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Reaction of (3-Aminopropyl)dimethylethoxysilane with Amine Catalysts on Silica Surfaces

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The gas-phase reaction of (3-aminopropyl)dimethylethoxysilane (APDMES) with silica with and without amine catalysts has been studied using infrared spectroscopy. Evidence is provided that shows that the aminosilane initially adsorbs via hydrogen bonding of both ethoxy and aminopropyl moieties of the silane with the surface hydroxyl groups. As the reaction proceeds, the number of silane molecules attached to the surface via a Si–O–Si linkage increases primarily at the expense of the number of H-bonded ethoxy groups. The conversion is due to a catalytic process involving the aminopropyl end of gaseous APDMES molecules. On the other hand, the H-bonded aminopropyl groups are less reactive and only a small portion of these groups participates in Si–O–Si bond formation. At the end of the reaction there remain about 50% of the adsorbed APDMES attached by the H-bonded aminopropyl group. Attempts to block the adsorption of the aminopropyl end through the use of the more strongly H-bonded triethylamine proved unsuccessful. The use of preadsorbed triethylamine or 1 : 10 mixtures of triethylamine/APDMES accelerates the reaction but in the end leads to the same final distribution of products on the surface.

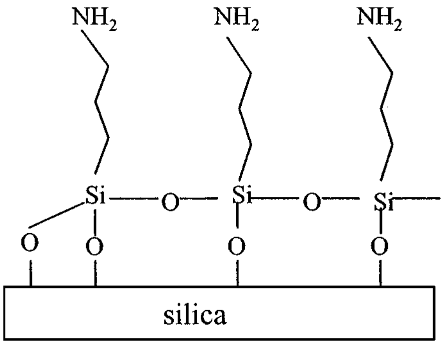
Key Words: **silica; aminopropylalkoxysilanes; infrared spectroscopy.**

INTRODUCTION

Among the silanating agents, aminopropylethoxysilanes are of special interest owing to their bifunctional nature. In the idealized scheme, the ethoxy moiety reacts with the surface hydroxyl groups to form a surface Si–O–Si bond whereas the amino functionality extends from the surface. The modified surface is often depicted by a uniform structured surface as shown in Scheme 1. The aminopropylsilane behaves as a "primer" molecule providing an anchor to the surface and a linkage point for the attachment of other molecules to the surface. The unique properties imparted by the amine group along with its capability for reaction with other functionalities have been the source of its popularity as a silanating agent.

While there is much debate on the nature of the adsorbed species, there is a general consensus that the idealized reaction depicted in Scheme 1 is a gross oversimplification of the modified surface. As with all organochloro- or organoalkoxysilanes a lack of reproducibility in film quality arises from an acute sensitivity to reaction conditions. Different deposition conditions such as reaction temperature, nature of the aminosilane (mono-, di-, or trialkoxy), silane concentration, incubation time, role of solvent, role of catalysts, postcuring, and, in particular, the amount of adsorbed water all affect the final structure of the adsorbed aminosilane layer. As a result, the adsorption of aminosilanes on silica conducted under different reactions conditions has been the subject of numerous infrared (1–18), NMR (19–25), XPS (26–29), and Raman (30, 31) spectroscopic studies.

There is an inherent variability common to all non-aqueous-based silanization processes because water is needed in the reaction. Silane adsorption does not occur in the absence of water. However, the presence of water also leads to deposition of polymerized products and the lack of reproducibility arises from a competition between formation of chemisorbed and polymerized products. The sensitivity to water is enhanced for aminopropylalkoxysilanes because the aminopropyl group self-catalyzes the formation of both chemisorbed and polymerized products (2). Further complications arise because the amine functionalities compete with the alkoxy moieties for surface sites (22). The adsorbed amine groups are H-bonded or protonated and the relative amounts depend on the amount of water present. Even in the absence of water, a modified surface as depicted in Scheme 1 is not expected. Given this acute sensitivity to reaction conditions, a more realistic picture of the possible structures on the surface is shown in Scheme 2 (22, 29). Clearly this variability



SCHEME 1

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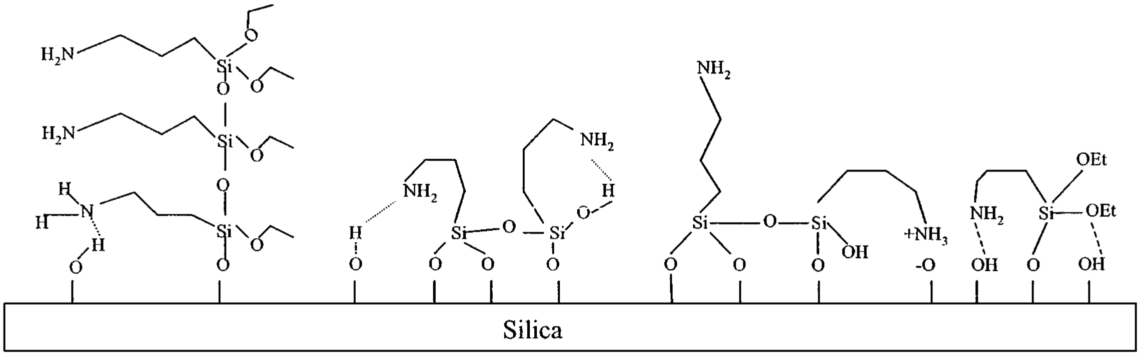


