13040 *J. Am. Chem. Soc.* **1996,** *118,* 13040−13045

Study of the Constitutive Superficial Water of Precipitated Amorphous Silicas using ^{1}H NMR: Broad-Line at 4 K and HR MAS at 300 K

C. Dorémieux-Morin,*,† L. Heeribout,† C. Dumousseaux,† J. Fraissard,† H. Hommel,‡ and A. P. Legrand‡

Contribution from the Laboratoire de Chimie des Surfaces, Université P. et M. Curie, Unité associée au CNRS - URA 1428, Casier 196, 4, place Jussieu, F 75252 Paris Cédex 05, France, and Laboratoire de Physique Quantique, ESPCI, Unité associée au CNRS - URA 1428, 10, rue Vauquelin, F 75005 Paris, France

Received June 19, 1996⊗

Abstract: Two silicas obtained by precipitation have been compared using two ^{1}H NMR techniques: broad-line at 4 K with simulation of the spectra and MAS at room temperature. Previous ^{29}Si high resolution NMR results have been used to interpret the spectra. Geminal silanols, single silanols, water molecules relatively strongly hydrogen-bonded to silanols, and water not interacting with OH groups have been characterized and quantified. Differences are found between the two precipitated silicas. Silanols, 70% of which can hydrogen-bond a water molecule, occupy all the surface of one of them. The other sample surface is not so crowded with silanols, and only 37% of them hydrogen-bond water molecules. Both geminal and single silanols hydrogen-bond water. Physisorbed water molecules not interacting with silanols can be equilibrated on both sample surfaces. Room temperature dehydration of the samples in vacuum is studied.

Introduction

Amorphous silicas have been extensively studied by means of NMR techniques, the spectra either of nuclei belonging to the silicas themselves (^{29}Si,[1−9] ^{17}O,[10] ^{1}H[1−3,7,11,12]) or of those present in modified silicas (previous nuclei and also ^{2}H, ^{13}C, ^{31}P, ^{14}N, ^{15}N[1,2]) being recorded. Important results on the structure of unmodified silicas have been obtained.

^{1}H High resolution NMR has been used to study the hydroxyl groups and hydration of silicas. The *isotropic* value of the chemical shift, δ_{iso}, is given by high resolution magic angle spinning NMR (MAS) or the more elaborate technique of combined rotation and multipulse spectroscopy (CRAMPS). Though not general, a relationship giving δ_{iso} in terms of the deprotonation energy ΔE_{DP}

$$d(\Delta E_{DP})/d(\delta_{iso}) = -84 \pm 12 \text{ kJ mol}^{-1} \text{ ppm}^{-1}$$

has been proposed for catalyst surface hydroxyl groups, when these groups are all bonded to elements (including Si) whose first coordination sphere consists solely of oxygen atoms.[13] The value of 1.7−2.5 ppm (all values are relative to TMS), attributed by different authors[1−2,14,15] to isolated silanol groups does not correspond to an easy deprotonation.[13] The *anisotropy* of the chemical shift, measured by using only a multipulse sequence, gives information about the symmetry of the O-H bonds. Schreiber and Vaughan[16] found 6.9 ppm for the axial anisotropy of a sample containing 1.6 OH group·nm^{-2} and Ernst[17] 5.5 ± 0.3 ppm, the coverage of his silica sample being 1.5 OH group.nm^{-2}. This anisotropy is 2 to 4 times smaller than for hydroxyl protons in other oxides.[16] Bernstein et al.[18] related this reduction to the rapid rotation of the OH groups around the Si-O axis. The Si-O-H angle is as (140 ± 5)°.[17]

Maciel et al.[1,2,10,12] published important CRAMPS results on a silica gel (S-679 from Fisher) at different stages of hydration. The samples were sealed in thin-walled glass tubes. A sample in equilibrium with the atmosphere shows three resolvable peaks which the authors attributed as follows: isolated SiOH at 1.7

---

* Correspondence to Dr. C. Dorémieux (E-mail address: cd@ccr.jussieu.fr). CNRS - URA1428, Université P. et M. Curie, Chimie des Surfaces, Casier 196 4, place Jussieu, 75252 Paris Cedex 05, France. Tel. 1 44275537. Fax 1 44275536.

† Université P. et M. Curie.

‡ ESPCI.

⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1996.

[1] Maciel, G. E.; Ellis, P. D. In *NMR Techniques in Catalysis*; Bell, A. T., Pines, A., Eds.; Marcel Dekker: New York, 1994; p 231, and refs therein.

[2] Maciel, G. E.; Bronnimann, C. E.; Zeigler, R. C.; Chuang, I-S.; Kinney, D. R.; Keiter, E. A. In *The Colloid Chemistry of Silica*; Bergna, H. E., Ed.; Adv. Chem. Ser. 234, American Chemical Society: Washington, DC: 1994; p 269, and refs therein.

[3] Maciel, G. E.; Bronnimann, C. E.; Hawkins, B. L. In *Advances in Magnetic Resonance: The Waugh Symposium*; Warren, W. S., Ed.; Academic Press: San Diego, 1990; Vol. 14, p 125.

[4] Chuang, I.-S.; Kinney, D. R.; Maciel, G. E. *J. Am. Chem. Soc.* **1993**, *115*, 8695.

[5] Chuang, I.-S.; Maciel, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 401.

[6] Legrand, A. P.; Hommel, H.; Tuel, A.; Vidal, A.; Balard, H.; Papirer, E.; Levitz, P.; Czernichowski, M.; Erre, R.; Van Damme, H.; Gallas, J. P.; Hemedy, J. F.; Lavalley, J. C.; Barres, O.; Burneau, A.; Grillet, Y. *Adv. Colloid Interfac. Sci.* **1990**, *33*, 91.

