Plasmachemical Dehydroxylation of High Surface Area Silica at Room Temperature

S. P. Godfrey and J. P. S. Badyal*

Department of Chemistry, Science Laboratories, Durham University, Durham DH1 3LE, England, U.K.

I. R. Little

*BP Amoco Chemicals, Sunbury-on-Thames, Middlesex TW16 7LL, England, U.K.*

Compared to conventional thermal and wet chemical methods, nonisothermal plasma treatment is found to be a viable alternative for carrying out dehydroxylation of porous silica. Changes in hydroxyl population and distribution within silica particles have been followed using solid state ^{1}H NMR, temperature programmed desorption, and optical emission spectroscopy.

Introduction

High surface area silica powders are used in a wide range of applications (e.g., as desiccants, additives in paints, inks, pharmaceuticals, and cosmetics).[1] Control of the silica surface hydroxyl density can have a profound impact upon its performance, e.g., in catalysis and chromatography.[1] Prior to any treatment, the surface contains a large hydroxyl population[1] together with physisorbed water.[2] Traditionally, thermal and chemical methods have been employed for changing the surface chemistry of silica. In the former case, heating to approximately 473 K causes loss of physisorbed water, and higher temperatures give rise to silanol (Si−OH) condensation to produce siloxanes (Si−O−Si), Scheme 1.[3] Above 1100 K,[1] there is total loss of surface hydroxyls; however, this is accompanied by sintering[4] and a drop in surface area. On the other hand, wet chemical modification of silica surfaces typically comprises reaction of hydroxyls with silane coupling agents;[1] e.g., hexamethyldisilazane converts hydroxyls to siloxanes according to (Scheme 2). However, the complete elimination of hydroxyls is impracticable due to the steric hindrance of trimethylsilyl groups blocking accessibility to neighboring surface hydroxyls.[5]

To overcome the drawbacks associated with conventional methods (large energy input, long treatment times, chemical waste, etc.) an alternative approach has been investigated using low-temperature ("cold") plasmas. Such partially ionized electrical discharges consist of ions, electrons, neutrals, and electromagnetic radiation, where the electron temperature ($T_e \approx 10\,000$ K) is much greater than the bulk gas temperature ($T_g \approx 300$ K).[6] Therefore, although the overall temperature of the system is close to ambient, the electrons possess sufficient energy to cause rupture and excitation of chemical bonds. It is this attribute which makes nonequilibrium plasmas so attractive for materials processing. Current areas of application include aerospace, automotives, microelectronics, optical coatings, packaging, lighting, and waste destruction.[7] For instance, plasma treatment of planar nonporous silica surfaces (where plasma penetration into the subsurface is not an issue) has already been investigated:[8] oxygen plasmas readily remove surface hydroxyls, while water plasmas are able to promote rehydroxylation. However, the nonisothermal electrical discharge dehydroxylation of the

SCHEME 1: Silanol Condensation Mechanism[3] (the Reaction May Be Considered with or without the Geminal Hydroxyls in Parentheses)
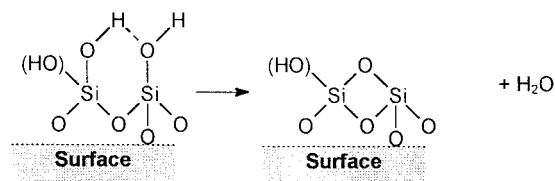
SCHEME 2: Silane Coupling Reaction[1]
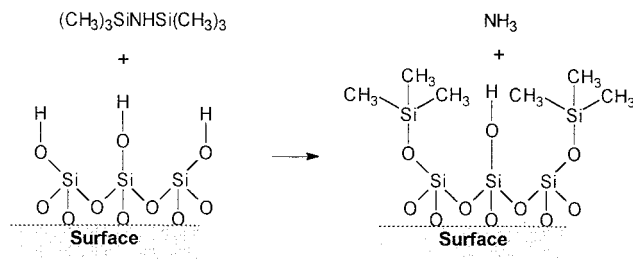
internal pores of high surface area silica particles has not been previously demonstrated.

