J. Am. Chem. Soc. **1983**, *105*, 1487-1493

^{29}Si NMR Study of Dehydrated/Rehydrated Silica Gel Using Cross Polarization and Magic-Angle Spinning

Dean W. Sindorf and Gary E. Maciel*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received July 26, 1982*

Abstract: A ^{29}Si NMR study was carried out on silica gel, using cross polarization and magic-angle spinning (CP/MAS). Spectra were examined on silica samples prepared at various stages of dehydration. It was found that the spectral changes observed in these experiments could not be accounted for by a single structural model of the types that have been advanced previously for silica surfaces. However, these ^{29}Si spectral features are consistent with a heterogeneous silica surface consisting of separate regions resembling the 100 face and 111 face of β-cristobalite.

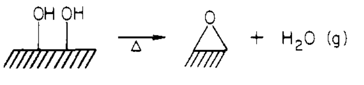
Introduction

1. ^{29}Si NMR Approach. Silica surfaces have become very important in both catalysis and chemical separations. Previous reports have shown that ^{29}Si NMR is a promising technique for the characterization of silica surfaces[1] and surface-derivatized silicas.[2,3] The combination of magic-angle spinning (MAS) and cross polarization (CP)[4,5] provides ^{29}Si NMR spectra with a high degree of structural resolution, permitting detailed study of structures and transformations at the silica surface.

The nature of the cross-polarization process, in which ^{29}Si spin polarization is derived from the proton-spin reservoir, discriminates against silicon nuclei in the interior of a silica particle and in favor of surface silicon atoms, which are much nearer the available (hydroxyl) protons. In an earlier report[1] it was shown that the ^{29}Si CP/MAS signals of surface silanol silicons, both $>$SiOH and $>$Si(OH)$_2$, are suitable for quantitative study. Thus, for these silicon nuclei, the hydrogen–silicon cross-polarization relaxation time (T_{HSi}) is found to be substantially shorter than the experimental cross-polarization time employed, which is in turn typically much shorter than the rotating-frame ^{1}H spin-lattice relaxation time ($T_{\rho\mathrm{H}}$). This is the relationship between the parameters that is needed for a maximum signal-to-noise ratio and a straightforward interpretation of intensities. For silicon atoms that have no directly attached OH groups, the same kind of relationship is precluded by the large T_{HSi} value.

In this paper we describe a detailed ^{29}Si CP/MAS NMR study of silica gel surfaces, exploring the quantitative relationships among structural features that can be derived from the ^{29}Si spectra. Special emphasis is placed on the effects of dehydration and rehydration of silica gels. Detailed studies of the interactions of silylating agents with silica gel surfaces are described elsewhere.[6-8]

2. Dehydration. Silica samples subjected to high temperatures under vacuum will experience a general loss in weight corresponding to the evolution of molecular water. This is believed to reflect primarily the condensation of adjacent hydroxyl groups to form siloxane bridges (eq 1) and to a lesser extent the elimination of physically adsorbed or bulk H$_2$O. Substantial evidence has indicated that the detailed nature of the rehydration of such a surface (i.e., the restoration of surface hydroxyls through exposure to water) is largely determined by kinetic factors. Since the siloxane bonds formed in dehydration are known to be hydrophobic,[9] they probably serve as poor sites for the initial specific adsorption of water necessary for the reverse of process (1). Iler[10] and others[9,11,12] have suggested that the rate-limiting step in rehydration may instead involve the association of molecular water with neighboring (uncondensed) hydroxyl groups. For highly dehydroxylated silica gels containing few residual silanols, rehydration is quite slow at normal temperatures and probably proceeds via the growth of patches of hydrated surface originating at these hydrophilic sites. This idea is supported by the observations of Volkov, Kiselev, and Lygin,[9] who found that the rehydration of silica samples heated from 900 °C to 1100 °C proceeded autocatalytically. Young and Bursh[11,12] have also reported that at pretreatment temperatures less than 425 °C, silica surfaces were rehydrated readily, whereas above this temperature rehydration became increasingly slower.



(1)

Since both dehydration and rehydration processes reflect basic underlying features of the organization of hydroxyl sites on the silica surface, studies of such phenomenon have traditionally played a central role in the development of theoretical models to describe surface structure. In this report a number of these models, along with their proposed dehydration and rehydration mechanisms, will be examined in some detail. Predictions based upon these explanations will then be compared with new experimental data obtained by using the techniques of solid-state ^{29}Si NMR.

Experimental Section

1. NMR Measurements. Most of the solid-state ^{29}Si NMR spectra were obtained at 11.88 MHz on a prototype JEOL FX-60QS NMR spectrometer, especially modified for the observation of this nucleus by using an external frequency synthesizer and mixers. Additional solid-state ^{29}Si spectra were acquired for samples requiring higher sensitivity at 39.75 MHz on a modified Nicolet NT-200 spectrometer, with a home-built CP/MAS probe. Design aspects of the iron-magnet probes have been described in detail elsewhere.[13] Magic-angle sample spinning was routinely carried out at 2.0–2.3-KHz spinning rates on the FX-60QS and 3.5–4.0 KHz on the NT200, with Kel-f or Delrin rotors of the bullet design. Typically, spectra were obtained by using a contact time of 10 ms and a pulse repetition time of 0.5–1.0 s.

All chemical shifts are reported with respect to the silicon resonance in liquid Me$_4$Si.

2. Silica Gels. Dehydration/rehydration studies were carried out on Fisher S-157 silica gel (surface area: 750 m^2/g by N$_2$ adsorption). In another report[6] involving quantitative studies of trimethylsilane bonding reactions, it is shown that this system exhibits no evidence for internal

---

[1] Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606–7607.

[2] Maciel, G. E.; Sindorf, D. W.; Bartuska, V. J. *J. Chromatogr.* **1981**, *205*, 438–443.

[3] Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 4263–4265.

[4] Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *8*, 1–79.

[5] Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–589.

[6] Sindorf, D. W. Ph.D. Dissertation, Colorado State University, June, 1982.

[7] Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.*, in press.

[8] Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.*, in press.

[9] Volkov, A. V.; Kiselev, A. V.; Lygin, V. I. *Zh. Fiz. Khim.* **1974**, *48*, 1214–1218.

[10] Iler, R. K. "The Chemistry of Silica, Solubility, Polymerization and Surface Properties and Biochemistry"; Wiley: New York, 1979.

[11] Young, G. J. *J. Colloid Sci.* **1958**, *13*, 67–85.