[7] *The Surface Properties of Silica*; Legrand, A. P., Ed.; Wiley: New York, to be published.

[8] Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1487.

[9] Leonardelli, S.; Facchini, L.; Frétigny, C.; Tougne, P.; Legrand, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 6412.

[10] Walter, T. H.; Turner, G. L.; Oldfield, E. *J. Magn. Reson.* **1988**, *76*, 106.

[11] Bronnimann, C. E.; Zeigler, R. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 2023.

[12] Kinney, D. R.; Chuang, I-S.; Maciel, G. E. *J. Am. Chem. Soc.* **1993**, *115*, 6786.

[13] Fleischer, U.; Kutzelnigg, W.; Bleiber, A.; Sauer, J. *J. Am. Chem. Soc.* **1993**, *115*, 7833.

[14] Bonardet, J. L.; Fraissard J.; de Ménorval L. C. *Proceedings of the 6th International Congress* Catalysis, B6; London, 1976.

[15] Rosenberger, H.; Ernst, H.; Scheler, G.; Jünger, I.; Sonnenberger, R. *Z. Phys. Chem. (Leipzig)* **1982**, *263*, 846.

[16] Schreiber, L. B.; Vaughan, R. W. *J. Catal.* **1975**, *40*, 226.

[17] Ernst, H. *Z. Phys. Chem. (Leipzig)* **1987**, *268*, 405.

[18] Bernstein, T.; Ernst, H.; Freude, D.; Jünger, I.; Sauer, J.; Staudte, B. *Z. Phys. Chem. (Leipzig)* **1981**, *262*, 1123.

S0002-7863(96)02057-4 CCC: $12.00

ppm; physisorbed water, a narrow signal at 3.5 ppm; hydrogen-bonded OH groups, a broad signal (at about 3.0 ppm). The width and the position of this last signal depends upon sample treatment. These attributions result from experiments on treated samples: evacuation (10^{-2} Torr, 25 °C) leads to almost complete disappearance of the signal at 3.5 ppm. The spectrum of the sample is little changed by vacuum treatment between 25 and 200 °C . Evacuation at 500 °C leaves only the relatively sharp peak of isolated SiOH groups at 1.7 ppm.

Combining CRAMPS and relaxation experiments on untreated silica gel and on a silica gel evacuated at 25 °C, Maciel et al.[1,2,11] showed that all the components of each spectrum relax at the same rate. However, the common T_1 value depends markedly on whether or not physisorbed water is present. It seems that the motion of the adsorbed water molecules provides a relaxation "sink" for all the protons on the surface. Introducing dipolar dephasing in the CRAMPS experiment, the same authors[1,2,11] confirmed that the 3 ppm signal corresponds to hydrogen-bonded silanols. These authors refined their experiments further by introducing a "mixing time" after the dephasing time. They concluded that spin equilibration arises from mutual dipolar coupling by spin diffusion. (Spin diffusion is defined as the process by which resolvable spin sets achieve thermal equilibrium with respect to each other following a perturbation of the system that leaves the different spin sets in different states of nuclear spin polarization.)[1,2] For the sample without molecular water, the apparent efficiency of spin diffusion between the two types of silanol proton implies a mean distance less than 1 nm between the hydrogen-bonded and isolated silanol protons. For the untreated sample, ^{1}H spin diffusion between water and silanol protons is almost inexistent on the microsecond-to-millisecond time scale. The authors[1,2,11] claimed that these ^{1}H CRAMPS results are consistent with previous IR results. Maciel's team[12] studied the interaction between water and the same silica surface using variable-temperature high resolution ^{1}H RMN, both MAS and CRAMPS. Several samples with different water concentrations were tested. Water physisorbed on the silica surface exhibits a freezing point depression of roughly 40 K relative to pure water. Molecular reorientation of physisorbed water at rates in the tens of kiloHertz range have been observed through interference with multi-pulse line narrowing.

There are a large number of studies of silica by ^{29}Si NMR.[1−9] In general, it is easy to distinguish between three different sites: geminal silanols give a line at −90 ppm, single silanols at −100 ppm and siloxane bridges at −110 ppm. A large body of knowledge is available from the ^{29}Si spectra of species subjected to different treatments. Maciel et al.[1] claimed that comparison of the ^{1}H and the ^{29}Si NMR results still presents many difficulties, due probably to spin dynamic effects which lead to different relaxation paths.[1] In particular, the attribution of the ^{1}H and ^{29}Si lines to definite identical species is not straightforward, because the respective evolutions as a function of the experimental parameters are not always closely related.[1] However, these authors contribute strongly to enhance the understanding of NMR results obtained with both nuclei. Interior hydroxyls of silica gel have been studied by ^{29}Si CP-MAS.[4] The results are the following: (i) there is no evidence for internal geminal silanols; (ii) hydroxyl groups of the internal single silanols undergo rapid rotation about the Si-OH bond axis; (iii) internal single silanols have a much smaller ^{1}H−^{1}H dipolar interaction than those on the surface; (iv) some of the internal single silanols may be accompanied by trapped water. Chuang and Maciel[5] also probed hydrogen bonding and the local environment of silanols on silica surfaces via nuclear spin cross polarization dynamics.

