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An Infrared Study of the Reaction of Octadecyltrichlorosilane with Silica

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The reaction of octadecyltrichlorosilane with a high surface area fumed silica was studied by infrared spectroscopy. We have found that the amount of water adsorbed on the surface was critical for adsorption to occur. We have shown that there is no direct reaction of octadecyltrichlorosilane (OTS) with the surface hydroxyl groups or adsorption with the first water layer bound to the surface of a fumed silica. Adsorption of the OTS does occur with the subsequent layers of water.

Introduction

The formation of monolayers by self-assembly of organochlorosilanes on various surfaces[1-4] and organosulfur compounds on gold[5,6] is well established. The durability of the self-assembled monolayer is highly dependent on the effectiveness of the anchoring to the surface. On gold, the attachment to the surface is due to an interaction of sulfur end groups with the gold surface. However, the nature of the attachment of the organochlorosilane with the surface is ill-defined.[7-9]

Octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$, henceforth denoted OTS) is the most common organochlorosilane used for the formation of self-assembled monolayers and, when reacted with silica surface, finds extensive use as a bonded phase in liquid chromatography applications.[10] A common mechanism proposed for attachment of the chlorosilane to the surface[7,11] involves the hydrolysis of the chlorosilane groups with water which is already on the surface of the substrate. The silanols which are formed then condense with the surface hydroxyl groups to form stable linkages to the substrate. In practice, a curing process is usually required to condense adjacent silanols attached to the organosilane to form a cross-linked "mat" on the surface.

Part of the difficulty in determining the nature of the attachment to the surface arises from the lack of direct spectral evidence. For high surface area metal oxides such as fumed silicas, infrared spectroscopy[12-15] and NMR[16,17] have been very successful in determining the nature of the attachment of chlorosilane molecules to the surface. For example, we have been able to determine the surface reaction of the chloromethylsilanes with silica by observing changes in the infrared bands due to surface hydroxyl groups and, in particular, to the formation of bands assigned to surface Si$_s$–O–Si, Si–Cl, and Si$_s$–Cl modes.[15]

The main problem in using infrared spectroscopy in the study of self-assembled monolayers is that the substrates have low surface area and therefore the bands due to the adsorbed species are weak in intensity. Nevertheless, we have been able to observe the complete disappearance of infrared bands due to Si–Cl modes[18] when OTS was added to mica, and recently, Angst and Simmons[8] using attenuated total reflectance on oxidized silicon wafers were able to detect bands to surface hydroxyl groups and adsorbed water. Upon addition of OTS, the band due to the surface hydroxyl groups decreased and new hydroxyl bands formed. Angst and Simmons attributed the new hydroxyl groups to silanol formation in the organosilane layer. The decrease in the band due to surface hydroxyl groups could be due to an interaction with the surface hydroxyl groups, but direct evidence for a surface covalent bond was not found. Further improvement in the quality of the adsorbed layer was realized by curing at 150 °C, and this was attributed to the formation of cross-linking between adsorbed OTS molecules.

Silberzan et al.[7] along with Angst and Simmons[8] have shown that the water content on the surface is vital for the formation of a complete monolayer. Angst and Simmons were able to obtain a tightly packed monolayer on a fully hydrated oxidized silicon wafer, whereas reaction with a dry silicon wafer gave a disordered monolayer with a lower surface coverage. Silberzan et al. concluded that the OTS reacted with the water layer on the surface and formed very few bonds with the surface.

The importance of surface anchoring sites in forming robust self-assembled monolayers of organochlorosilanes has been demonstrated by Granick and co-workers[4,9,20] in their studies using mica substrate. The attractive feature of mica is that it can be cleaved to form molecularly smooth surfaces over several square centimeters and thus is ideal for use as a substrate in adsorption experiments, particularly in the surface force apparatus.[21] However, a freshly cleaved surface of mica does not contain surface hydroxyl groups as anchoring sites. Using standard

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procedures which had been successful for forming self-assembled OTS monolayers on other substrates, Granick and co-workers found that OTS did not form durable monolayers on mica. They attributed this to the lack of surface hydroxyl groups as anchoring sites as well as to mica's smooth surface which does not allow for strong mechanical adhesion.

Initial strategies for forming strong films have focused on the surface modification of mica using either plasma treatment[4] or chemical modification[20] to incorporate anchoring sites. In both cases, the quality of the surface layer was sensitive to the water concentration used in the preparation. However, Kessel and Granick[9] have recently produced robust monolayers on mica without using any surface modification of the mica. They have been successful in producing good quality films on mica using alkylsilanols and have attributed the durability of the film to the formation of a cross-linked net via the condensation of adjacent silanols. Although it is clear that the presence of water is important for the reaction, the role of surface hydroxyl groups and the nature of the surface attachment in the formation of self-assembled monolayers of OTS remain unclear.

