

A Fourier Transform Infrared (FTIR) Study of the Reaction of Triethoxysilane (TES) and Bis[3-triethoxysilylpropyl]tetrasulfane (TESPT) with the Surface of Amorphous Silica

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The interaction of triethoxysilane (TES) and bis[3-triethoxysilylpropyl]tetrasulfane (TESPT) with silica has been studied by IR spectroscopy. TES has been adsorbed onto silica pretreated at different temperatures, from the gas phase and, also, by a liquid-phase procedure. The analysis of the Si–H stretching and deformation modes, the C–H stretching and deformation modes, the SiO–H stretching, and the C–O–Si stretching modes has allowed us to investigate the structure of the adsorbed species and propose a chemisorption/desorption mechanism. The spectral features of hydrogen-bonded TES and those of three different chemisorbed species (with the formation of one, two, and three Si–O–silica bonds, respectively) have been identified. It has been concluded that the first interaction involves terminal free silanols, which actually exist also on the wet silica surface. The second and third Si–O–silica bonds are established by opening the nearest siloxane bridges. The silanization process is faster when performed in the liquid phase, because of the presence of some water in the reaction medium and the long time of reaction applied. The presence of a small amount of water promotes the adsorption reaction, likely by hydrolyzing the adsorbate. The spectroscopic data suggest that TESPT is bonded, after typical liquid-phase contact, through two Si–O–silica siloxane bridges with one remaining ethoxy group. The extent of polycondensation of the silanes seems very limited, if at all, under our conditions.

Introduction

Amorphous silica¹ is an inexpensive and easily available commercial material that has many different industrial applications, including use as an adsorbent, a pigment, a catalyst support, a filler for rubber and other polymers, an electric insulator, an acoustic insulator, an optical material, and so on. It is also used for biological and pharmaceutical applications.

Structurally, amorphous silica is a quite covalent oxide material² whose surface behavior is dominated by the chemistry of the terminal silanol groups³ that are either isolated, vicinal, or geminal.⁴ These groups, although being weakly Brønsted acidic,⁵ are able to establish quite strong but easily reversible hydrogen bondings with polar molecules⁶ that are the key phenomena occurring in adsorption–desorption cycles. Silanol groups lying nearby also make hydrogen bonds with each other, which results in chains of hydrogen-bonded hydroxyls⁷ whose interaction with adsorbates is weaker than that of free silanols.⁸ The silanols make the surface of hydroxylated silicas hydrophilic, and even more active in adsorption when wet. It is well-known that hydrogen bondings also occur between the silica silanol groups and unpolar molecules such as hydrocarbons,^{6,7,9} which allows silicas to be used for the adsorption of these compounds also. However, this interaction is weaker than that

with polar molecules. Nevertheless, van der Waals interactions also may have a relevant effect in this case.¹⁰

Thermal treatment with a consequent extensive dehydroxylation can be performed to limit silica hydrophilicity. Silanols condense under these conditions, which results in surface siloxane bridges. However, the surface of high-temperature-treated silicas is quite reactive.¹¹ To make silica hydrophobic, a surface chemical treatment can be performed. Chemical reactions with organic compounds such as alcohols¹² or organosilanes¹³ allow the conversion of surface silanols to nonpolar groups. Typical molecules that allow these reactions include monoalkoxysilanes, dialkoxysilanes, and trialkoxysilanes.¹⁴ These reactants allow the simultaneous disappearance of silanols and the bonding to the silica surface of organic groups that can interact with nonpolar species. This is what is done when silica is used as a filler for rubber. Silica typically is modified with bis[3-triethoxysilylpropyl]tetrasulfane (TESPT), which improves its reinforcing capability by promoting filler/polymer interaction and reducing filler/filler interaction, therefore increasing the dispersion of the silica into the matrix; this TESPT also acts as an integral component of the curing system, to enhance cross-linking network properties.¹⁵

Several spectroscopic techniques have been used to study the surface modification of silica with alkoxysilanes. In particular, IR spectroscopy has found several applications.^{16–18} However, the actual structures of the species bound on silica, and the nature of the filler/elastomer interactions, are still under investigation.^{19–21}

Here, we will summarize the results of a study of the interaction of triethoxysilane (TES, (CH₃CH₂–O)₃Si–H) and

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of TESPT with an amorphous silica surface. The former compound contains the alkoxy groups that allow reaction with the surface. Moreover, it has the advantage of being volatile, therefore allowing gas/solid interaction, and it contains an easily IR-detectable and sensitive bond (the Si–H bond) whose stretching frequency can be used as a probe for the structure of the adsorbed species. Studies of the TES/silica interaction have been recently reported,^{22,23} mostly based on electrophoresis and magic angle spinning–nuclear magnetic resonance (MAS NMR) spectroscopy with some IR data; a study of the interaction of TES with germania, using inelastic electron tunneling spectroscopy (IETS), has also been published.²⁴ The results that we obtained with TES will allow us to interpret those obtained for the liquid-phase TESPT/silica interaction, therefore gaining information that can explain the behavior of the resulting filler/rubber composite.

Experimental Section

The amorphous precipitated silica material used in the present study is Zeosil 1165 MP ($165 \pm 20 \text{ m}^2/\text{g}$), supplied by Rhône Poulenc in form of “micropearls”. Modified SiO₂ samples were prepared by contacting the SiO₂ micropearls, in ambient atmosphere, with liquid triethoxysilane (TES, (CH₃CH₂–O)₃–Si–H), purchased from Aldrich, or bis[3-triethoxysilylpropyl]-tetrasulfane (TESPT), kindly provided by Pirelli Pneumatici, S.p.A. Silica and the silane were dispersed in CH₂Cl₂ and maintained under slow agitation until complete solvent evaporation occurred. The powder was then kept under static vacuum overnight and subsequently introduced in vials that contained argon. These were placed in a thermal bath for 2–3 h at 423 K in the case of TESPT, and for 12 h at 323 K when the more-volatile TES was used. Finally, the samples were washed again with CH₂Cl₂ in a Soxhlet and dried under static vacuum. A “poly-TES” sample was also prepared by hydrolyzing TES in distilled water, aging for 5 h, filtering, washing with distilled water, and drying at 300 K under vacuum. These powders were later subjected to outgassing upon IR experiments.

Fourier transform infrared (FTIR) analyses were performed both on pure and modified SiO₂ samples. The spectra were recorded on a Nicolet Nexus Fourier Transform instrument that was provided with a DTGS KBr detector. For each spectrum, 100 scans in the range 4000–400 cm^{–1} were recorded, with a resolution of 4 cm^{–1}. The spectra are shown with an absorbance scale; in the pictures that present more than one spectrum, the absorbance scale refers only to the first spectrum from the bottom, whereas the others are shifted without any scale modifications.

The characterization of the surface activity of the SiO₂–TES system was performed using pressed disks (2.5 cm in diameter) of pure SiO₂ powder. The disk weight was calibrated to have, in all cases, the best spectral conditions. The disks were prepared in air and then located inside an IR cell connected to a conventional manipulation/outgassing ramp that allows the disk to stay, alternatively, in the IR beam path or inside an oven. The samples were treated by outgassing at room temperature or higher temperature (823 or 973 K) in the IR cell. Spectra were collected after the pretreatment and after adsorption of TES, which was distilled under vacuum and then contacted with the sample surface through the ramp. The adsorption procedure involves contact of the pretreated sample disk with vapors at room temperature or 373 K and at a pressure of 15 Torr for 20 min, and outgassing in steps from room temperature to higher temperatures (up to 773 K).

The spectra of the gases that evolve inside the cell during the evacuation procedure also were collected, to gain information about TES thermal desorption mechanism.