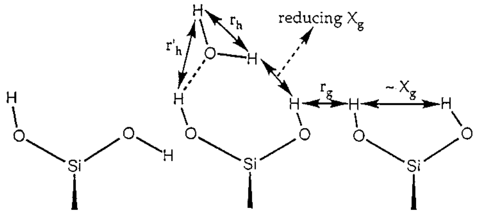

Figure 1. Meaning of some distance parameters of magnetic configurations used for simulating ^{1}H broad-line NMR spectra. The subscript "h" is for "hydrogen-bonded complex" and the subscript "g" for "geminal". Changes on geminal silanol hydration.

The aim of this paper is to present results on two different silicas prepared by precipitation, using ^{1}H NMR both broad-line of "rigid lattice" with simulation of the spectra and magic angle spinning (MAS) at room temperature. The samples are either dehydrated or not, in order to study quantitatively the nature of the silanols (single, hydrogen-bonded or geminal) and the interaction between hydration water and silanols. Previous results from ^{29}Si NMR on the same samples[6] will be used in the interpretation of these results.

Experimental Section

The chosen samples, denoted P and G, are from Rhône-Poulenc. Their preparations are described in patents, refs 19 and 20, respectively, and their physical characteristics are given in ref 6; the specific surface area of P measured by BET(N_2) is about the same as that of silicas obtained by pyrohydrolysis (200 m^2/g). The BET(N_2) specific surface area of G is 392 m^2/g. Both silicas have a rough surface and are not perceived by N_2 molecules as microporous.[6] The distribution of mesopores is wide for P, from 16 to 80 nm with two maxima at 30 and 46 nm and narrower for G, from 10 to 40 nm with a maximum at 24 nm.[6] In contrast to P, sample G consists of dense aggregates with badly defined outlines.[6] The samples were sealed in cylindrical glass ampules without or with vacuum pretreatment at room temperature for various times. They are denoted P_m or G_n where m or n are the approximate coefficients of their formulas expressed as SiO_2, m or n H_2O, in other words, the amount of total constitutive water per SiO_2 after pretreatment (including molecular water and the contribution of OH groups).

Broad-line spectra were recorded at 60 MHz as the derivative of absorption relative to the main applied magnetic field.[21] The experiment temperature was 4 K in order to avoid translation and rotation of the oxyhydrogenated species. Details of the experiments can be found in ref 22. High resolution ^{1}H MAS spectra were recorded at room temperature at 400 MHz with 3 kHz spinning rate,[21] and, for one sample, at 500 MHz with 10 kHz spinning rate. The signal for the probe and the empty glass ampule was subtracted from the crude signal in both techniques.

The simulated broad-line spectra correspond to the weighted sum of the following contributions of the various species for which the magnetic configurations have been calculated: (i) H_2O and, more generally, protons taken two-by-two: a **r**-distant two-spin configuration,[23] denoted $\mathbf{r}_w$ for water and $\mathbf{r}_g$ for geminal OH groups (Figure 1); (ii) $H_2O\cdots HOSi$: a magnetic configuration with three spins at the vertices of an isosceles triangle,[24−26] where $\mathbf{r}_h$ is the base and $\mathbf{r}'_h$ the equal sides (**h** for "hydrogen-bonded species") (Figure 1); (iii) silanols: in this case, a pure Lorentzian function (parameter in Tesla),

---

(19) Patent FR 8715275, Nov 4, 1987

(20) Patent EP 18866, June 13, 1983.

(21) Batamack, P.; Dorémieux-Morin, C.; Fraissard, J.; Freude, D. *J. Phys. Chem.* **1991**, *95*, 3790.

(22) Semmer, V.; Batamack, P.; Dorémieux-Morin, C.; Vincent, R.; Fraissard, J. *J. Catal.* **1996**, *160*.

(23) Pake, G. E. *J. Chem. Phys.* **1948**, *16*, 327.

(24) Andrew, E. R.; Finch, N. D. *Proc. Phys. Soc.* **1957**, *70B*, 980.

(25) Dorémieux-Morin, C. *J. Magn. Reson.* **1976**, *21*, 419.

(26) Dorémieux-Morin, C. *J. Magn. Reson.* **1979**, *33*, 505.

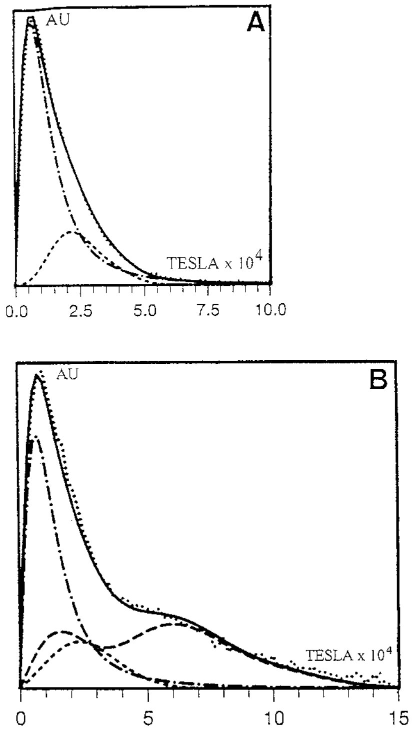

Figure 2. ^{1}H broad-line half-derivative absorption spectra of two P silicas at 4 K. (A) $P_{0.12}$ and (B) $P_{0.22}$. ··· experimental spectra; continuous line, simulated spectra; — · —, - - , single silanols; — — —, geminal silanols; - -, $H_2O\cdots HOSi$ species.