In this study we have used transmission infrared spectroscopy to investigate the reaction of OTS with a high surface area silica powder. Infrared spectroscopy can easily discriminate between adsorbed water and surface hydroxyl groups on such silica and therefore may be useful in distinguishing between the roles of water and surface hydroxyl groups in the adsorption of OTS. It is important to note that the chemistry for the formation of self-assembled monolayers on low area surfaces may be different from the high surface area silica. The packing order and density of self-assembled monolayers are higher on low area surfaces and the distribution and density of surface hydroxyl groups on the substrate are different.

Infrared studies of reactions on high area metal oxides have almost exclusively been reported for reactions occurring at the solid/vapor interface mainly because of the experimental difficulties encountered in recording spectra of the reactions at the solid/liquid interface.[22] In fundamental studies of the interaction at the surface of silica (or any other oxide material), it is important to be able to control and modify the surface hydroxyl groups of the oxide in a reproducible manner. The number and types of surface hydroxyl groups are well documented,[23-25] and these are discussed later in the Results and Discussion section. In studies at the solid/vapor interface, the surface quality is easily controlled by thermal pretreatment under evacuation before exposure to the vapor of the adsorbate. However, when OTS and other molecules with low vapor pressure are studied, the reaction with silica has to be performed at the solid/liquid interface. In order to distinguish between adsorption/reaction with water on the surface and surface hydroxyl groups, it is important to control the surface quality of the substrate in the same manner as can be done in studies at the solid/vapor interface. We have therefore designed two cells which enable us to control this surface quality before exposure to the adsorbate in solution. A brief description of these cells is included in this report.

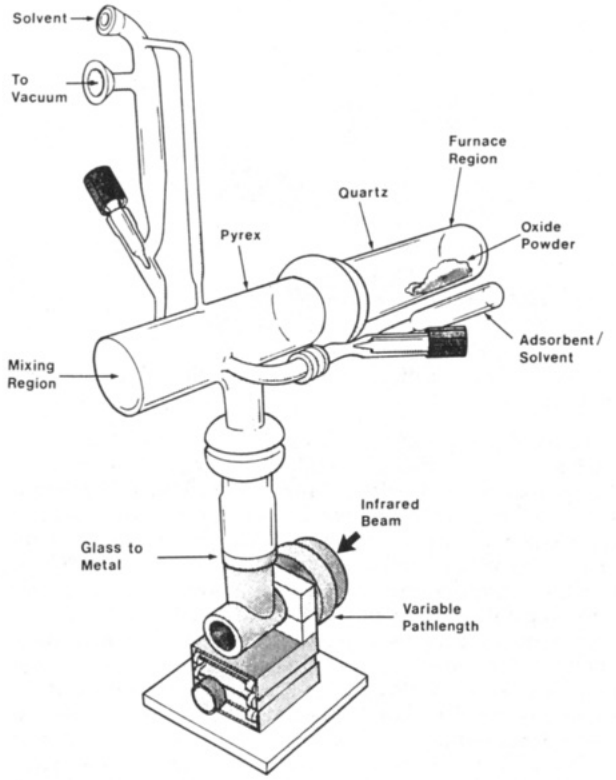

Figure 1. The in situ liquid infrared cell.

Experimental Section

The fumed silica used in this study was Aerosil 380 obtained from Degussa A. G. Frankfurt. The measured BET (N_2) surface area was 375 m^2/g. OTS and CCl_4 were obtained from Aldrich. The CCl_4 was dried over molecular sieve and distilled prior to use. The OTS was used as received. Fresh solutions of OTS in CCl_4 were prepared before each experiment. The degree of polymerization of the OTS in CCl_4 was checked by IR. We did not detect any bands due to Si–O–Si of Si–OH modes in the spectrum.

Infrared spectra were recorded on a Bomem Michelson 102 FTIR equipped with a CsI beamsplitter and a DTGS detector. Typically 25 scans at 4-cm^{-1} resolution were recorded for each spectrum. These required approximately 3 min to collect. In settling experiments (employing the in situ mixing cell to be described later) single interferograms were collected at 1-min intervals and postprocessed using the MULTI option of the Spectra Calc collection module. When using the in situ mixing cell the FTIR was mounted vertically against the wall to provide sufficient clearance for the cell and stirring plate.

In order to investigate the reaction of OTS with silica, it is important to be able to control the number and the type of surface hydroxyl groups and water content of the surface of the silica before treatment with the OTS solution. We have designed two cells specifically for this purpose. The first is designated as the "in situ liquid cell" and is shown in Figure 1. The second, designated as the "in situ mixing cell" is a derivation of the first and was designed for settling studies which will be described in detail elsewhere.[26]

The upper section of the cell shown in Figure 1 contains a quartz furnace region and a Pyrex mixing region with three outlets for solvent and adsorbate addition as well as cell evacuation. The lower metal section contains the variable path length optical cell which is shown in detail in Figure 2. Two ZnSe windows were attached to the metal base with an epoxy resin. ZnSe was used because of its chemical inertness to most solvents and because it is optically transparent above 650 cm^{-1}. The path length of the cell is defined by the distance between the two ZnSe windows and this could be varied between 25 μm and 1 cm. The path length selected was dependent on the solvent and the quantity of silica used in the experiment.

