Inaccessible Hydroxyl Groups on Silica Are Accessible in Supercritical CO_2

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The three main types of hydroxyl groups on a silica surface are classified as isolated, hydrogen bonded, and inaccessible. The isolated and hydrogen bonded groups are the most important as these readily exchange with D_2O and thus are exposed to reactant molecules. However, it has generally been accepted that the inaccessible groups do not participate in surface reactions as only a small fraction of these groups exchange with D_2O. It is shown that the inaccessible hydroxyl groups on nonporous fumed silica and mesoporous MCM-48 silica powders and films fully exchange with D_2O and are reactive with octadecylydimethylchlorosilane when supercritical CO_2 is used as the solvent. Furthermore, it is found that the CO_2 penetrating the regions containing the inaccessible groups is not removed by simple evacuation but rather slowly diffuses from the silica over periods of months.

Introduction

The existence of isolated, hydrogen bonded, and inaccessible hydroxyl groups (silanols) on the surface of siliceous material was first established more than 40 years ago.[1−5] While the absolute population density of each type of silanol continues to be debated, it is generally agreed that the isolated silanols are the most important as they are the primary sites for physisorption and chemisorption processes. While the hydrogen bonded groups are also accessible to adsorbates, these silanols are much less reactive and can be eliminated from the surface by heating at 450 °C. The inaccessible silanols have been the least studied as they lie in regions that are not accessible by gaseous adsorbates. On a fully hydroxylated fumed silica, the total silanol density has been estimated at 3 OH/nm^2 and about 1.2−1.5 OH/nm^2 with activation at 450 °C.[3]

Much of our understanding about the nature of the various silanol groups has been derived from early infrared studies on fumed silica.[2−4] The accepted picture of these silanol species has changed very little in the intervening 40 years. Perhaps the most significant changes occurred in the late 1970s and early 1980s. Morrow et al. showed that heating silica above 450 °C results in defective or "strained siloxane" sites that are very reactive with a variety of molecules.[6−8] The number of these sites increases with activation temperature, but even after heating at 1000 °C, these sites are relatively few in number. The other significant discovery came from the pioneering ^{29}Si NMR studies by Maciel et al.[9] The NMR work showed that the isolated silanols are subdivided into two types, single and geminal silanols.

The presence of inaccessible hydroxyl groups on fumed silica was first reported by Hockey et al.[10,11] An IR band near 3650 cm^{-1} in fumed silica was found to increase in intensity with the pressure used to form self-supporting disks. The band at 3650 cm^{-1} was assigned to isolated silanol perturbed by steric hindrance as a result of interparticle contact. These regions of interparticle contact are thought to be located where the primary particles of a fumed silica coalesce to form larger agglomerates. In addition, such perturbed silanols may be found along defect lines in films and grain boundaries within zeolites.[12] These regions, in effect, constitute a surface area that is not probed by the nitrogen sorption techniques that are traditionally used to determine surface area. The term "inaccessible" is used to describe these silanols as they do not exchange with D_2O and are not involved in physisorption or chemisorption of reactant molecules. There is little mention of these silanols in the literature, which this is understandable given the inaccessible nature of these sites.

The purpose of this paper is to show that the "inaccessible" silanols are, in fact, accessible. In particular, we show that these sites can exchange with D_2O and are reactive with an octadecylsilane when the reactions are conducted using supercritical CO_2 (SCF CO_2) as a solvent. This is not unique to fumed silica and is shown to also occur in mesoporous SiO_2 powders and films. This shows that the term inaccessible no longer applies when describing these sites, and therefore we use the term interparticle silanols to denote them. We also show that the penetration of the CO_2 into these interparticle regions has implications for performing surface modification reactions in SCF CO_2. It is also shown that the CO_2 slowly diffuses out from these regions, which leads to a significant level of gaseous CO_2 in the modified materials.

Experimental Section

Two nonporous fumed silicas were used in this study, Aerosil 380 from Degussa AG with a surface area of 380 m^2 g^{-1} and Cab-O-Sil M5 from Cabot Corporation with a surface area of 200 m^2 g^{-1}. Two porous silicas were also used in the study, mesoporous silica powders with the MCM-48 structure and mesoporous three-dimensional cubic silica films dip-coated onto Si-coated 13-mm-diameter Ge windows. The Ge windows were obtained from Harrick Scientific and coated with a 100-Å-thick Si film by sputtering. The experimental techniques for synthesis of the mesoporous powder and films can be found elsewhere.[13]

The Si layer was used to produce stable silica coatings. While dip-coated films did form directly on the Ge windows, it was