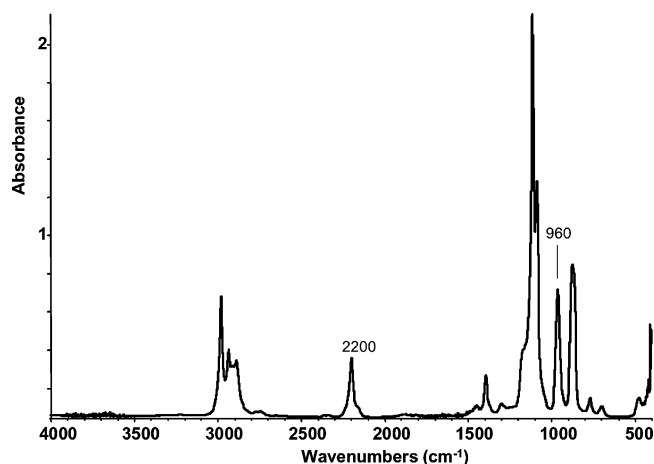


Figure 1. FTIR spectrum of TES vapor.

The spectra of the modified SiO₂ samples and of the poly-TES sample were collected similarly after outgassing at room temperature and higher temperatures.

Results and Discussion

Study of the Gas–Solid TES/Silica Interaction. The spectrum of gaseous TES is reported in Figure 1. In the 3000–2800 cm^{–1} region, we find C–H stretching bands of the ethoxy groups, and the corresponding deformation bands in the 1500–1200 cm^{–1} range. The very strong bands in the 1200–1000 cm^{–1} range are due to the C–O–Si asymmetric stretching modes, whereas the bands in the 1000–600 cm^{–1} region are likely due to the C–C stretchings, the Si–H deformation, and the C–O–Si symmetric stretching modes. The C–O–Si rocking modes are responsible for the bands below 500 cm^{–1}.^{25,26}

The sharp band at 2200 cm^{–1} is due to the Si–H stretching of the silane bond. It presents weak and broad components at both sides, as expected for a parallel vibration mode of a symmetrical top molecule.²⁷

The spectrum of liquid TES presents, as expected, the same bands but with considerable shifts, and the absence, obviously, of rotovibrational components. However, it shows some dissolved water, and the exact position of the bands seems to be quite dependent on the degree of drying.

The spectra related to the experiment of TES adsorption at room temperature over a silica disk pretreated at 973 K are reported in Figures 2 and 3.

After the thermal pretreatment (spectrum a in Figures 2 and 3), the silica presents a very sharp and almost symmetric O–H stretching band of silanol groups, centered at 3746 cm^{–1}.

After contact with TES vapor (spectrum b in Figures 2 and 3), this band has fully disappeared, whereas a very broad and weak absorption is found in the 3600–3200 cm^{–1} region (see spectrum b in Figure 2). New bands in the C–H stretching and deformation regions and in the Si–H stretching region reveal the presence of adsorbed TES.

After contact at room temperature (see spectrum b in Figures 2 and 3), the main Si–H maximum is located at 2227 cm^{–1}; however, it presents an evident shoulder near 2256 cm^{–1}, a weak component near 2180 cm^{–1}, and a further tail toward 2300 cm^{–1}. After outgassing at increasing temperatures (spectra c–h on the right-hand side of Figure 3), the lower-frequency components decrease in intensity faster than those at higher frequencies. After outgassing at 573 K (spectrum f in Figure 3), the band at 2256 cm^{–1} represents the main maximum. Upon treatment at 773 K

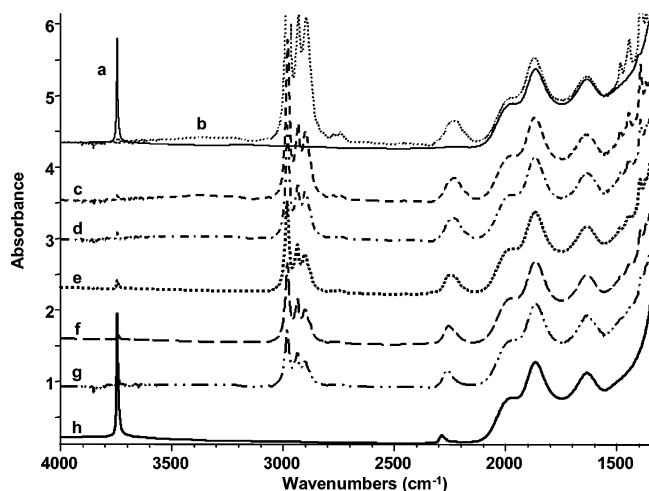


Figure 2. FTIR spectra of SiO₂ after thermal treatment at 973 K: SiO₂ alone (spectrum a), after adsorption of TES at room temperature (spectrum b), outgassed at room temperature (spectrum c), outgassed at 373 K (spectrum d), outgassed at 473 K (spectrum e), outgassed at 573 K (spectrum f), outgassed at 673 K (spectrum g), and outgassed at 773 K (spectrum h).

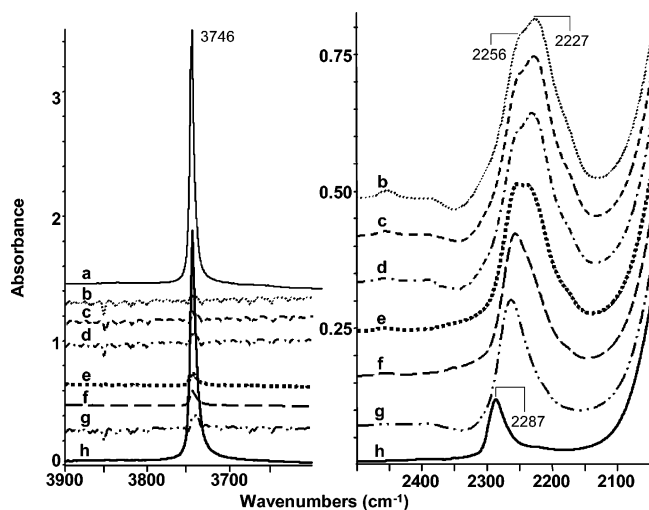


Figure 3. FTIR spectra of SiO₂ after thermal treatment at 973 K: SiO₂ alone (spectrum a), after adsorption of TES at room temperature (spectrum b), outgassed at room temperature (spectrum c), outgassed at 373 K (spectrum d), outgassed at 473 K (spectrum e), outgassed at 573 K (spectrum f), outgassed at 673 K (spectrum g), and outgassed at 773 K (spectrum h). The O-H stretching region is shown on the left, and the Si-H stretching region is shown on the right.

(spectrum h in Figure 3), the band is displaced, although weakened, at 2287 cm⁻¹. Upon outgassing below 773 K (spectra b–g on the left-hand side of Figures 2 and 3), the O–H stretching of the silanols is still extremely weak. Only outgassing at 773 K (see spectrum h on the left-hand side of Figure 3) allows the O–H stretching mode to be completely restored. On the other hand, under these conditions, the C–H stretching and deformation modes disappear completely (see spectrum h in Figure 2).

In Figures 4 and 5, the spectra reported are relative to TES adsorption on a silica disk pretreated by outgassing at 823 K for 1 h. Even in this case, evidence is provided for the adsorption and the progressive desorption or decomposition of TES by the presence and progressive disappearance of the C–H stretching and deformation bands in the ranges of 3000–2800 cm⁻¹ and 1500–1300 cm⁻¹, and by the presence of the Si–H stretching band. In this region, its main maximum when the sample is still in contact with the vapor (spectrum b on the right-hand

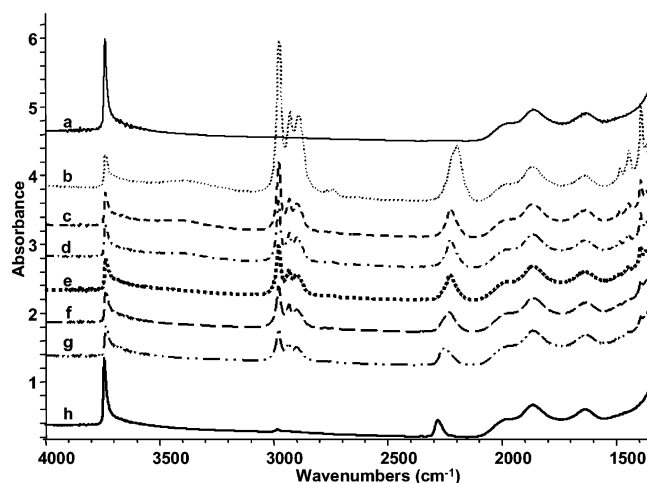


Figure 4. FTIR spectra of SiO₂ after thermal treatment at 823 K: SiO₂ alone (spectrum a), after adsorption of TES at room temperature (spectrum b), outgassed at room temperature (spectrum c), outgassed at 373 K (spectrum d), outgassed at 473 K (spectrum e), outgassed at 573 K (spectrum f), outgassed at 673 K (spectrum g), and outgassed at 773 K (spectrum h).