[12] Young, G. J.; Bursh, T. P. *J. Colloid Sci.* **1960**, *15*, 361–369.

[13] Bartuska, V. J.; Maciel, G. E. *J. Magn. Reson.* **1981**, *42*, 312–321.

0002-7863/83/1505-1487$01.50/0

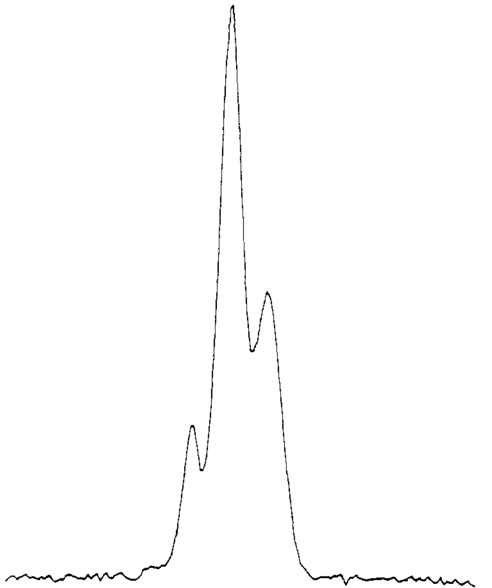


Figure 1. CP/MAS ^{29}Si NMR spectrum of Fisher S-157 silica saturated with liquid water. Algebraically larger values correspond to lower shieldings.

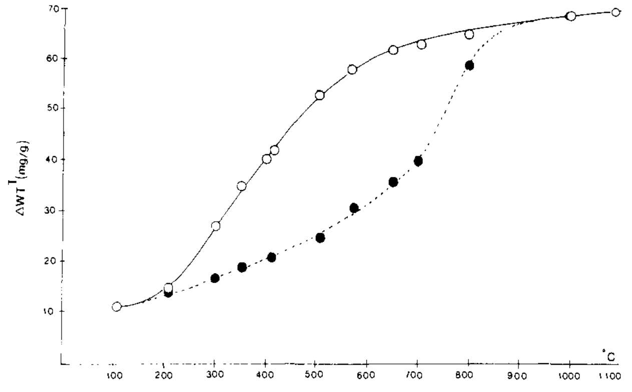


Figure 2. Weight loss vs. dehydration temperature for Fisher S-157 silica: (○) data obtained for dehydrated samples, (●) data obtained for rehydrated samples.

SiOH groups or regions of solute-inaccessible surface. A surface concentration of 5.2 hydroxyls per 100 Å^2 was measured for fully hydrated S-157 silica, of which 30% were attributed to surface geminal-hydroxyl silanol sites. Additional silica gel systems that were used in relaxation studies in the present report are described in ref 6.

3. **Dehydration.** Dehydration experiments were carried out in a tube furnace capable of reaching temperatures of 1100 °C. A 10-g sample of silica gel was placed in a preweighed quartz tube that could be independently sealed by using a fritted stopcock fitting. The stopcock was attached via vacuum tubing to a vacuum source (10^{-5} torr). The sample tube was briefly evacuated, sealed and weighed, and then placed in the furnace (under vacuum) and allowed to dry at a specified temperature for a period of 18 h. At the end of this time the cell was sealed, detached from the vacuum line, and removed from the furnace. After a cooling period, the weight of the sample and tube was measured. For several samples weights were also determined at intermediate stages of dehydration. In all cases at least 90% of the observed weight loss occurred during the first 4 h of drying.

4. **Rehydration.** Approximately 2-g samples of dried silica were placed in preweighed glass ampule vials. After weighing, the vials were filled with liquid water, and the resulting silica suspension was allowed to stand at ambient temperature for a period of 12 h. After this time the excess water was removed by evacuation at 20 °C to approximate dryness and then at 160 °C for 4 h. The sample was then reweighed and the weight gain due to rehydration determined.

Results

1. **General ^{29}Si NMR Features.** Figure 1 shows the structural resolution obtainable in a CP/MAS ^{29}Si spectrum of a silica gel (S-157) in the most favorable cases. Chemical shifts are given with the convention that higher shielding corresponds to algebraically lower values. The low-intensity peak at −89 ppm has been assigned previously[1] on the basis of chemical shift correlations and relaxation data to geminal-hydroxyl silanol sites ($(\gg SiO)_2Si(OH)_2$). Similarly, the peak at −100 ppm has been assigned to single hydroxyl silanol sites, $(\gg SiO)_3SiOH$, and the peak at −109 ppm to surface silicons of the $(\gg SiO)_4Si^*$ type.

Proton rotating-frame spin–lattice relaxation studies were carried out on selected silica gel samples by using (a) the variable contact-time method[1,5] and (b) a pulse sequence involving spin-locking the proton magnetization, waiting a variable time period (t), and then cross polarizing to ^{29}Si. The two methods yielded comparable results. $T_{1\rho H}$ was found to range from 11–21 ms for "wet" silica gels with abundant adsorbed water to 60–110 ms for samples that had been heated under vacuum at temperatures >100 °C. Very short $T_{1\rho H}$ values (3–6 ms) were measured for samples in which both H_2O and HCl were adsorbed on the surface, suggesting that hydroxyl proton exchange might be involved in the mechanism of rotating-frame ^{1}H relaxation in these systems.

Proton T_1's for a number of different silica gels and bonded-phase materials were measured by using a pulse sequence[14] involving inversion–recovery of the proton magnetization followed by spin-locking, cross polarization, and observation of ^{29}Si. Observed T_1 values varied from 60 to 400 ms and, as in the case of $T_{1\rho}$ relaxation, were somewhat sensitive to the degree of surface hydration. In this case, however, such effects did not result in T_1 magnitude changes exceeding about 30%.

For highly dehydrated silica surfaces containing widely spaced hydroxyl protons, one may be justifiably concerned that equilibrium may not be fully established in the proton reservoir during cross polarization. Such a condition might lead to a distortion in spectral intensities because (1) protons associated with different silicon species may relax at different rates in the rotating frame and (2) the intensity achieved from cross polarization may be dominated by near-neighbor protons. (This effect might result in a distortion in the relative intensities associated with geminal and single hydroxyl sites on the surface.) In either situation one would expect to observe significant differences in relative spectral intensities as the experimental contact time is varied. To explore this possibility, we examined two of the dehydrated samples used in this study (samples heated to 417 °C and 507 °C) over a range of contact times between 3 and 30 ms. It was found that the ratio of geminal-hydroxyl site intensity (−91 ppm peak) to single-hydroxyl site intensity (−100 ppm peak) remained essentially constant for contact times >7 ms. Measured values of T_{HSi} and $T_{1\rho H}$ were, in addition, quite similar to values observed for fully hydrated samples (i.e., 2–5 ms for T_{HSi} and about 100 ms for $T_{1\rho H}$). From these results we conclude that intensity distortions originating from relaxation effects are probably not a major source of error in these measurements.