Table 1. Formulas, $SiO_x(OH)_y(H_2O\cdots HO)_z(H_2O)_u$, of P_m and G_n Samples from ^{1}H Broad-Line NMR Results[a]

sample	x in SiO_x	y in $(OH)_y$ ± 0.004	z in $(H_2O\cdots HO)_z$ ± 0.004	u in $(H_2O)_u$ ± 0.004	f_g' ± 0.03
$P_{0.12}$	1.88	0.24	0	0	0.18
$P_{0.18}$	1.88	0.184	0.056	0	0.17
$P_{0.22}$	1.88	0.142	0.098	0	0.16
$P_{0.24}$	1.88	0.125	0.115	0	0.15
$P_{0.40}$	1.88	0.070	0.170	0.110	0.21
$G_{0.15}$	1.86	0.266	0.014	0	0.17
$G_{0.20}$	1.86	0.225	0.055	0	0.15
$G_{0.38}$	1.86	0.210	0.070	0.165	0.16
$G_{0.45}$	1.86	0.176	0.104	0.201	0.15

[a] {including geminal silanols assumed from the f_g values (4)}, where m and n are the approximate coefficients of their formula expressed as SiO_2, m/n H_2O, in other words the amount of total constitutive water (water and OH form) per SiO_2; the calculations are normalized to the f_s values of 0.20 and 0.24 for P_m and G_n, respectively.[4] The symbol f_g' expresses the number of geminal silanols per silanol, none of them interacting with molecular water. The $\mathbf{r}$ value of the two-spin configuration used to determine f_g' is 230 pm, from the results obtained with $P_{0.12}$.

Table 2. Distance Parameters Used for the Simulation of the ^{1}H Broad Line NMR spectra of P_m and G_n Samples

sample	Lorentzian function parameter (10^{-4} T)	$H_2O\cdots HOSi$ distance parameters (pm) $\mathbf{r_h}$; $\mathbf{r'h}$; $\mathbf{X_h}$	geminal two-spin distance parameters (pm) $\mathbf{r_g}$; $\mathbf{X_g}$	H_2O distance parameters (pm) $\mathbf{r_w}$; $\mathbf{X_w}$
$P_{0.12}$	1.95 ± 0.05		230; 285	
$P_{0.18}$	2.04 ± 0.05	155; 225; 228	230; 245	
$P_{0.22}$	2.11 ± 0.05	159; 231; 235	230; 255	
$P_{0.24}$	2.04 ± 0.05	155; 225; 230	230; 250	
$P_{0.40}$	1.99 ± 0.05	140; 196; 210	230; 250	165; 225
$G_{0.15}$	1.66 ± 0.04	165; 231; 240	230; 275	
$G_{0.20}$	1.81 ± 0.05	165; 231; 262	230; 275	
$G_{0.38}$	2.51 ± 0.05	147; 210; 210	230; 270	165; 220
$G_{0.45}$	2.28 ± 0.05	142; 199; 230	230; 270	165; 230

[a] The accuracy on $\mathbf{r}$ values for water molecules (140−165 pm) is ±2 pm; for geminal hydroxyl $\mathbf{r}$, $H_2O\cdots HOSi$ $\mathbf{r'}$ and all $\mathbf{X}$ values it is ± 5 pm.

or a two-spin configuration[27] as mentioned above. Each of the corresponding functions (except the Lorentzian) was convoluted by a Gaussian which allows for the interactions between the protons of the configuration and the other magnetic spins outside the configuration. As the ^{29}Si and ^{17}O nuclei are diluted, the parameter of each Gaussian was related to a ^{1}H−^{1}H distance, $\mathbf{X_i}$ ($\mathbf{i} = \mathbf{w}$, $\mathbf{g}$ or $\mathbf{h}$) close to the shortest distance between a proton of the configuration considered and a proton outside it. As no dehydroxylation could occur during the room temperature pretreatment, the quantitative results[28] were expressed on the basis of two ratios determined by Legrand et al.[6] using ^{29}Si MAS NMR: (i) f_s: number of silanol Si, whether single or geminal, per Si (the f_s value is 0.20 and 0.24 for P and G, respectively); (ii) f_g: number of $Si(OH)_2$ groups per silanol, whether single or geminal (the f_g value is 0.18 and 0.17 for P and G, respectively). We define as f_g' the number of $Si(OH)_2$ per silanol, neither of them interacting with water molecules. It results that the sample formulas (for fully hydroxylated samples without molecular water) are $SiO_{2.12}H_{0.24}$ and $SiO_{2.14}H_{0.28}$ for P and G, respectively.

Results

The broad-line spectrum of the most dehydrated P sample, $P_{0.12}$, indicates that molecular water is absent. This spectrum is simulated by using two contributions: (i) a Lorentzian derivative for magnetically diluted OH groups[29] which can be located on solid surfaces;[30] (ii) a two-spin contribution for which the smallest H−H distance is in the 220-235 pm range, denoted $\mathbf{r_g}$. Such a low precision on $\mathbf{r_g}$ is due to the fact that the experimental spectrum was unresolved (Figure 2A).

From the 0.18 f_g value,[6] determined by ^{29}Si NMR, the fraction of H atoms belonging to geminal silanols corresponds to 0.31 of all silanol H atoms of $P_{0.12}$. The relative concentration of the protons responsible for the two-spin signal was in acceptable agreement with the 0.31 value, a striking result which supports the attributions of the peaks: we assume, therefore, that the two-spin contribution represents geminal OH group resonance. The $\mathbf{r_g}$ distance parameter used for the simulation giving the assumed number of protons as geminal OH is 230 ± 2 pm. The results are given in Table 1. The magnetic configuration ^{1}H−^{1}H distances are in Table 2.