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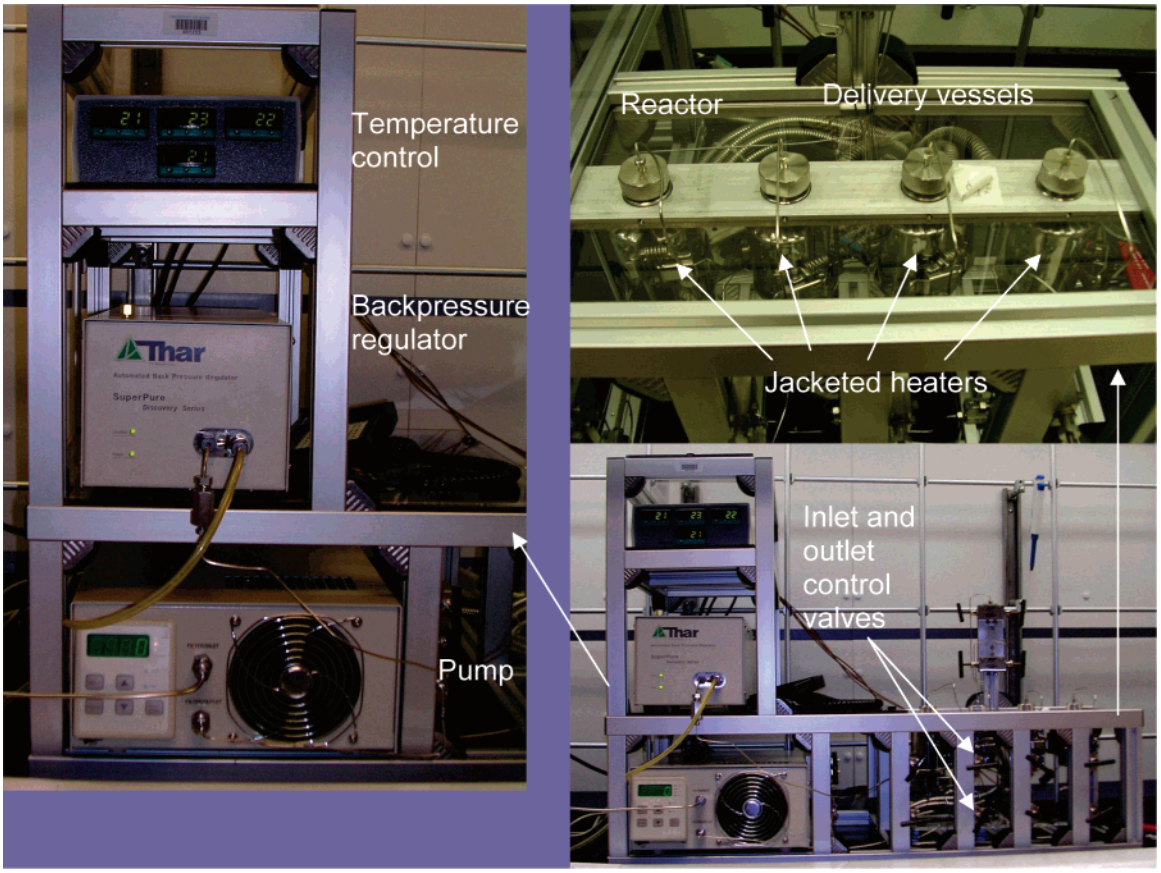

Figure 1. Supercritical CO_2 deposition system.

found that these films were removed when placed in contact with aqueous solutions. The method used for dip-coating the silica film is described in detail elsewhere.[13] Silane modification of the silicas was conducted using a two-step base-catalyzed reaction.[14] Triethylamine (TEA) and 90% D_2O were used as obtained from Aldrich Chemical. Octadecyldimethylchlorosilane (ODMCS, 70% in toluene) was used as obtained from Gelest.

All IR spectra were recorded on ABB FTLA 2000 spectrometers. Transmission spectra of the fumed silica powders were recorded by pressing approximately 50 mg of the powder into self-supported 13-mm-diameter disks using minimal pressure (~100 psi). The pressed disks were placed inside an evacuable IR cell connected to a standard glass vacuum line.[15] Spectra of the SiO_2 film deposited on the Ge windows were recorded in transmission. MCM-48 powder is not amenable to transmission measurement as the large particle size (approximately 2 μm) leads to scattering of the IR beam. IR spectra of the MCM-48 powder were recorded in diffuse reflectance IR Fourier transform (DRIFT) using a Praying Mantis diffuse reflectance apparatus from Harrick Scientific. KBr powder was used to record the reference for the DRIFT spectra. All spectra were recorded at 4 cm^{-1} resolution using 100 scans requiring approximately 2 min of collection time.

