(100 MHz, CDCl$_3$) δ 15.49, 28.56, 28.72, 56.26, 113.08, 124.77, 127.98, 128.92, 145.91, 151.58; IR (neat) (cm^{-1}) 3018, 2985, 2970, 2930, 1750, 1699, 1695, 1684, 1674, 1619, 1501, 1449, 1376; HRMS calcd for $C_{10}H_{12}O$ 148.0888, found 148.0888 ± 0.0006 amu.

2,5-Dimethoxybicyclo[4.2.0]octa-1,3,5-triene (Scheme II, Entry 3).[11a] ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.29 (s, 4 H), 3.82 (s, 6 H), 6.61 (s, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 29.28, 56.41, 113.84, 130.17, 148.05; IR (KBr) (cm^{-1}) 3023, 2999, 2971, 1593, 1492, 1456, 1440; HRMS calcd for $C_{10}H_{12}O_2$ 164.08372, found 164.08379 ± 0.0006 amu.

2-Methylbicyclo[4.2.0]octa-1,3,5-triene (Scheme II, Entry 4).[11b] ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.19 (s, 3 H), 3.12 (s, 4 H), 6.87 (d, J = 6.9 Hz, 1 H), 6.97 (d, J = 8.2 Hz, 1 H), 7.10 (t, J = 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 28.49, 29.71, 119.79, 127.19, 127.41, 132.38, 144.53, 145.39; IR (neat) (cm^{-1}) 2924, 1611, 1591, 1457, 1340, 1260, 1100.

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Ammonia-Catalyzed Silylation Reactions of Cab-O-Sil with Methoxymethylsilanes

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Abstract: The reactions of methoxymethylsilanes with Cab-O-Sil in dry toluene medium in the presence of ammonia were investigated as a model system to understand the role of ammonia as a catalyst in the silylation of silica surfaces. Diffuse reflectance sampling technique and FTIR spectroscopy were used for this study. Ammonia was found to be a true catalyst under the reaction conditions used. It catalyzes the direct condensation reaction of unhydrolyzed methoxymethylsilanes with "dry" Cab-O-Sil permitting surface structural information to be inferred. High-temperature post-reaction curing is unnecessary for silylation to occur on either "wet" or "dry" Cab-O-Sil in the presence of ammonia. Monolayer or greater than monolayer surface converage is obtained for methoxymethylsilane reactions with Cab-O-Sil when ammonia is present and is about 12 times the surface coverage obtained in the absence of ammonia.

The utility of organosilane-modified surfaces has been demonstrated in a variety of fields ranging from their use as stationary phases for chromatography,[1] antimicrobials,[2] catalysts,[3] immobilized enzymes,[4] and fiber reinforced composites.[5] To better tailor surfaces with specific properties, it is necessary to understand how reaction conditions affect reaction mechanisms and surface structure. With this goal in mind, we have undertaken a detailed study of a model system consisting of Cab-O-Sil (a very pure, high surface area silica) modified with methoxymethylsilanes (the simplest alkoxyalkylsilanes) from dry toluene medium. We have found diffuse reflectance FTIR spectroscopy to be a useful quantitative tool[6,7] as well as an ideal sampling technique for these materials.[8] A previous report[9] addressed the role of surface-adsorbed water and post-reaction curing temperature on reaction mechanism and relative silane loading.

The use of an amine during silylation of silica surfaces with chlorosilanes from nonaqueous medium is recommended for the synthesis of reversed-phase chromatography packings.[10-12] The amine shifts the equilibrium by binding the acid formed in the reaction. The mechanistic aspects of similar reactions have been studied in homogeneous[13] medium. Kinkel and Unger[14] assumed the same mechanistic aspects to be applicable to reactions in a heterogeneous phase. The presence of a base is also known to increase the silane loading when alkoxysilanes are used. Few systematic studies have been done to understand the role played by a base in the silylation reaction with alkoxysilanes. As early as 1967, it was observed[15] that the addition of *n*-propylamine when treating silica with triethoxyethylsilane produces a more hydrophobic surface. Stark et al.[16] used radiochemical tracer techniques to investigate the specific roles of silane functional groups, condensation catalyst, and adsorbed water on adsorbate–adsorbent interactions. They reported that the addition of anhydrous ammonia prior to the vapor-phase adsorption of trimethylsilanol resulted in a 9-fold increase in the concentration of the bound silane. Kaas and Kardos[17] used infrared spectroscopy to show that the presence of *n*-propylamine at 1:1 mole ratio with ethyltriethoxysilane greatly enhanced the concentration of the silane bound to a Cab-O-Sil wafer. Although the concentration of *n*-propylamine was not varied, its presence was found to accelerate the surface reaction of other silanes. The amine func-