The experimental and simulated MAS spectra of $P_{0.12}$ at 10 kHz spinning rate (Figure 3) show three signals: (i) a doublet at 1.8 and 1.1 ppm with an intensity ratio of 0.9 (±20%); (ii) a signal at 3.8 ± 0.2 ppm twice as wide as each part of the doublet and not well resolved. Maciel's team[1,2,11] has found hydrogen-bonded silanols resonating about 3 ppm and this attribution can also be valid *a priori* for the 3.8 ppm signal. However, the relative weight of this 3.8 ppm signal is 0.26−0.39, in good agreement with the expected value of 0.31 if this signal was attributed to geminal silanols. These proposals will be discussed later.

The experimental broad-line spectra of the other samples, either P_m ($m \geq 0.18$) or G_n ($n \geq 0.15$) proved the presence of molecular water, indicated by the relatively important contribution in the 6 10^{-4} T domain (Figures 2B and 5). Moreover, geminal silanol groups were assumed to be characterized by the 230 pm $\mathbf{r_g}$ value found for $P_{0.12}$. The concentration of

---

[27] Porte, A. L.; Gutowsky, H. S.; Boggs, J. E. *J. Chem. Phys.* **1962**, *36*, 1695.

[28] Dorémieux-Morin, C.; Hommel, H.; Heeribout, L.; Legrand, A. P.; Dumont, E.; Fraissard, J. 11th Specialized Colloquium AMPERE on Catalysis; Menton, France, 1993.

[29] Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon: Oxford, 1961; Chapter IV.

[30] Freude, D.; Schmiedel, H. *Phys. Stat. Sol.* **1972**, *54*, 631.

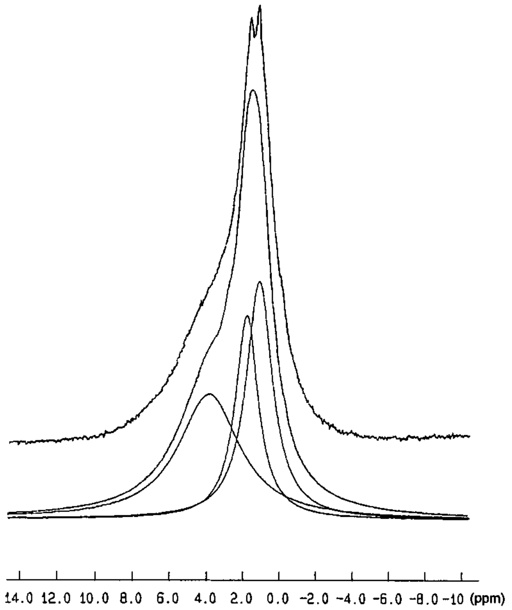

Figure 3. ^1H MAS spectra (experimental, simulated and components) of sample $P_{0.12}$ (500 MHz, 10 kHz spinning rate). The experimental spectrum can be spotted by the noise of its drawing.

geminal silanol H, which could differ from its value for $P_{0.12}$, remained to be determined by fitting. The simulated spectra contained the following contributions: (i) SiOH still diluted; (ii) $Si(OH)_2$ groups; (iii) water molecules relatively strongly hydrogen-bonded to hydroxyl groups; (iv) only for the non- or less dehydrated samples ($P_{0.40}$, $G_{0.45}$ and $G_{0.38}$), water molecules not interacting with hydroxyl groups. The results are presented in Table 1, the samples being formulated as $SiO_x(OH)_y(H_2O\cdots HO)_z(H_2O)_u$. The magnetic configuration $^1H-^1H$ distances are in Table 2. Given the assumptions proposed above, the f_g' ratio is approximately constant for both the P and G samples, whatever the m or n value (Table 1).

The MAS spectra of P and G at 400 MHz and 3 kHz spinning rate are given in Figures 4 and 6, respectively; MAS spectra were not recorded for $G_{0.38}$ and $G_{0.45}$. They contain a 2.2 ppm peak of SiOH groups and, depending on the water content, a broad signal at 3.9−4.7 ppm attributable to rapidly exchanging H atoms.[21] Moreover, for P samples containing some molecular water (Figure 4B−E), a shoulder of the peak for exchanging H atoms, at about 7 ppm, is present. This signal is also present for G, as a shoulder for $G_{0.15}$ (Figure 6A) but is well defined for $G_{0.20}$ (Figure 6B). The chemical analysis of the samples[6] excludes the possibility that this signal corresponds to NH_4^+ protons. Freude recently attributed such a peak,[31] which is always narrow, to silanol groups hydrogen-bonded to O atoms (framework O atoms in the case of zeolites).

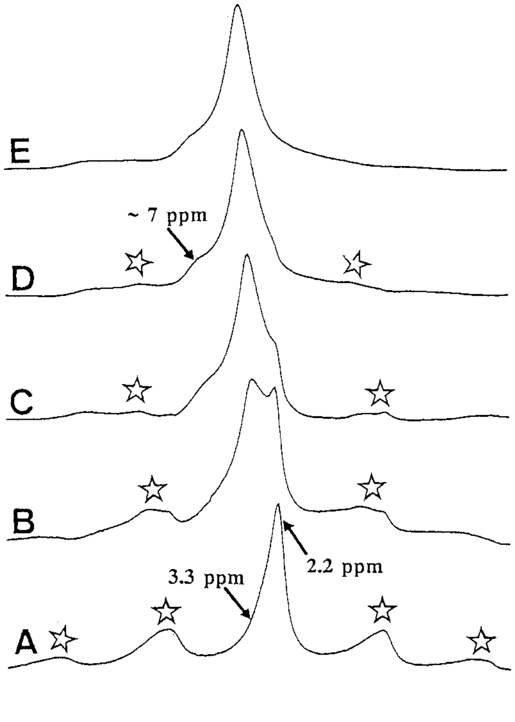

Figure 4. ^1H MAS spectra of P silicas (400 MHz, 3 kHz spinning rate): (A) $P_{0.12}$; (B) $P_{0.18}$; (C) $P_{0.22}$; (D) $P_{0.24}$; (E) $P_{0.40}$. * indicates spinning side-bands.