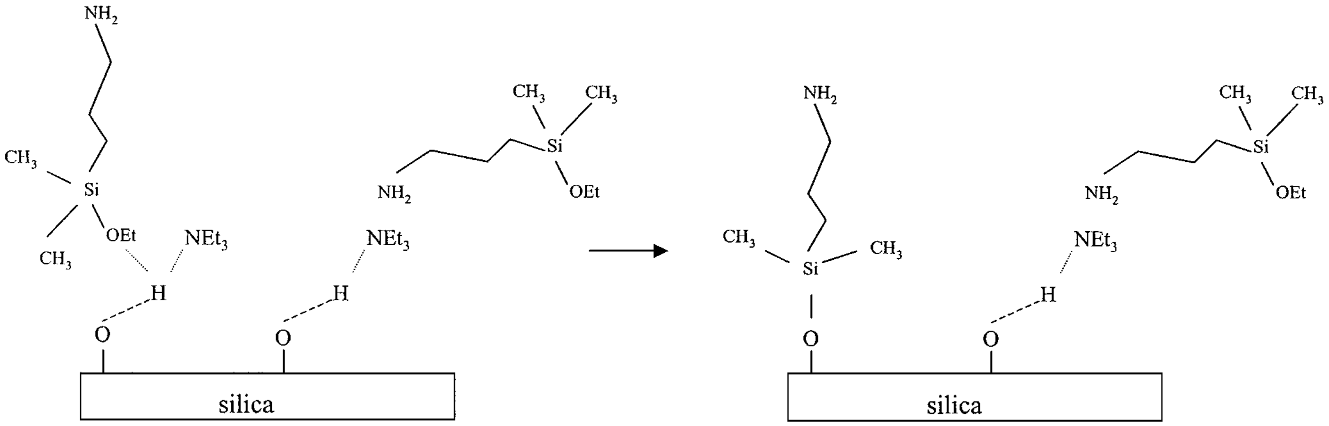
SCHEME 2

in the number and type of adsorbed species is not desirable, as it will translate to variability in subsequent attachment chemistries.

In this paper we have investigated a possible reaction scheme that eliminates polymerization of the aminopropylsilane and also reduces the number of silane molecules adsorbed via the aminopropyl functionality. The first step, elimination of polymerization, requires a means of excluding trace quantities of water. Removal of water is best accomplished with a gas-phase reaction. It is difficult to eliminate the adsorption of trace quantities of water from nonaqueous solvents (32) whereas adsorbed water is easily removed from fumed silica by gas-phase evacuation at room temperature (33). The use of a gas-phase process also allows for much higher reaction temperatures than can be tolerated in solution reactions. This is important because water is not needed at high reaction temperatures. A direct reaction of gaseous alkoxy- or chlorosilanes with surface hydroxyl groups on silica occurs at 300°C (34, 35).

An elevated reaction temperature may not be required in the reaction of aminopropylsilanes with silica. The gas-phase reaction should occur at room temperature owing to the autocatalytic behavior of the aminopropyl functionality. It is known that amines form a strong H-bond with the surface hydroxyl groups and these sites then react with an incoming alkoxysilane to form a surface Si–O–Si bond (36, 37). As a consequence, it may be possible to use an external amine to increase the number of free aminopropyl groups extending from the surface (28). In essence, an amine such as triethylamine is preadsorbed on the silica surface or added with the aminopropylsilane in a 1 : 1 mixture (see Scheme 3). The adsorption of triethylamine serves two purposes. First, it is a stronger base than propylamine and therefore could potentially block the adsorption of the aminopropyl functionality of the silane. Second, the preadsorbed TEA catalyzes the reaction of the ethoxy ends of the silane to the surface.

In our work, the monoalkoxysilane, $NH_2(CH_2)_3Si(CH_3)_2OCH_3$ (APDMES), is used instead of its more common triethoxysilane counterpart, $NH_2(CH_2)_3Si(OCH_3)_3$ (APTES), for several reasons. First, APDMES has sufficient vapor pressure for gas-phase adsorption studies. Adsorption of APTES would require elevated temperatures (38, 39) or the reaction would have to be carried out in solution. Second, we use APDMES instead of APTES because both di- and trialkoxysilanes displace adsorbed triethylamine (TEA) from the silica surface (36). Both di- and trialkoxysilane form stronger H-bonds with the silanols because they adsorb through two and three alkoxy groups per molecule. In contrast, the monoalkoxysilane does not form a stronger H-bond with the silanols than TEA and is displaced only when the silane reacts to from a covalently attached species. Therefore, it is likely that the monoethoxy-based APDMES would displace



SCHEME 3

the adsorbed TEA only when a surface Si–O–Si covalent bond is formed, thus giving rise to a modified surface more akin to the picture described in Scheme 1 (28, 40).

