

# Hydroxylation and Dehydroxylation Behavior of Silica Glass Fracture Surfaces

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**The hydroxylation and dehydroxylation behavior of amorphous silica fracture surfaces was studied using temperature-programmed static SIMS. The results show that vacuum heat treatments result in more extensive condensation of silanol groups on the silica glass fracture surface as compared to fumed silica (Cabosil). This is attributed to differences in the distribution of silanol groups on the two silica surfaces. The rehydration kinetics of the dehydroxylated silica fracture surfaces showed two distinct reaction rates—an initial rapid increase in the silanol concentration, followed by a slower rehydration for longer dosing times. The slower rehydration reaction was shown to follow first-order reaction kinetics with the reaction rate constant, suggesting hydrolysis of strained siloxane bonds on three-membered silicate ring structures. The much faster initial rehydration is attributed to the hydrolysis of extremely strained siloxane bonds in two-membered, edge-shared tetrahedral rings. The effect of the dehydration time and temperature (i.e., thermal history of the surface) on the rehydration kinetics is also discussed.**

## I. Introduction

THE surface properties of silica are important in many fields including photonics, microelectronics, catalysis, soil chemistry, and chromatography. In addition, because silica is the dominant component in most multicomponent glasses, a detailed understanding of the chemistry of silica surfaces can also impact our understanding of the surface chemistry of many different commercial glass products, including substrates for flat panel displays, optical coatings, and biological sensors. More generally, surface chemistry has a significant effect on the strength, chemical durability, optical quality, and adhesion properties of silica and alkali-silicate glasses. Surface chemical phenomena can result in compositional as well as structural changes at the glass surface, which may significantly alter the properties of the glass. For example, during the formation of a surface, the glass will minimize the number of high-energy surface sites by modifying its surface composition through atomic rearrangement. A glass surface exposed to the ambient environment will minimize high-energy surface sites such as strained bonds by adsorbing water from the atmosphere. In general, though, most silicate glass surfaces are expected to acquire a hydrated surface layer. The kinetics of this hydration depend on the bulk glass composition and thermal history of the surface.<sup>1</sup> In the end, it is the concentration and

distribution of surface hydroxyl groups that control the adsorptivity of the glass surface under any given set of conditions.

Thus, one of the major issues of concern in surface studies of glasses is the degree of hydroxylation of the surface. Silanol (Si–OH) groups on silica surfaces have been extensively studied in the past several decades; however, the majority of these studies have been conducted on high-surface-area porous silica gels and powders. This is because for bulk glasses (with low specific surface area), the absolute concentration of surface hydroxyl groups is too low to meet the signal sensitivity requirements of most analytical techniques. High-surface-area silica gels and powders allow the use of spectroscopic techniques such as FTIR, Raman, and NMR to detect surface silanol groups. But there are several factors that must be considered to relate the studies of high-surface-area silica to silica glass surfaces.

Surface chemistry studies have been conducted on a variety of different silica surfaces including dried gels, precipitated silicas, and fumed silica powders, and which have been processed by a number of different chemical, mechanical, and thermal procedures. Since the structure and reactivity of the silica are strong functions of the thermal and chemical history of the sample, it is not surprising that there are numerous inconsistencies in the results that have been reported for these different silicas. For example, variations in pore size, shape, and geometry between different silica powders and gels have been shown to affect the water adsorption and desorption kinetics of these surfaces. Similarly, the processing of silica glass fibers may create reactive surface sites that do not even exist on high-surface-area silicas. And in studies of polymer adhesion to silica glass, where direct correlation with the processing history of the glass surface is desired, it is necessary to probe the bulk silica glass surface directly. In light of these issues, it is apparent that the results obtained from studies on silica gels and powders may not fully reflect the surface structure and reactivity of planar, nonporous, low-specific-surface-area silica glass surfaces.

The intent of this work is to describe the hydroxylation/dehydroxylation behavior of planar, silica glass surfaces directly, and in addition, to compare these results to those obtained for high-surface-area silica (Cabosil) treated in a similar way (in this study and also reported in the literature). Kinetic data on the dehydration and rehydration of heat-treated silica surfaces are included, and are interpreted in terms of the distribution of silanol groups and the nature of the strained siloxane bonds at the silica surface.

Very little work has been reported about methods to quantitatively measure silanols on low-surface-area amorphous silicas or multicomponent glasses. X-ray photoelectron spectroscopy (XPS) has been used in the past to study silanol groups on low-surface-area planar samples by using special peak deconvolution algorithms<sup>2</sup> or by chemical derivatization techniques to tag the silanol groups.<sup>3</sup> However, both of these methods are based on indirect measurement of the silanol groups, which can pose problems for some analyses. A few previous studies have shown that static SIMS and related techniques are sensitive to the presence of silanols on low-surface-area silicas, and hence provide a means for the direct measurement of the surface silanol concentration.<sup>4–6</sup>

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Sneh and George used laser-induced thermal desorption (LITD) and temperature-programmed desorption (TPD) to study the hydroxyl coverage of well-defined thermally oxidized Si (100) surfaces.<sup>7</sup> They found a good correlation between the concentration and thermal stability of silanol groups on the planar silica surfaces with values obtained in previous studies using high-surface-area silica gels and powders.