The supercritical fluid deposition reactor used for the experiments is reported here for the first time. Figure 1 is a schematic depicting the system. The system was custom-built by Applitech corporation and is based on an atomic layer deposition system described elsewhere.[16] The system consists of a modified HPLC pump capable of pressurizing liquid CO_2, delivered from a siphon tank, into the supercritical phase. SCF CO_2 was delivered to one of three 10-cm^3 heated delivery vessels where a reactant was dissolved. The reactants were then delivered to a 25-cm^3 heated reactor vessel containing the powder or substrate to be modified. The pressure in the system was maintained by the pump and a back pressure regulator capable of purging the vessels with a SCF CO_2 flow rate as low as 0.5 mL min^{-1}.

D_2O exposure experiments were performed by first pressurizing the silica material in the reaction chamber to 200 atm at a temperature of 50 °C. At the same time, 200 μL of D_2O was placed in a delivery vessel and dissolved in CO_2 at 250 atm. CO_2 was then flowed through the chamber at a rate of 1 mL min^{-1} to remove adsorbed water from the silica.[17] The D_2O was then delivered to the reaction vessel by the 50 atm pressure gradient. With both vessels open to each other, the pressure was allowed to equilibrate between the two vessels for 20 min, allowing for sufficient exposure of silica to D_2O. After the D_2O exposure, the reaction vessel was closed off from the D_2O delivery vessel and purged with pure CO_2 for 5 min. This process was repeated for a total of three exposures.

The base-catalyzed silane modification of MCM-48 was performed in a manner similar to the D_2O exposure. In this reaction, the silica was first exposed to the TEA catalyst for a period of 10 min, followed by a 5 min purge. The ODMCS was then delivered to the silica and exposed for 5 min, followed by a 5 min purge. In those experiments where the silica was exposed solely to SCF CO_2, the CO_2 addition was performed by pressurizing the silicas in the reactor and purging at a rate of 1 mL min^{-1} for a period of 1 h.

Results and Discussion

D_2O Exchange Experiments. Figure 2a shows a typical IR spectrum of M5 silica evacuated at 400 °C. The principle features of interest in the spectrum are the peak located at 3747 cm^{-1} due to isolated silanols and a weaker band at 3650 cm^{-1}

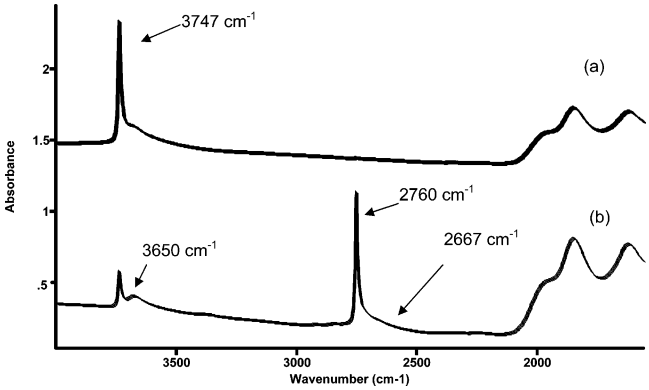

Figure 2. IR spectra of a M5 SiO_2 disk (a) evacuated at 400 °C followed by (b) exposure to 90% D_2O vapor at 400 °C. Both spectra were recorded under vacuum at room temperature.

that has been attributed to interparticle silanols. As noted in the Introduction, the term inaccessible has been applied to these silanols based on the evidence that they exchange to a small degree with D_2O. Thus, the exposure of the silica to a D_2O seeded SCF CO_2 is the key experiment to test the accessibility of these groups in this solvent system.

For comparative purposes, the spectral changes observed upon exposure of the M5 silica to D_2O vapor at 400 °C are shown in Figure 2b. A shift from 3747 to 2755 cm^{-1} is clearly observed for the isolated silanols. A 90% exchange of the isolated groups occurs because of the 90% D_2O/H_2O composition of the vapor used in this work. This was done for illustrative purposes since the spectrum contains bands both for nondeuterated and deuterated silanols. It is well-known that repeated exposures to 100% D_2O vapor result in the complete exchange of the isolated silanols, resulting in the disappearance of the band at 3747 cm^{-1}.[17] It is also noted that both spectra in Figure 2 do not contain a broad band centered at 3550 cm^{-1} due to hydrogen bonded groups. The hydrogen bonded groups are eliminated from the surface by heating to 400 °C. For our purposes, Figure 2b clearly shows that the band due to interparticle silanols at 3650 cm^{-1} has approximately the same intensity as before exposure to D_2O vapor. Furthermore, the spectrum shows that this band does not shift to any large extent upon exposure to D_2O vapor as there is only a weak inflection at 2667 cm^{-1} on the low-frequency side of the isolated SiOD peak at 2760 cm^{-1}. In other words, the interparticle silanols show very little exchange with repeated exposure of D_2O vapor at 400 °C.