EXPERIMENTAL

The fumed silica (Aerosil A380, surface area (BET N_2) of 375 $m^2\ g^{-1}$) from DeGussa AG was evacuated at 400°C for 30 min followed by cooling to room temperature. This pretreatment removes the H-bonded silanols leaving isolated silanols on the surface (33).

Detailed procedures of the thin-film experiments and *in situ* gas cell are given elsewhere (34). Infrared spectra were collected on a Bomem Michelson 102 FTIR equipped with a CsI beam splitter and a DTGS detector. Typically, 100 scans were coadded at 4 cm^{-1} resolution. Each scan required approximately 6 s. Spectra are reported as difference spectra and, as such, positive bands are due to species formed on the surface and negative bands refer to bonds removed from the surface.

The time evolution of adsorbed aminosilanes required a shorter acquisition time (ca. 10 s) than the 600 s needed to obtain 100 scans on the Bomem 102 FTIR. These experiments were performed on a Bomem 155S FTIR equipped with a wide-band MCT detector. Spectra of sufficient signal-to-noise ratios could be acquired within 10 s with this spectrometer. The trade-off in using this spectrometer is that it has a lower wavenumber cutoff of 500 cm^{-1}.

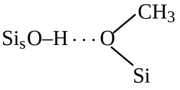
The ethoxydimethylsilane and amines were purchased from Aldrich and the APDMES was purchased from United Chemical Technologies. All reagents were transferred as received to glass bulbs using standard freeze–thaw methods. The purity of the reagents was checked periodically by FTIR.

RESULTS AND DISCUSSION

Adsorption of $NH_2CH_2CH_2CH_3$ and $(CH_3)_3SiOC_2H_5$

The possible interactions of APDMES with the SiOH surface groups involve H-bonding with the alkoxy or amino group or formation of a covalent Si–O–Si bond. To aid in deciphering between the spectral features expected for each possibility we have performed separate experiments involving the adsorption of propylamine and ethoxytrimethylsilane on silica. A tabulation of the key bands (those referenced in the text) and their assignments is provided in Table 1.

TABLE 1
Infrared Bands and Assignments

Assignments	Bands (cm^{-1})	Comment
	Negative bands	
$Si_sO–H$ str.	3747	Silica: OH str. mode
$Si_sO–H$ str.	973	Silica: Si–O str. mode of Si_sOH
Si_s O–H bend.	840, 760	Silica: OH bend. mode
	Positive bands	
$Si_sO–H \cdots NH_2$ asymm. str.	3370	N-H asymm. str. of H-bonded NH_2 GROUP
	3350	OH str. mode of H-bonded Si_sOH group to alkoxy group
N–H str.	3346	Free amine
$Si_sO–H \cdots NH_2$ symm. str. (H-bond)	3305	N–H symm. str. of H-bonded NH_2 group
OCH_3 str.	2979	
$Si_sO–H \cdots NH_2$ (H-bond)	2750	O–H str. mode of Si_sOH H-bonded group to NH_2 group
NH_2 bend.	1622	Free NH_2 group
$Si_sOH \cdots NH_2$ bend.	1596	N–H bend of NH_2 H-bonded to Si_sOH group
$Si–CH_3$ bend.	1265	
Si–O–C asymm. str.	1118	Alkoxy gas phase
Si–O–C symm. str.	1087	Alkoxy gas phase
$Si_s–O–Si$ str.	1080	Chemisorbed silane
$Si_s–OH \cdots NH_2$ (tentative)	1000/996	Si–O str. of SiOH group H-bonded to NH_2 group
$Si_s–O–H \cdots NH_2$ bend	945	OH bending mode of SiOH H-bonded to NH_2 group

The spectra of gas-phase propylamine and propylamine adsorbed on silica are shown in Figs. 1b and 2b, respectively. The changes to the bands that occur due to surface hydroxyl groups are similar to those changes observed for H-bonding of TEA on silica (40, 41) and are assigned accordingly. Negative bands in the difference spectra are SiO–H stretching mode (3747 cm^{-1}), Si–OH stretching mode (973 cm^{-1}), and SiO–H bending modes (840 and 760 cm^{-1}) (42). H-bonding with the amine weakens the O–H bond, resulting in a downward shift of the SiO–H stretching mode at 3747 cm^{-1} to 2750 cm^{-1} and an upward shift of the SiO–H bending modes at 840 and 760 cm^{-1} to 945 cm^{-1}. The N–H stretching mode at 3346 cm^{-1} and bending mode at 1622 cm^{-1} for the gaseous molecule shift to 3370 and 1596 cm^{-1}, respectively. These frequency shifts are consistent with an increase in N–H bond strength and this is expected for H-bonding of the N atom of the amine with the surface SiOH groups.