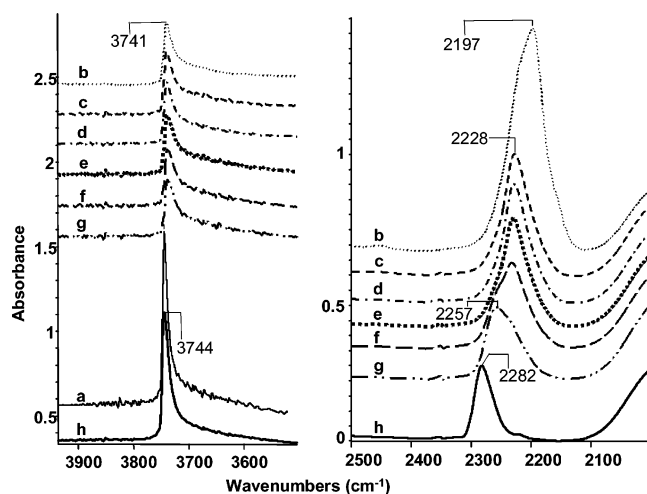


Figure 5. FTIR spectra of SiO₂ after thermal treatment at 823 K: SiO₂ alone (spectrum a), after adsorption of TES at room temperature (spectrum b), outgassed at room temperature (spectrum c), outgassed at 373 K (spectrum d), outgassed at 473 K (spectrum e), outgassed at 573 K (spectrum f), outgassed at 673 K (spectrum g), and outgassed at 773 K (spectrum h). The O–H stretching region is shown on the left, and the Si–H stretching region is shown on the right.

side of Figures 4 and 5) is located at 2197 cm⁻¹, i.e., very close to the position observed for TES vapor. However, a pronounced shoulder is already observed near 2220 cm⁻¹, and another weak component can be envisaged near 2250 cm⁻¹ (see spectrum b on the right-hand side of Figure 5). By outgassing at room temperature (spectrum c on the right-hand side of Figure 5), the component at 2197 cm⁻¹ disappears almost completely but a band centered at 2228 cm⁻¹ is now very evident. After outgassing at 573 K (spectrum f in Figure 5), this band seems to decrease in intensity but the shoulder near 2260 cm⁻¹ certainly becomes more pronounced. This feature becomes the main maximum after outgassing at 673 K, whereas it shifts to 2282 cm⁻¹ after outgassing at 773 K.

The spectra in the Si–H region provide clear evidence of the formation of four different species on the silica surface, characterized by the position of the Si–H stretching near 2180–2200, 2230, 2255, and 2280 cm⁻¹. The almost-perfect coincidence of the first band with that of the TES vapor, together

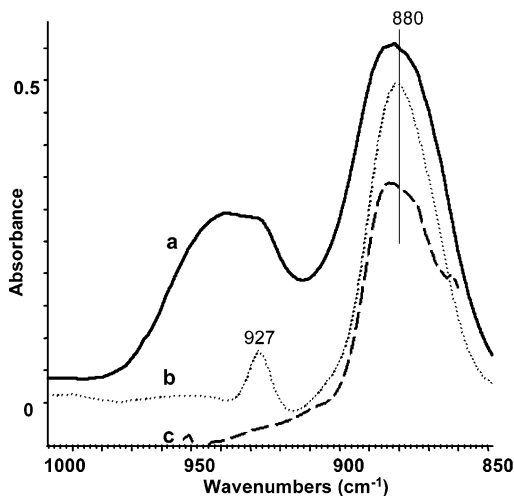
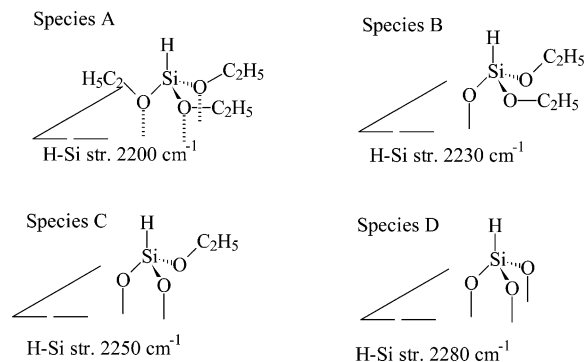


Figure 6. FTIR spectra of the adsorbed species arising from TES in the 1000–800 cm^{-1} window after outgassing at room temperature (spectrum a), 573 K (spectrum b), and 773 K (spectrum c).

SCHEME 1: Hypothetical Structure for Adsorbed TES Species. The Symbol “ \angle ” Represents the Silica Surface Plane.



with the easy desorption of this species by simple outgassing at room temperature, is consistent with its assignment to a weakly adsorbed molecular TES species. In contrast, the total absence of C–H bands after outgassing at 773 K suggests that the band at 2280 cm^{-1} is due to a chemisorbed species that has lost the three ethoxy groups. By parallelism, it seems reasonable to assign bands near 2230 and 2255 cm^{-1} to adsorbed species that have lost one and two ethoxy groups, respectively. In Scheme 1, the hypothetical structures for these species are reported. We can note that a band at 2300 cm^{-1} was previously reported to be formed over “reactive silica” after contact with hydrogen and was assigned to a Si–H bond over a surface silicon reactive center of the silica.²⁸

The aforementioned interpretation finds additional support in the spectra recorded in the region of 1000–800 cm^{-1} , which are available because of a window in the silica skeletal spectrum. In this region, adsorbed TES exhibits, after outgassing at room temperature, two evident bands (spectrum a in Figure 6): a main band, centered near 880 cm^{-1} , and a weaker band that is composed by several features. We can find an evident component at 927 cm^{-1} , a broader one with a maximum at 937 cm^{-1} and, possibly, a further shoulder at higher frequencies. These features correspond to the Si–H stretching at 2200 cm^{-1} . By outgassing at increasing temperature, the main band decreases in intensity without shifting significantly. In contrast, the broad feature at 950–930 cm^{-1} progressively decreases up to disappear, whereas the sharp component at 927 cm^{-1} also disappears after heating at 773 K, when the Si–H stretching is found near 2280 cm^{-1} .

In agreement with Lin,²⁶ the band at 880 cm^{-1} is due to the Si–H bending mode. This observation should indicate that this mode actually is quite insensitive to the state of the molecule, in contrast to the corresponding stretching mode. On the other hand, the bands at 950–900 cm^{-1} could be due to the C–C stretching mode of the ethoxy groups. This band has, in fact, been detected at 960 cm^{-1} for TEOS²⁵ and is observable near 940 cm^{-1} for liquid TES and at 960 cm^{-1} for gaseous TES (see Figure 1). The total disappearance of this band when outgassing is performed at 573 K and the Si–H stretching is at 2280 cm^{-1} is in full agreement with the identification of this species as species D. The sharp band at 927 cm^{-1} could be assigned to species C, whereas the broader feature at 950–930 cm^{-1} , which is likely split, could be due to species B and A.

The comparison of the overall spectra of the disks after the outgassing pretreatments (see spectrum a in Figures 2 and Figure 4) shows that the band of the surface free silanol groups (3750–3600 cm^{-1}) is much more intense, if compared to those of the overtones of the bulk vibrations (2100–1500 cm^{-1}) when the sample is outgassed at 823 K rather than at 973 K. Note that the samples do not have the same weight, so the comparison of the absolute intensity of the bands has no meaning. The lower relative intensity of the O–H band is proof of surface dehydroxylation and/or a decrease of the external surface area caused by sintering.