The exchange with D_2O vapor at 400 °C differs from the results obtained in SCF CO_2. The IR spectra of the SiOD spectral region for the SCF-exchanged and vacuum-exchanged M5 are presented in Figures 3a and 3b, respectively. Both the SCF CO_2 and vacuum-exchanged SiO_2 exhibit strong bands near 2755 cm^{-1} due to the deuterated isolated silanols. In actuality, the band is at 2761 cm^{-1} in Figure 3a. This is because the isolated SiOH band of Cab-O-Sil M5 in air appears at 3741 cm^{-1} and at 3747 cm^{-1} when recorded after evacuation at 400 °C. However, the SCF-treated SiO_2 also exhibits a band located at 2680 cm^{-1}. This band falls directly where we would expect the deuterated interparticle silanol species to be located.

To verify this assignment, spectra were recorded after the samples were exposed to air. A deuterated silica will readily exchange back to the nondeuterated form when left exposed to air. This reverse exchange is an equilibrium-driven diffusion process resulting from a very low concentration of D_2O in air. Figure 4 presents the IR spectra of the deuterated M5 silica after 72 h in air at room temperature. For comparison, the spectrum of the deuterated M5 immediately after treatment is

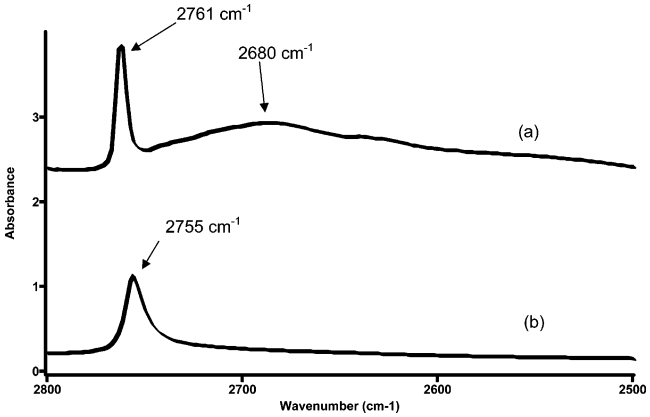

Figure 3. IR spectra of (a) M5 SiO_2 after D_2O exposure in 200 bar SCF CO_2 and (b) the same as Figure 2b.

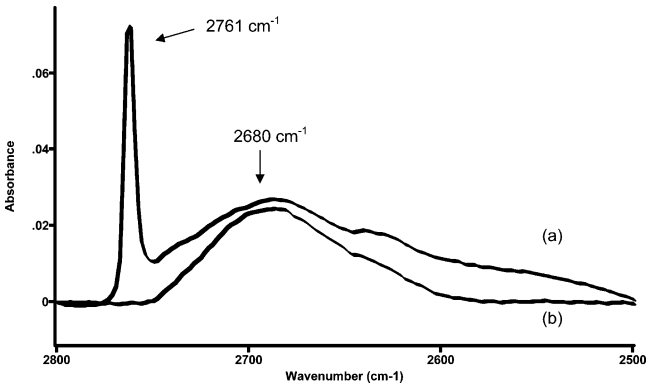

Figure 4. IR spectra of (a) M5 SiO_2 scanned immediately after D_2O exposure at 250 bar SCF CO_2 and (b) recorded again 72 h later.

also shown in this figure. After 72 h in air, the isolated SiOD band has completely disappeared due to conversion of these groups back to isolated SiOH while the band at 2680 cm^{-1} assigned to deuterated interparticle silanols does not decrease in intensity. This lack of exchange is attributed to the inability of gaseous H_2O to penetrate into the location within the material that contains these interparticle silanols.