In this work, temperature-programmed static SIMS has been used to measure the surface silanol concentration of various silica glass samples as a function of various heat treatment and hydration conditions. Most of the experiments were performed on vacuum-fractured surfaces. Vacuum-fracture surfaces provide a convenient method to create a reproducible, contaminant-free surface on which subsequent heat treatment and/or water adsorption experiments could be conducted. Silica surfaces created in vacuum by fracture are ideal "models" for studying the molecular-level relaxation/rearrangement processes that take place at silica surfaces during and after the propagation of a crack tip. These surfaces can also be used to follow the evolution of glass (melt) surfaces at high temperatures, and the changes they undergo during exposure to the ambient atmosphere.

## II. Experimental Procedure

In this study, fused silica rods were used. The silica rods were 6.35 mm diameter, high-purity amorphous silica rods (Suprasil 2) obtained from Heraeus Amersil. These rods were cut into 25.4 mm long pieces and were notched to produce smooth "mirror regions" during fracture. The rods were cleaned by sonicating in acetone and methanol before fracturing. The silica rods were subsequently fractured either in air or under vacuum. All of the subsequent analyses were performed on the fracture surfaces.

The fracture of the silica rods under vacuum was performed in the preparation chamber of the two-chamber UHV system. The preparation chamber contained a fracture stage for *in vacuo* fracturing of samples, a gas doser for exposing the surface to ultra-high-purity H<sub>2</sub>O, and a quadrupole mass spectrometer for monitoring the gas purity. The base pressure of the preparation chamber was  $1 \times 10^{-8}$  torr ( $1.3 \times 10^{-6}$  Pa). After pumpdown of the chamber to its base pressure, water vapor was introduced into the chamber through the variable leak valve to the desired partial pressure, ranging from  $1 \times 10^{-7}$  torr ( $1.3 \times 10^{-5}$  Pa) to 10 torr (1333.2 Pa). The sample was then fractured and the fracture surface exposed to water vapor for the desired amount of time. The system was then pumped back down to the base pressure and the sample transferred to the analysis chamber.

The static SIMS analyses were performed in the analysis chamber of the UHV system described above. The base pressure of the analysis chamber was  $1 \times 10^{-9}$  torr ( $1.3 \times 10^{-7}$  Pa). A Kratos Mini Beam I gun was used to produce a fast atom beam (FAB) source. This gun produces a neutral atom beam by resonant charge exchange of a noble gas ion beam with the background gas. The use of a neutral beam eliminates the charging problems normally encountered during the analysis of insulators. Ultra-high-purity argon gas was used for the ion/neutral beam generation. The typical operating parameters for the gun were 2 keV beam energy and 10 nA/cm<sup>2</sup> current density. The analyzer used was an Extranuclear quadrupole mass spectrometer tuned to the positive ion spectrum. The analyzer chamber was also equipped with a boron nitride coated graphite heater which allowed the sample to be heated up to 800°C and also allowed for static SIMS spectra to be collected at elevated sample temperatures. All of the static SIMS spectra discussed in this paper were collected either at room temperature or at a sample temperature of 200°C as a function of time. For most experiments, spectra were collected only for the peaks of interest, namely, *m/z* 28, 29, 30 (Si<sup>+</sup> isotopes), 44 (SiO<sup>+</sup>), and 45 (SiOH<sup>+</sup>), to minimize the acquisition time. A detailed description of the UHV system and the experimental procedures used in this study are given elsewhere.<sup>8,9</sup>

## III. Results

Figure 1 plots the SiOH<sup>+</sup>/Si<sup>+</sup> peak area ratios and the silanol concentration for a silica surface created under vacuum at  $1 \times 10^{-9}$  torr ( $1.3 \times 10^{-7}$  Pa) as a function of time after fracture. The silanol concentration was calculated from the normalized SiOH<sup>+</sup>/Si<sup>+</sup> peak area ratios obtained from the corresponding SIMS spectra. The quantification of the SiOH<sup>+</sup>/Si<sup>+</sup> peak area ratios to obtain the corresponding silanol concentrations has been explained in detail in previous publications.<sup>8,9</sup> It can be seen that the surface silanol concentration initially increases with time before stabilizing at about 2.6 OH/nm<sup>2</sup>. This initial gradual increase in the silanol concentration with time has been attributed to the time required for the adsorption of water on the silica surface to reach equilibrium at a pressure of  $1 \times 10^{-9}$  torr ( $1.3 \times 10^{-7}$  Pa).<sup>10</sup> It has also been shown that the equilibrium silanol concentration of 2.6 OH/nm<sup>2</sup> obtained is the number of silanol groups required to hydrolyze all of the strained siloxane bonds that form on a reconstructed vacuum fracture surface.<sup>10</sup>