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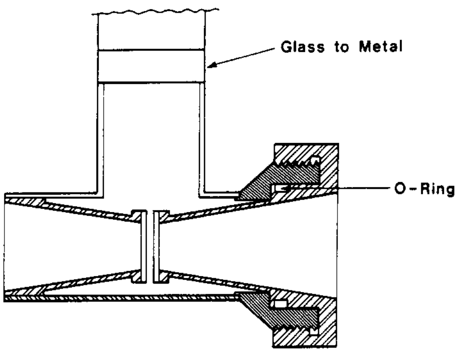


Figure 2. Cross sections of the in situ liquid cell optical compartment.

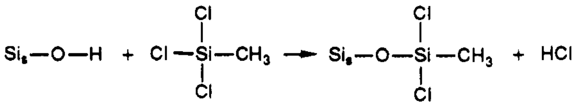
The following procedure was used for operating the in situ liquid cell. A graduated glass bulb containing a solution of the adsorbate (transferred under dry nitrogen and degassed by several freeze–thaw cycles) was clamped to the side arm of the cell prior to evacuation. The silica was placed in the quartz furnace region (quartz is used so that activation temperatures up to 1100 °C can be reached) and the entire cell was evacuated. The silica used in the preparation of the suspension was usually first degassed under vacuum at a desired temperature. Chemical modification could be performed at this time through addition of gases to the cell. The silica was allowed to cool to room temperature and a reference spectrum of the evacuated cell was recorded. Addition of the solvent was accomplished without exposing the silica to air. The solvent (~60 mL) was contained in an evacuated glass bulb which was attached to the cell at the solvent outlet (indicated in Figure 1) and was then transferred to the cell using standard vacuum line techniques. An infrared spectrum of the solvent was recorded. The cell was then rotated in order to transfer the solvent and the silica into the mixing region (a stirring bar was added to this section of the cell prior to evacuation). After mixing, the cell was rotated back to its original position, the suspension filled the optical cell, and a spectrum was recorded. Known quantities of adsorbate located in the graduated bulb could be added to the suspension when the cell was rotated back into the stirring position.

With the capability of selecting path lengths between 25 μm and 1 cm, the cell could be used with most nonaqueous solvents. The main drawback to this cell arises from the fact that the mixing and spectroscopic regions are separated. During transfer between sections some of the silica would adhere to the side of the cell, thus rendering quantitative analysis difficult. In addition, the spectroscopic analysis must be performed rapidly for suspensions that are not stable as the suspended particles settle out of the beam area.

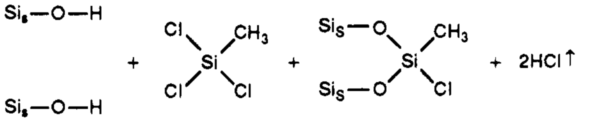
In order to circumvent these problems, a second cell was designed primarily to study settling effects. This cell operated in the same manner as the in situ liquid cell above. The main difference is that the mixing region and the spectroscopic region have been combined into one section and therefore most of the adhesion and settling problems associated with the in situ liquid cell were avoided. Spectra are acquired in situ while the suspension is being mixed and the amount adsorbed can be determined by taking advantage of the fact that the suspended silica particles settle out of the beam area. Spectra are acquired at equally spaced intervals and the adsorbate remaining in solution is determined by monitoring the decrease in intensity of a band due to the adsorbate and a band due to the silica as the particles settle out of the beam region. If all the adsorbate is attached to the surface, then the bands due to silica and the bands due to the adsorbate should decrease at the same rate. Because of the large path lengths associated with this cell (approximately 2.5 cm), we have used only CCl_4 as a solvent. If narrower path lengths were required, the in situ liquid cell was used. A new cell combining a variable path length with in situ mixing capabilities is currently being evaluated.

Results and Discussion

The gas phase reaction of trichloromethylsilane with the surface silanol groups has been studied by many authors.[12-15] It is known to occur at elevated temperatures (>300 °C) according to the following reactions:



$$Si_s{-}O{-}H + Cl{-}\underset{Cl}{\overset{Cl}{Si}}{-}CH_3 \rightarrow Si_s{-}O{-}\underset{Cl}{\overset{Cl}{Si}}{-}CH_3 + HCl \quad (1)$$



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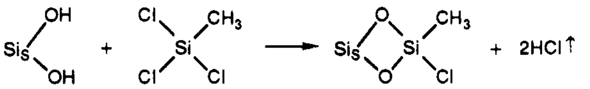

(3)

Reaction below 200 °C is negligible.[14] The possibility of the reaction of OTS proceeding at room temperature in solution in this manner is unlikely and one purpose of our work is to remove this from consideration as a possible mechanism for anchoring the silane to the surface. Our first set of adsorption experiments with OTS were therefore performed in the absence of water to verify that OTS does not react directly with the surface hydroxyl groups.