Reaction of Silanes with the Interparticle Silanols. In the extremely high pressures of SCF CO_2, the interparticle silanols become accessible to D_2O, and an exchange is possible. Therefore, it should be possible to use SCF CO_2 as a medium to deliver reactant molecules into these previously inaccessible regions. This is demonstrated with the functionalization of MCM-48 silica with ODMCS catalyzed by TEA.[14] We have selected this specific reaction and this specific silica for several reasons. Modification of silica with a silane containing an octadecyl moiety is a very common practice. The silane has a very low vapor pressure, and thus the reaction is not carried out in the gas phase but rather is conducted in nonaqueous liquids or, as shown here, in SCF CO_2. A monochlorosilane rather than the more commonly used trichloro counterpart was chosen because there is no possibility of polymerized products depositing on the surface of the silica. Furthermore, the ODMCS is one of the largest silanating agents used to modify siliceous materials and is clearly much larger than D_2O. Thus, the ODMCS represents a good test molecule to determine the accessibility of the inaccessible groups for silane reaction. MCM-48 was selected as the silica because the unmodified powder exhibits strong isolated and interparticle silanol bands at 3747 and 3650 cm^{-1}, respectively. Thus, it is easy to discern if these groups on the MCM-48 silica participate in the reaction with ODMCS.

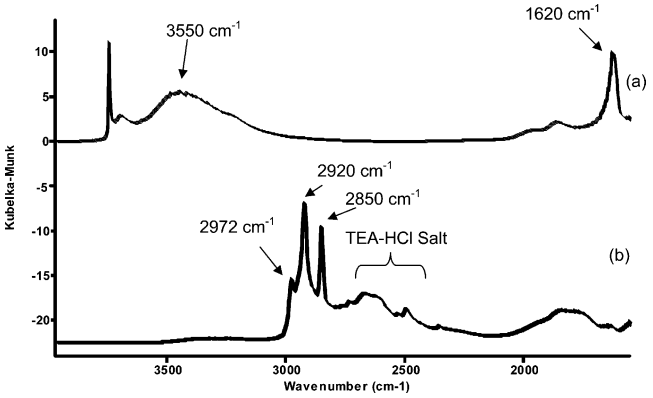

Figure 5. IR spectra of mesoporous silica MCM-48 (a) recorded in air and (b) recorded in air after the TEA-catalyzed addition of ODMCS.

Figure 5 shows the DRIFT spectra of MCM-48 powder before and after ODMCS modification in supercritical fluid. The modification was carried out by first exposing the MCM-48 powder to TEA followed by exposure to ODMCS at 200 atm and 80 °C. The spectrum of the untreated MCM-48 differs from the spectrum of M5 shown in Figure 2. This is because the MCM-48 sample was recorded in air whereas the spectrum shown in Figure 2 was recorded after evacuation at 400 °C. Thus the spectrum of the MCM-48 shown in Figure 5a contains a broad band centered at 3550 cm^{-1} due to surface water that is superimposed on a broad band due to hydrogen bonded silanols. The presence of adsorbed water is confirmed by the appearance of the water bending mode located at 1620 cm^{-1}. The spectrum of the modified powder in Figure 5b shows no IR bands at 3747 or 3650 cm^{-1}, indicating complete reaction of both the isolated and interparticle silanols. The peaks in Figure 5b at 2920 and 2850 cm^{-1} are due to CH_2 stretching modes of the octadecyl chains whereas the small peak located at 2972 cm^{-1} is due to the CH_3 modes from the methyl groups of the silane. Additional peaks located in the range of 2740−2490 cm^{-1} are due to TEA−HCl salt species that form as a byproduct of the surface reaction. The salt stays in the pore after the reaction but may be removed by sublimation in a vacuum or by flushing with water. Again, this simple surface reaction shows that the interparticle silanols are reactive and that they are accessible to molecules even larger than water when introduced via SCF CO_2.

The above results with D_2O exchange and ODMCS clearly show that the term inaccessible no longer applies to these interparticle hydroxyl groups. We view this as an interesting point on its own but note that it remains to be determined if the silicas modified in SCF CO_2 exhibit different properties from those produced by conventional gas- or liquid-phase modification. While this lies outside the scope of this paper, we do note one potential drawback in the use of SCF CO_2 as a solvent for surface treatments of silica. This potential drawback arises from the penetration of SCF CO_2 in these interparticle regions.

Interactions of SCF CO_2 with Silica. To better understand the interactions between the interparticle silanols and SCF CO_2, a separate set of experiments was performed using three different silica materials having different surface areas and different relative amounts of interparticle silanols. Figure 6 shows the IR spectra of (a) cubic mesoporous templated silica film on a Ge window, (b) Aerosil 380, and (c) Cab-O−Sil M5. The relative surface area can be estimated from the relative intensity of the isolated peak relative to the bulk modes located below 2000 cm^{-1}. The templated silica film has a much higher intensity of the isolated silanol to the bulk mode and thus has the highest