The silanol concentrations as a function of heat treatment temperature under vacuum for a silica vacuum fracture surface and for a fumed silica powder (Cabosil) are plotted in Fig. 2. The silanol concentrations were measured after a 12 h hold at the temperature of interest in the vacuum system. It can be seen that although both silica surfaces show comparable silanol concentrations after heat treatments to 200°C, the condensation of silanol groups occurs at lower temperature on the fracture surface. This difference in dehydroxylation behavior between the Cabosil powder and the fracture surface may be due to kinetics, but more likely reflects differences in the surface structure (distribution of silanol groups, degree of strain of the siloxane bonds, etc.) between the two silicas. This effect will be examined in more detail in the next section.

Figure 3 compares the rehydration kinetics for silica fracture surfaces dehydrated at 500°C for 20 h under vacuum for different dosing pressures of water vapor. The plot shows that the equilibrium silanol concentration of the fracture surface has decreased substantially after the heat treatments relative to the vacuum fracture surface. It can be seen that for all of the dosing pressures, the rehydration kinetics can be differentiated into two distinct parts: an initial rapid increase in the silanol concentration, followed by slower rehydration kinetics for longer dosing times. The

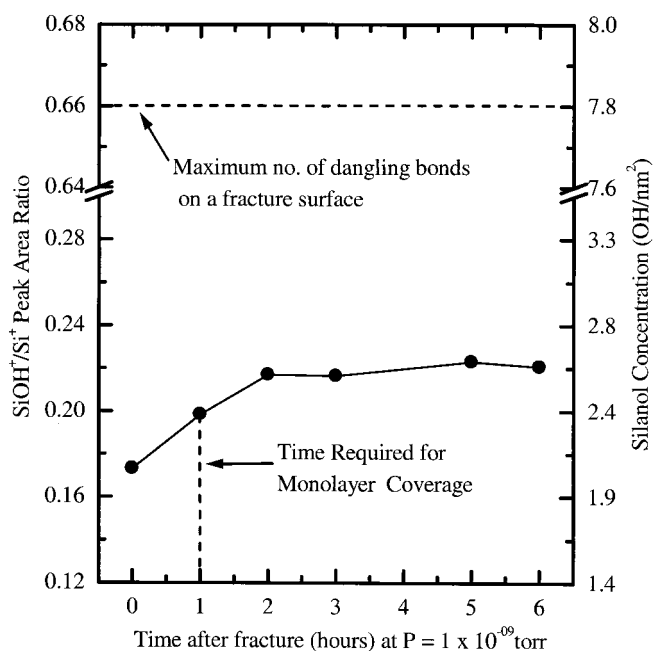
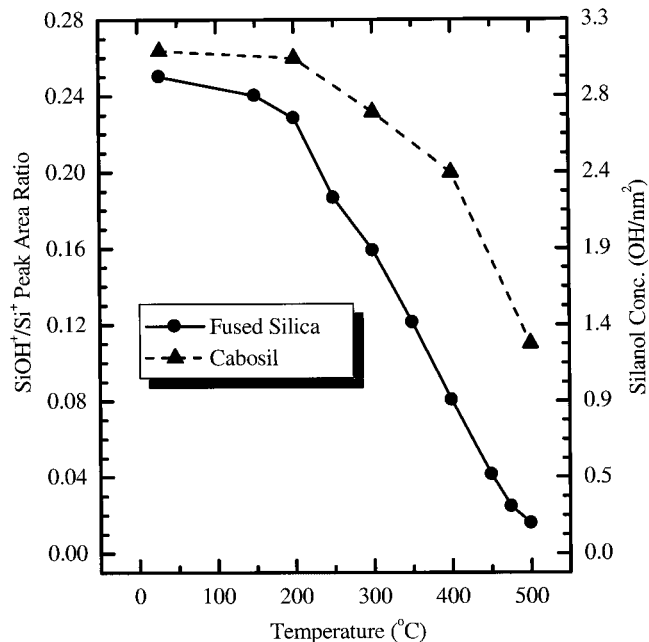