2. **Dehydration/Rehydration Studies.** Gravimetric data obtained for dehydrated and rehydrated samples are plotted as a function of dehydration temperature in Figure 2. The values indicated in the figure (ΔWT) are in milligrams lost per gram of *original* silica gel. The data shown for rehydrated samples are the net loss of sample weight following both dehydration and rehydration procedures.

The sigmoidal shape of the plot of weight loss vs. dehydration temperature shown in Figure 2 is typical of the general behavior found in these kinds of studies. At low temperatures (<100 °C) there is a rapid loss of physically adsorbed or bulk molecular water, corresponding in this case to about 10 mg/g. Data reported elsewhere[7] indicate that this process may continue to a lesser extent up to temperatures as high as 300 °C. However, at about 150 °C and higher the observed weight loss reflects primarily the condensation of hydroxyl groups on the silica surface. The data of Figure 2 show that this process occurs quite efficiently at

---

[14] Sullivan, M. J.; Maciel, G. E. *Anal. Chem.* **1982**, *54*, 1615–1623.

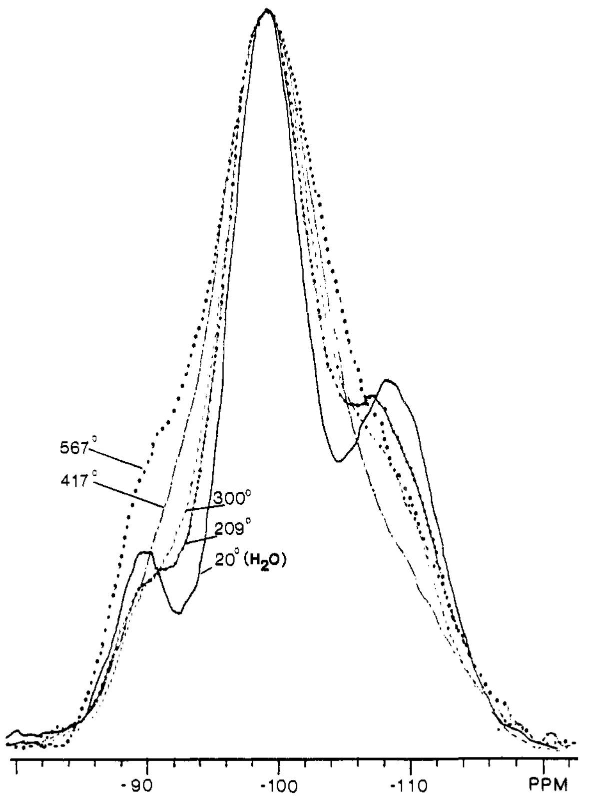


Figure 3. 39.75-MHz ^{29}Si CP/MAS NMR spectra obtained for dehydrated S-157 silica dehydrated at 209–567 °C. A spectrum for a water-saturated sample, 20 °C (H_2O), is included for comparison. All spectra are normalized to the amplitude of the central resonance.

temperatures from 150 °C to 550 °C but less readily at higher dehydration temperatures. Even at the highest temperature obtainable with this experimental apparatus (1100 °C), the non-zero slope of the dehydration curve indicates that at least some residual hydroxyl groups are probably present on the silica surface. In this high-temperature regime, Curthoyes et al.[15] have determined that at 700, 800, and 1000 °C the remaining surface hydroxyl density is about 1.2, 0.9, and 0.4 OH per 100 Å^2, respectively. For Fisher S-157 silica (with a surface area of 750 m^2/g), this corresponds to about 13, 10, and 4.6 mg of bound H_2O per gram of silica. With the data of Figure 2 this suggests that complete dehydration in this situation would involve a total weight loss of about 74 mg/g.

The rehydration data in Figure 2 show that at temperatures up to about 500 °C, most, but not all, of the silanol groups removed in dehydration are restored following exposure to liquid water. At higher temperatures, however, rehydration becomes increasingly inefficient. Although kinetic aspects of rehydration were not pursued in these studies, these data are qualitatively consistent with the observation of Volkin, Young, and others described above (i.e., that rehydration will be rapid for samples heated at low dehydration temperatures but will become increasingly slower at higher temperatures). At very high temperatures (>800 °C), rehydration can be extremely slow, as shown by the work of Agzamkhodzhaev et al.[16] who found that a surface dehydrated at 900 °C for 10 h required several years of standing in liquid water at ambient temperature to become fully rehydrated. It is unlikely therefore that rehydrated samples prepared in this study represent true equilibrium surface conditions. Instead, particularly for samples dehydrated at high temperatures, silanol groups restored by exposure to liquid water will probably reflect a kinetically active subset of condensed structures at the silica surface.

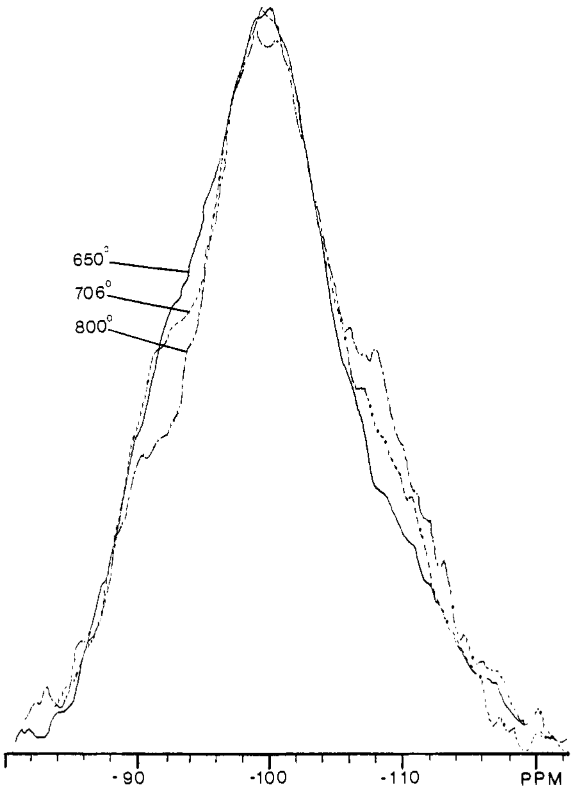


Figure 4. 39.75-MHz ^{29}Si CP/MAS spectra of S-157 silica gel dehydrated at 650–800 °C.