Experimental Section

For comparison, conventional thermal dehydroxylation of silica was carried out in a nitrogen atmosphere (BOC 99.998%, dried through activated 3A molecular sieve (Aldrich) to give less than 1.0 ppm$_v$ of H_2O) at a flow rate of 3.0 dm^3 h^{-1}. Typically, 1 g of mesoporous silica (EP10X amorphous silica, Crosfield Ltd., pore volume = 1.81 cm^3 g^{-1}, particle size ≈ 100 μm) was loaded into a quartz microreactor and heated at 1 K min^{-1} to temperatures between 373 and 1073 K using a Eurotherm controller. The temperature was then kept constant for 5 h, prior to cooling at 5 K min^{-1} back down to 298 K. The composition of gases leaving the furnace was sampled in real time via a heated fine capillary tube connected to a computer controlled Vacuum Generators SX 200 quadrupole mass spectrometer.

An inductively coupled 13.56 MHz rotating plasma reactor was used to treat the silica powder. The chamber was pumped

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* To whom correspondence should be addressed.

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TABLE 1: Solid State ¹H NMR Data for Thermally Treated Silica

silica treatment	proton number			percentage		ratio of hydrogen bonded to isolated hydroxyls
	total	hydrogen bonded	isolated	hydrogen bonded	isolated	
untreated[a]	0.75 ± 0.01					
373 K[a]	0.29 ± 0.01					
473 K	0.27 ± 0.01	0.20 ± 0.01	0.07 ± 0.01	74 ± 2	26 ± 2	2.9 ± 0.2
573 K	0.24 ± 0.01	0.15 ± 0.01	0.09 ± 0.01	61 ± 3	39 ± 3	1.6 ± 0.1
673 K	0.14 ± 0.01	0.15 ± 0.01	0.07 ± 0.01	49 ± 2	51 ± 2	0.96 ± 0.04
773 K	0.12 ± 0.01	0.07 ± 0.01	0.07 ± 0.01	40 ± 2	60 ± 2	0.67 ± 0.02
873 K	0.10 ± 0.01	0.05 ± 0.01	0.09 ± 0.01	12 ± 1	88 ± 1	0.14 ± 0.02
973 K	0.05 ± 0.01	0.01 ± 0.01	0.05 ± 0.01	2 ± 2	98 ± 2	0.02 ± 0.01
1073 K	0.04 ± 0.01	0.00 ± 0.01	0.04 ± 0.01	0 ± 1	100 ± 1	0.00 ± 0.01

[a] Not deconvolved due to the presence of physisorbed water.

by a 33 dm³ h⁻¹ Edwards E2M2 Fomblin rotary pump via a liquid nitrogen cold trap to yield a base pressure of 1 x 10⁻³ mbar (with a leak rate better than 3.5 x 10⁻⁸ mol s⁻¹).[9] Prior to each experiment, the reactor was scrubbed with detergent, rinsed with isopropyl alcohol, dried in an oven, and then cleaned in situ using a 0.3 mbar air plasma at 30 W. One gram of silica powder was then loaded into the reactor and evacuated down to base pressure. At this stage, the silica had become effectively vacuum-dry. Argon (BOC 99.998%), helium (BOC 99.999%), oxygen (Air Products 99.995%), or carbon tetrafluoride (Air Products 99.7%) gas was then introduced into the plasma chamber via a fine leak valve. At this stage, rotation of the reactor commenced and the glow discharge was ignited. Upon completion of plasma treatment, agitation of the particles was stopped, the rf power supply was switched off, and the chamber was evacuated back to its original base pressure, prior to bringing up under a nitrogen atmosphere ($H_2O < 1.0$ ppm$_v$).

An Ocean Optics Inc. SD 1000 fiber optic spectrometer was used for real time optical emission spectroscopy (OES) diagnostics of the electrical discharge during dehydroxylation. In particular, the intensity of the hydrogen H_α emission line at 656.3 nm[10] was taken as being characteristic of hydroxyl removal.