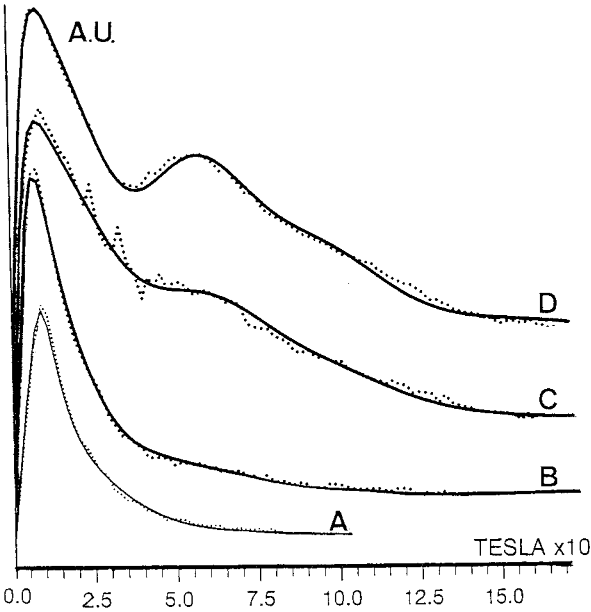

Figure 5. ^1H broad-line half-derivative absorption spectra of G silicas at 4K: (A) $G_{0.15}$; (B) $G_{0.20}$; (C) $G_{0.38}$; (D) $G_{0.45}$. ···, experimental spectra; continuous line, simulated spectra.

Discussion

Let us first consider the "dry" $P_{0.12}$ sample. In order to simplify this discussion we use the following sets of initials (Table 3): G for all geminal silanols, S for all single silanols, HG for hydrogen-bonded geminal silanols; HS for hydrogen-bonded single silanols; NHG for non-hydrogen-bonded geminal silanols; NHS for non-hydrogen-bonded single silanols.

In view of its intensity, we proposed to attribute the 3.8 ppm peak of the $P_{0.12}$ MAS spectrum to geminal silanols. However, Maciel and Ellis's attribution of a 3 ppm signal to hydrogen-bonded silanol H on the S-679 Fisher gel surface[1,2,11] could also be valid for P and G signals at 3.8 ppm. In this case, all non-hydrogen-bonded silanol H (belonging to NHG and NHS) would resonate at 1.8 or 1.1 ppm (Figure 4), one of these signals corresponding probably to geminal silanols and the other to single ones. Chuang and Maciel's recent results[5] on two different "dry" silica samples showed (NHG/G) and (NHS/S) to be 46−47% and 53−58%, respectively. Assuming (NHG/G) and (NHS/S) values to differ not much between these author samples and P, which seems likely, NHG/NHS is about 0.18. As there are two H atoms per geminal silanol, the H atom relative concentrations in these NHG and NHS, would be 0.37, far from the 0.9 ratio of the 1.8 to 1.1 ppm signal intensities.

Assuming that the 3.8 ppm signal of the $P_{0.12}$ ^1H MAS spectrum at high spinning rate can be attributed to geminal

Table 3

Abbreviations and symbols

f_s	number of silanol Si, whether single or geminal, per Si (the f_s value is 0.20 and 0.24 for P and G, respectively)
f_g	number of $Si(OH)_2$ groups per silanol, whether single or geminal (the f_g value is 0.18 and 0.17 for P and G, respectively)
f_g'	number of $Si(OH)_2$ per silanol, neither of them interacting with water molecules

Silanol Concentrations of Sample $P_{0.12}$, Which Contains No Molecular Water

S	all single silanols	G	all geminal silanols
HS	hydrogen-bonded single silanols	HG	hydrogen-bonded geminal silanols
NHS	non-hydrogen-bonded single silanols	NHG	non-hydrogen-bonded geminal silanols

$S = HS + NHS$ $G = HG + NHG$

$f_g = G/(S + G)$

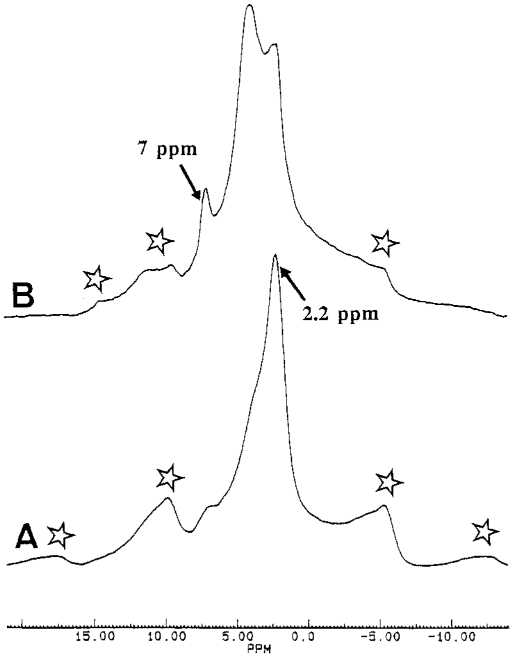

Figure 6. ^1H MAS spectra of G silicas (400 MHz, 3 kHz spinning rate): (A) $G_{0.15}$ and (B) $G_{0.20}$;. * indicates spinning side-bands.