^{29}Si CP/MAS spectra of dehydrated samples obtained at 39.75 MHz are shown in Figure 3 (20–567 °C) and Figure 4 (650–800 °C). Similar results, with poorer S/N, were obtained at 11.88 MHz (not shown). Examination of these spectra reveals that at increasing dehydration temperatures the apparent line widths become larger. One possible explanation of this behavior is that on water-saturated surfaces a rapid translational diffusion of water brings about the averaging of ^{29}Si chemical shifts of most of the silanol groups interacting strongly via hydrogen bonding with the adsorbed water. The removal of surface molecular water could result in a "freezing in" of surface geometries that give rise to a dispersion of chemical shifts, accounting for the sharp increase in line widths evident in going from a water-saturated surface at 20 °C to an essentially water-free surface at 209 °C. At dehydration temperatures higher than about 300 °C, most, if not all, molecular water will probably have been removed, so another explanation is needed for the changes in line shape—possibly longer range chemical shift perturbations arising from the condensation of neighboring silanol sites on the silica surface.

Despite the disappointingly poor quality of resolution, the spectra of Figures 3 and 4 show certain features that give evidence for substantial structural changes. In particular, a comparison of the apparent amplitude of the shoulder at −91 ppm (associated with surface geminal-hydroxyl sites) to that of the resonance at −100 ppm (associated with single-hydroxyl sites) shows that the relative fractional population of geminal-hydroxyl sites decreases as the temperature is raised from 20 °C to about 300 °C and then increases abruptly at higher temperatures, reaching a maximum at about 650 °C. At temperatures beyond 650 °C, the −91 ppm resonance again exhibits a qualitative decrease in amplitude with respect to the central resonance.

For spectra of the corresponding rehydrated samples (shown in Figure 5), similar, if somewhat less complicated, behavior is evident. In this case the relative intensity of the −91 ppm resonance increases for samples heated from 209 °C to 507 °C and then decreases at progressively higher temperatures. Interestingly, these spectra also show substantially better resolution than the corresponding spectra of dehydrated samples, even when samples with similar total hydroxyl content are compared (rehydrated 706 °C

---

(15) Curthoys, G.; Davydov, V. Y.; Kiselev, A. V.; Kiselev, S. A.; Kuznetsav, B. V. *J. Colloid Interface Sci.* **1974**, *48*, 58–72.

(16) Agzamkhodzhaev, A. A.; Zhuravlev, L. T.; Kiselev, A. V.; Shengeliya, K. Ya. *Kolloidn. Zh.* **1974**, *36*, 1145–1148.

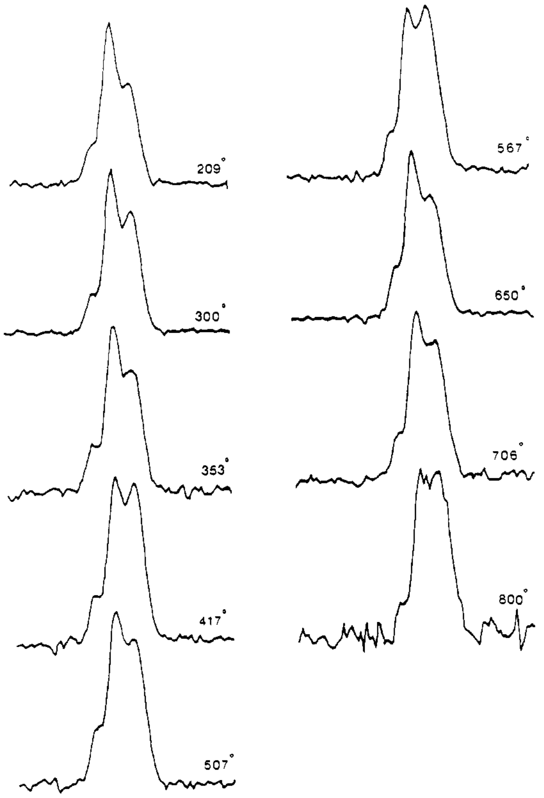


Figure 5. 11.88-MHz ^{29}Si CP/MAS NMR spectra of rehydrated silica gel samples.

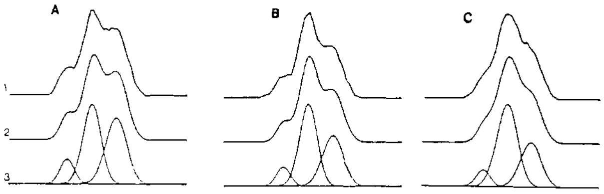


Figure 6. Examples of the application of the Nicolet curve-fitting program to ^{29}Si CP/MAS spectra of S-157 silica: (1) actual 11.88-MHz spectrum (digitized), (2) synthetic spectrum, (3) component Gaussian lines; (A) heated to 507 °C (rehydrated), (B) heated to 209 °C (rehydrated, (C) heated to 353 °C (dehydrated).

and dehydrated 417 °C, for example). The reason for this is not known but may indicate that the subset of condensed silanol groups giving rise to the largest broadening effects is also the subset most easily rehydrated following exposure to liquid water.

To place the general observations presented above on at least a semiquantitative basis, the spectral features of Figures 3–5 were subjected to a line-shape analysis, by using the Nicolet curve-fitting program NTC-CAP. ^{29}Si spectra obtained at 11.88 MHz were plotted on chart paper and digitized manually. These data (40 points per spectrum) were then entered as a data set into the Nicolet 1180 computer (spectra obtained at 39.75 MHz were analyzed directly). Synthetic spectra were generated with NTC-CAP by using a function consisting of three Gaussian lines. The nine associated variables (height, width, and chemical shift for each of the three peaks) were adjusted to minimize the root-mean-square error between the observed and calculated spectrum (similar procedures using Lorentzian lines gave much poorer agreement with the actual line shapes). Examples of the application of these methods are shown in Figure 6. Relative peak areas were generated by the program and were used to calculate the apparent fractional population of surface geminal sites, defined as f_g.

