangle$ β-cristobalite surface model to account for the observed concentrations of 3-membered rings. This concentration of rings could perhaps be accomodated by dehydroxylation of 6-membered rings present on the terminating surface of a continuous random network * or by dehydroxylation of the mixed $\langle 111 \rangle / \langle 100 \rangle$ β-cristobalite surface [14].

* Of course 3-membered rings can form from a variety of precursor structures in a continuous random network (CRN); however 6-membered rings which are abundant in a CRN are obvious precursors for 3-membered rings according to the above scheme.

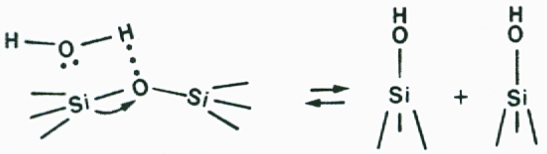
3.4. Consequences of 3-membered rings

The pseudo-first-order hydrolysis rate constant of 3-membered rings on the dehydroxylated gel surface, $K = 5.2(\pm 0.5) \times 10^{-3}$ min^{-1} [15], is comparable to the hydrolysis rate constant of the model compound, hexamethylcyclotrisiloxane ($K = 3.8 \times 10^{-3}$ min^{-1} [16]) and more than 75 × greater than the hydrolysis rate constant of unstrained a-SiO_2 [17]. Since hydrolysis occurs by

Table 1
Mulliken charges on oxygen in $(HO)_6Si_2O$ calculated by Gibbs [19] at the 6-31G* level for various Si–O–Si bond angles and Si–O bond lengths

ϕ	d (Si–O), Å			
	1.592	1.602	1.622	1.642
120°			−0.945	
130°			−0.930	
140°			−0.920	
150°	−0.880	−0.890	−0.909	−0.926
170°			−0.880	

water adsorption followed by dissociative chemisorption [18]:



Either of these steps could be rate determining. Based on studies of highly-strained, 2-membered rings, Bunker et al. [17] concluded that the initial adsorption step is rate-limiting. The subsequent dissociative step is very rapid, presumably due to the ring strain. They argue that the enhanced hydrolysis rate results from greater accessibility of nucleophilic oxygen to the silicon nucleus and/or altered acid/base properties of the siloxane bond due to the ring strain.

The manner in which acid/base properties change with ring strain is disputed on theoretical grounds. Molecular orbital calculations performed by Gibbs [19] on $(HO)_6Si_2O$ at the 6–31G* level (see table 1) indicate that the Mulliken charge on the bridging oxygen increases as ϕ is reduced and d is increased (increased oxygen basicity with ring strain, increased siloxane bond ionicity). Consistent with this result, calculations by Tossell [20] using the quantum mechanical technique of a coupled Hartree–Fock perturbation theory [21] on 2- and 3-membered rings ($H_4Si_2O_2$ and $H_6Si_3O_3$) show that the Si 2p binding energy increases and the O 1s binding energy decreases as ϕ is reduced from 133° to 91°. However, calculations based on a tight binding formalism (see, e.g., refs. [22,23]) show the opposite dependence of siloxane bond ionicity on ϕ: as shown in table 2, ionicity decreases as ϕ is reduced and d is reduced [23]. A trend of decreasing ionicity with decreasing ϕ

Table 2
Siloxane bond ionicities calculated by Hollinger et al. [23] for various Si–O–Si bond angles and Si–O bond lengths

ϕ	d (Si–O), Å			
	1.58	1.61	1.65	1.70
132°	0.44	0.449	0.461	0.471
144°	0.461	0.467	0.488	0.494
156°	0.498	0.508	0.504	–
168°	0.529	0.536	–	–

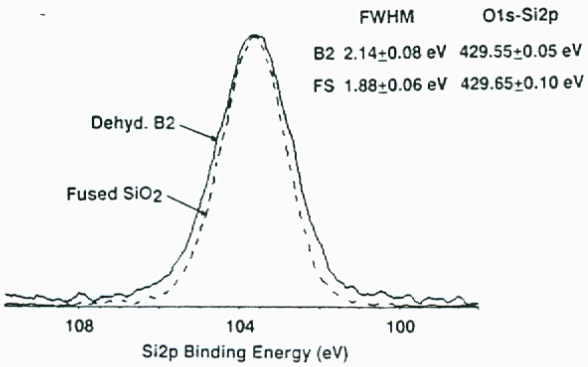


Fig. 5. Si 2p spectrum of a silica gel (B2) after heating to 650°C for 24 h in vacuo and fracturing in vacuo compared to that of conventional a-SiO_2 (FS) fractured in vacuo.

appears to be consistent with the ^{29}Si NMR results obtained for dehydroxylated gels (fig. 4) and silicon nuclei in $Si–Si_{4-m}O_m$ environments [24]: both the formation of 3-membered rings and replacement of oxygen with silicon on $Si–Si_{4-m}O_m$ (reduced ionicity) cause the Q^4 resonance to shift toward less negative values.