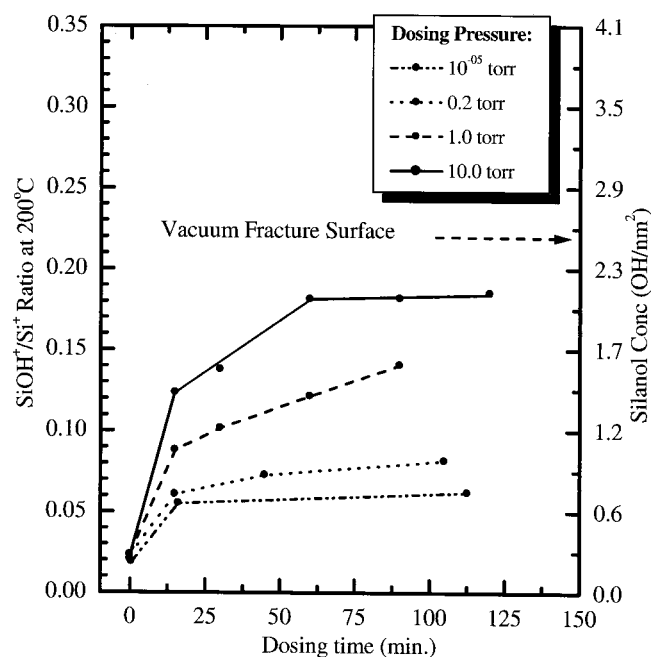
Fig. 1. Silanol concentration vs "time after fracture" for a silica glass fractured under vacuum at  $1 \times 10^{-9}$  torr ( $1.3 \times 10^{-7}$  Pa).



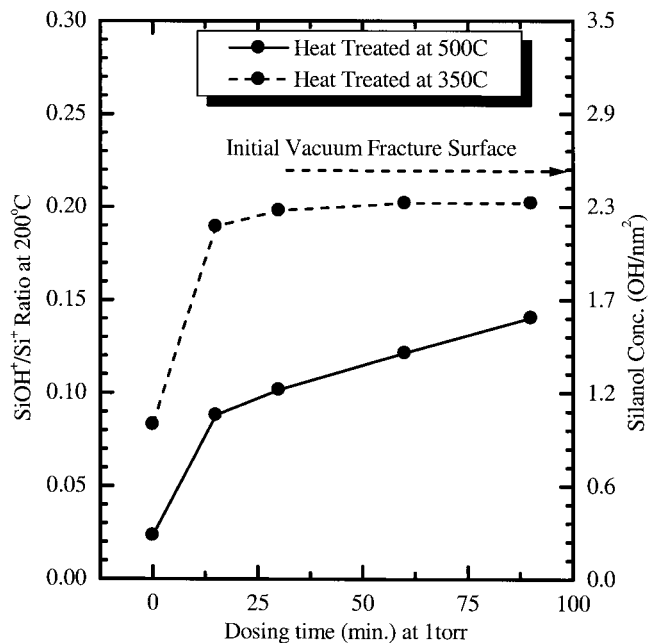
**Fig. 2.** Silanol concentration as a function of heat treatment temperature under vacuum for a silica glass (vacuum) fracture surface and for fumed silica powder.

rate of rehydration is also seen to be dependent on the dosing pressure of water, being higher at higher partial pressures of water vapor. Another important observation is that for all of the dosing pressures, the silanol concentration obtained after rehydration is lower than the initial silanol concentration of the silica surface fractured at  $1 \times 10^{-9}$  torr ( $1.3 \times 10^{-7}$  Pa). This indicates that structural relaxation of the surface has taken place during the heat treatments.

The effect of the dehydration time and temperature on the condensation of silanol groups, and on the subsequent rehydration kinetics of the fracture surfaces, was also investigated. Figure 4 compares the rehydration kinetics at 1 torr (133.3 Pa) for silica

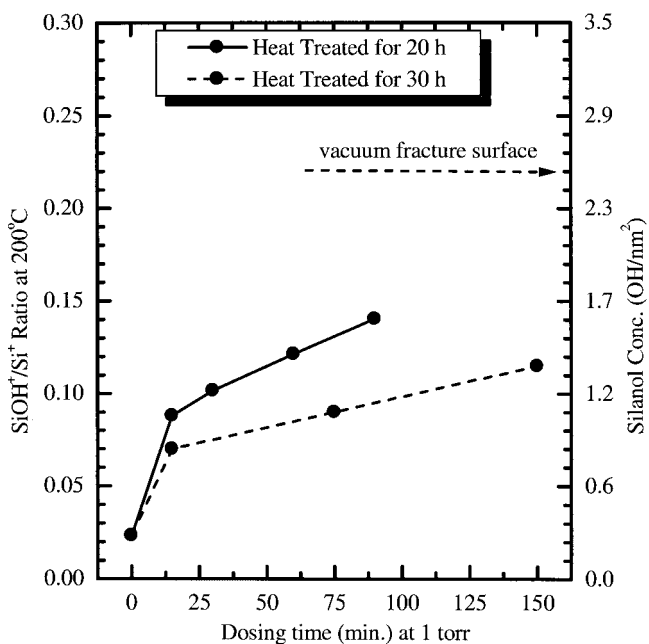


**Fig. 3.** Rehydration kinetics for silica fracture surfaces heat-treated at 500°C for 20 h for different dosing pressures.