Discussion

1. Models for the Silica Surface. X-ray work on silicas suggests that the structure most closely resembles that of the β-cristobalite, or similar crystalline phases,[17] a view also supported by bulk density studies.[18] Most prevalent descriptions of the silica surface are thus based upon an assumed similarity to various crystallographic faces of these forms of silicon dioxide. Three such models are considered here.

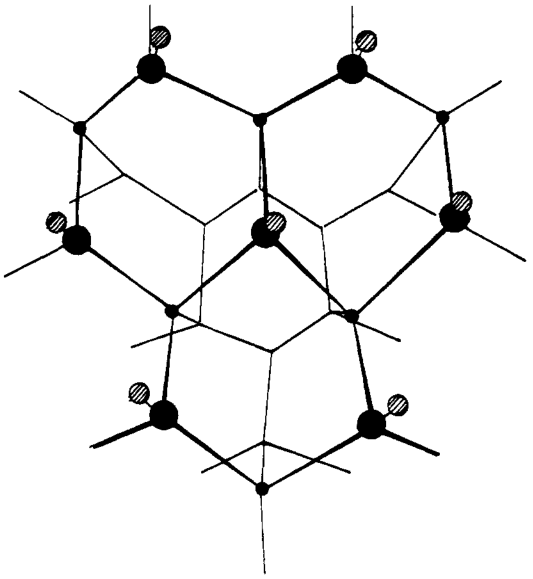


Figure 7. Surface model (β-cristobalite 111) proposed by DeBoer and Vleeskins showing the arrangement of surface hydroxyls (shaded circles), silanol silicons (●), and cross-polarizable lattice silicons, $(SiO)_4Si^*$ (•).

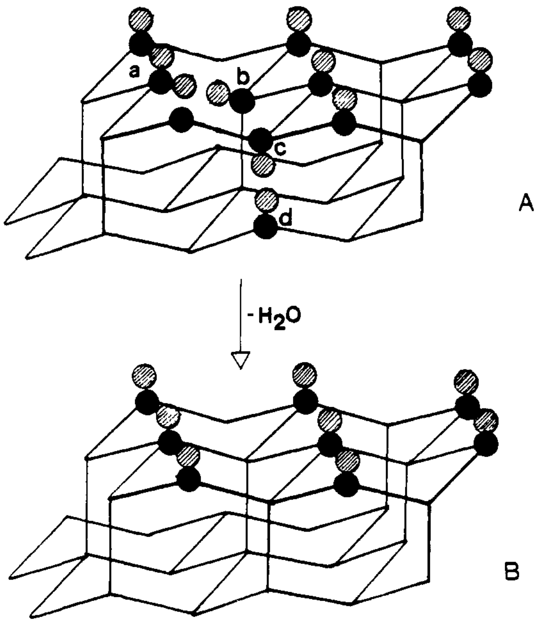


Figure 8. Mechanism of dehydration proposed by Hockey, showing the surface of silica gel (A) before dehydration and (B) after dehydration: (shaded circles) hydroxyls; (●) silanol silicons. Hydroxyl pairs ab and cd arise from additional silanol sites created from defects in lattice structure.

In 1958 DeBoer and Vleeskins[19] suggested a model based on the 111 face of β-cristobalite or similar faces of β-tridymite, as represented in Figure 7. On such ideal surfaces, hydroxyl groups are separated by about 5 Å and are arranged in a hexagonal array that corresponds to an OH concentration of 4.55 per 100 Å^2, close

---

[17] Frondel, C. "The System of Minerology of Dana", 7th ed.; Wiley: New York, 1962; Vol. 3 (Silica Minerals), p 154.

[18] Skinner, B. J.; Appleman, D. E. *Am. Mineral.* **1963**, *48*, 854–867.

[19] DeBoer, J. H.; Vleeskins, J. M. *Proc. K. Ned. Akad. Wet., Ser. B: Palaeontol., Geol., Phys., Chem.* **1958**, *B61*, 85–93.

to the value of 4.6 these authors found in dehydration/rehydration studies of various silica gels. They hypothesized that their experimental procedure (termed "annealing") produced a similar, thermally stable surface structure that resulted from the reorganization and removal of surface irregularities.

The mechanism for dehydration and rehydration of such a surface has been addressed in more depth by Hockey,[20] who postulated that the higher and widely variable values measured for the hydroxyl density of untreated silicas arise from the presence of defects in lattice structure. As illustrated in Figure 8A, such defects may occur either on the surface, giving rise to adjacent geminal (a) and single (b) hydroxyl sites, or in the interior, producing a pair of single hydroxyl sites (c and d). Because of their relatively close proximity, hydroxyls on such silanol pairs might be expected to condense readily at moderate temperatures, resulting in the regular (β-cristobalite) surface shown in Figure 8B. Upon exposure to water, underlying strain imposed by the crystal lattice is presumed to favor restoration of the original structural configuration, leading to the rehydration of surface sites a and b. Because of their lower accessibility, however, sites c and d may not be as easily regenerated. Hockey proposed that, as in the case of annealed glass, such lattice strain may be relaxed by subjecting the materials to sufficiently high temperatures. Presumably, under these conditions all lattice defects (a, b, c, d) will be eliminated permanently. At higher temperatures, further dehydration would involve condensation reactions between hydroxyls on the regular crystalline surface (Figure 8B). Because of highly unfavorable internuclear distances, siloxane bonds formed in this process are expected to be thermodynamically unstable and, according to Hockey, may be rehydrated readily in the presence of H_2O.

The DeBoer–Vleeskins model, with the lattice-defect mechanism of Hockey, does have a number of difficulties. For example, some studies[21,22] have indicated that a substantial fraction of the surface hydroxyls are "paired" (spacially adjacent), even on surfaces heated beyond the hypothetical annealing temperatures (about 450 °C) of DeBoer and Vleeskins. This is inconsistent with the geometry of the 111 face of β-cristobalite, where all surface OH groups are separated by at least 5 Å. Reducing the hydroxyl density of such a model much below 4.6 per 100 Å^2 also appears rather infeasible, considering the constraints imposed by the underlying lattice. In actual situations, however, surface OH concentrations of less than 1.0 per 100 Å^2 have been measured for highly dehydrated silica samples, with little observed decrease in overall surface area.