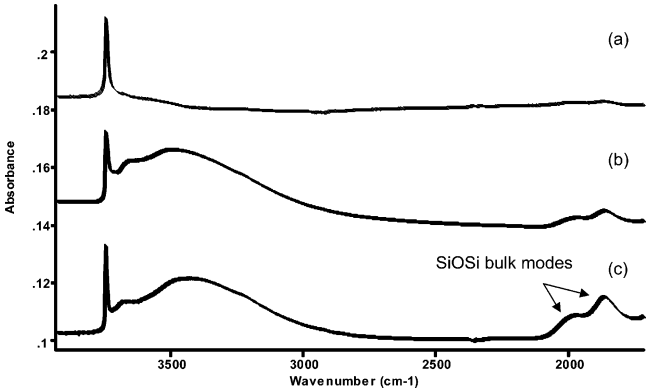

Figure 6. IR spectra of (a) templated silica film, (b) A380, and (c) M5 recorded in air.

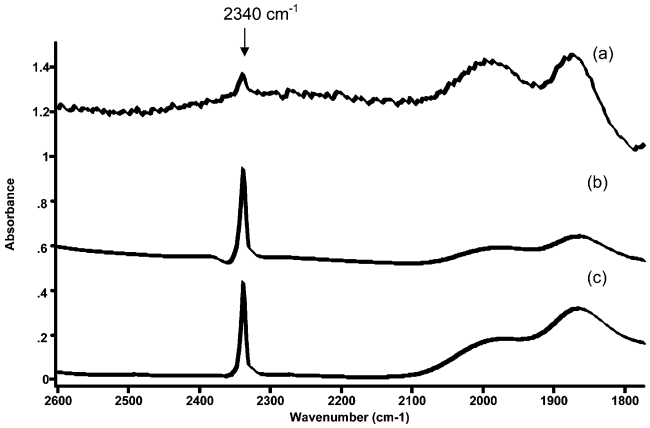

Figure 7. IR spectra of (a) templated silica film, (b) A380, and (c) M5 after 1 h exposure to SCF CO_2 at 200 bar and 100 °C.

surface area. Each material was exposed to SCF CO_2 at 200 atm and 50 °C for a period of 1 h. The IR spectra for the three materials after CO_2 exposure in the CO_2 spectral region is presented in Figure 7. Each material incorporates CO_2 to varying degrees after exposure. This incorporation is denoted by the strong single peak located at 2340 cm^{-1}. The presence of a single peak shows that the CO_2 is liquidlike as gaseous CO_2 would have the characteristic P−R branches. Clearly, the spectra show that the incorporation of CO_2 does not correlate with surface area. For example, the silica film that has the highest surface area has the lowest uptake of CO_2. Perhaps a more interesting aspect of this CO_2 band is that it does not diminish in intensity with evacuation for 1 h at room temperature. This suggests that the CO_2 remains trapped in the interparticle region of the silica. However, it is noted that the CO_2 slowly diffuses from the silica with time. This is clearly seen in Figure 8, which shows the spectra of M5 SiO_2 directly after exposure to SCF CO_2 and after one month at ambient conditions. In this case, the overall area of the CO_2 peak is reduced by a factor of 2 after one month in air. This result indicates a slow diffusion from the interparticle region by the CO_2. The amount of CO_2 incorporated in the interparticle regions is significant. We have found that this has important implications when using SCF CO_2 for large scale (>50 g) batch modification of silica powders. After modification, these larger batches require "aging" in open containers to allow for the expulsion of the CO_2.

The data presented in Table 1 and Figure 9 show that there is a direct correlation between the uptake of CO_2 in the silica and the relative amount of interparticle silanols. The relative amounts of CO_2 incorporation and the number of interparticle silanols were calculated using the integrated area of the bands

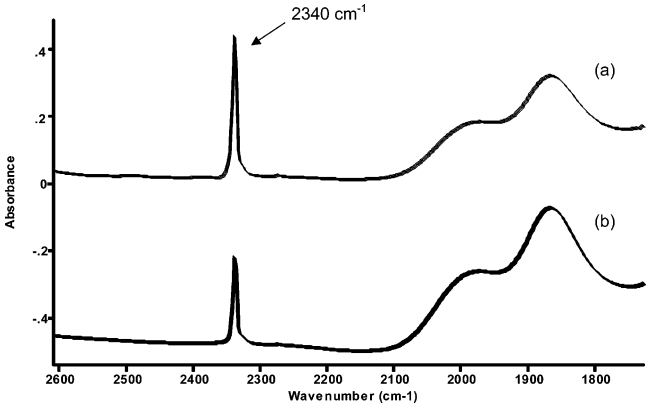

Figure 8. IR spectra of M5 after exposure to 200 bar SCF CO_2. Spectra were recorded (a) immediately after exposure and (b) 1 month later.