The amount of adsorbed water which is present in an "as received" fumed silica will vary with the relative humidity of the atmosphere.[27] The amount of adsorbed water on an "as received" silica as measured by the integrated intensity of the deformation mode[28] at 1620 cm^{-1} did not change when exposed to a relative humidity of 90% over a period of several days. From microbalance measurements[27,29] it is shown to be in the range of 2.5–4.0 H_2O molecules/nm^2. Evacuation at temperatures between ambient and 150 °C will eliminate the molecularly adsorbed water from the surface, and this exposes the underlying surface hydroxyl groups. These surface hydroxyl groups fall into two main types, isolated and geminal groups which are identified by a sharp infrared band at 3747 cm^{-1} (3688 cm^{-1} in CCl_4) and hydrogen-bonded groups which are characterized by a broad band centred at 3520 cm^{-1}. The total hydroxyl density[30] for a fumed silica degassed at 150 °C is 3.1 OH/nm^2 of which 1.1 OH/nm^2 are due to the isolated/geminal groups. With evacuation at 450 °C the hydrogen-bonded groups are removed leaving a surface containing only isolated/geminal groups at a density of 1.4 OH/nm^2. Figures 3 and 4 show the results of adding OTS to silica which has been previously outgassed at 150 and 400 °C. Figures 5 and 6 show the corresponding difference spectra. For neither reaction did we observe any spectral changes of the surface hydroxyl groups with addition of OTS. (In some of our experiments, we stirred the solutions for a period of up to 2 days without detecting any spectral changes. The detection limit is estimated to be about 3% of the measured peak intensity at 3688 cm^{-1}).

This nonreactivity may be the result of the inability of the OTS molecules to displace the physisorbed CCl_4 from the surface. The band due to isolated/geminal groups is shifted to 3688 cm^{-1} in CCl_4 and this shift is similar to the shift to 3690 cm^{-1} measured for physisorbed trichloromethylsilane adsorbed from the vapour phase.[26] To investigate this possibility, we have obtained spectra of a dehydrated silica placed in contact with pure OTS. When OTS was added directly to a silica degassed at 150 °C (see

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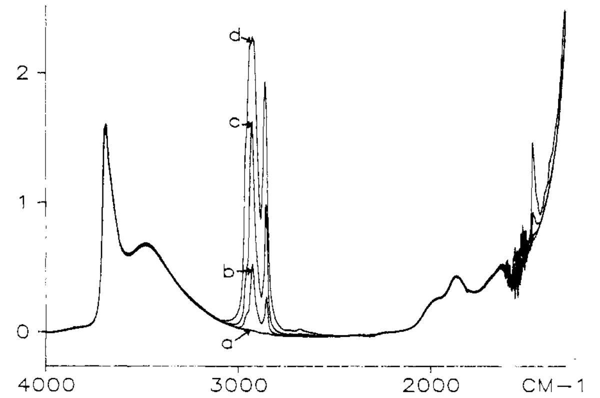

Figure 3. Addition of OTS to Aerosil 380 degassed at 150 °C and dispersed in CCl_4. Spectra shown are (a) Aerosil 380 followed by addition of (b) 52 μmol/g, (c) 162 μmol/g, and (d) 410 μmol/g OTS. The reference was recorded with the cell filled with CCl_4.

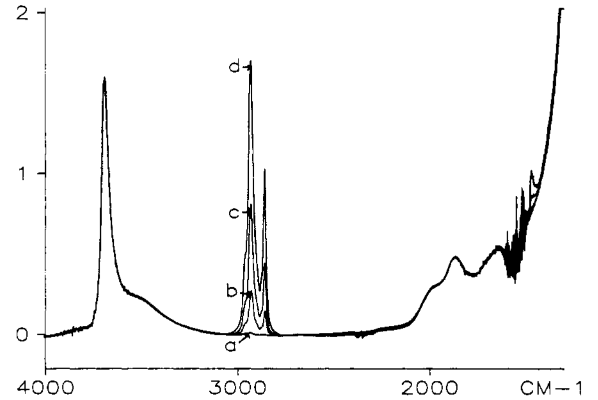

Figure 4. Addition of OTS to Aerosil 380 degassed at 400 °C and dispersed in CCl_4 Spectra shown are (a) Aerosil 380 followed by addition of (b) 65 μmol/g, (c) 115 μmol/g, and (d) 200 μmol/g OTS.

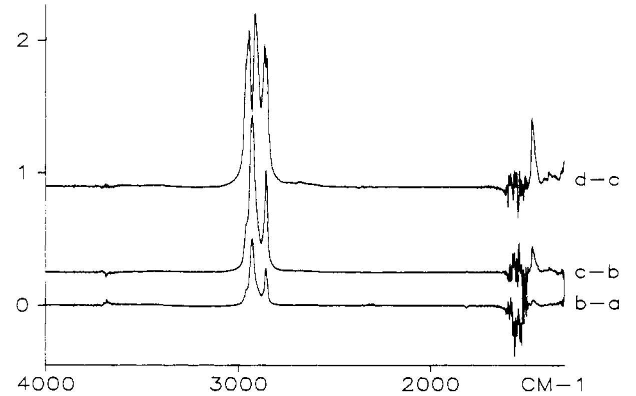

Figure 5. Difference spectra for curves shown in Figure 3. The labels a to d are defined in Figure 3.