A surface model that eliminates some of the inadequacies of the DeBoer–Vleeskins structure and predicts the existence of paired hydroxyl groups at all levels of dehydration was proposed by Peri and Hensley.[21] In this description (shown in Figure 9A) the surface of virgin silica gel is assumed to be similar to the 100 face of β-cristobalite. Each surface silicon is connected to a geminal pair of hydroxyl groups, the paired groups located in rows. Calculations based on such a surface give a OH concentration of 7.9 per 100 Å^2, in close agreement with a number of early experimental values measured for unheated silica. According to the Peri–Hensley model, the process of dehydration first involves the random condensation of hydroxyls groups along surface rows. A silica surface partially dehydrated by this mechanism is shown in Figure 9B. Assuming random condensation reactions, the concentration of hydroxyl groups on the surface following this dehydration process is predicted to be 4.56 OH per 100 Å^2.

It is important to note that in the Peri–Hensley model only paired hydroxyl groups remain on the surface after dehydration. Referring to Figure 9B, these consist of **a** sites (geminal pairs) and **b** sites (vicinal pairs). Thermodynamically, this dehydrated surface should be quite stable, since only small deformations of the lattice have been assumed. Further dehydration of the surface proposed in this model might involve the condensation of vicinal pairs into siloxane linkages, where the two participating SiO_4 tetrahedra are connected by an edge (eq 2). Formation of such linkages would probably be difficult, and the resultant highly strained structures might be expected to rehydrate rather easily. Peri and Hensley have calculated that maximal dehydration by this second mechanism should result in a surface with 1.2 widely separated geminal hydroxyl sites per 100 Å^2 of surface. Other possible mechanisms, such as the condensation of geminal pairs to form >Si=O type groups, are not considered likely on the basis of the known chemistry of silicon. Unlike DeBoer and Vleeskin's structure, no clear mechanism for the formation of isolated single OH groups has been suggested on the basis of this model.

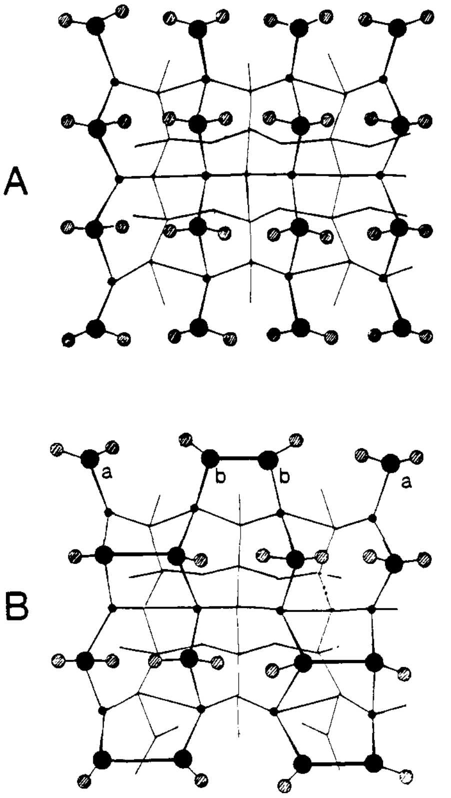
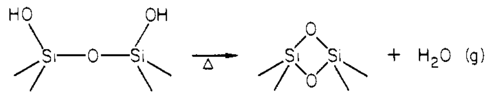


Figure 9. Surface geometry (β-cristobalite 100 face) including mechanism of dehydration suggested by Peri and Hensley: (A) completely hydrated, (B) following partial dehydration. In B, b sites are "vicinal pairs" formed from the condensation of adjacent geminal hydroxyl sites (a). (Shaded circles) Hydroxyls; (●) surface silanol silicons; (•) cross-polarizable lattice-type silicons.



(2)

An alternate model in which the surface is similar to the 111 face of β-cristobalite, but holds randomly distributed single-hydroxyl silanols, has also been postulated.[21] The formation of single hydroxyls, vicinal hydroxyl pairs, and surface condensation of adjacent hydroxyl groups would be possible on such a surface. Full dehydration by the condensation of all possible pairs results in a minimum density of 1.5 OH per 100 Å^2. As with the DeBoer model, no geminal hydroxyl groups would be expected at any stage of dehydration.

2. Dehydration/Rehydration Experiments. An important parameter that is extracted directly from relative ^{29}Si NMR intensities in the −90 and −100 ppm spectral regions is the fraction of silanol sites present as geminal sites, f_g. For dehydrated and rehydrated samples, f_g is plotted as a function of dehydration temperature in Figure 10. Error bars reflect only the general reproducibility of the deconvolution fitting procedures used in evaluating f_g and thus at best can be considered as very rough confidence limits of the accuracy of these data. In some cases, particularly for the more poorly resolved spectra, several shallow

---

(20) Hockey, J. A. *Chem. Ind.* (*London*) **1965**, 57–63.

(21) Peri, J. B.; Hensley, A. L., Jr. *J. Phys. Chem.* **1968**, *72*, 2926–2933.

(22) Peri, J. B. *J. Phys. Chem.* **1966**, *70*, 2937–2945.

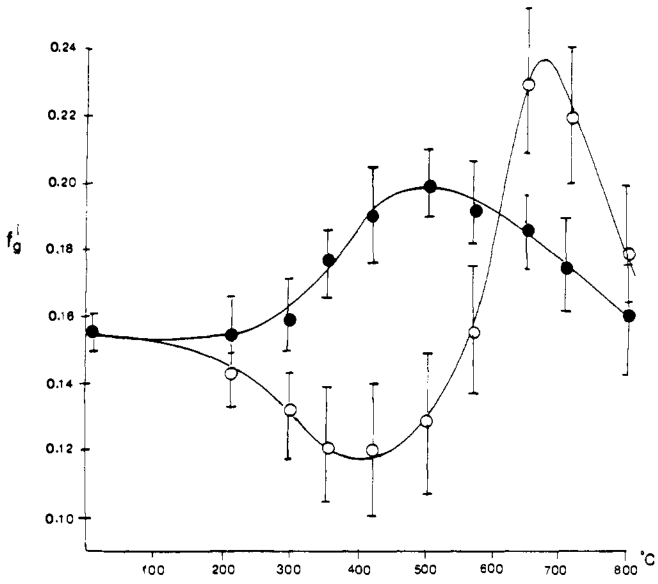


Figure 10. Plot of fractional population of geminal sites measured for dehydrated and rehydrated samples vs. dehydration temperature.

local root-mean-square minima could be found in the fitting process if relative chemical shifts were allowed unconstrained variability. A final evaluation of relative peak areas in these cases required constraint on the three resonance positions to values within 1 ppm of the mean values obtained in well-resolved spectra.