There is one additional band of interest appearing at 996 cm^{-1}. The assignment of this band remains uncertain. One possibility is that it is due to a H-bonded Si–O stretching mode of a surface silanol (40). The Si–OH bond is strengthened with formation of a H-bond and this would translate in an upward shift of the band at 973 cm^{-1}. This is consistent with observed spectral shifts obtained when compared to adsorbed TEA. TEA forms a stronger H-bond than propylamine as evidenced by a larger shift to 2660 cm^{-1} (2750 cm^{-1} for propylamine) in the SiO–H stretching mode. From spectroscopic arguments, a stronger H-bond would produce an upward shift in both the Si–OH stretching mode at 973 cm^{-1} and the SiO–H bending modes at 840 and 760 cm^{-1}. This does occur as the Si–OH stretching mode and Si–OH bending mode appear at 1000 and 953 cm^{-1} for TEA adsorption as compared to 996 and 945 cm^{-1} for adsorbed propylamine.

However, a second possibility is that the band at 996 cm^{-1} is the high-frequency side of a broader positive peak due to

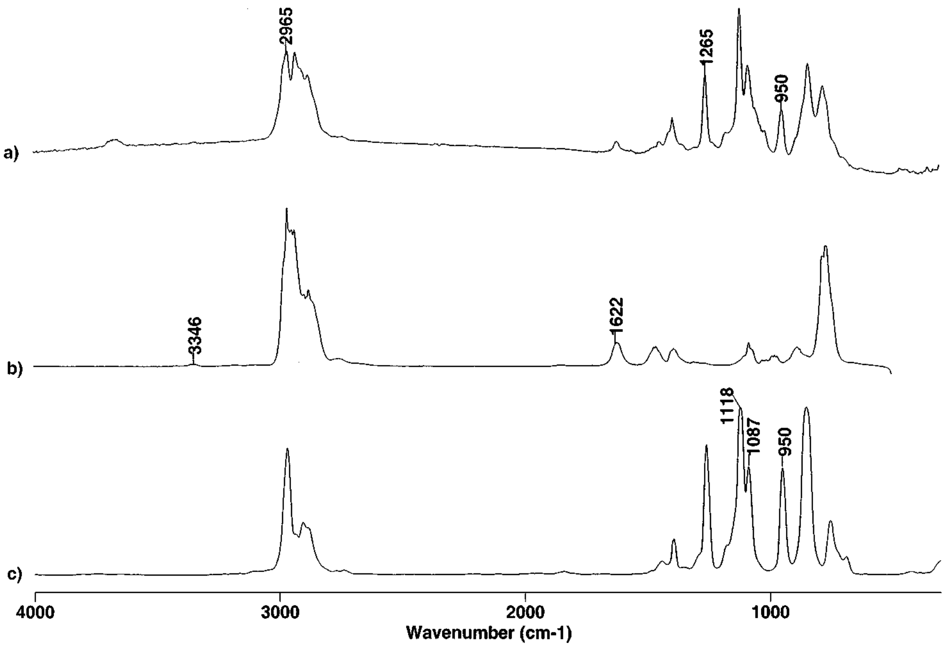


FIG. 1. Gas-phase spectrum of (a) APDMES, (b) propylamine, and (c) $(C_2H_5O)Si(CH_3)_3$.

the shifted H-bonded SiO–H bending mode. The appearance of a separate band at 996 cm^{-1} arises from the superposition of the negative Si–O stretching mode at 973 cm^{-1}. The 1000 cm^{-1} peak maximum would appear as a shift to higher frequency as the H-bonded SiOH bending mode shifts to higher frequency. For our purposes, we leave this band unassigned and simply state that the appearance of positive features between 1005 and 900 cm^{-1} is evidence of H-bonded species with the surface SiOH groups.

H-bonding of the surface SiOH with the ethoxy groups is weaker than H-bonded amines. The gas-phase spectrum of $(CH_3)_3SiOC_2H_5$ and that of adsorbed $(CH_3)_3SiOC_2H_5$ on silica are shown in Figs. 1c and 2c, respectively. The addition of $(CH_3)_3SiOC_2H_5$ to silica gives rise to spectral trends similar to those of its methoxy counterpart (35). The H-bond between the ethoxy group and SiOH shifts the SiO–H stretching mode at 3747 cm^{-1} to 3350 cm^{-1} and this is much less than the shift