**Fig. 4.** Comparison between the rehydration kinetics at 1 torr (133.3 Pa) for two silica fracture surfaces heat-treated at 500° and 350°C, respectively, for 20 h.

surfaces heat-treated at 350° and 500°C, respectively, for 20 h each. It can be seen that the sample heat-treated at 350°C shows faster rehydration kinetics compared to the sample that has been heat-treated at 500°C. The surface silanol concentration of the 350°C heat-treated sample also equilibrates at a higher value as compared to the sample heat-treated at 500°C. Figure 5 shows the effect of the heat treatment time on the rehydration kinetics of the sample surfaces. The plot compares the rehydration kinetics at 1 torr (133.3 Pa) for two silica fracture surfaces heat-treated at 500°C for 20 and 30 h, respectively. In this case, both of the heat treatments result in similar initial silanol concentrations. However, the sample heat-treated for longer times shows slower rehydration



**Fig. 5.** Effect of heat treatment time on the rehydration kinetics for silica fracture surfaces at 500°C.

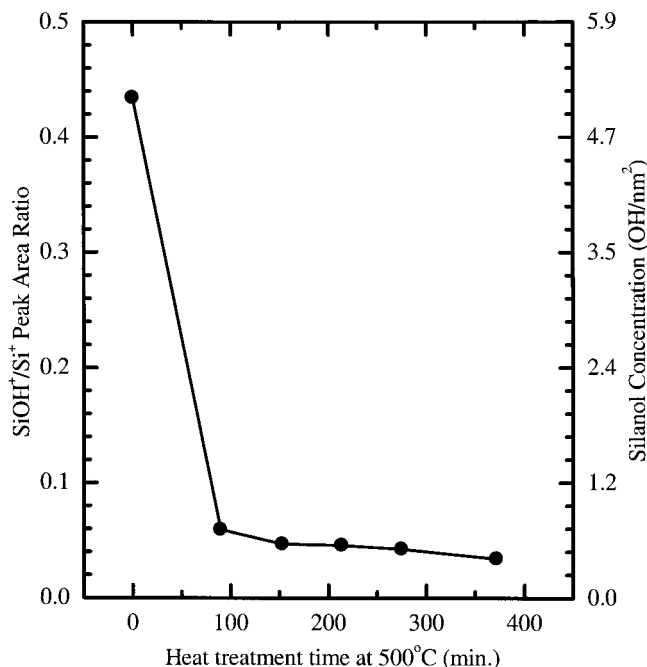


Fig. 6. Silanol concentration at a silica fracture surface as a function of heat treatment time at 500°C.

kinetics, which indicates a greater degree of structural relaxation having taken place on this surface.

The time dependence of the condensation of silanol groups at 500°C is shown in Fig. 6. The majority of the silanol groups on the fracture surface condense within a couple of hours. Although an early study by Morrow and Cody had suggested that the condensation of silanol groups and the formation of strained siloxane bonds on a silica surface are only temperature dependent,<sup>11</sup> most other studies on high-surface-area silica powders have claimed that there is a strong time dependence to the condensation of hydroxyl groups on silica surfaces.<sup>12</sup> This may reflect the conductance-limited transport of molecular water out of the pores of the high-surface-area silica powders used in those studies. In one of the other studies on low-surface-area silica, Sneh and George also observed relatively fast condensation times for silanol groups on thermally grown silica films on silicon wafers.<sup>7</sup>

Figure 7 plots the silanol concentration for silica fracture surfaces after 20 h dehydration, or after 4 h rehydration at 10 torr (1333.2 Pa), as a function of heat treatment temperature. It can be seen that dehydroxylation of the silica surface is reversible on rehydration at 10 torr (1333.2 Pa) for heat treatment at temperatures less than 350–400°C. However, heat treatments at higher temperatures make the dehydration progressively irreversible in that rehydration at 10 torr (1333.2 Pa) does not restore the silanol concentration of the surface to its initial value. It can also be seen that the higher the temperature of the dehydration treatment, the lower the silanol concentration obtained after rehydroxylation at 10 torr (1333.2 Pa).