The general behavior of the curves in Figure 10 is consistent with the qualitative observations given above. For dehydrated samples, the relative apparent population of the surface geminal sites decreases from an initial value of about 15.5% at 20 °C to a value of about 12% at 350–400 °C. Above 400 °C there is a sharp increase in the relative population of geminal sites, which reaches a maximum of approximately 24% at 650 °C and then decreases again at higher dehydration temperatures. For rehydrated samples, the fractional geminal site population appears to go through a simple maximum of about 20% at 500 °C.

While illustrating the distribution of silanol types present on silica surfaces at various stages of hydration, Figure 10 does not give much insight into the nature of the dehydration and rehydration mechanisms themselves. For this purpose the data are best represented in terms of the fraction of initial sites (geminal and single) that remain on the silica surface as a function of dehydration temperature.

Using the gravimetric data summarized in Figure 2, one can estimate the total fractional OH content remaining after treatment (F_{OH}) by the following equation:

$$F_{OH} = \frac{(\Delta W^m - W^m{}_{H_2O}) - (\Delta W^T - W^T{}_{H_2O})}{(\Delta W^m - W^m{}_{H_2O})} \tag{3}$$

where ΔW^m is the weight loss at complete dehydration (estimated at 74 mg/g) and ΔW^T is the weight loss appropriate for a given dehydration temperature; $W^T{}_{H_2O}$ and $W^m{}_{H_2O}$ are the portions of the weight change attributable to the elimination of adsorbed molecular H_2O at a given temperature T and at maximum dehydration, respectively. Results reported elsewhere[7] show that for the S-157 silica used in this study, $W^m{}_{H_2O}$ amounts to about 14 mg/g and equals $W^T{}_{H_2O}$ for samples heated beyond 300 °C. Equation 3 is also valid for rehydrated samples with $W^m{}_{H_2O} - W^{160}{}_{H_2O} \simeq 4$ mg/g.

The fraction of geminal sites remaining after dehydration, or after dehydration followed by rehydration (F_g), is given by eq 4,

$$F_g = \frac{f_g^i(1 + f_g^T)}{f_g^T(1 + f_g^i)} F_{OH} \tag{4}$$

where f_g^i and f_g^T are the estimated relative silanol populations of geminal sites on the initial and heat-treated surfaces, respectively (values extracted from Figure 10). The fraction of residual single-hydroxyl sites (F_l) is obtained in a similar manner.

$$F_l = \frac{(1 - f_g^i)(1 + f_g^T)}{(1 - f_g^T)(1 + f_g^T)} F_{OH} \tag{5}$$

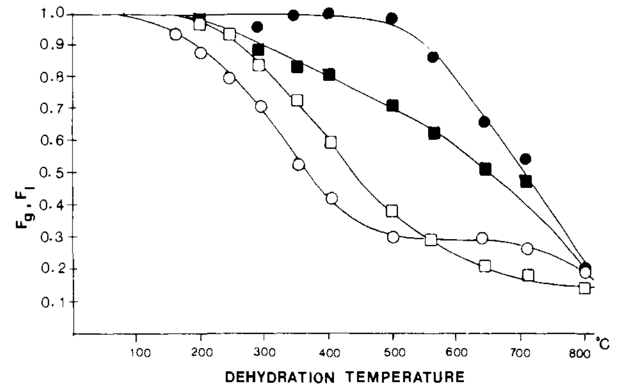


Figure 11. Estimated fractions of original single-hydroxyl and geminal-hydroxyl sites remaining vs. dehydration temperature: (○) geminal sites after dehydration, (●) geminal sites following rehydration, (□) single sites after dehydration, (■) single sites following rehydration.

On the basis of the data of Figures 2 and 10 and the expressions just presented, the fractional residual populations of both geminal and single OH sites have been calculated and are plotted as a function of dehydration temperature in Figure 11. These curves show that the general behavior of the single-hydroxyl sites (squares) follows that observed for the overall hydroxyl population in Figure 2. Dehydration of these sites proceeds efficiently as the temperature is increased from 200 to 500 °C, but less readily at higher temperatures. Rehydration efficiency for single-hydroxyl sites is reasonably high for samples preheated to moderate temperatures (≤500 °C) but falls off quickly as the temperature is increased beyond this point.

From a comparison of this behavior with that exhibited by the geminal-hydroxyl sites (circles), some interesting features emerge. First, the dehydration data in Figure 11 show that at low to moderate temperatures (200–500 °C), although condensation reactions occur simultaneously among both single- and geminal-hydroxyl silanols, they occur preferentially for the geminal-hydroxyl sites. In this same temperature regime, virtually 100% of the geminal-hydroxyl sites eliminated in dehydration are restored following exposure to liquid water. (In general only about half of the single-hydroxyl silanols are recovered under these same conditions.) At temperatures beyond 500 °C, but less than 700 °C, the surface concentration of geminal-hydroxyl sites remains essentially constant. Surprisingly, however, the restorability of geminal sites decreases precipitously for dehydration temperatures greater than 500 °C. At very high temperatures (>700 °C) further elimination of geminal sites occurs, and, as in the case of single-hydroxyl sites, rehydration is practically nonexistent under these experimental conditions.

3. Dehydration/Rehydration Results and Silica Gel Models. The ^{29}Si NMR spectrum of unheated silica gel (Figure 1) is consistent with the model of DeBoer and Vleeskins (111 cristobalite face) if the initial 15% geminal-hydroxyl site population can be attributed to lattice defects of the type shown as a in Figure 8. Even without this assumption, the fact that the majority of surface sites (85%) are of the single-hydroxyl type strongly suggests that the more prevalent structural form is in closest agreement with this kind of geometry. Macroscopically, the overall behavior of the silica gel in dehydration and rehydration studies is thus expected to follow predictions based on single-hydroxyl silanol sites in an environment corresponding to this model. As was mentioned previously, such a correspondence is indeed evident in the relative similarity of the gravitemetric dehydration/rehydration data of Figure 8 and the ^{29}Si NMR data of single-hydroxyl sites given in Figure 11.