On the other hand, spectrum a in Figure 5 shows that, after pretreating silica by outgassing at 823 K for 1 h, the IR band due to the O–H stretching of the surface free silanol groups presents an evident tail in the 3740–3600 cm^{-1} range. This tail is not present for silica outgassed at 973 K (see spectrum a in Figure 3). For silica that has been outgassed at 823 K (Figure 5), the main maximum at 3744 cm^{-1} disappears after contact with TES, but a maximum is now observed near 3741 cm^{-1} and the tail is also essentially still present. This provides evidence of a lack of reactivity of the OH groups responsible for the band at 3741 cm^{-1} and the tail, which still exist on the sample that was outgassed at 823 K but are destroyed after outgassing at 973 K. Our data suggest that the maximum at 3741 cm^{-1} and the tail, resisting interaction with TES, are likely due to free silanol groups located on micropores that cannot be entered by TES and are destroyed by sintering at higher temperatures.

The analysis of the Si–H stretching band of the surface silane bonds (2300–2100 cm^{-1}) shows a much greater intensity in relation to the bands of the overtones of the bulk vibrations (2100–1500 cm^{-1}) if the sample is contacted with TES vapor after pretreatment by outgassing at 823 K rather than at 973 K. This parallels the intensity of the main band near 3744 cm^{-1} that, in fact, has fully disappeared upon adsorption of TES in both cases. This suggests that the adsorption of TES from the gas at room temperature occurs by reaction with surface free silanol groups that are well-exposed on the silica surface, the amount of which is reduced by increasing the outgassing temperature.

The spectra reported in Figures 7 and 8 are relative to the TES adsorption experiment on a silica disk pretreated by outgassing at room temperature. After this pretreatment, the silica disk presents a very strong and broad absorption in the 3750–2500 cm^{-1} region with a main maximum around 3500 cm^{-1} and a component near 3650 cm^{-1} . The adsorption of TES results in strong bands in the 3000–2800 cm^{-1} and 2300–2100 cm^{-1} regions, and below 1500 cm^{-1} . The subtraction spectrum shown in the inset in Figure 7 shows that, although the band of free silanols at 3746 cm^{-1} is not evident in the broad overlap

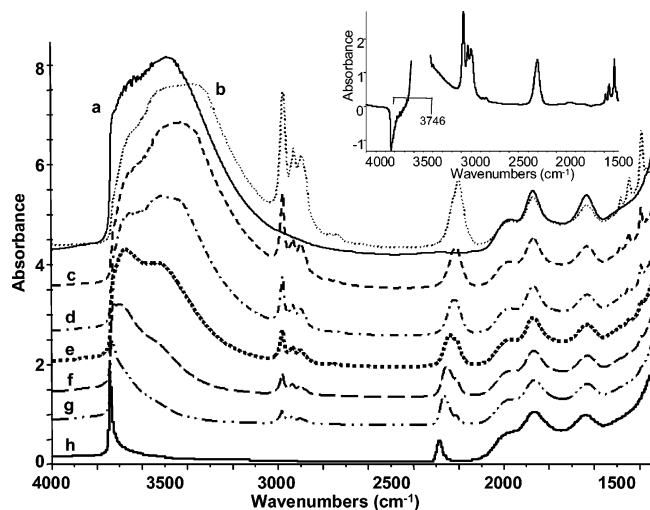


Figure 7. FTIR spectra of SiO₂ after outgassing at room temperature: SiO₂ alone (spectrum a), after adsorption of TES at room temperature (spectrum b), outgassed at room temperature (spectrum c), outgassed at 373 K (spectrum d), outgassed at 473 K (spectrum e), outgassed at 573 K (spectrum f), outgassed at 673 K (spectrum g), and outgassed at 773 K (spectrum h). Inset shows the spectral subtraction of spectrum d – spectrum a.

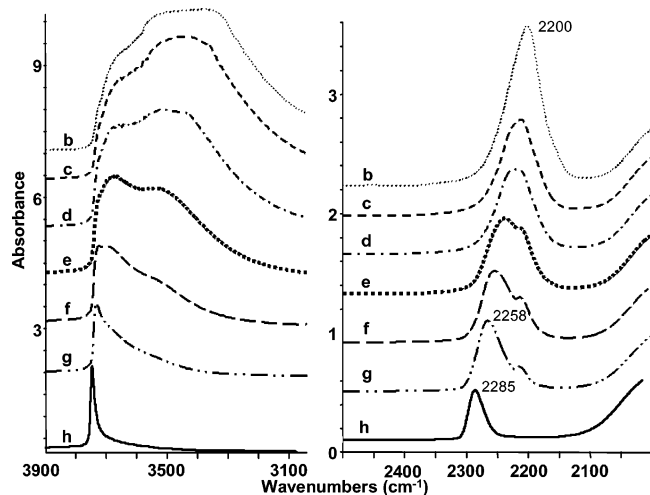
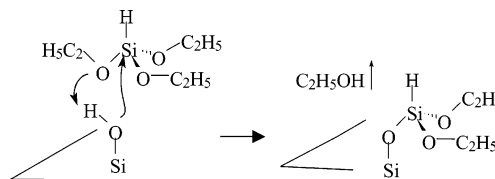


Figure 8. FTIR spectra of SiO₂ after outgassing at room temperature: after adsorption of TES at room temperature (spectrum b), outgassed at room temperature (spectrum c), outgassed at 373 K (spectrum d), outgassed at 473 K (spectrum e), outgassed at 573 K (spectrum f), outgassed at 673 K (spectrum g), and outgassed at 773 K (spectrum h). The O–H stretching region is shown on the left, and the Si–H stretching region is shown on the right.

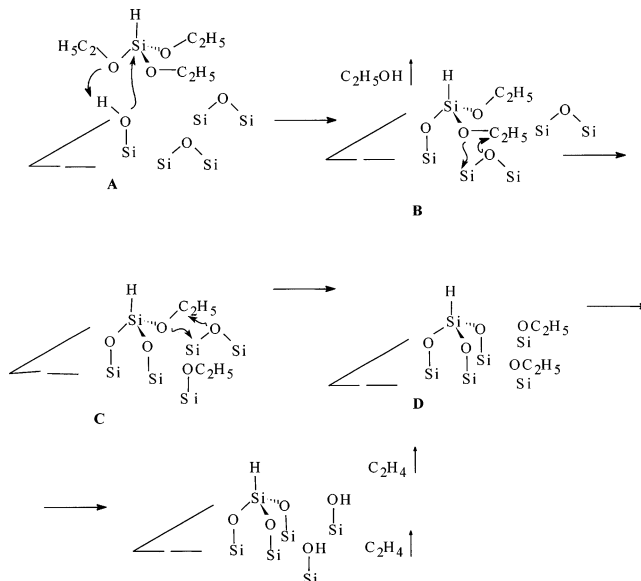
of the OH groups of silica (also reported in spectrum a in Figure 7), it actually exists and appears as a negative sharp band in the subtraction. Therefore, free terminal silanols exist, even after outgassing at room temperature, and they also are reactive toward TES under these conditions. No other negative feature is observed in the subtraction, therefore suggesting that only the free silanols are reactive toward TES at the vapor/solid interface at room temperature.

The behavior of the Si–H stretching band is similar to that of the previous experiments, with the main maximum observed first near 2200 cm^{−1} and shifting upward by outgassing as usual (see Figure 8, right-hand side). Even in this case, the C–H bands decrease in intensity and fully disappear (see spectrum h in Figure 7) when outgassing at 773 K, as the Si–H band shifts from near 2260 cm^{−1} to above 2280 cm^{−1}. The intensity ratio between the Si–H stretching and the bulk overtones is similar

SCHEME 2: Likely Mechanism for the Formation of Adsorbed TES Species B.