#### IV. Discussion

It was shown in Fig. 2 that the amorphous fused silica fracture surface dehydrated to a greater extent than the fumed silica (Cabosil) surfaces for the same heat treatment temperature. More specifically, the final silanol concentration of 2.3 OH/nm<sup>2</sup> measured at 500°C for the fused silica surface is much lower than the value obtained for the Cabosil in this study, as well as in other reported studies of Cabosil.<sup>13</sup> In addition, it is lower than the previously reported values for other high-surface-area silica powders.<sup>14</sup> Since temperature-programmed static SIMS measures the silanol concentration only at the surface of the silica samples,

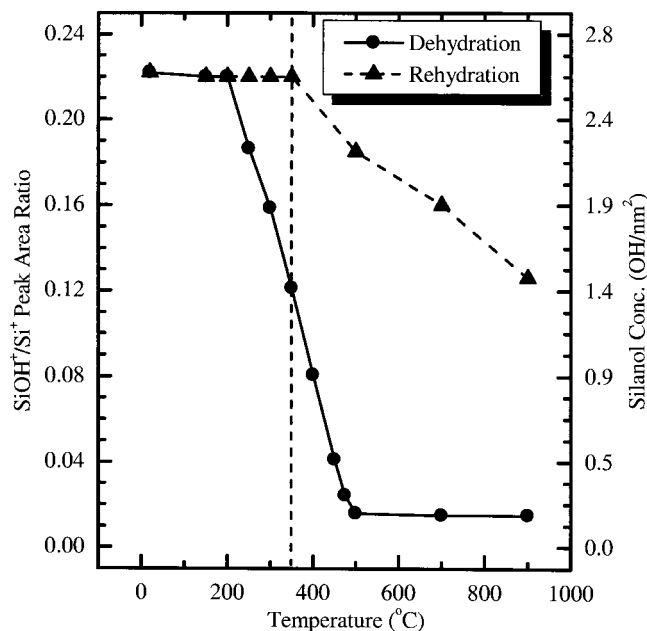


Fig. 7. Equilibrium silanol concentration for vacuum fracture silica surfaces as a function of heat treatment temperature after dehydration, and after subsequent rehydration at 10 torr (1333.2 Pa).

kinetic effects related to conductance-limited transport of hydroxyl groups out of pores should not factor into the measured values of the OH concentrations for Cabosil as a function of temperature. Therefore, it appears likely that the difference in silanol concentrations measured here, between the silica fracture surface and Cabosil as a function of the heat treatment temperature, is a real chemical effect and reflects differences in the surface structure of the two silicas. These differences may be related to the number and/or degree of strained surface siloxane bonds, or to the distribution of silanol groups on the surface.

In a previous publication, the formation of a vacuum fracture surface was modeled as a three-step process: rupturing of Si–O–Si bonds to form broken Si\* and Si–O\* bonds, reconstruction of the surface to form both strained and unstrained siloxane bonds, and lastly, reaction of water vapor with those strained siloxane bonds belonging to two- and three-membered silica rings to form surface silanol groups.<sup>10</sup> By this model, all of the silanol groups that form on a reconstructed silica fracture surface must be created by the hydrolysis of the strained surface siloxane bonds; therefore, all of the silanol groups that form in this way are paired. In contrast, the frozen high-temperature liquid surface of Cabosil can be expected to exhibit a more random distribution of silanols across the silica surface. For a random distribution of silanol groups, it has been well established<sup>11,15</sup> that paired, vicinal groups begin to condense at temperatures ~200–300°C, while the isolated silanol groups require temperature as high as 700–800°C to condense due to the limited mobility of these surface OH groups. In the case of the silica fracture surface, condensation of a greater number of silanol groups can take place at a lower temperature because more of the silanol groups are paired. Thus, the difference in the distribution of silanol groups on the fracture surface, as compared to frozen liquid silica surfaces such as Cabosil, could explain the differences observed in the condensation behavior of the two silicas as a function of temperature.

The rehydration kinetics of the dehydroxylated silica fracture surfaces were shown to involve two distinct reaction rates, an initial rapid increase in the silanol concentration followed by a slower rehydration for longer dosing times (Fig. 3). These kinetic experiments were performed to obtain information about the concentration, reactivity, and type of strained siloxane bonds that are present on dehydrated silica surfaces. Previous FTIR studies have reported the presence of a number of strained siloxane sites