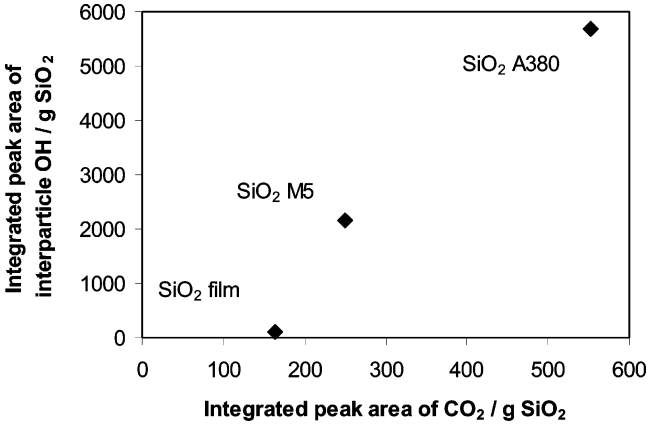

Figure 9. Relative CO_2 incorporation as a function of the relative number of interparticle silanols per gram of SiO_2.

TABLE 1: Material Properties of Templated Mesoporous Silica Film, A380, and M5

material	pore size (nm)	surface area (m^2/g)	interparticle SiOH (peak area/g SiO_2)	CO_2 incorporation (peak area/g SiO_2)
film	3.6	1900	105	163
A380		389	5691	551
M5		200	2166	250

at 2340 and 3650 cm^{-1}, respectively. These values were then normalized to the integrated intensity of the bulk silica mode located at 1870 cm^{-1}. Normalization to a bulk mode produces a relative value per mass of silica. Table 1 summarizes the material properties of the three silicas as well as the relative amounts CO_2 and interparticle silanols.

Figure 9 is a plot of the amount of CO_2 incorporation per gram of SiO_2 with respect to the relative interparticle hydroxyl population per gram of SiO_2 for each of the three materials. It can be seen that there is a positive relationship between the amount of CO_2 incorporated into the material and the amount of interparticle silanols in the material. The results shown in Figure 9 indicate that the incorporation of CO_2 into the silicas is not related to the surface area or the number of isolated silanols but to the interparticle hydroxyl population. We recall that the SiO_2 film that has the highest surface area (and highest number isolated silanols per gram) has the lowest amount of CO_2 uptake per gram. This finding adds further evidence that the interparticle hydroxyl region becomes accessible at the high pressures involved in SCF processes and that the incorporation of CO_2 in these regions is the reason for the slow diffusion.

Additional proof of an interaction between CO_2 and the interparticle groups is provided by the IR spectra shown in

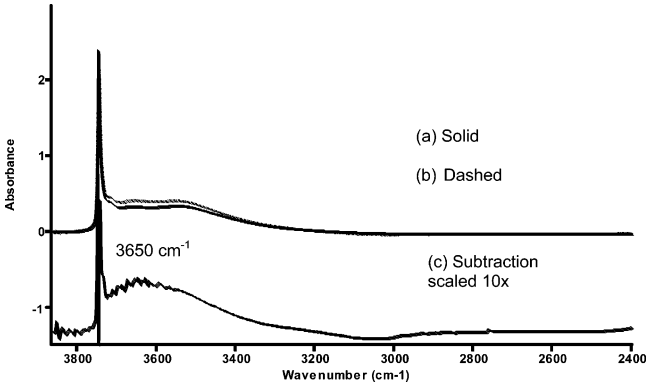

Figure 10. IR spectra of the hydroxyl region for M5 (a) before exposure to CO_2, (b) after CO_2 exposure at 200 bar 50 °C for 1 h, and (c) part b − part a. All spectra were recorded under evacuation at room temperature. The ordinate scale for part c is multiplied by a factor of 10.

Figure 10. Figure 10 shows the spectra of M5 silica evacuated at room temperature before and after CO_2 treatment. The bottom spectrum in Figure 10 is a spectral subtraction of the material before and after treatment scaled up by a factor of 10 to better illustrate the pertinent features. The isolated hydroxyl peak after CO_2 exposure remains virtually unchanged, exhibiting a slight broadening which gives rise to the "artifacts" produced in the subtracted spectrum. Interaction of the SCF CO_2 with the isolated silanols is expected to cause a shift of the band at 3747 cm^{-1} to approximately 3690 cm^{-1} due to weak van der Waals interactions. This is not observed. The slight broadening of the 3747 cm^{-1} peak is perhaps due to a change in the environment of the isolated hydroxyl species, i.e., a loss of homogeneity. This loss of homogeneity may be due to a change in the packing density of the primary particles due to the very high pressures involved supercritical processing. The main difference after exposure to CO_2 is the appearance of a broad band centered near 3650 cm^{-1}, which is the same frequency as the interparticle hydroxyl peak. We believe this result is due to a compaction of the primary particles within the hard agglomerates thereby increasing the total interparticle hydroxyl population. This result is in agreement with the findings of Hockey's group.[11,18,19] In those papers, they found that the compression of fumed silicas to fabricate transmission disks increased the population of interparticle silanols.