Figure 7), the band due to free hydroxyl groups shifted to 3688 cm^{-1}. The shift to 3688 cm^{-1} is due to physisorption of OTS and is identical to the shift observed when CCl_4 is the solvent. The broad feature centered at 3400 cm^{-1} is due to hydrogen-bonded hydroxyl groups. The intensity of these bands did not change with contact time. We therefore have no evidence for the direct reaction of the OTS with the surface hydroxyl groups of silica in the absence of water.

The results obtained for the adsorption of OTS to a hydrated silica in its "as received" state is shown in Figure 8 and in the difference spectra shown in Figure 9. The most obvious changes occurred rapidly with the first dosage of OTS and continued very slowly and to a much lesser extent with subsequent additions of OTS. With the first addition of OTS there was a decrease in bands located at 3707 and 3614 cm^{-1} and this was accompanied by a small decrease in the broad band near 3400 cm^{-1} and in the region between 1690 and 1640 cm^{-1}. The two bands at 3707 and 3614 cm^{-1} are present in the spectrum (Figure 9e) of CCl_4 used as the solvent. Bascom[31] has previously shown that the bands at 3707 and 3614 cm^{-1} are due to molecular water dissolved in CCl_4, and the decrease in these bands can be attributed to the reaction of the OTS with molecular water dissolved in the solvent. For the "as received" silica the band due to isolated/geminal hydroxyl groups is located at 3676 cm^{-1}. The shift from 3688 to 3676 cm^{-1} is due to the extension of the high-frequency

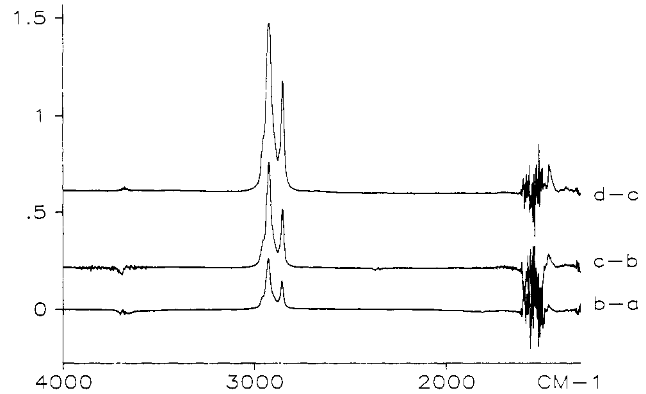

Figure 6. Difference spectra for curves shown in Figure 4. The labels a to d are defined in Figure 4.

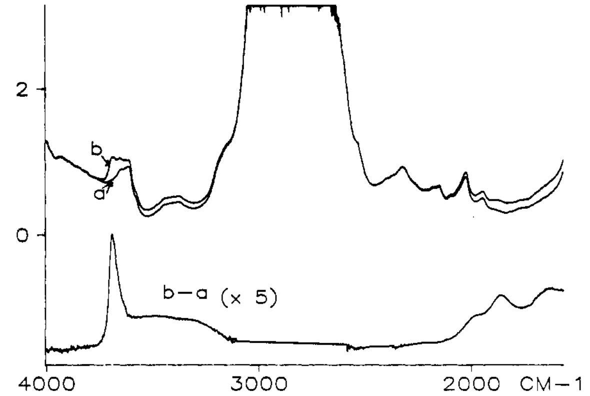

Figure 7. Infrared spectra of (a) OTS and (b) Aerosil 380 degassed at 150 °C and dispersed in OTS.

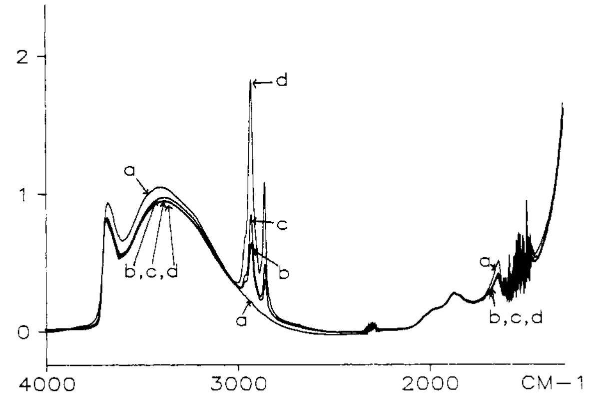

Figure 8. Addition of OTS to an "as received" Aerosil 380 dispersed in CCl_4. Spectra shown are (a) Aerosil 380 followed by addition of (b) 50 μmol/g, (c) 100 μmol/g, and (d) 250 μmol/g OTS.

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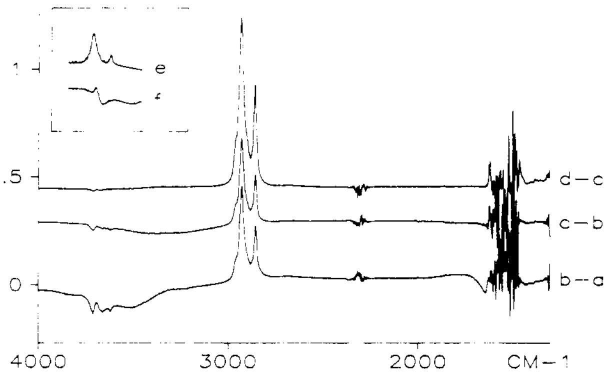

Figure 9. Difference spectra for curves shown in Figure 8. The spectrum e in the box is the CCl_4 used as the solvent and f is the spectrum obtained by subtracting the bands shown in spectrum e from the spectrum labeled b–a.