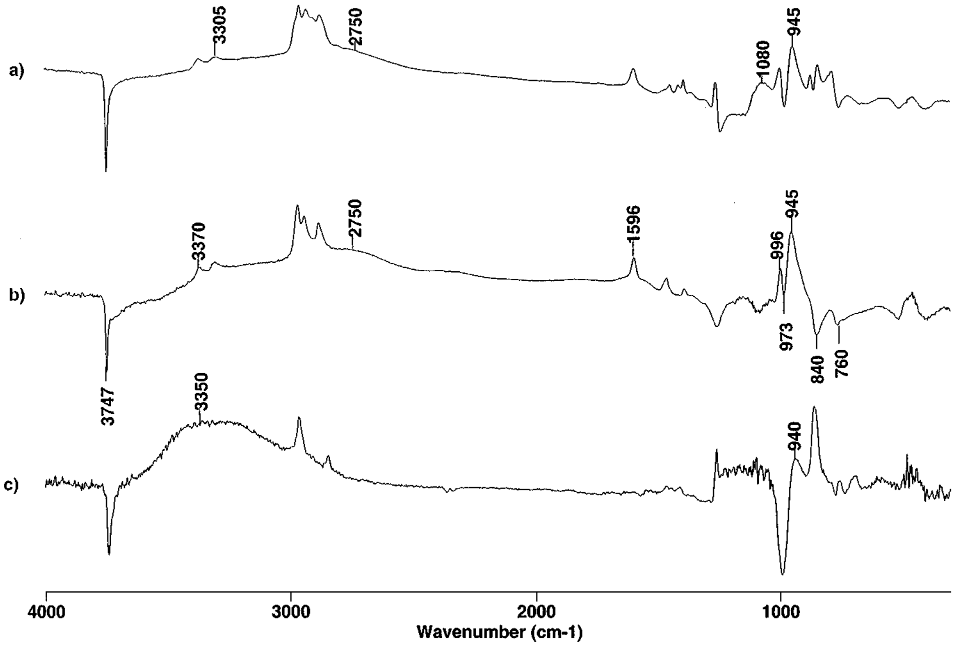
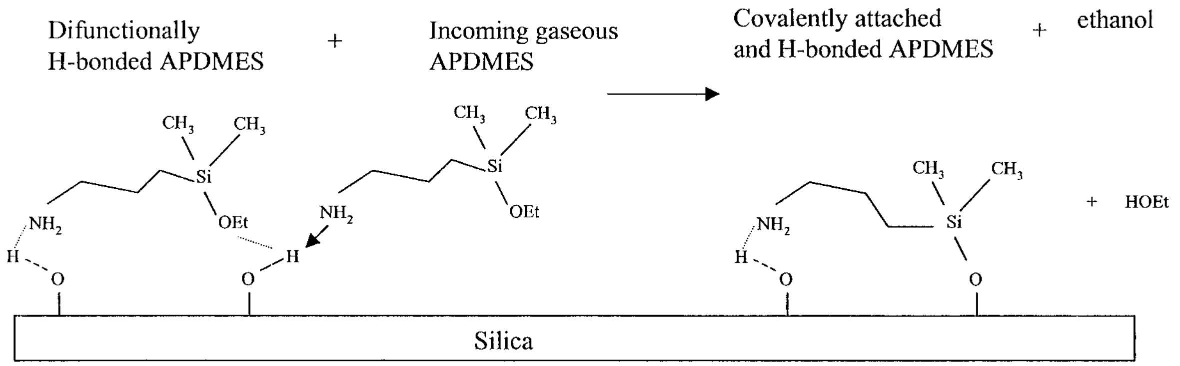


FIG. 2. Addition of excess (a) APDMES, (b) propylamine, and (c) $(C_2H_5O)Si(CH_3)_3$ vapor to a thin silica film at room temperature for 10 min, followed by evacuation for 5 min.



SCHEME 4

to 2750 cm^{-1} obtained for propylamine. In the low-frequency region, the SiO–H bending mode shifts upward to 940 cm^{-1} and the strong alkoxy modes for the gaseous molecule at 1118 and 1087 cm^{-1} disappear and are replaced by a broad and ill-defined feature located in the 1200–1000 cm^{-1} region. One additional band in the low-frequency region is possible. When chloro- or alkoxysilanes are reacted at elevated temperatures, a band at 1080 cm^{-1} appears and this is assigned to a surface Si–O–Si bond (34, 35).

APDMES Added at Room Temperature

The gas-phase spectrum of APDMES is shown in Fig. 1a. The assignments for the key bands (5, 9) are listed in Table 1. Figure 2a is the difference spectrum obtained after addition of excess APDMES to silica at room temperature for 10 min followed by evacuation for 5 min. From a comparison to the spectra obtained for adsorption of propylamine and $(CH_3)_3SiOC_2H_5$ (Figs. 2b and 2c), it is clear that the adsorption of APDMES on silica arises from H-bonding with the aminopropyl group and covalent attachment through a reaction with the ethoxy end of the molecule.

The normally weak N–H stretching modes in the gas-phase molecule are more intense upon adsorption of the APDMES on the silica. These bands along with the appearance of SiO–H stretching at 2750 cm^{-1}, N–H bending mode at 1596 cm^{-1} along with bands at 996 cm^{-1} and 945 cm^{-1} (see Fig. 2a), are identical to those obtained for adsorbed propylamine. It is also noted that there is no band at 1622 cm^{-1} due to the bending mode of the free amine. Therefore, we conclude that the aminopropyl group of each adsorbed APDMES molecule is H-bonded to a surface silanol group.