silanols, the presence of the two signals at 1.1 and 1.8 ppm is relatively easy to understand, also in the light of Chuang and Maciel's results.[5] From these results the NHS/S value is 53−58%, as mentioned above. Therefore the ratio HS/NHS is 47−42 / 53−58, between 0.89 and 0.72. The simulation data of the high-speed MAS spectrum of $P_{0.12}$, giving 0.9 (±20%) for the ratio of the H atom concentrations for the 1.8 and 1.1 ppm doublet, can be considered to be in agreement with ref 5. The 1.1 ppm signal would correspond to NHS and that at 1.8 ppm to HS. We confirm, therefore, the attribution of the 3.8 ppm signal to geminal silanol H atoms.

Table 1 shows that f_g' remains about constant for P and G samples whatever the degree of hydration. This is to be compared with the results from Sindorf and Maciel,[8] and Leonardelli et al.[9] using ^{29}Si NMR, who obtained a nearly constant f_g value for different more or less hydrated samples.

When molecular water remains in the samples, there are hydrogen bonds between OH groups and H_2O, identified by the $\mathbf{r_h}$ and $\mathbf{r'_h}$ values used with the isosceles three-spin magnetic configuration (Table 2); Iler has already demonstrated such hydrogen bond formation[32] confirmed by Kinney et al.[12] using variable-temperature high resolution ^1H NMR. These $\mathbf{r'_h}$ values show that the hydrogen bonds are relatively strong, corresponding to oxygen−oxygen distances of about 250−255 pm, straight bonds and OH lengths of 100 pm being assumed.

Are all the oxy-hydrogenated species located on the silica surfaces?

According to the S BET(N_2) values,[6] the mean available surface area per P sample silanol is 0.10 nm^2 (Table 3). The typical surface area per OH group being 0.12 nm^2, almost every silanol can be on the surface, which is probably strained; however, a few silanols can be located "inside" the particles, as previously observed[4] in silica gels. For the P silica, the largest experimental number of $H_2O{\cdots}HO$ groups per silanol is 0.71 (Table 4). This number is in acceptable agreement with the specific surface area, some strain of the surface being assumed {0.14 nm^2 per hydrogen-bonded group (Table 3), the typical surface area per water molecule being 0.16 nm^2}. In air, for equilibrated P silica, water molecules "free" of interaction with OH groups are located upon those H_2O which are hydrogen-bonded to OH. The mean surface area then available per "free" water molecule {0.22 nm^2 (Table 3)}, corresponding to 0.46 of such water molecules per silanol (Table 4), shows that the surface is not densely covered with water molecules not interacting with OH groups.

Table 4. Available Mean Area per Oxyhydrogenated Species at Maximum Concentration

	mean surface area/silanol (nm^2)	mean surface area/$H_2O{\cdots}HO$ at max. exptl concn (nm^2)	mean surface area/free H_2O at max. exptl concn (nm^2)
silica P	0.10	0.14	0.22
silica G	0.17	0.46	0.24

Table 5. Mean Number of $H_2O{\cdots}HO$ and Water Molecules Not Interacting with OH Groups, per Silanol Group

sample	$P_{0.12}$	$P_{0.18}$	$P_{0.22}$	$P_{0.24}$	$P_{0.40}$
$H_2O{\cdots}HO$ per silanol	0	0.23	0.41	0.48	0.71
H_2O not interacting with OH, per silanol	0	0	0	0	0.46

sample	$G_{0.15}$	$G_{0.20}$	$G_{0.38}$	$G_{0.45}$
$H_2O{\cdots}HO$ per silanol	0.05	0.20	0.25	0.37
H_2O not interacting with OH, per silanol	0	0	0.59	0.72

For sample G, the mean available surface area per silanol being 0.17 nm^2 (Table 3), the silanols do not fill the surface; they are either clustered or randomly distributed over this surface.[33] The Lorentzian derivative shape of the diluted silanol broad-line spectrum does not exclude the possibility that there are parts of the surface without silanols. The large mean surface area available per silanol would allow each of them to hydrogen-bond a water molecule, but this is not the case: the highest experimental number of $H_2O{\cdots}HO$ groups per silanol is 0.37 (Table 4). On the room temperature equilibrated G sample, 0.72 of a "free" water molecule per silanol is present (Table 4).

The MAS signal at about 7 ppm is observed only in the spectra of P and G samples containing some molecular water. As this peak corresponds to silanols hydrogen-bonded to O atoms,[31] the silanol hydrogen bonds must concern either

---

(31) Freude, D. *Chem. Phys. Lett.* **1995** *235*, 69.