Quantification of the proton signal intensity associated with surface hydroxyls on the silica surface was achieved by using solid state ¹H NMR undertaken on a Varian Unity Plus 300-MHz spectrometer. Silica samples were transferred into 5-mm-o.d. silicon nitride rotors with push-on caps in a nitrogen atmosphere glovebox (i.e., without exposure of the material to air). Static solid echo NMR experiments[11] acquired 32 transients using a 90° pulse−15 ms delay−90° pulse sequence with a 5-s recycle delay and a 1000-kHz spectral width. The background signal of the rotor was removed for each set of data. The measured integral between 100 and −100 kHz was divided by the weight of silica contained in the sample rotor to yield the number of protons per unit mass, subsequently referred to as the "proton number". ¹H magic angle spinning NMR experiments were used to compare the proportion of isolated and hydrogen bonded hydroxyls following surface dehydroxylation. Thirty-two transients were acquired using a 90° pulse, 5-s recycle delay, 100-kHz spectral width, and a 4−8 kHz magic angle spinning speed. Again, the background signal of the empty rotor was subtracted for each spectrum. The hydroxyl distribution was then calculated by deconvolving the spectra into isolated and hydrogen bonded hydroxyl environments at 1.7 and 3.0 ppm, respectively.[12−14]

Nitrogen gas sorption measurements at 77 K were performed on a PMI sorptometer. Seven data points in the range $0.04 < p/p_o < 0.25$ were collected following in situ degassing of each silica sample at 473 K for 16 h. The gradient of the BET graph
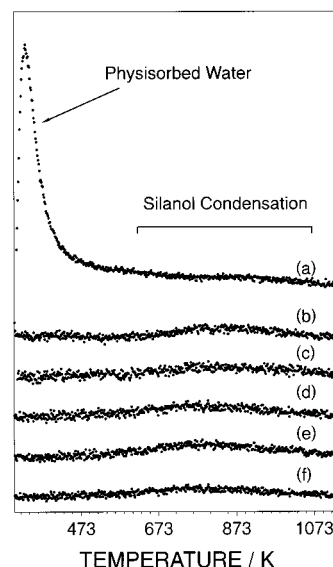

Figure 1. Temperature programmed desorption of silica: (a) no prior treatment; (b) vacuum-dried; (c) argon plasma treated; (d) helium plasma treated; (e) oxygen plasma treated; (f) carbon tetrafluoride plasma treated.

over the selected p/p_o range was always found to be constant within experimental error.[15]

Results

(a) Conventional Thermal Dehydroxylation.

Temperature programmed desorption spectra of untreated silica display the loss of physisorbed water as a sharp peak at ≈350 K, and a broad water peak due to silanol condensation at higher temperatures (≈720 K),[2,16] Figure 1.

Static solid echo NMR experiments were used to follow the changes in the hydroxyl density at the silica surface during thermal dehydroxylation, Table 1. Also ¹H MAS NMR was used to compare the relative proportion of isolated versus hydrogen bonded hydroxyls. As-received silica was found to exhibit a broad resonance around 3 ppm attributable to the overlap of physisorbed water (3.3 ppm), hydrogen bonded hydroxyls (3.0 ppm), and a small number of isolated hydroxyls (1.8 ppm),[12−14,17] Figure 2. Loss of physisorbed water at 373 K caused the main peak at 3.0 ppm to diminish at the expense of the 1.8 ppm component (a small amount of physisorbed water remains at this temperature[2]). Peak deconvolution of the NMR spectra into hydrogen bonded and isolated hydroxyl chemical environments was carried out for samples heated above 473 K (at which point all physisorbed water is lost[2]), Table 1 and Figure 3. Higher temperatures gave rise to the loss of hydrogen bonded and isolated silanols, until eventually only a small number of isolated