In contrast to the bands obtained for adsorbed $(CH_3)_3SiOC_2H_5$, the spectrum of adsorbed APDMES does not show a broad band at 3350 cm^{-1}, indicating that few SiOH groups are perturbed by H-bonding with the ethoxy groups. However, the ethoxy group is interacting with surface sites because the spectrum in Fig. 2a shows no ethoxy modes at 1118 and 1087 cm^{-1}. Furthermore, there is no C–H stretching mode of the ethoxy group at 2979 cm^{-1}. Unlike the ethoxy modes at 1118 and 1087 cm^{-1}, the OCH_3 stretching mode at 2979 cm^{-1} is not structure sensitive and appears for both free and H-bonded groups (36). The decrease in intensity of the 2979 cm^{-1} band is proof of the removal of ethoxy groups and along with the appearance of a band at 1080 cm^{-1} (Si–O–Si) provides direct evidence of covalent attachment of APDMES by a self-catalyzed surface reaction between the ethoxy group and the surface silanols. It is noted that the 1080 cm^{-1} band is not obtained when alkoxysilanes are added to silica under the same reaction conditions, (35) but this band does appear when amine catalysts are used (36).

The picture that emerges (shown in Scheme 4) is that each APDMES molecule is difunctionally adsorbed to two surface hydroxyl groups. Supporting proof is provided by a comparison of the relative band intensities of adsorbed APDMES to the relative band intensities for adsorbed propylamine and $(CH_3)_3SiOC_2H_5$. For example, propylamine adsorbs only by a 1 : 1 H-bonding interaction with the surface SiOH groups. Thus, the ratio of the 1596/3747 cm^{-1} (i.e., N–H mode of H-bonded amine/free SiOH groups removed by H-bonding to amine group) integrated band intensities obtained for propylamine represents the value expected for the same ratio obtained if all APDMES is adsorbed only by H-bonding of the aminopropyl groups to the surface SiOH groups. The 1596/3747 cm^{-1} band intensity ratio obtained for adsorbed APDMES is 50% of that obtained for adsorbed propylamine. This shows that half of the perturbed silanols are H-bonded with the aminopropyl group. Similarly, by comparing the 1080/3747 cm^{-1} band intensity ratio in the spectrum obtained for the high-temperature reaction (150°C) of $(CH_3)_3SiOC_2H_5$ (i.e., all SiOH groups removed by formation of a Si–O–Si surface bond) to the value obtained for adsorbed APDMES, we estimate that 45% of the SiOH groups participate in formation of Si–O–Si bonds. This value is consistent with 50% of the SiOH groups participating in a H-bond with the aminopropyl group. Thus, each APDMES molecule is adsorbed with two silanols. One silanol is H-bonding with the aminopropyl group and the second silanol is removed through a reaction with the ethoxy group to form a surface Si–O–Si bond. In the end, the chemisorbed APDMES have few, if any free aminopropyl groups extending from the surface.

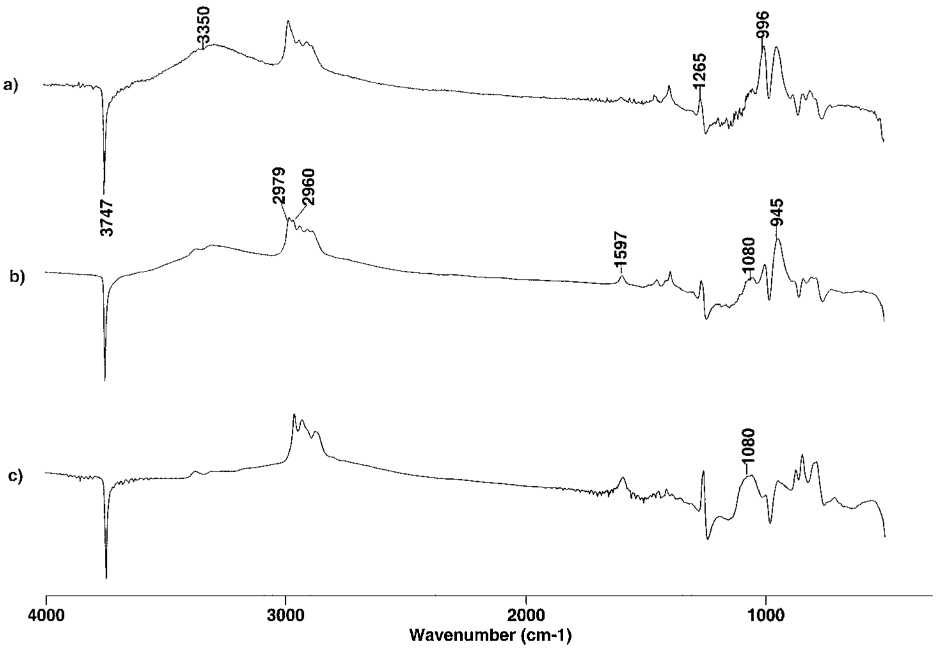


FIG. 3. Addition of excess APDMES vapor to a thin silica film at room temperature for (a) 10 s, (b) 1 min, and (c) 2 h.