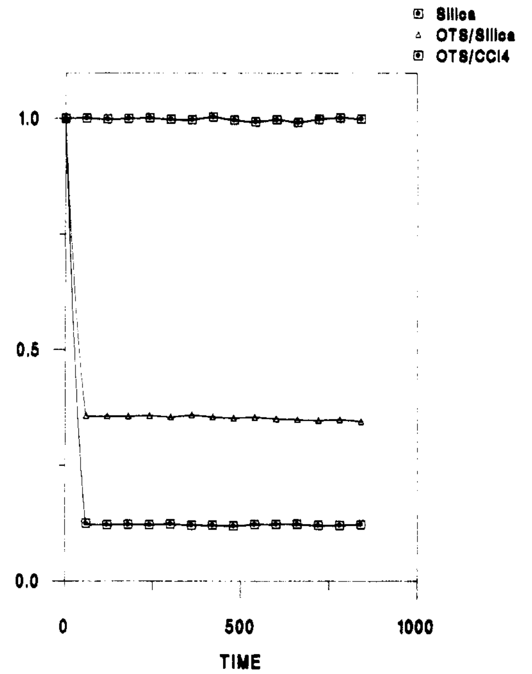

Figure 10. Settling experiment after addition of 50 μmol/g OTS on an "as received" Aerosil 380. Values for Aerosil 380 and OTS were calculated from the intensity of the band at 3400 and 2920 cm^{-1}, respectively. The ordinate values were obtained by rationing the intensity of the above bands to the measured intensity of the bands in the mixed suspension prior to settling.

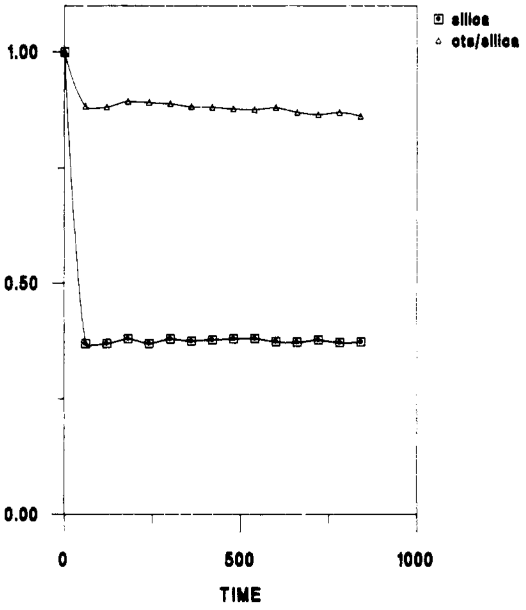

Figure 11. Settling experiment after addition of 250 μmol/g OTS on an "as received" Aerosil 380.

tail of the band at 3400 cm^{-1} into the region containing the band at 3688 cm^{-1}. The bands at 3707 and 3614 cm^{-1} overlap the region containing the band at 3676 cm^{-1} making it difficult to differentiate between spectral changes in the band at 3676 cm^{-1} from the changes arising from reaction with the molecular water in the solvent. We have therefore subtracted the bands shown in curve 9e from the spectrum shown in Figure 9a–b, and the result is shown in Figure 9f. The spectrum shown in Figure 9f is the result of a shift to higher frequency (the inflection point in the curve is at 3676 cm^{-1}) and this occurs because the underlying broad band centered at 3400 cm^{-1} is reduced in intensity.

The decrease in the band at 3400 cm^{-1} and between 1690 and 1640 cm^{-1} is the result of reaction with water on the surface of the silica. Adsorbed water on silica has a deformation mode at 1620 cm^{-1} but the exact nature of the diminution in this region cannot be defined in these experiments because it is masked by a strong absorption of the solvent (CCl_4) in this region. The decrease between 1690 and 1640 cm^{-1} represents a decrease in the high-frequency side of the water deformation mode. For this reason it is difficult to calculate the amount of OTS which has reacted with the surface water. Nevertheless, the level of adsorption of OTS with the surface water would appear to be small and this is in accord with the settling measurements which are detailed in the curves shown in Figures 10 and 11.