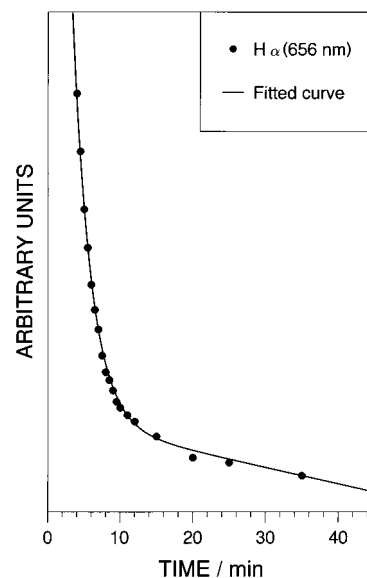**TABLE 2: Solid State ^{1}H NMR Data for Vacuum Dried and Plasma Treated Silica (0.4 mbar, 60 W, and 15 min)**

| silica treatment | proton number | | | percentage | | ratio of hydrogen bonded to isolated hydroxyls |
	total	hydrogen bonded	isolated	hydrogen bonded	isolated	
vacuum dried	0.34 ± 0.01	0.24 ± 0.01	0.10 ± 0.01	72 ± 2	28 ± 2	2.6 ± 0.1
argon plasma	0.28 ± 0.01	0.18 ± 0.01	0.10 ± 0.01	63 ± 1	37 ± 1	1.8 ± 0.1
helium plasma	0.28 ± 0.01	0.18 ± 0.01	0.10 ± 0.01	65 ± 1	35 ± 1	1.9 ± 0.1
oxygen plasma	0.26 ± 0.01	0.10 ± 0.01	0.16 ± 0.01	39 ± 3	61 ± 3	0.64 ± 0.02
CF$_4$ plasma	0.19 ± 0.01	0.14 ± 0.01	0.05 ± 0.01	74 ± 2	26 ± 2	2.9 ± 0.2
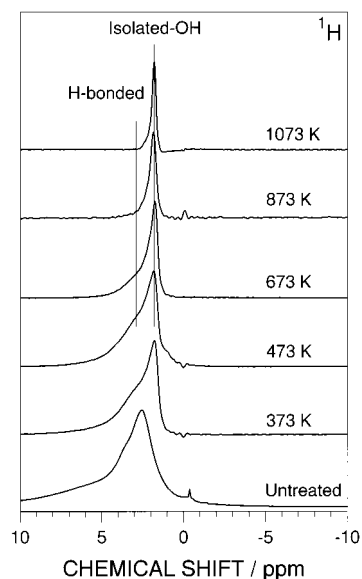
Figure 2. ^{1}H MAS NMR spectra, 299.945 MHz (90° pulse, 5-s relaxation decay), of silica heated under nitrogen at different temperatures (all spectra have been normalized for intensity).
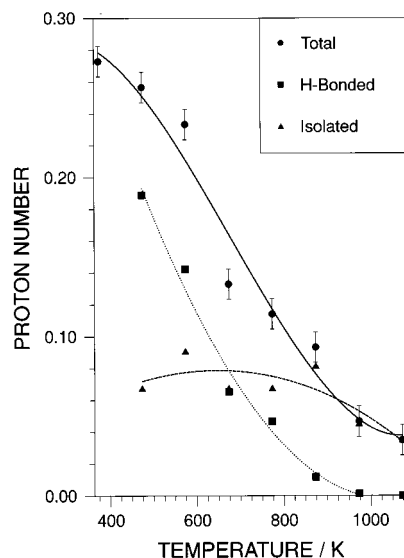
Figure 3. Effect of temperature upon hydroxyl distribution.

Figure 4. Optical emission spectroscopy of the 656-nm H$_\alpha$ line decay during oxygen plasma treatment of silica.

hydroxyl groups remained at around 1073 K. In summary, raising the temperature reduced the hydroxyl density at the silica surface, while the relative proportion of isolated hydroxyls increases, Figure 3. This is in good agreement with other spectroscopic and chemical investigations. [1,18−20]

(b) Plasma Dehydroxylation.

Temperature programmed desorption showed that vacuum-drying of silica removes physisorbed water, whereas the silanol condensation feature associated with higher temperatures is retained, Figure 1. Subsequent plasma treatment using various feed gases was found to lead to further dehydroxylation of the silica surface. This was evident from the observed attenuation of the high-temperature TPD peak and the rapid decline in intensity of the hydrogen H$_\alpha$ line at 656 nm detected by optical emission spectroscopy during plasma exposure, Figures 1 and 4, respectively.