Time Evolution of APDMES Adsorbed on Silica

The competition of ethoxy and amine groups for surface sites was studied by monitoring the time evolution of the adsorption process. In a separate experiment, we exposed the APDMES vapor to the thin film of silica and recorded spectra as a function of reaction time. Typical spectra obtained at 10 s, 1 min, and 2 h incubation times are shown in Fig. 3. A plot of the change in band integrated intensities with incubation time is shown in Fig. 4. During the initial 5 min, the spectra showed a steady increase in the amount of APDMES adsorbed on the surface silanol group. The amount of adsorbed APDMES was monitored from the intensity of the $SiCH_3$ bending mode at 1265 cm^{-1}. The band at 1265 cm^{-1} increased in intensity and this was mirrored by a decrease in the SiOH band at 3747 cm^{-1} (see Fig. 4). Curve 3a shows that the SiOH groups are H-bonded with both amine (identified by a positive band at 1595 cm^{-1}) (1, 3, 9, 43) and ethoxy ends (band at 3350 cm^{-1}) (35, 44) and form a covalent Si–O–Si linkage (band at 1080 cm^{-1}). The catalytic behavior of the aminopropyl group is evident as even after only 10 s of contact approximately 10% of the SiOH groups are converted to a Si–O–Si bond.

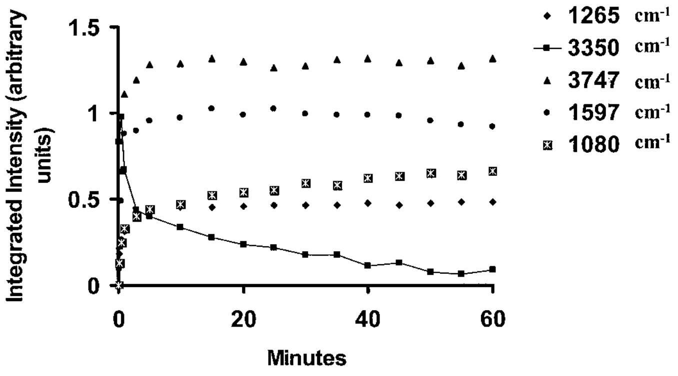


FIG. 4. Change in integrated band intensity with contact time for adsorbed APDMES on silica. The ordinate values for each curve have been arbitrarily scaled for clarity and a line is drawn through the 3350 cm^{-1} curve to emphasize that it passes through a maximum.

After about 5 min of contact time, there was no further change in the intensity of the 3747 cm^{-1} band indicating that all available SiOH surface sites were covered. We refer to the period between 5 min and 2 h as stage II. The time evolution in band intensities in stage II showed different trends for the ethoxy and aminopropyl ends of the molecule. These changes continue over a 2 h period. After 2 h of incubation there were no further changes detected in the spectrum.

For the ethoxy end, there is a uniform decrease in the intensity of the bands due to H-bonded SiOH groups with the ethoxy moieties (bands at 3350, 996, and 945 cm^{-1}) and the OCH_3 band at 2979 cm^{-1}. This uniform decrease is accompanied by an increase in the intensity of the band due to Si–O–Si bonds (band at 1080 cm^{-1}). This shows that the primary mechanism for removal of the H-bonded ethoxy is through conversion to a Si–O–Si bond. From the 1080/3747 cm^{-1} band ratio we estimate that at 5 min 22% of the SiOH groups are converted to Si–O–Si. At 1 h this number is 45% and at 2 h the value is 50%.

It is possible that some of the H-bonded ethoxy groups are displaced from the surface by the aminopropyl end of an incoming gaseous APDMES molecule. There is a 20% increase in the amount of adsorbed APDMES from the beginning to the end of stage II. In this case, the APDMES would remain anchored through the H-bonded aminopropyl end and have the ethoxy group dangling out from the surface. However, the strong ethoxy modes at 1118 or 1087 cm^{-1} were not detected at any time during the experiment. Furthermore, it is noted that we observed a uniform decrease in intensity of the band at 2979 cm^{-1} (not shown in Fig. 4) and this is consistent with removal of the ethoxy modes only through formation of a surface Si–O–Si bond.

During stage II there is only a small decrease in the intensity of the N–H bending mode at 1595 cm^{-1} showing that there is little change in the number of H-bonded aminopropyl groups. From the 1596/3747 cm^{-1} band ratio, about 65% of the SiOH groups are H-bonded by the aminopropyl end at 5 min and this decreases to about 50% after 2 h. Over this same period, there is only a 20% increase in the amount of adsorbed APDMES showing that a relatively small fraction of the original H-bonded aminopropyl groups are displaced by incoming gaseous APDMES molecules giving rise to a Si–O–Si bonded species. Most of the H-bonded aminopropyl groups are impervious to the presence of the gaseous APDMES molecules. This is in contradiction to the effect of preadsorbed TEA or propylamine in the reaction of methylalkoxysilanes with silica (36, 37). In this case the gaseous methylalkoxysilanes form a Si–O–Si surface bond removing all adsorbed amine in the process. Without the preadsorbed amine the methylalkoxysilanes form only H-bonds with the surface SiOH groups (35). On the other hand, there is a clear catalytic effect of the aminopropyl group on the H-bonded ethoxy groups. This catalytic process most likely occurs with the aminopropyl group of a gaseous APDMES molecule. Proof of this was provided by other experiments in which the excess APDMES was evacuated at set time intervals during the time evolution experiment. During the evacuated period (up to 1 h) there was no change in the intensity of the Si–O–Si band at 1080 cm^{-1}. An increase in the intensity of the Si–O–Si band occurred only in the presence of gaseous APDMES.