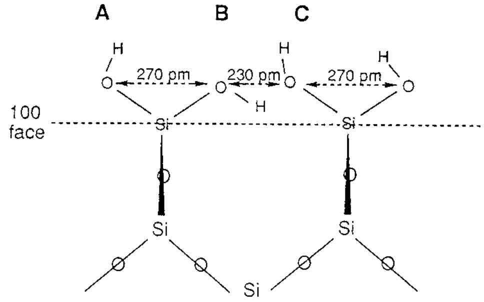

Figure 7. Localization of geminal silanols on the model 100 face of β-cristobalite.[1,4,5]

molecular water O atoms or neighboring surface O atoms. As mentioned previously, the hydrogen atoms of silanols hydrogen-bonded to water molecules are part of the chemically exchanging H, corresponding to the broad MAS signal between 3.9 and 4.7 ppm. Therefore, the protons resonating at 7 ppm are probably hydrogen-bonded to other silanol O atoms or to siloxane ones. The siloxane O atoms are more "basic" than those of the hydrogen-bonded silanols, and the stronger the hydrogen bonds, the larger the corresponding ^1H chemical shift. For this reason, we assume that the high 7 ppm chemical shift corresponds to silanols hydrogen-bonded to siloxane O atoms. The following result also supports this assumption: the relative concentration of these silanol H atoms, which is always low, is lower for P than for G samples (Figure 3B−E and Figure 6). This is in agreement with the idea that siloxane groups are more likely to be present on the G surface than on the silanol-crowded P surface. These silanols cannot be identified with the hydrogen-bonded ones of Fisher gel S-679, resonating at about 3.5 ppm.[1,2,11]

New results can be inferred from the geminal silanol H−H distances.

The $\mathbf{r_g}$ value found for geminal silanols at the surface of $P_{0.12}$, 230 pm, is equal to the smallest O-O distance of OH groups, BC, at the model surface of the 100 face of β-cristobalite[1,4,5] (Figure 7); this is likely the mean distance between the protons of these OH groups, belonging to geminal silanols. However, this value does not correspond to the intra-group distance, which is about 270 pm (AB in Figure 7), but to the inter-group one (Figure 7). It results that geminal silanols on $P_{0.12}$ are each other's neighbors, gathered into clusters, in agreement with the β-cristobalite 100 face surface model.[1,4,5]

We assumed the geminal inter-silanol H−H distance to be the 230 pm $\mathbf{r_g}$ value of the two-spin magnetic configuration for both P and G. For the dry $P_{0.12}$ sample, the distance parameter $\mathbf{X_g}$ is found to be 285 pm (Table 2), a little larger than the 270 pm geminal intra-silanol H−H distance (Figure 1); this is not surprising, because geminal silanols are in rows about 500 pm apart (cf Figure 4B in ref 5). The dependence of the distance parameter on hydration must be discussed. It should be kept in mind that, generally, **"X"** does not express a definite distance but an apparent mean distance which corresponds to the coefficient of the Gaussian function used to describe the broadening of magnetic configuration spectra by nuclei outside the configurations. Introducing new H atoms (of water molecules) at distances of a geminal H shorter than the largest "distance" parameter of the **g** two-spin configuration, $\mathbf{X_g}$, would tend to decrease this $\mathbf{X_g}$ value (Figure 1). The hydrated silanol H atom itself is then considered to belong to a group of three-spins at the apices of an isosceles triangle. For G samples $\mathbf{X_g}$ is constant whatever the hydration level, about 270 pm (Table 2), the average distance to be expected for the intra-geminal H−H distance (AB in Figure 7).[1,11,5] The $\mathbf{X_g}$ value does not decrease for G, though $\mathbf{X_h}$ for the hydrogen-bonded species is always smaller than $\mathbf{X_g}$ (Table 2); this shows that geminal silanols are gathered into large clusters compared to the number of these geminal silanols which can be hydrogen-bonded. For all hydrated P samples, $\mathbf{X_g}$ is about 250 pm (Table 2). Such low values of $\mathbf{X_g}$ are understandable if the clusters of geminal silanols are smaller for P silica than for G.

Conclusion

^1H broad-line NMR at 4 K with simulation of the spectra and ^1H MAS NMR of hydrated and room temperature in vacuum dehydrated precipitated silicas (P and G)[6,7] provide quantitative results about the surface of these samples.

On a P sample containing no molecular water, single silanols, hydrogen-bonded and not hydrogen-bonded are evidenced on a 10 kHz spectrum by two MAS signals at 1.8 and 1.1 ppm. Another signal at about 3.8 ppm is attributed to geminal silanols, in agreement with the broad-line spectrum. Physisorbed water molecules at the surface of P and G samples equilibrated in air can be eliminated under vacuum at room temperature. Some of these water molecules interact with silanols, giving relatively strong hydrogen bonds; other water molecules do not interact directly with silanols. For both samples, single and geminal OH groups are roughly statistically hydrated, and geminal silanols are gathered in clusters on surfaces corresponding to the 100 face of β-cristobalite, as proposed by Maciel and Ellis.[1,4,5] A MAS signal at 7 ppm, recently attributed to silanols hydrogen-bonded to O atoms[31] and which appears in the spectra of the hydrated samples, probably corresponds to a small number of silanols hydrogen-bonded to siloxane O atoms.

Differences are found between the two precipitated silicas, P and gel G. Silanols occupy almost all the P sample surface, but only 70% of them can hydrogen-bond a water molecule, probably because of steric hindrance. The G surface is not so crowded with silanols, and only 37% of them hydrogen-bond water molecules. The geminal silanol clusters are probably smaller for P than for G silica.

Maciel and Ellis[1] stated that "at the present stage, it seems preferable to develop each of ^1H and ^{29}Si high resolution NMR study on its own to its most remote consequences before trying to compare closely all aspects on the same samples". Though this will remain true for some time, using some ^{29}Si NMR results in order to understand our ^1H NMR results appears to us essential and hopeful.

JA962057K

---

(32) Iler, R. K. *The Chemistry of Silica. Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*; Wiley-Interscience: New York, 1979.

(33) Fraissard, J.; Solomon, I; Caillat, R.; Elston, J.; Imelik, B. *J. Chim. Phys.* 1963, 676.