Vacuum dried silica, and silica subjected to a variety of plasma treatments were also analyzed by ^{1}H NMR, Table 2 and Figure 5. A 55% reduction in the total number of protons occurred in the former case, corresponding to the loss of physisorbed water without any disturbance of the surface hydroxyls.[21] Noble gas plasma treatment produced a small drop in the overall concentration of hydroxyl groups, while the relative proportion of isolated hydroxyls was slightly enhanced, Figure 6. Oxygen plasma treatment also resulted in surface dehydroxylation, but with a much greater loss of hydrogen bonded hydroxyls, accompanied by an increase in the absolute number of isolated hydroxyls. Carbon tetrafluoride plasmas were found to be the most effective at stripping hydroxyls from the silica surface. In this case, the hydroxyl distribution was markedly different compared to the other plasma treatments: the ratio of hydrogen bonded to isolated hydroxyls remained similar to that for vacuum-dried silica (although the concentrations were significantly less), Table 2.

Optimization of the CF$_4$ glow discharge operating conditions was pursued using a 3-level-2-factor (power and pressure) experimental design, Table 3.[22] It was found that a combination of high power and pressure were the most effective at removing surface hydroxyls. Further improvement was achieved by using Simplex optimization.[23] CF$_4$ plasma treatment at 60-W power and 0.5-mbar pressure yielded a total hydroxyl number comparable to a conventional thermal activation at 773 K, Figure

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TABLE 3: Solid State ^1H NMR Data for CF_4 Plasma Factorial Experiments and Simplex Optimization (15-min Treatment Time)
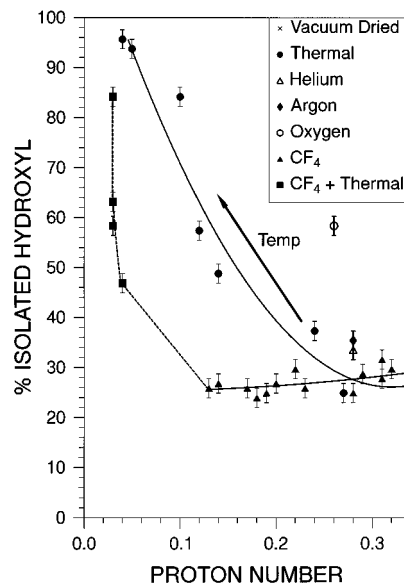
	proton number			percentage		ratio of hydrogen
silica treatment	total	hydrogen bonded	isolated	hydrogen bonded	isolated	bonded to isolated hydroxyls
CF_4 20 W, 0.1 mbar	0.32 ± 0.02	0.23 ± 0.02	0.09 ± 0.02	71 ± 1	29 ± 1	2.4 ± 0.1
CF_4 20 W, 0.3 mbar	0.29 ± 0.03	0.20 ± 0.03	0.09 ± 0.03	70 ± 1	30 ± 1	2.3 ± 0.1
CF_4 20 W, 0.4 mbar	0.28 ± 0.01	0.21 ± 0.01	0.07 ± 0.01	74 ± 2	26 ± 2	2.9 ± 0.1
CF_4 40 W, 0.1 mbar	0.31 ± 0.01	0.21 ± 0.01	0.10 ± 0.01	67 ± 1	33 ± 1	2.0 ± 0.1
CF_4 40 W, 0.3 mbar	0.22 ± 0.01	0.15 ± 0.01	0.07 ± 0.01	69 ± 3	31 ± 3	2.2 ± 0.1
CF_4 40 W, 0.4 mbar	0.20 ± 0.01	0.14 ± 0.01	0.06 ± 0.01	72 ± 1	28 ± 1	2.6 ± 0.1
CF_4 60 W, 0.1 mbar	0.31 ± 0.02	0.22 ± 0.02	0.09 ± 0.02	71 ± 2	29 ± 2	2.4 ± 0.1
CF_4 60 W, 0.3 mbar	0.23 ± 0.01	0.17 ± 0.01	0.06 ± 0.01	73 ± 1	27 ± 1	2.8 ± 0.1
CF_4 60 W, 0.4 mbar	0.19 ± 0.01	0.14 ± 0.01	0.05 ± 0.01	74 ± 2	26 ± 2	2.9 ± 0.2
CF_4 60 W, 0.5 mbar	0.13 ± 0.01	0.09 ± 0.01	0.04 ± 0.01	73 ± 2	27 ± 2	2.7 ± 0.1
CF_4 60 W, 0.6 mbar	0.17 ± 0.02	0.12 ± 0.02	0.05 ± 0.02	73 ± 2	27 ± 2	2.7 ± 0.1
CF_4 80 W, 0.5 mbar	0.18 ± 0.02	0.13 ± 0.02	0.05 ± 0.02	75 ± 3	25 ± 3	3.0 ± 0.2
CF_4 80 W, 0.6 mbar	0.14 ± 0.01	0.10 ± 0.01	0.04 ± 0.01	72 ± 1	28 ± 1	2.6 ± 0.1
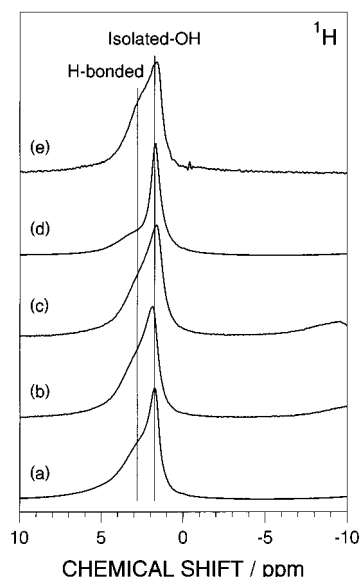
Figure 5. ^1H MAS NMR spectra, 299.945 MHz (90° pulse, 5-s relaxation decay), of silica: (a) vacuum-dried; (b) argon plasma treated; (c) helium plasma treated; (d) oxygen plasma treated; (e) carbon tetrafluoride. (The minor variation in width of the ^1H resonances can be attributed to the slightly different magic angle spinning speeds employed during data acquisition.[50])