In these experiments the silica was suspended in the in situ settling cell using the preparative procedures detailed above. A spectrum was taken to establish the initial concentration. After the first addition of OTS (50 μmol/g) the spectra showed that the silica depletion from the beam area in the settling experiment was 86% whereas for OTS it was 65%. (For comparison, the settling curve for a solution of OTS in CCl_4 is also shown in Figure 10. In this case the OTS had reacted with the small amount of molecular water in the CCl_4. There was no decrease in the intensity of the infrared bands of OTS with time. Therefore, any decrease in the amount of OTS must be due to adsorption on the silica particle.) From the differences in the two plots, the adsorbed quantity of OTS is then calculated to be 37 μmol/g or 5.8×10^{-2} OTS molecules/nm^2. This is about 2 orders of magnitude below the hydroxyl concentration (3.1 OH/nm^2) or the amount of water which is on the silica surface (2.5–4.0 H_2O/nm^2). Also, it is well below the value of 5 OTS molecules/nm^2, which is reported for a tightly packed monolayer.[1] Further addition of OTS did little to affect the total amount of adsorbed OTS: With the addition of 250 μmol/g of OTS (see Figure 11) the calculated adsorbed quantity corresponds only to a density of 8.0×10^{-2} OTS molecule/nm^2. There is a low level of adsorption of OTS on the silica surface with this level of water on the silica.

In our next experiment we increased the amount of water adsorbed on the silica surface relative to the "as received" silica. This silica, which we refer to as a superhydrated silica, was prepared by forming a dispersion of the "as received" silica in water. After evaporation of the water the silica was ground into a powder and redispersed in CCl_4. The amount of adsorbed water as measured by the integrated intensity of the deformation mode[28] at 1620

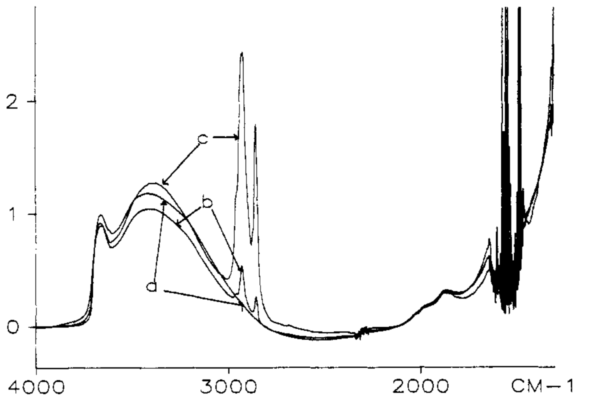

Figure 12. Addition of OTS to a superhydrated Aerosil 380 dispersed in CCl_4. Spectra shown are (a) Aerosil 380 followed by addition of (b) 50 μmol/g and (c) 500 μmol/g OTS.

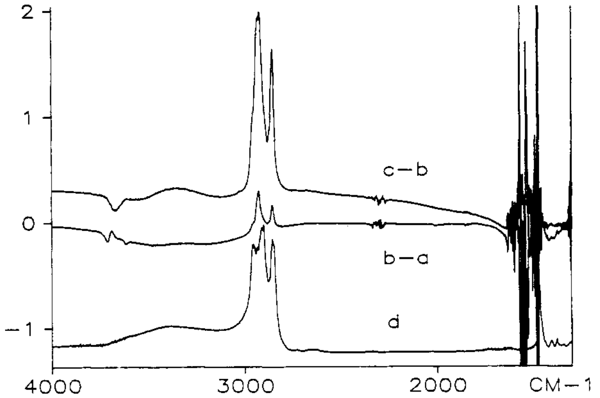

Figure 13. Difference spectra for curves shown in Figure 11. Labels a to c are defined in Figure 11. Curve d is the spectrum of the OTS polysiloxane. The curve shown in spectrum d is reduced by a factor of 2 in intensity relative to the absorbance scale.

cm^{-1} using a pressed disk and recorded in air was about a factor of 1.8 greater than an "as received" silica.

The results obtained for the adsorption of OTS on the superhydrated silica are shown in Figures 12 and 13. The spectrum recorded after the first addition of OTS (50 μmol/g) is shown in Figure 12b and the spectral changes are shown in the difference spectrum in Figure 13b–a. The difference spectrum shown in Figure 13b–a is similar to the difference spectrum recorded for the "as received" silica shown in Figure 9b–a. However, the amount of OTS adsorbed on the superhydrated silica was 90% or 46 μmol/g, which is higher than the 67% or 37 μmol/g obtained using an "as received" silica. When additional quantities of OTS were added to the superhydrated silica, the results were quite different to the results on an "as received" silica. In the latter case, we did not detect any further changes in the spectrum, but for the former, continued reaction was observed. The OTS was added in incremental amounts to the superhydrated silica and this was continued until we did not detect any further changes in the bands due to adsorbed water or surface hydroxyl groups. The final spectra are shown in Figure 12c and in Figure 13c–b. In this spectra, it is noticed that there has been a further decrease in the intensity of the high-frequency side of the band at 1620 cm^{-1} and this was accompanied by a decrease in the band at 3665 cm^{-1} along with the formation of a broad band centered at 3350 cm^{-1}.