The possible altered electronic environments of silicon and oxygen that result from the formation of 3-membered rings should influence not only the ^{29}Si NMR chemical shifts but also the Si 2p and O 1s binding energies (BE). In order to estimate the magnitude of the expected shift in BE, fig. 3 shows the Si 2p binding energy as a function of ϕ based on the linear relationship established by Devine [24] for Si in $Si–Si_{4-m}O_m$ environments, $-d(\delta)/d(BE) \approx 14.4$ ppm/eV. The BE scale in fig. 3 associates the most common ϕ in a-SiO_2 (147°) with the authors' most commonly measured BE for a-SiO_2 (103.6 eV). From fig. 3 it is seen that a reduction in ϕ of 9° is predicted to result in a 0.35 eV reduction in Si 2p BE.

Figure 5 compares the Si 2p XPS spectra of conventional a-SiO_2 and a silica gel dehydroxylated at 650°C and fractured in vacuum. The gel exhibits a broader envelope of Si 2p BE (FWHM $= 2.14 \pm 0.08$ eV compared with 1.88 ± 0.06 eV) consistent with the broad ^{29}Si NMR envelope, presumably due to the more varied environments of silicon in the dehydroxylated, high surface area gel than in a-SiO_2. However, comparisons of the O 1s and Si 2p peak positions indicate that XPS is not sufficiently sensitive to resolve the ionicity

issue: O 1s–Si 2p = 429.55 ± 0.05 eV for the gel compared with 429.65 ± 0.10 eV for conventional a-SiO_2. Therefore the 0.07 eV shift ($Si_{c3}/Si \times 0.35$ eV) expected from theory [24] falls within the uncertainty of the measurement.

Studies employing photochemical probe molecules adsorbed on the silicon surface provide indirect evidence of the altered acid/base properties resulting from the formation of 3-membered rings. DeMayo et al. [25] find that the most inhomogeneous silica surface, as judged by multiple exponential decay of pyrene probe molecules, is that which results after heating to 700 °C. Subsequent adsorption of water renders the surface much more homogeneous. This is consistent with a partially dehydroxylated surface at 700 °C comprising Q^2, Q^3, and two different Q^4 sites with quite different acid/base character. The main effect of water adsorption is elimination of strained Q^4 sites (fig. 4), suggesting that these sites are largely responsible for the surface inhomogeneities.

In addition to altered chemical properties, the formation of 3-membered rings appears to be correlated with a change in density of the silica skeleton [26,27]. Figure 6 shows the skeletal density of an acid-catalyzed silica gel as a function of temperature during a constant heating rate experiment. Above 500 °C, the skeletal density exceeds the density of conventional a-SiO_2 and reaches a maximum value within a temperature range where we find the concentration of 3-membered rings to be maximized. Heating to higher temperatures promotes viscous sintering [1], eliminating most of the 3-membered rings [6] and reducing the skeletal density to that of conventional a-SiO_2. Similar results were observed by Vasconcellos and coworkers [27]. These results are consistent with studies of neutron compacted a-SiO_2: exposure of a-SiO_2 to an integrated flux of > 10 eV neutrons of $10^{20}/cm^2$ causes a dramatic increase in the relative intensity of the D2 band (10 ×) [28] accompanied by an increase in skeletal density of ~ 5%, apparently due to the formation of denser, 3-member rings at the expense of larger rings [29].

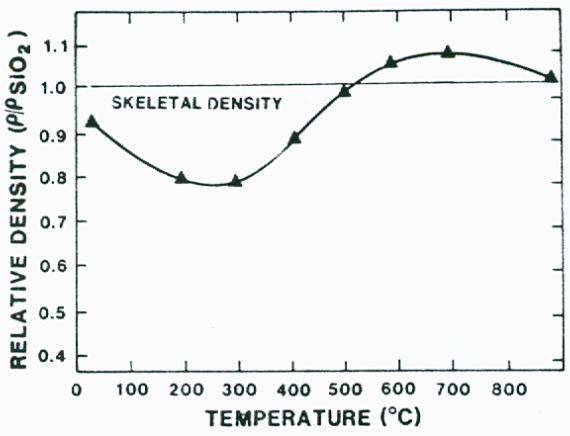


Fig. 6. Skeletal density of a silica gel versus temperature for a constant heating rate of 1 °C/min.

4. Summary

Due to their high surface areas (generally > 500 m^2/g), structural studies of bulk gels provide surface sensitive information that is pertinent to all a-SiO_2 surfaces. Raman and ^{29}Si NMR studies indicate that dehydroxylation of the silica surface above 200 °C results in the formation of strained, cyclic trisiloxanes (3-membered rings). Estimates of the maximum experimentally observed concentration of 3-membered rings correspond to approximately 2.2–4.5/nm^2 or incorporation of about 28–58% of the surface silicons in 3-membered rings. Although 6-membered rings are obvious precursors for 3-membered rings, the experimentally observed concentration of 3-membered rings is less than expected from dehydroxylation of the ⟨111⟩ face of β-cristobalite, arguing against pure ⟨111⟩ β-cristobalite as an appropriate structural model of the a-SiO_2 surface. Instead this concentration of 3-membered rings could perhaps be accommodated by dehydroxylation of a continuous random network or a mixed ⟨111⟩/⟨100⟩ cristobalite surface. Consequences of 3-membered ring formation are enhanced hydrolysis rates and greater skeletal densities. Conventional XPS is not sufficiently sensitive to detect possible altered acid/base properties resulting from ring strain, suggesting future experiments employing monochromatic or synchrotron energy sources.

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