Figure 6. Comparison of the hydroxyl distribution between thermal, plasma, and combined plasma−thermal treatments of high surface area silica.

6. However, the hydroxyl distribution was very different, with a higher proportion of hydrogen bonded hydroxyls, and the remaining isolated hydroxyl density at the silica surface being similar to that achievable by 1073 K thermal activation.

These optimum CF_4 plasma conditions were then combined with subsequent heating under dry nitrogen in order to see whether the hydroxyl distribution relaxed toward the expected thermodynamic equilibrium associated with conventional thermal treatment, Figure 7 and Table 4. It was found that annealing to 773 K reduced the total number of hydroxyls to that equivalent to a 1073 K thermal activation (in fact the number of isolated hydroxyls was 50% lower). Heating to higher temperatures did not produce any further drop in total hydroxyl population; however, some of the hydrogen bonded hydroxyls converted to isolated hydroxyls, thereby shifting the overall distribution toward the expected 1073 K thermal equivalent, Figure 6.

BET surface area analysis confirmed that no significant loss of porosity occurred during any of the plasma treatments, Table 5.

Discussion

It has been shown that bulk dehydroxylation of high surface area silica powder can be controlled by nonisothermal plasma exposure. This is consistent with our previous investigation, where we demonstrated that Phillips ethylene polymerization catalyst precursors supported on silica could be activated by plasma treatment.[24] It is of interest to note that depending upon the conditions employed, the electrical discharge can access either the whole porous material[24] or just its surface.[25]

It can be calculated by using the perfect gas equation that at a typical operating plasma pressure of 0.4 mbar, on average, there will be less than one atom/molecule within each pore.[26] Furthermore the pores in mesoporous silica are much smaller in size (between 2 and 50 nm) compared to the plasma Debye length ($2 \mu m < \lambda_D < 7$ mm) under such conditions.[6,7] Therefore plasma ignition within the pores is unlikely. Rather, penetration of excited species (electrons, ions, and metastables) together with electromagnetic radiation is more probable. The negative charge associated with the plasma sheath potential adjacent to a particle surface will cause incident electrons to be retarded as they approach the silica surface.[7] Ions and short-lived metastables will predominately interact with the near surface region due to rapid loss of kinetic energy via collisions with the pore