The drawback associated with the slow expulsion of the CO_2 from the silica should be viewed in relation to the many advantages of chemical modification of silica conducted in SCF CO_2. There is the obvious advantage of using an environmentally benign solvent that spontaneously separates from the silica. There is no "caking" of the silica as found with other nonaqueous solvents because the modified powder retains its original texture.[17] Moreover, SCF CO_2 has the unique ability to remove the adsorbed water layer on the silica,[17] and this is important for water-sensitive reactions such as silanization.[20]

Conclusions

By using supercritical carbon dioxide as a delivery medium, we have shown that the interparticle silanols on silica can exchange with D_2O. In addition, the interparticle silanols were also found to participate in reactions with the fairly large octadecyl silane, ODMCS, when delivered in SCF CO_2.

By studying the interactions of SCF CO_2 with silicas of varying surface areas and interparticle hydroxyl content, we have shown that CO_2 is incorporated into the interparticle regions attributed to the location of the inaccessible groups. The amount

of CO_2 incorporation was found to be independent of surface area and related to the relative amount of interparticle groups within a given silica sample. We also found that the CO_2 remains inside these interparticle regions and slowly diffuses from the silica over long periods of time.

Finally, it was shown that the high pressures involved in SCF CO_2 processing may in fact generate more interparticle hydroxyl species within fumed silica. The increase is attributed to compaction of silica particles by the high pressure thereby generating more sterically hindered interparticle regions and thus creating more interparticle species.

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References and Notes

(1) Iler, R. K. *The Chemistry of Silica*; John Wiley and Sons: New York, 1979.

(2) Hair, M. L. *Infrared Spectroscopy in Surface Chemistry*; Marcel Dekker: New York, 1967.

(3) Morrow, B. A. Surface Groups on Oxides. In *Spectroscopic Analysis of Heterogeneous Catalysts, Part A: Methods of Surface Analysis*; Fierro, J. L. G., Ed.; Elsevier: Amsterdam, 1990.

(4) Kiselev, A. V.; Lygin, V. I. *Infrared Spectra of Surface Compounds*; John Wiley and Sons: New York, 1975.

(5) Little, L. H. *Infrared Spectra of Adsorbed Species*; Academic Press: New York, 1966.

(6) Morrow, B. A.; Cody, I. A. *J. Phys. Chem.* **1976**, *80*, 1995.

(7) Morrow, B. A.; Cody, I. A. *J. Phys. Chem.* **1976**, *80*, 1998.

(8) Morrow, B. A.; Cody, I. A.; Lee, L. S. M. *J. Phys. Chem.* **1976**, *80*, 2761.

(9) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606.

(10) Armistead, C. G.; Tyler, A. J.; Hambleton, F. H.; Mitchell, S. A.; Hockey, J. A. *J. Phys. Chem.* **1969**, *73*, 3947.

(11) Hambleton, F. H.; Hockey, J. A.; Taylor, J. A. G. *Nature* **1965**, *208*, 138.

(12) McCool, B. Unpublished work.

(13) McCool, B. A.; Hill, N.; DiCarlo, J.; DeSisto, W. J. *J. Membr. Sci.* **2003**, *218*, 55.

(14) Tripp, C. P.; Hair, M. L. *J. Phys. Chem.* **1993**, *97*, 5693.

(15) Tripp, C. P.; Hair, M. L. *Langmuir* **1991**, *7*, 923.

(16) McCool, B. A.; DeSisto, W. J. *Ind. Eng. Chem. Res.* **2004**, *43*, 2478.

(17) Tripp, C. P.; Combes, J. R. *Langmuir* **1998**, *14*, 7348.

(18) Hambleton, F. H.; Hockey, J. A.; Taylor, J. A. G. *Trans. Faraday Soc.* **1966**, *62*, 801.

(19) Armistead, G. G.; Tyler, A. J.; Hambleton, F. H.; Mitchell, S. A.; Hockey, J. A. *J. Phys. Chem.* **1969**, *73*, 3947.

(20) Combes, J. R.; White, L. D.; Tripp, C. P. *Langmuir* **1999**, *15*, 7870.