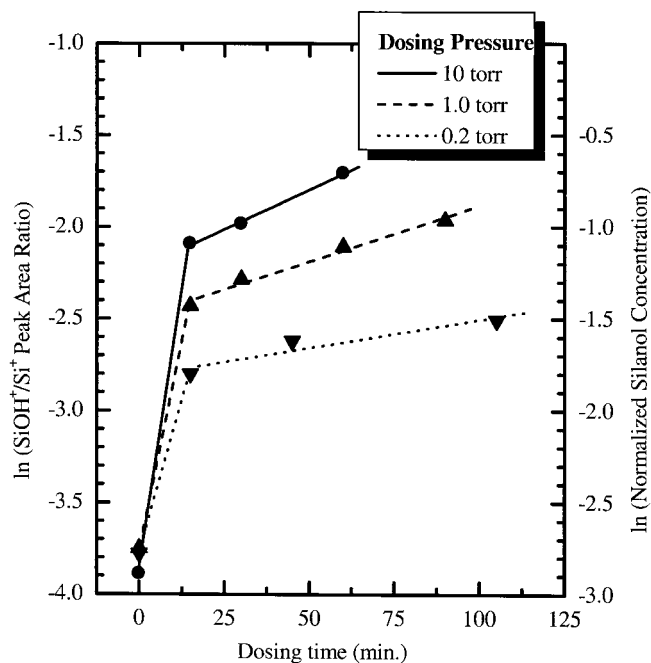


Fig. 8. Plot of the normalized silanol concentration versus dosing time for various dosing pressures.

on silica powders with varying degrees of reactivity.<sup>11,16,17</sup> The kinetics of rehydration were modeled either as a single-step process following first-order kinetics or as a two-step process with each step following first-order kinetics. Bunker *et al.* used a similar approach to describe the kinetics of rehydration of strained siloxane defects on dehydrated Cabosil.<sup>18</sup>

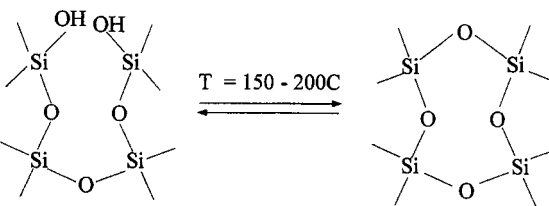
A reaction following first-order kinetics is given by the equation

$$c(t) = c_0 \exp[kt] \quad (1)$$

where  $c$  is the concentration of silanol groups,  $t$  is the dosing time, and  $k$  is the reaction rate constant. From this equation, it is clear that  $\ln[\text{OH}]$  should vary linearly with time for a reaction that follows first-order kinetics. The results plotted in Fig. 8 show that for all dosing pressures, the rehydration reaction shows two stages. The initial stage of rehydration is characterized by very rapid kinetics, while for longer dosing times the rehydration reaction displays a slower reaction rate. These data require expansion of Eq. (1) to include two reaction rate constants (but unfortunately there is insufficient data at short times to make a meaningful fit). Nevertheless, the fact that two distinct stages can be distinguished for the rehydration reaction suggests that at least two different types of strained siloxane sites are present on the dehydroxylated silica fracture surface, and each has a different reaction rate with water.

Based on our model for the formation of a silica fracture surface under vacuum, the majority of the silanol groups that form on a silica fracture surface after the fracture event are created by the hydrolysis of strained siloxane bonds belonging to two- and three-membered silicate rings.<sup>10</sup> On dehydration of the fracture surface, condensation of these silanol groups would reform strained siloxane bonds in these two types of closed ring structures. The condensation of silanol groups to form three-membered silicate rings is known to occur at temperatures  $\sim 200$ – $300^\circ\text{C}$ , whereas the formation of edge-shared, two-membered tetrahedral rings is generally thought to occur at temperatures  $>500^\circ\text{C}$ .<sup>19</sup> However, edge-shared tetrahedral ring defects have been shown to form at temperatures as low as  $300$ – $400^\circ\text{C}$  on Cabosil samples.<sup>11</sup> Therefore, it is likely that both types of defects would be present on the surface of the silica fracture surfaces dehydrated to  $500^\circ\text{C}$ , and that the two reaction rates observed on rehydration correspond to the rehydration of these two types of strained siloxane bond

a.



b.

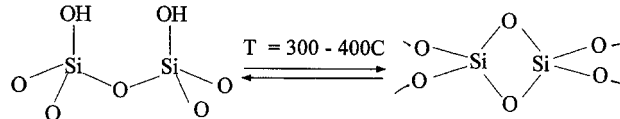


Fig. 9. Dehydration of silanol groups on the silica surface to produce strained siloxane bonds belonging to (a) three-membered silicate rings, and (b) edge-shared, two-membered silicate rings. (Adapted from Michalski and Bunker.<sup>19</sup>)

defects. Since the degree of strain of Si–O–Si bonds in edge-shared tetrahedra is much greater than in three-membered rings (14 vs 4 kcal/mol),<sup>20</sup> the rehydration rate for two-membered rings would be greater than for three-membered rings.