SCHEME 3: Hypothesis for the Sequential Formation of Species A, B, C, and D.



on the sample outgassed at room temperature and on the sample outgassed at 823 K, suggesting that this temperature destroys hydrogen-bonded silanols but not the isolated ones, which are very likely exposed on corners or edges of the surface. These are the sites for TES reactive adsorption.

A possible mechanism for this reaction is shown in Scheme 2. It seems likely that one ethoxy group of TES should be lost as ethanol, which, under the conditions of our experiment, probably leaves the surface when the outgassing occurs.

One common feature of the three experiments described so far is that the O–H stretching band at 3746 cm^{−1}, which disappeared after TES adsorption at room temperature in all cases, reappeared only after outgassing at 773 K. At this point, the adsorption is approximately as intense as that in the thermally pretreated samples. On the other hand, TES is still strongly adsorbed in the form of species D, whose main band falls near 2285 cm^{−1}. This phenomenon indicates that a mechanism occurs that restores or recreates the free surface OH groups without a desorption of TES, implying instead the conversion of species B and C to species D.

In Scheme 3, we neglect the possibility of a condensation of adsorbed TES molecules to produce adsorbed “siloxane” species of “surface poly-TES”, such as those reported by Ketelson.^{22,23} This is actually a possible explanation for the conversion of an adsorbed TES species to another one (such as species B into C), with a loss of CH species without the appearance of OH species. On the other hand, we have very good proof that adsorbed TES such as species B is formed on isolated OH groups and it seems quite unlikely that several isolated OH groups can be close enough to allow condensation of adsorbed TES species. In any case, this will be discussed later in this study.

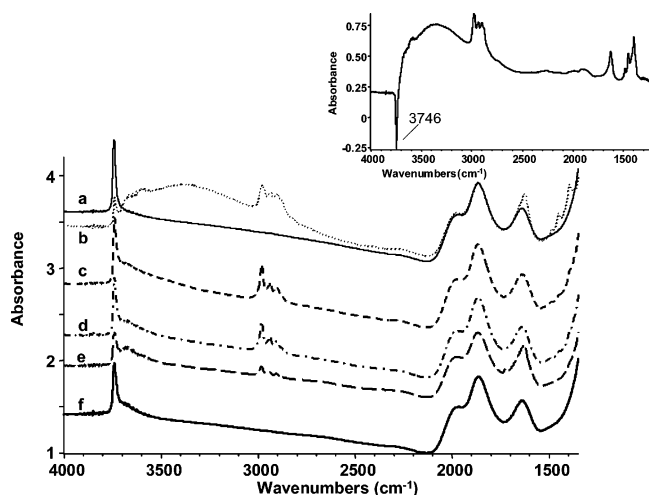


Figure 9. FTIR spectra of SiO₂ after thermal treatment at 823 K: SiO₂ alone (spectrum a), after adsorption of EtOH at room temperature (spectrum b), outgassed at 473 K (spectrum c), outgassed at 573 K (spectrum d), outgassed at 673 K (spectrum e), and outgassed at 773 K (spectrum f). Inset shows the spectral subtraction of spectrum b – spectrum a.

Study of the Gas–Solid Ethanol/Silica Interaction. To gain further information about the mechanism of the TES/silica interaction, we also investigated the interaction of ethanol with silica under similar conditions.

In Figure 9, spectra are reported relative to an ethanol adsorption experiment on a silica disk pretreated by outgassing at 823 K for 1 h. The spectra show the formation of the C–H stretching and deformation bands, which resist outgassing up to 673 K but have fully disappeared after outgassing at 773 K. The subtraction spectrum highlights that the O–H stretching at 3746 cm⁻¹ is definitely affected upon adsorption. However, after contact at room temperature, only a small portion of the O–H stretching band is actually eroded and reappears upon outgassing at 773 K.

This shows that ethanol is far less reactive than TES with the surface silanols. On the other hand, although hydrogen-bonded forms of ethanol are certainly formed at room temperature, as described by previous authors (e.g., Jeziorowski et al.²⁹), ethoxy groups resist outgassing above 373 K and are fully destroyed only upon outgassing at 773 K. This proves that the ethoxy groups bonded to silica do not resist outgassing at 773 K.

In Figure 10, the spectra recorded in the C–H stretching and deformation regions for TES and ethanol species adsorbed on silica are compared. After TES adsorption at room temperature, in the C–H stretching region, the spectrum presents three maxima—at 2978, 2931, and 2894 cm⁻¹, the last being quite broad. After outgassing at 573 K, the spectrum seems slightly more complex, with more evident shoulders at 2947 and 2876 cm⁻¹, and the main maxima have shifted upward to 2981, 2935, and 2901 cm⁻¹. The spectrum of the species that results from the adsorption of ethanol after outgassing at the same temperature again presents three main maxima, at even higher frequencies—2984, 2939, and 2906 cm⁻¹—with even more evident components at 2952 and 2882 cm⁻¹.

In the C–H deformation region, the bands for TES adsorbed at room temperature are observed at 1484, 1455 (weak), 1445, 1393, and 1369 cm⁻¹. All bands shift slightly higher when outgassing at 573 K, assuming a position similar to those of the species that results from ethanol adsorption at room temperature and subsequent outgassing at 573 K, which are located at 1489, 1457, 1450, 1397, and 1373 cm⁻¹.

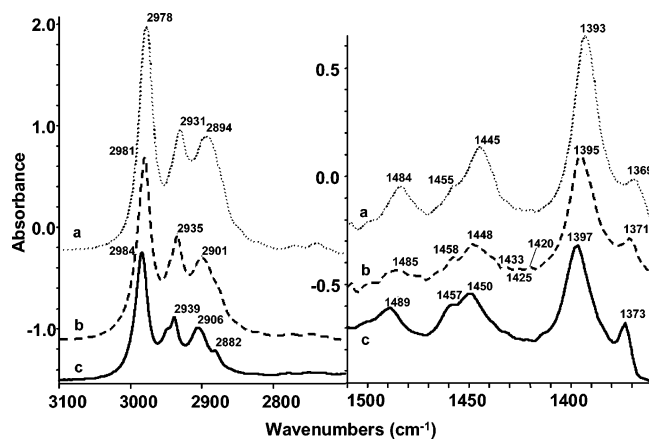


Figure 10. FTIR spectra of the C–H stretching (left) and deformation (right) regions: TES-treated SiO₂ after outgassing at room temperature (spectrum a), after outgassing at 573 K (spectrum b), and ethanol-treated SiO₂ outgassed at 573 K (spectrum c).

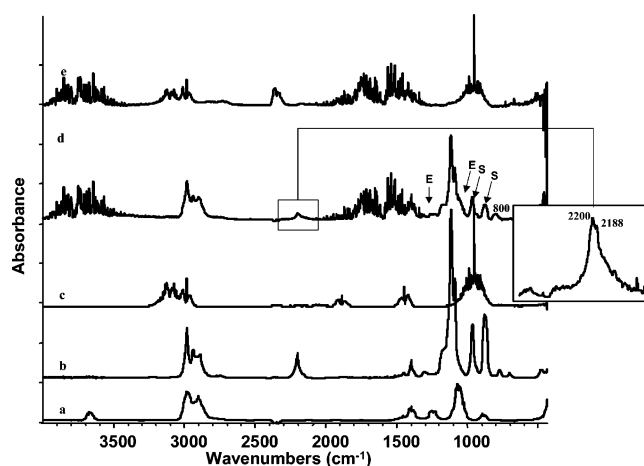


Figure 11. FTIR spectra of gases evolving from TES-treated SiO₂ surface, under static vacuum, at increasing temperatures and comparison spectra of pure gases: ethanol (spectrum a), TES (spectrum b), ethylene (spectrum c), and gas evolved from TES-treated silica after heat treatment under static vacuum at 573 K (spectrum d) and 723 K (spectrum e).