In the spectrum of the superhydrated silica the band due to isolated/geminal hydroxyl groups is located at 3665 cm^{-1}. The diminution in intensity (about 10%) of this band could be due to the reaction of the hydrolyzed OTS with the surface to form a siloxane linkage, or this band could be shifted to lower frequency due to a hydrogen-bonding interaction with the hydrolyzed or polymerized OTS. A broad band located at 3350 cm^{-1} is observed in the spectrum of polymerized OTS (see Figure 13d) and is expected for trisilanols.[32,33] Therefore, we assign the band at 3350 cm^{-1} to silanols attached to the chlorosilane head group of hydrolyzed or polymerized OTS and not to hydrogen bonded surface hydroxyl groups. The possibility of physisorption with the isolated/geminal sites cannot be discounted because the perturbed band may be broad and weak and masked by the spectral changes occurring for the adsorbed water. There is no clear evidence supporting the formation of a surface Si–O–Si linkage or the physisorption of a octadecyltrisilanol or polymerized OTS with the surface hydroxyl groups. However, it is unlikely that the decrease in the band at 3665 cm^{-1} is due to a physisorption of polymerized OTS: In a separate experiment (see Figure 14), we added the polymerized OTS represented by the spectrum shown in Figure 13d to a hydrated silica and did not observe any changes in the band at 3665 cm^{-1}.

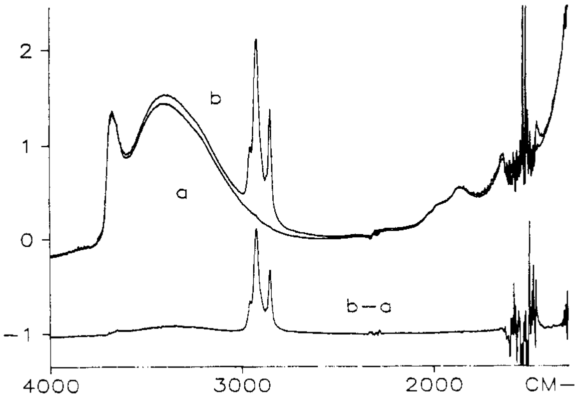

Figure 14. Addition of polymerized OTS to a superhydrated Aerosil 380 dispersed in CCl_4. Spectra shown are (a) Aerosil 380 followed by addition of (b) 35 mg/g of polymerized OTS.

It is evident that the excess layer of water on the superhydrated silica is more reactive with OTS than the first layer of adsorbed water which is found on an "as received" silica. Although the level of adsorbed water was about twice that on an "as received" silica, the amount of OTS adsorbed on the superhydrated silica calculated from settling experiments (0.5 OTS molecule/nm^2) is about an order of magnitude higher than the value obtained for an "as received" silica. These results are consistent with the existence of multilayered water on the surface of silica. The first layer of water is strongly bonded to the surface and does not participate in the hydrolysis of the chlorosilane head group of the OTS molecule. Subsequent layers would be less strongly bonded to the surface and, being more like bulk water in character, would be able to participate in direct hydrolysis of the OTS. It is possible that hydrolysis of the OTS may in fact occur in solution[2,8] rather than with the adsorbed water at the surface. Our experiments have shown that OTS does react with molecular water dissolved in CCl_4 and we point out that the excess layer of water is less well bound to the surface and would dissolve more readily in solution.

This is in accord with experiments reported some time ago both by Hair and Hertl[34] and by Bascom and Timmons.[35] In the former work, the authors report quantitative measurements of the adsorption of ammonia on

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(32) Ishida, H.; Koenig, J. L. *Appl. Spectrosc.* **1978**, *32*, 462.
(33) Ishida, H.; Koenig, J. L. *Appl. Spectrosc.* **1978**, *32*, 469.
(34) Hair, M. L.; Hertl, W. *J. Phys. Chem.* **1969**, *73*, 4269.
(35) Bascom, W. D.; Timmons, R. B. *J. Phys. Chem.* **1972**, *76*, 3192.

silica surfaces which had been purposely covered with excess water. On surfaces where the amount of water was increased above the number of hydroxyl groups on the surface, there was an increase of up to 3 times in the amount of ammonia which could be adsorbed. However, this ammonia was physically adsorbed and gave the normal spectrum of the ammonia molecule. Not until more water was added could the NH_4^+ ion be detected. The Bascom and Timmons conclusions are similar. They studied the kinetics of the hydrolysis of the ethoxysilane $(C_2H_5)_3SiOC_2H_5$ on silica which had been pretreated with varying quantities of adsorbed water. A major increase in the kinetics of the reaction is reported when the coverage of water exceeded a monolayer.

The relative importance of the reaction of OTS with surface hydroxyl groups and with water may be different in the self-assembled monolayers of OTS on low surface area substrates than was observed for the silica. Clearly, the packing order and density are much higher for self-assembled monolayers of OTS on low area surfaces than on the high surface area silica. Nevertheless, our results are consistent with results reported by Carson and Granick[20] for the adsorption of OTS on mica where it was found that an optimum level of water was necessary to form robust films: Too little water and an incomplete monolayer formed, whereas with thick water layers the OTS polymerized with the water on the surface and could easily be floated off.

In conclusion, our results have shown that there is no direct reaction of OTS with the surface hydroxyl groups and only to a small extent with the first water layer bound to the surface of a fumed silica. Hydrolysis and adsorption of the OTS does occur with the subsequent layers of water.

Registry No. OTS, 112-04-9; H_2O, 7732-18-5; SiO_2, 7631-86-9.