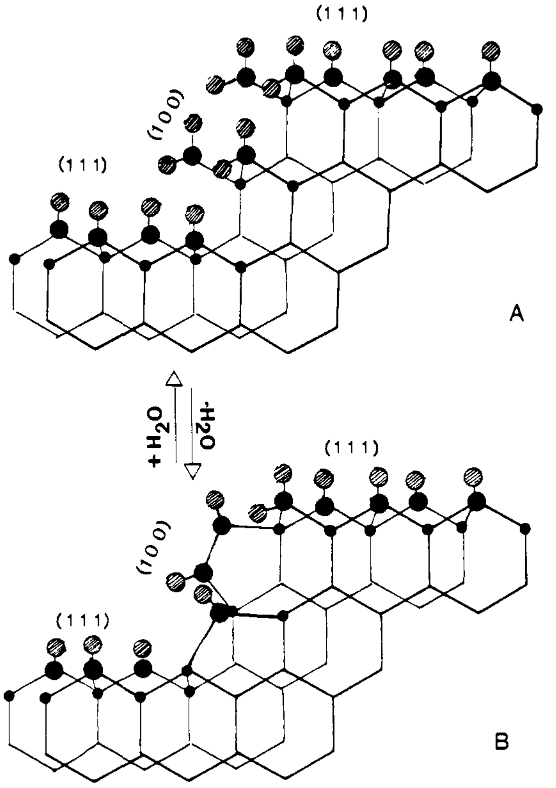


Figure 12. Mixed-surface model showing proposed mechanism of reversible dehydration on 100 surface planes: (A) original surface, (B) partially dehydrated surface.

The nominally inverse relationship between rehydration efficiency and dehydration temperature exhibited in both of these figures is consistent with a dehydration mechanism that is kinetically controlled by the surface concentration of residual silanol groups. Because equilibrium was not completely achieved under the relatively mild rehydration procedures employed in this study, the kind of plateau behavior in the concentration of hydroxyl groups reported by DeBoer and Vleeskins for fully "annealed" silica gels was not observed. Nevertheless, CP/MAS ^{29}Si NMR provides a check of certain predictions of the Hockey mechanism for dehydration and rehydration.

If the 15%-abundant geminal sites on unheated silica gel arise from surface defects of type a in Figure 8, then the Hockey dehydration model predicts that their relative population should decrease with increasing dehydration temperatures. Because of underlying lattice strain, restoration of such sites following exposure to water may be possible for silica samples heated from low to moderate temperatures (500 °C). For samples heated to higher temperatures, however, the removal of strain by annealing is predicted to result in defect-free silica surfaces containing only single-hydroxyl silanol sites. The data of Figures 10 and 11 are in clear conflict with these expectations, since they indicate that some geminal sites are present at all degrees of hydration. Highly dehydrated surfaces actually show an increase in the relative population of geminal groups as temperatures are increased beyond the hypothetical annealing point of DeBoer and Vleeskins. Hence, while the DeBoer–Vleeskins model may describe the behavior of the more prevalent single-hydroxyl sites, it is incompatible with changes observed in the surface population of geminal sites.

According to the model of Peri and Hensley, unheated silica surfaces contain silanol sites of only the geminal-hydroxyl type. Although inconsistent with ^{29}Si spectra of completely hydrated materials, this model may explain the behavior observed for the geminal silanol population if regions of 100 and 111 surfaces are assumed to exist simultaneously in the silica gel samples. For sections of 100 surface, the Peri–Hensley model predicts that the relative concentration of geminal sites will decrease as temperatures are increased from low to moderate values. This will arise from the random condensation of adjacent hydroxyls along rows of geminal silanols and result in pairs of vicinal-silanol sites having chemical structures of the single-hydroxyl type (e.g., b of Figure 8B). For maximum dehydration via this mechanism, Peri concluded that about 15% of the original geminal sites will remain on the surface. These sites will be well separated from other surface hydroxyls and may therefore be resistant to subsequent dehydroxylation. This behavior is qualitatively consistent with the dehydration data exhibited for geminal sites in Figure 11. At low to moderate temperatures, these sites condense more readily than single silanols. At higher temperatures (500–700 °C) a plateau is reached in which little further reduction in the geminal silanol population occurs. This could correspond to the maximum level of dehydration permitted by the mechanism suggested by Peri, leaving only vicinal pairs and condensation-resistant, isolated geminal groups on the 100 silica surface.

The data in Figure 11 indicate that for 500–700 °C dehydration about 30% of the original geminal sites remain. Although higher than the 15% levels predicted by Peri, the possible presence of geminal-hydroxyl sites associated with edges and corners that separate surface planes and nonrandom condensation processes may account for this.

Rehydration data also support the presence of structures corresponding to 100-face surface regions, if interpretation is based upon kinetic factors rather than the thermodynamic arguments of Peri and Hensley. Condensation reactions between adjacent hydroxyls of geminal sites give rise to "vicinal pairs" of residual single-hydroxyl species interconnected by single siloxane bonds, as illustrated in Figure 12 for a hypothetical section of 100 surface, joining two sections of 111 surface. In contrast, processes occurring exclusively on the 111 faces must result in hydrophobic siloxane bridges that may be many bonds removed from nearest-neighbor hydroxyls.

The assumption of a kinetically controlled rehydration mechanism that requires as a rate-limiting step the initial adsorption of molecular water leads to the prediction of preferential restoration of geminal sites associated with vicinal pairs, since in this case two hydroxyls are available for H_2O adsorption. This prediction is consistent with the data in Figure 12, which show that for surfaces heated to moderate temperatures, the elimination/restoration of geminal sites is essentially a reversible process. Single-hydroxyl silanol sites are only partially recovered under identical conditions. The drop in the rehydration efficiency of geminal sites for samples dehydrated above 500 °C may reflect the second dehydration mechanism proposed by Peri and Hensley, involving the rotation of silicon tetrahedra associated with vicinal-hydroxyl pairs to form edge-linked condensation structures that are interconnected by two siloxane bonds (eq 2). As in the case of dehydration reactions on faces of the 111 type, these groups have no directly associated hydroxyls, and from a kinetic viewpoint would therefore not be expected to rehydrate easily under the mild conditions of this study.

In summary, consideration of ^{29}Si NMR intensities in dehydration and rehydration studies of silica gel have shown that no single, previously proposed model gives a completely adequate description of the surface structure and behavior. The present evidence indicates that the silica surface is quite heterogeneous and may contain segments of surface resembling both the 111 and 100 faces of cristobalite. On both types of surface, rehydration efficiency appears to be dictated primarily by kinetic rather than thermodynamic factors.

Acknowledgements. We gratefully acknowledge partial support of this research by the U.S. Department of Energy (Contract No. De-AT20-81LC10652 from the Laramie Energy Technology Center) and the assistance of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE 78-18581.

Registry No. Silicon-29, 14304-87-1.