In the last case, the spectrum is certainly due to ethoxy groups that have been formed by the condensation of the silica silanols with the ethanol. The spectrum obtained from TES adsorption is a little different but progressively evolves toward it. This observation suggests that the spectrum converts from that of ethoxy groups that belong to TES adsorbed species to ethoxy groups that are bonded to the silica surface, meaning that, upon progressive outgassing at increasing temperature, some of the ethoxy groups of the TES adsorbed species transfer onto the silica surface.

Study of the Gases Evolved upon Thermal Treatment of TES Adsorbed on Silica. To better evaluate the high-temperature behavior observed in our experiments, we recorded the spectra of the gases evolved upon the thermal treatment of silica with preadsorbed TES (spectra d and e in Figure 11). The spectra are compared with those of gaseous ethanol (see spectrum a in Figure 11), TES (see spectrum b in Figure 11 and see Figure 1) and ethylene (see spectrum c in Figure 11).

The spectra recorded after treatment under static vacuum at low temperature (e.g., 573 K) show the features of gaseous TES, gaseous water, and gaseous ethanol (see the bands highlighted by arrows with E), proving that at least a portion of TES actually adsorbs by condensation on surface silanols, following our

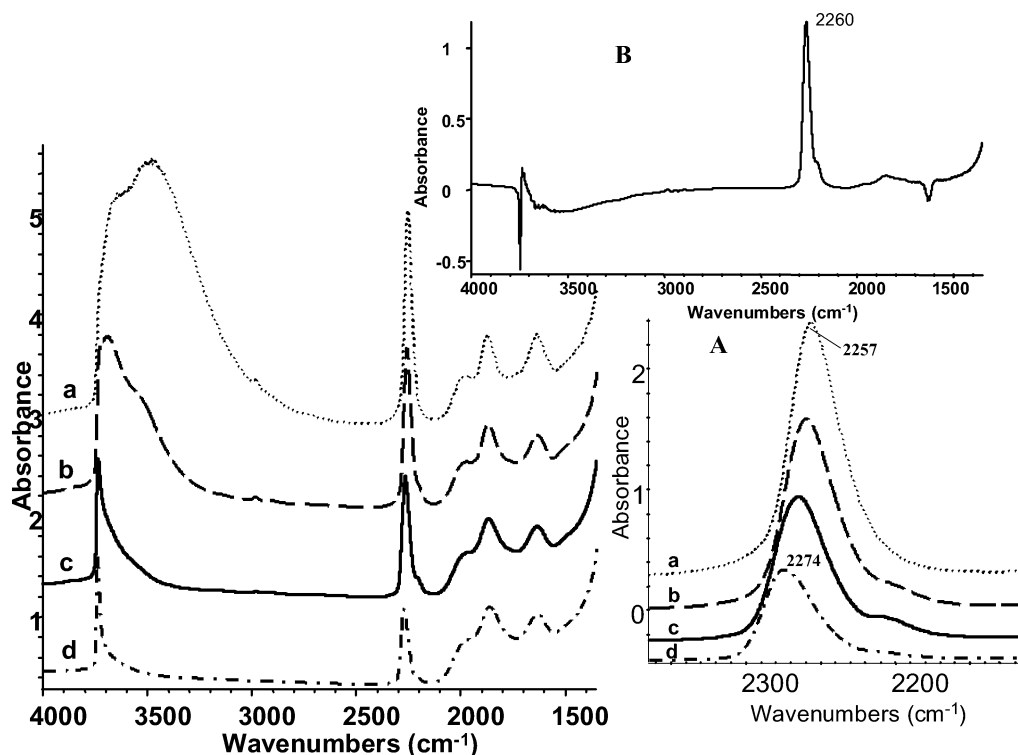


Figure 12. FTIR spectra of TES-modified SiO_2 outgassed at increasing temperatures: room temperature (spectrum a), 473 K (spectrum b), 673 K (spectrum c), and 773 K (spectrum d). Inset A shows the Si-H stretching region, and inset B shows the subtraction spectrum between TES-modified SiO_2 and pure SiO_2 . Both samples were outgassed at 473 K.

reaction Scheme 1. However, the Si-H stretching region (a new component at 2188 cm^{-1}) and the Si-O-C (or Si-O-Si) symmetric stretching region (a band at 800 cm^{-1} , and different absorption ratios) clearly show features that are due to neither TES nor ethanol, but certainly are due to another silane (see the bands highlighted by arrows with S). It seems likely that two TES molecules could have condensed, forming the siloxane $(\text{C}_2\text{H}_5\text{-O})_2\text{-SiH-O-SiH-(OC}_2\text{H}_5)_2$.

The spectrum taken after adsorbed TES was heated at $>673\text{ K}$ (namely, at 723 K) shows very evident bands of gaseous ethylene. This supports the mechanism proposed in Scheme 3. It seems interesting to remark that we did not observe gas-phase diethyl ether, which is expected to be the product (or the primary product) of the condensation of TES species among each other. This suggests that "poly-TES" species, such as those created after liquid-phase contact between TES and silica by Ketelson et al.,^{22,23} do not form in relevant amounts under our conditions.

Study of the TES/Silica Interaction via Liquid Solution Reaction. Figure 12 shows the spectra of a pressed disk of pure silica modified with TES through liquid-phase reaction, after outgassing at increasing temperatures. The strong band at 2257 cm^{-1} indicates the presence of adsorbed TES. On the other hand, the C-H stretching and deformation bands are very weak already at room temperature and are not present at all after outgassing at 773 K .

The progressive outgassing steps do not alter the Si-H band frequency until 523 K ; from this point forward, a gradual shift is observed that reaches 2274 cm^{-1} after outgassing at 773 K .

The spectra that we obtained are different from those reported by Ketelson et al.^{22,23} that actually showed the Si-H band at 2250 cm^{-1} , even stronger than ours in relation to the bulk absorptions of silica, and also very strong C-H stretching and bending modes.

The spectral features of the species obtained after outgassing at 773 K are almost identical to those found after pure silica

came into contact with TES vapor, so we can suppose that, at the end of the experiment, the same species D has been formed. In contrast, at $<773\text{ K}$, the spectra obtained for silica modified with TES in the liquid phase differ from those obtained for silica after the adsorption of TES from the gas phase. In particular, the differences are the following:

- (1) The Si-H stretching band is observed already at 2257 cm^{-1} , after outgassing at room temperature, which suggests that a species similar to C is formed directly;
- (2) This band is much more intense, implying the generation of a much greater quantity of bonded species;
- (3) The C-H bands are almost nonexistent, which could mean that ethoxy groups have been hydrolyzed upon liquid-phase reaction.

Figures 13 and 14 compare the spectra of a pure silica sample and silica modified with TES, both outgassed at 300 K and 523 K . Interestingly, the sample with TES shows a much-less-intense absorption in the $3200\text{--}2600\text{ cm}^{-1}$ region (stretching of hydrogen-bonded water) and near 1630 cm^{-1} , where the scissoring mode of molecular water is superimposed over a skeletal overtone mode of the bulk silica. This means that the TES-modified sample contains much less water. On the other hand, from the TES-free sample, one can detect the sharp peak at 3747 cm^{-1} that is due to free silanols, even if not very evident, whereas the same peak is definitely not present in the spectrum of TES-containing silica. However, under both outgassing conditions, TES-containing silica absorbs more than pure silica in the $3730\text{--}3650\text{ cm}^{-1}$ region. This can be seen clearly in the corresponding subtraction spectra where bands of terminal silanols and water are observed as negative bands (downward), whereas the Si-H stretching is observed upward together with an absorption in the $3730\text{--}3650\text{ cm}^{-1}$ region (marked with an asterisk, *, in Figures 13 and 14). These bands could be associated with silanol groups that belong to the ex-TES Si atom, therefore providing evidence for a species we call C' (see

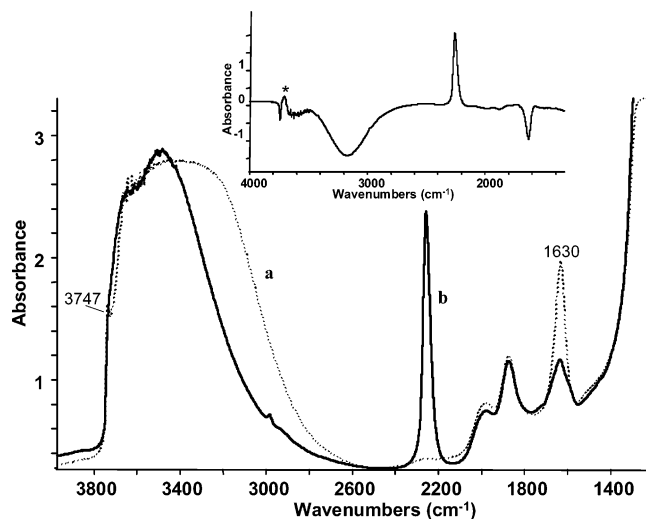


Figure 13. FTIR spectra after outgassing at room temperature: pure silica (spectrum a) and TES-modified silica (spectrum b). Inset shows the subtraction spectrum defined as spectrum b – spectrum a.