TABLE 4: Solid State ^{1}H NMR Data for Optimum CF$_4$ Plasma Treatment (0.5 mbar, 60 W and 15 min) with Subsequent Thermal Treatment

	proton number			percentage		ratio of hydrogen bonded to isolated hydroxyls
silica treatment	total	hydrogen bonded	isolated	hydrogen bonded	isolated	
CF$_4$ + 773 K	0.04 ± 0.02	0.02 ± 0.02	0.02 ± 0.02	51 ± 4	49 ± 4	1.0 ± 0.1
CF$_4$ + 873 K	0.03 ± 0.02	0.01 ± 0.02	0.02 ± 0.02	39 ± 4	61 ± 4	0.64 ± 0.1
CF$_4$ + 973 K	0.03 ± 0.02	0.01 ± 0.02	0.02 ± 0.02	34 ± 3	66 ± 3	0.52 ± 0.07
CF$_4$ + 1073 K	0.03 ± 0.02	0.00 ± 0.02	0.03 ± 0.02	12 ± 4	88 ± 4	0.14 ± 0.05
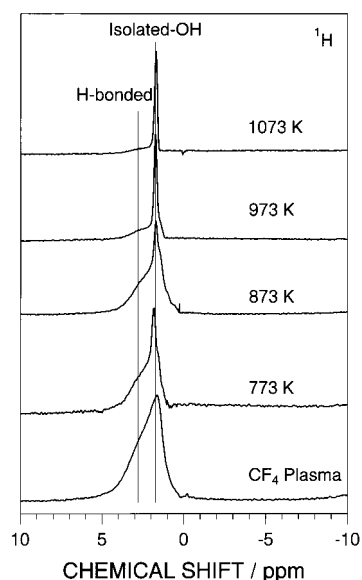
Figure 7. ^{1}H MAS NMR spectra, 299.945 MHz (90° pulse, 5 s relaxation decay), of optimum carbon tetrafluoride plasma treatment of silica followed by annealing.

TABLE 5: BET Surface Areas

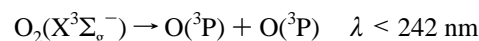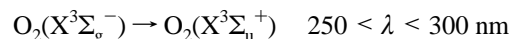| treatment	BET surface area/m^2 g^{-1}
untreated	333 ± 3
optimum CF$_4$ plasma	320 ± 4

walls.[27,28] This leaves long-lived neutrals and photochemistry as potential candidates for bulk modification. In the case of noble gases, the intense $M(I)$ emission lines of argon (106.7 and 104.8 nm) and helium (58.4 nm) superimposed on a weak, broad continuum between 105−155 nm and 58−110 nm, respectively,[29] are not able to penetrate throughout the whole particle, since silica attenuates wavelengths shorter than 160 nm.[30] Consequently the effect of noble gas plasma treatment must be confined to the surface region of the silica particles and therefore accounts for the minor changes seen in total hydroxyl population.

Oxygen plasmas contain additional chemically active species. These include neutral ground-state (e.g., O, O$_2$, O$_3$) and metastable (e.g., O$_2$(a$^1\Delta_g$)) species, as well as positively charged (e.g., O$^+$, O$_2^+$, O$_3^+$, O$_4^+$) and negatively charged (e.g., O$^-$, O$_2^-$, O$_3^-$, O$_4^-$) ions.[31,32] Atomic oxygen is considered to be the predominant reactive constituent.[31] Again, electron, ion, and metastable bombardment will be localized to the particle surface. Permeation of some atomic oxygen species into the whole particle is likely,[33] although atomic oxygen will also undergo surface recombination processes:[32,34]

$$O + O \text{ (surface)} \rightarrow O_2$$
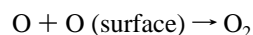
Direct photoexcitation of molecular oxygen within the pores is an alternative source of atomic species. Plasma UV radiation in the 240−250-nm range (O$_2$ A$^3\Sigma^+_u$ − X$^3\Pi^-_g$ transition)[10] is

longer in wavelength compared to the silica absorption threshold at 160 nm and therefore will penetrate throughout the particle to produce excited and ground-state atomic oxygen within the pores:

$$O_2(X^3\Sigma_g^-) \rightarrow O_2(X^3\Sigma_u^+) \quad 250 < \lambda < 300 \text{ nm}$$

$$O_2(X^3\Sigma_g^-) \rightarrow O(^3P) + O(^3P) \quad \lambda < 242 \text{ nm}$$