Assuming first-order kinetics, the reaction rate constant was calculated for the slower part of the hydration reaction using the slope of the  $\ln[\text{OH}]$  at long dosing times (Fig. 8). The OH concentration was normalized to the maximum surface silanol concentration ( $4.5/\text{nm}^2$  for this type of silica).<sup>10</sup> The rate constant obtained at 1 torr (133.3 Pa) was calculated to be  $6 \times 10^{-3}/\text{min}$ . This can be compared to a rate constant reported in the literature for the hydrolysis of three-membered silicate ring structures in silica gel ( $\sim 2 \times 10^{-4}/\text{min}$ ),<sup>18,20,21</sup> and is consistent with the idea that the slower hydrolysis reaction corresponds to the hydration of strained siloxane bonds belonging to three-membered silicate rings. (The difference of approximately a factor of 30 may be due to the microporous nature of the silica gel vs the nonporous silica glass fracture surface studied here.) The hydrolysis rate constant for the initial part of the hydration curve in Fig. 3 was so rapid that it was not possible to collect a sufficient number of data points to enable an accurate calculation of the rate constant. Using the hydrolysis rate constants obtained in the literature for different siloxane ring sizes, it can be calculated that edge-shared tetrahedral rings will react with water  $\sim 10^4$ – $10^5$  times as fast as three-membered tetrahedral rings.<sup>22,23</sup> Therefore, the initial rapid rehydration kinetics observed in the rehydration plots most likely correspond to the rehydration of highly strained edge-shared, two-membered silicate rings. The hydration and dehydration of these two types of ring defects are shown schematically in Fig. 9.

Figures 4 and 5 indicate that the concentration and the degree of strain associated with the strained siloxane bonds belonging to these silicate ring structures have a strong dependence on the temperature and time of dehydration. Figure 4 compares the rehydration kinetics for silica fracture surfaces heat-treated at  $350^\circ\text{C}$  and  $500^\circ\text{C}$ . The samples heat-treated at  $350^\circ\text{C}$  essentially showed only a single rehydration rate, which is consistent with the fact that the lower heat treatment temperature would only result in the formation of three-membered tetrahedral ring defects, and not two-membered defects.<sup>11</sup> Figure 5 compares the rehydration rates for samples heat-treated for 20 and 30 h at  $500^\circ\text{C}$ . The longer heat treatment times resulted in slower rates of rehydration. This indicates that, unlike the silanol condensation reaction, relaxation of the surface siloxane bonds that are formed during dehydration has a strong time dependence. This is not entirely unexpected when we consider that the glass structure is made up of a network of Si–O–Si bonds, wherein relaxation of the surface siloxane

bonds would require some extended relaxation of the underlying silica network. Therefore, a longer heat treatment time would allow for this more extensive, in-depth, relaxation. It can also be seen in Fig. 7 that the longer heat treatment times reduce the rate of rehydration mainly in the latter stage of the rehydration. This part of the rehydration curve corresponds to hydrolysis of the three-membered silicate rings. Thus, it can be inferred that most of the structural relaxation that is taking place at elevated temperatures is associated with relaxation of the larger three-membered rings. Since the edge-shared tetrahedral rings result in highly distorted and constrained Si–O–Si bond angles, it appears that very little relaxation of these two-membered rings takes place during the heat treatments.

An overall description of the dehydration/rehydration behavior of the silica fracture surfaces is evident in Fig. 7. The plot shows that at elevated temperatures ( $>350^{\circ}$ – $400^{\circ}$ C), the dehydroxylation of the silica fracture surface becomes progressively irreversible due to the relaxation of the strained siloxane bonds at the silica surface. Similar hydroxylation/dehydroxylation curves have been reported for a wide variety of high-surface-area silica powders by a number of researchers.<sup>13,24</sup> However, the results of this study demonstrate that although the overall dehydration behavior of bulk silica fracture surfaces is qualitatively similar to high-surface-area silica powders such as Cabosil, there can exist significant differences in the dehydration kinetics between different types of silicas due to differences in the distribution of silanol groups, and the concentration and type of strained siloxane bonds on the silica surfaces.

## V. Summary

Silanol groups on (vacuum) fracture surfaces of silica glass were found to condense to a greater extent at lower temperatures than has been previously measured on other types of silica such as Cabosil. This was attributed to a difference in the spatial distribution of silanols on these surfaces, and specifically to a greater degree of pairing of silanol groups on the silica fracture surface as compared to Cabosil.

The rehydration kinetics of the dehydroxylated silica fracture surfaces showed two distinct reaction rates, an initial rapid increase in the silanol concentration, followed by a slower rehydration for longer dosing times. The reaction rate constant for the slower rehydration reaction was similar to reported rate constants for the hydrolysis of siloxane bonds belonging to three-membered silicate rings. It has been postulated, therefore, that the initial more rapid rehydration is caused by the hydrolysis of extremely strained siloxane bonds in two-membered, edge-shared tetrahedral rings, and that the slower rehydration reaction is due to the hydrolysis of lesser-strained siloxane bonds in three-membered silicate rings.

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