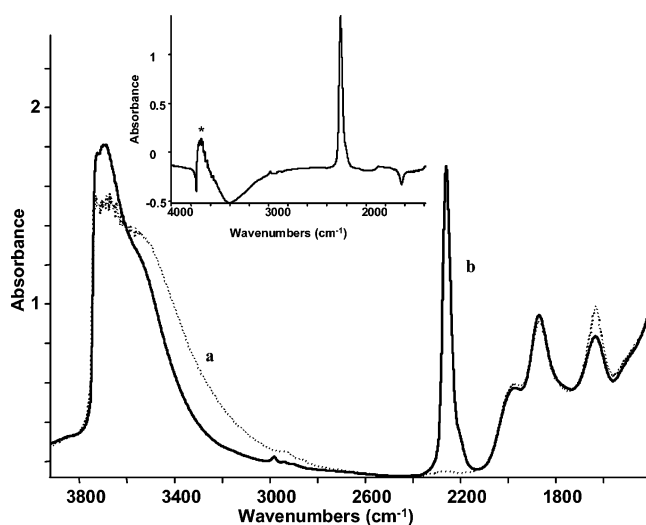
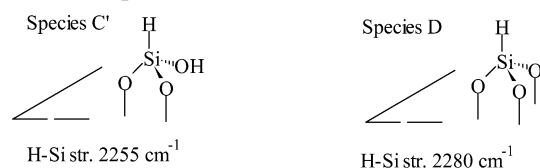


Figure 14. FTIR spectra after outgassing at 523 K: pure silica (spectrum a) and TES-modified silica (spectrum b). Inset shows the subtraction spectrum defined as spectrum b – spectrum a.

SCHEME 4: Species Detected over Silica Modified with TES with a Liquid-Phase Procedure.



Scheme 4), that results from adsorbed TES but contains silanol groups due to TES hydrolysis. The identification of the species responsible for the Si–H stretching band at 2256 cm^{-1} as a silane species that contains a silanol group agrees with the assignment given by Low²⁸ of a band at 2266 cm^{-1} to a similar species obtained by the reaction of “reactive silica” with water.

These data show, consequently, that the ethoxy groups of TES are almost completely hydrolyzed after the liquid-phase procedure. Therefore, our material is different from that described by Ketelson et al.,^{22,23} which instead presents a big amount of carbon in the form of ethoxy groups. These authors concluded that multilayered polymeric TES species were adsorbed on their sample. In our case, the similarity of the

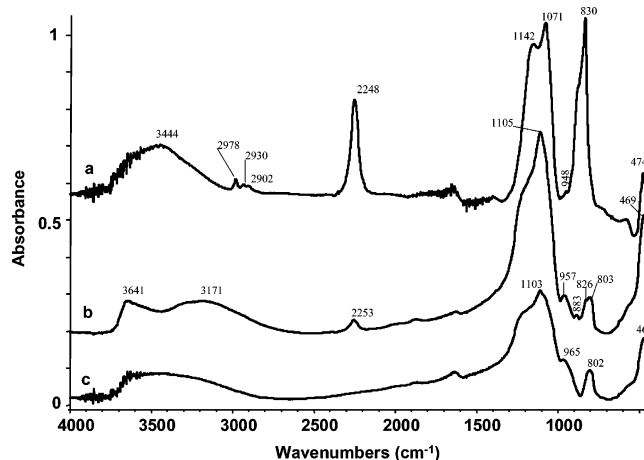


Figure 15. FTIR spectra of KBr pressed disks: poly-TES (spectrum a), TES-modified silica (spectrum b), and pure silica (spectrum c).

spectra to those obtained by gas adsorption suggests that most of the TES species are, instead, monomeric.

Study of the “Poly-TES” Material. Figure 15 shows the spectrum of our “poly-TES” material (spectrum a) recorded on a KBr pressed disk, compared with spectra from similar KBr pressed disks of TES-modified silica (spectrum b in Figure 15) and of silica (spectrum c in Figure 15).

The spectrum of poly-TES shows a very strong band at 2248 cm^{-1} , which is due to the Si–H stretching modes, whereas that of TES-modified silica presents much-less-intense Si–H stretching modes, at $\sim 2253 \text{ cm}^{-1}$. This frequency is slightly lower than that observed for the same material as a pure self-supporting disk (see spectrum a in Figures 12 and 13).

The spectrum of poly-TES also shows C–H stretchings at 2978, 2930, and 2902 cm^{-1} , which are similar to those observed after TES adsorption on silica from the gas phase, but much weaker. In the Si–O–Si stretching and bending modes (region below 1300 cm^{-1}), the spectrum of poly-TES is definitely different from that of silica. For example, the intensity of the split symmetric stretching mode (near 800 cm^{-1}) is even more intense than that of the asymmetric stretching mode (1200–1000 cm^{-1}), whereas the rocking mode near 450 cm^{-1} is very weak. The 3700–3000 cm^{-1} range presents a broad band that is due to hydrogen-bonded OH groups or water too, whereas the more-evident feature of silica and TES-modified silica at 3700–3600 cm^{-1} is not observed for poly-TES.

In any case, the overall features we have observed for TES-modified silica cannot be very well compared with those of poly-TES, which suggests that polymeric species of TES are not predominant in our TES-modified silica, if present at all.

Study of the TESPT/Silica Interaction via Liquid Solution Reaction. The spectra of a silica sample modified with TESPT are reported in Figure 16. The presence of TESPT is evident from the C–H stretching and deformation bands in the 3000–2800 cm^{-1} and in the 1500–1300 cm^{-1} regions, respectively. We can remark that the C–S and the S–S stretching modes fall to $<900 \text{ cm}^{-1}$ and, therefore, are not detectable in these samples. On the other hand, the O–H stretching band is also quite evidently perturbed. Interestingly, the subtraction result between the spectra of a TESPT-modified silica and pure silica treated in the same conditions, together with the “positive” C–H stretching and deformation bands of adsorbed TESPT, also shows a sharp negative band at 3747 cm^{-1} , which again proves that TESPT, similar to TES, primarily or exclusively reacts with the free silanols.

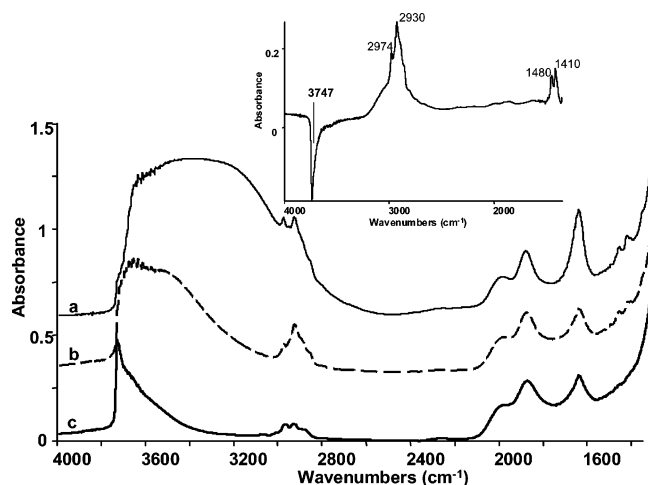


Figure 16. FTIR spectra of TESPT-modified SiO₂ outgassed at increasing temperatures: room temperature (spectrum a), 473 K (spectrum b), and 673 K (spectrum c). Inset shows the subtraction spectrum between TESPT-modified SiO₂ and pure SiO₂. Both samples were outgassed at 473 K.