APDMES Adsorbed in a 1:1 Mixture with Triethylamine

Clearly, our time evolution experiments show that in order to reduce thenumber of H-bonded aminopropyl groups it will be necessary to block the aminopropyl groups from adsorbing at the initial stage of the reaction. As shown in Scheme 3, one possibility is to use a more strongly adsorbed TEA to block the aminopropyl end from adsorbing on the surface. The spectrum obtained after addition of the 1 : 1 mixture of APDMES and TEA for 1 min, followed by evacuation, is shown in Fig. 5a. The bands are due to triethylamine adsorbed on silica (40). As predicted, the initial step in the 1 : 1 mixture is adsorption of TEA on the surface. However, the use of preadsorbed TEA had little effect on the final orientation of the adsorbed APDMES. The spectrum obtained after repeated exposures of the mixture for a total incubation time of 20 min is shown in Fig. 5b. This spectrum is similar to that obtained for a 2 h exposure of APDMES alone. The difference in strength of the H-bonds between adsorbed TEA and aminopropyl groups is small (45) and most likely insufficient to block the aminopropyl group from displacing TEA H-bonded to the surface SiOH groups. A more likely scenario is that a dynamic exchange can occur between the two adsorbed amine groups on the surface. In separate experiments we added excess propylamine to a surface pretreated with TEA and found that propylamine quickly displaced all the preadsorbed TEA on the surface. The same occurs in the reverse process when

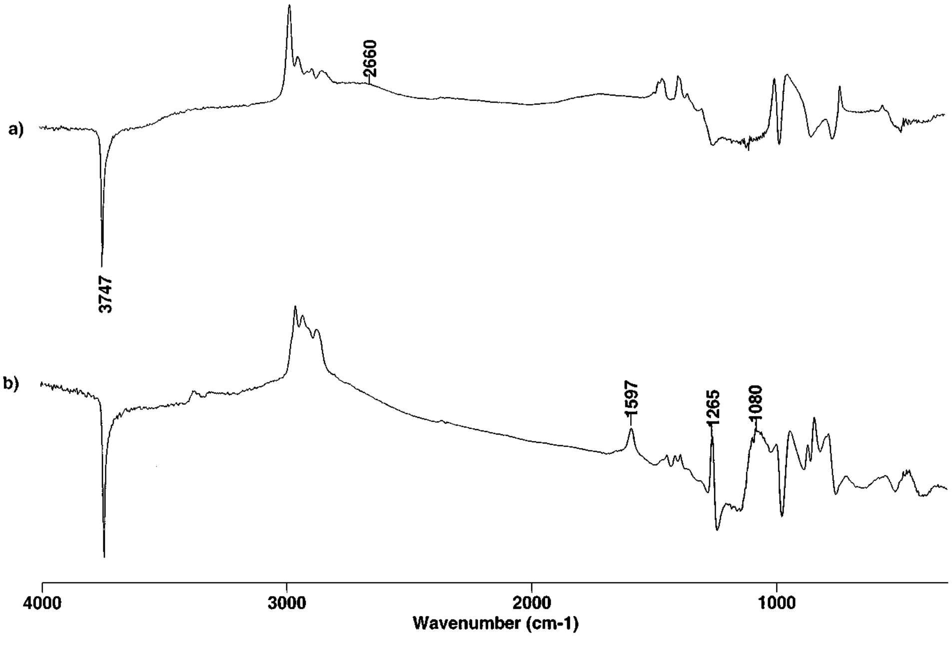


FIG. 5. Addition of a 1 : 1 mixture of APDMES and triethylamine at room temperature to silica for (a) 1 min and (b) 20 min. The gaseous mixture was evacuated prior to recording each spectrum.

propylamine is preadsorbed on the surface. Addition of excess TEA quickly displaced all adsorbed propylamine from the surface.

Although the use of a base catalyst does not change the final outcome it does, however, accelerate the reaction time. A faster reaction time may be desirable when conducting reactions from solution where slow hydrolysis and polymerization occur with water.

CONCLUSION

The initial adsorption of APDMES on silica occurs by H-bonding with both the aminopropyl and ethoxy ends of the molecule with the surface SiOH groups. The H-bonded ethoxy groups are converted to a Si–O–Si bond by a catalytic process involving the aminopropyl groups of an incoming gaseous APDMES molecule. On the other hand, a small portion of the H-bonded aminopropyl groups is removed by formation of a Si–O–Si bond through the ethoxy end of gaseous APDMES molecules. Most of the H-bonded aminopropyl groups do not participate in further reaction on the surface. The use of a mixture of TEA and APDMES does not change the final outcome of the reaction but does, however, accelerate the rate of reaction.

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