This is supported by previous studies where vacuum ultraviolet (VUV) irradiation generated by excimer lamps (from plasma sources) is shown to be effective at removing hydroxyls from planar silica surfaces via a photoassisted condensation mechanism.[35−39] Analogous reactions must be in operation during oxygen plasma treatment of high surface area silica.

CF$_4$ plasmas were found to be the most effective at bulk silica dehydroxylation. The predominant chemically reactive constituent of a CF$_4$ glow discharge is atomic fluorine together with a small concentration of CF, CF$_2$, and CF$_3$ radicals (there is no deposition[40,41]).[42] Therefore, the most likely reactive plasma species which could penetrate throughout the silica particles are UV radiation (CF (A$^2\Sigma$−X$^2\Pi$, B$^2\Delta$−X$^2\Pi$) and CF$_2$ (A^{1}B$_1$−X^{1}A$_1$) in the range 220−270 nm)[10] and fluorine atoms either diffusing from the plasma into the particle or being produced within the pores via CF$_4$ photodissociation:[43]

$$CF_4 \rightarrow CF_3 + F \quad \lambda < 236 \text{ nm}$$
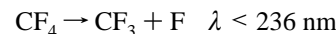
Since the distribution of hydrogen bonded and isolated hydroxyls was found to be similar to that for vacuum-dried silica, Figure 7, hydroxyl loss must occur via an indiscriminate mechanism (unlike thermal dehydroxylation, Scheme 1), perhaps forming small quantities of HF,[44] as well as minor etching to produce volatile SiF$_4$ and O$_2$.[6,45,46] Any etching process must be slow,[47] because an insignificant change in BET surface area is measured, Table 5. The optimum conditions for CF$_4$ plasma treatment of silica yielded hydroxyl densities equivalent to a 773 K conventional thermal treatment with the benefit of taking less than 2% of the time and consuming 1% of the energy. These high gas pressure and power conditions will enhance atomic fluorine and VUV production within the discharge,[42,48] consequently causing greater surface dehydroxylation.[49]

Subsequent thermal treatment at 773 K of CF$_4$ plasma modified silica further reduced the total hydroxyl population due to thermal reaction pathways leading to preferential surface condensation of the remaining hydrogen bonded surface hydroxyls, Scheme 1. Higher temperatures (873 → 1073 K) resulted in no further dehydroxylation of the silica (within the detection limits of the ^{1}H NMR experiment), rather the proportion of isolated hydroxyls increased toward thermodynamic equilibrium at this temperature. This indicates that hydrogen bonding breaks down at the silica surface to produce isolated hydroxyls. Mechanistically, this probably involves the interaction of protons with oxygen atoms adjacent to siloxane

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SCHEME 3: Surface Migration of Hydroxyls[1]
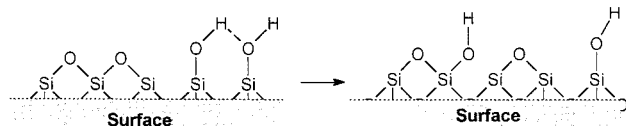
bridges, to generate new surface hydroxyls, which are displaced relative to their initial position,[1] Scheme 3.

Conclusions

Plasma treatment provides a quick and energy efficient means for bulk dehydroxylation of high surface area silica. It has been shown that CF_4 plasma treatment at room temperature is equivalent to a 773 K thermal activation in terms of total hydroxyl population on the silica surface. This is accompanied by a marked shift in the overall hydroxyl distribution, with the number of isolated hydroxyls being similar to that achieved by a 1073 K conventional thermal treatment. Other benefits include the fact that this is accomplished in less than 2% of the time with 1% of the energy consumption.

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