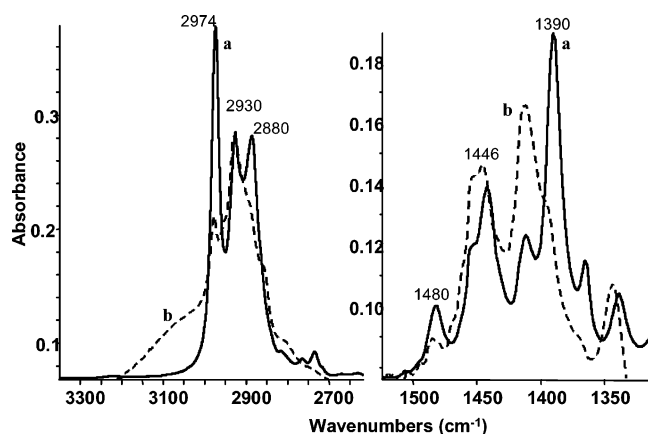


Figure 17. FTIR spectrum of liquid TESPT (spectrum a) and the subtraction spectrum between TESPT-modified SiO₂ and pure SiO₂ (spectrum b). The C–H stretching region is shown on the left, and the C–H deformation region is shown on the right.

The C–H stretching and deformation bands of free TESPT and TESPT adsorbed on silica are compared in Figure 17.

It is very evident that the stronger stretching and deformation bands of free TESPT at 2974 and at 1390 cm⁻¹ (which are certainly due to the asymmetric stretching and the symmetric deformation of the methyl groups of the ethoxy species, respectively) have strongly diminished (relative to the others) in the case of adsorbed TESPT. The components near 2880 cm⁻¹ and at ~1480–1450 cm⁻¹ (where the symmetric stretching and the asymmetric deformation of the methyl groups, respectively, fall but are superimposed onto modes of the methylene groups), have perhaps decreased slightly. The band near 2930 cm⁻¹, primarily due to asymmetric stretching of the methylenes, becomes, by far, the strongest one in the case of adsorbed TESPT. This definitely suggests that the amount of methyl groups decreased, with respect to the amount of methylene groups. This observation is consistent with the partial loss of ethoxy groups, where, in fact, methyl groups are located, upon the reaction between TESPT and silica. Instead, the chains of the silane, where most methylene groups are located, are unaffected. On the other hand, the permanence of the bands of methyl groups, although strongly decreased in intensity, indicates that species bonded once or twice to the surface predominate. The lack of detection of new O–H bands in the region of

3720–3650 cm⁻¹ in this case could indicate that hydrolysis of the ethoxy groups of TESPT is not as easy as that with TES, possibly because of the lower overall polarity of the TESPT molecule.

Conclusions

Gas-Phase Adsorption of Triethoxysilane (TES). All available data support reaction Scheme 3 concerning the gas–solid triethoxysilane (TES)/silica interaction. The data indicate that the condensation of TES with the isolated free silanol groups occurs, which results in the chemisorbed species B from the hydrogen-bonded TES species A.

Two mechanisms seem to be the most reasonable in regard to the conversion of species B into C and species C into D. The first consists of the reaction of the adsorbed TES species B (or C) with a second nearby silanol, with the development of ethanol, i.e., the same mechanism that allows the formation of species B. This mechanism implies the disappearance of one silanol group for every additional bond formed between TES and the silica surface. Therefore, it cannot explain the restoration of surface silanols. On the other hand, this mechanism, which seems possible for the formation of species C from B (two nearby OH groups are needed), is very unlikely to allow the formation of species D from C, because it would need three nearby OH groups with the proper geometry and reactivity.

It also seems possible that species B (or C) react with nearby siloxane bridges and open them, as shown in Scheme 3. In this case, a surface siloxane bridge is converted to an ethoxide species, which, however, decomposes at high temperature, resulting in ethylene and a new silanol. Every time a siloxane bridge reacts, a new OH group is formed. However, if it were to occur two times, for the conversion of species B into species D, the number of final OH groups should be twice that of the original population. On the other hand, it seems also possible that, in many cases, the two OH groups formed are sufficiently close together to condense with each other, recreating water and a siloxane bridge. This could occur for roughly half of the cases.

Liquid-Phase Adsorption of TES. The TES-modified silica, produced by liquid-phase reaction, is characterized by the Si–H stretching band at 2255 cm⁻¹ or above. The comparison with the results that concern gas-phase TES/silica interaction, as well as the detection of new O–H bands in the 3730–3650 cm⁻¹ region, suggest that the main species are D and C', where two Si–O–Si bridges are already formed between the ex-TES and the silica surface, whereas one OH group is bonded to the ex-TES Si atom. Further heating causes the conversion of such species C' into species D. The IR spectra show that the treatment of silica with TES strongly decreases the amount of adsorbed water.

The data also show that the main active site for TES reactive adsorption are, even when contact occurs in the liquid phase, the free terminal silanol groups. However, the low intensity of the C–H stretching and deformation bands for this sample suggests that the hydrolysis of most of the ethoxy groups occurred. This could be associated to the presence of some water in liquid TES, as mentioned previously, but also, or mostly, to the water present in silica (as shown in Figure 12 and spectrum c in Figure 14), which has not been dried before reaction.

It seems reasonable to propose that the greater extent of grafting of TES in the liquid-phase process, with respect to the gas-phase adsorption, is due to the higher degree of hydrolysis associated to the presence of some water in the reaction medium and the long time of reaction applied.

Poly-TES. The product of TES polycondensation in the presence of water—which we call “poly-TES”—is characterized by the Si–H stretching mode at 2248 cm^{-1} . It also presents very weak C–H bands, proving that polycondensation has actually occurred. It also shows characteristic vibrational modes that are associated with stretchings and deformations of Si–O–Si bridges.

The observed features do not fit with those of TES-modified silica, which suggests that, after our preparation procedure, polycondensation is not the predominant phenomenon, if it occurs at all. This observation also differentiates our poly-TES material from that reported by Ketelson et al.,^{22,23} whose preparation procedure was, in fact, noticeably different.

Liquid-Phase Adsorption of Bis[3-triethoxysilylpropyl]-tetrasulfane (TESPT). The results obtained with bis[3-triethoxysilylpropyl]tetrasulfane (TESPT)-modified silica seem to agree with those that result from the investigation of the TES/silica interaction. The spectra of TESPT adsorbed on silica clearly show the strong decrease of the absorption bands of the methyl groups, which are present only in the ethoxy moieties of TESPT, with respect to those of methylenes, both present in the ethoxy groups and in the chain. Again, the band of isolated free silanols is affected upon interaction. This suggests that TESPT, similar to TES, reacts by condensation with free silanols and possibly further condenses on nearby siloxane bridges too. One ethoxy group could remain bonded to the Si atom of the adsorbed TESPT. This behavior could be associated to the lower water content and the less-easy interaction with water of TESPT with respect to TES, because of the bigger hydrophobic chain. In any case, the residual presence of ethoxy groups gives the idea that “polycondensation” of TESPT is very limited upon our preparation procedure, if it occurs at all.

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Note Added after ASAP Posting. This paper was originally released to the Web 2/4/2004. Some of the features in Scheme 3 (particularly arrows in the depictions for species A, B, and C) did not translate well in the initially published version of

this paper. The corrected version, with the amended version of Scheme 3, was posted on 2/10/2004.

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