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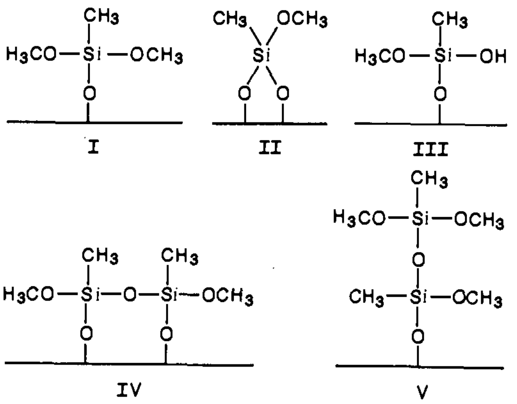
Chart I



tionality in the (3-aminopropyl)triethoxysilane (APTS) molecule was said to self-catalyze its reaction with Cab-O-Sil, and addition of *n*-propylamine had no effect on the rate of surface reaction. They concluded that "the mechanism by which the amine catalyzes the reaction between alkoxysilanes and silica surfaces is not known". In a similar study, Gent and Hsu[5] used *n*-propylamine to increase the surface coverage of vinyldimethylethoxysilane on Cab-O-Sil wafers as determined by near-infrared spectroscopy. Although no experimental evidence was given, they speculated that *n*-propylamine was probably involved in a base-catalyzed interchange reaction involving silanol groups on the silica surface and the silane. Koenig and Shih[18] used Raman spectroscopy to study the reaction of vinyltriethoxysilane with Cab-O-Sil and glass microspheres in the presence and absence of ammonia. They speculated the existence of $\equiv SiNH_2$ groups on the glass microspheres after reaction with ammonia which were said to be responsible for the increase in silane loading.

We have found[9] that both post-reaction curing and surface-adsorbed water play crucial roles in silylating Cab-O-Sil with methoxymethylsilanes in the absence of a catalyst. Neither the role of post-reaction curing nor the effect of surface-adsorbed water has previously been investigated when silylation reactions are carried out in the presence of an amine. Whether the amine is a true catalyst or it is consumed in the reaction has not been verified. The mechanism by which amine catalyzes the silylation reaction is also unknown. Amines have been referred to as both a hydrolysis[15] and a condensation[16] catalyst. The amine could be involved in the reaction mechanism leading to either (i) the hydrolysis of alkoxy groups on the silane (shown here for monomethoxysilane for simplicity)

$$R_3SiOCH_3 + H_2O \rightarrow R_3SiOH + CH_3OH \tag{1}$$

or (ii) the condensation between the hydrolyzed silane and surface hydroxyls

$$R_3SiOH + HOSi\equiv \rightarrow R_3Si{-}O{-}Si\equiv + H_2O \tag{2}$$

or (iii) the direct condensation of unhydrolyzed silane with surface hydroxyls

$$R_3SiOCH_3 + HO{-}Si\equiv \rightarrow R_3Si{-}O{-}Si\equiv + CH_3OH \tag{3}$$

or any combination of the above.

In many applications, surfaces are modified with silylating agents containing more than one reactive group (e.g., $CH_3{-}Si{-}(OCH_3)_3$). In addition to single attachment to the surface (I), multiple bonds of silane with the surface can occur (II). Hydrolysis and no subsequent condensation may occur (III) or siloxane bonds may be formed between adjacent silanes to form "horizontal" (IV) or "vertical" (V) polymers. If the mechanism of reaction can be understood, it may be possible to deduce the structure of the silylated surface. Then one can speculate as to which of the structures I–V is the most prevalent.

We have extended our study of the reaction of methoxymethylsilanes with Cab-O-Sil to include the effect of bases. This report describes the effect of ammonia on the extent of silylation, methoxy group loss, silane loading, and mechanism of reaction. Whether ammonia is truly a catalyst is also addressed, and the effects of surface-adsorbed water and post-reaction curing temperature are discussed. The information obtained suggests certain conclusions concerning the surface structure of methoxymethylsilane-modified Cab-O-Sil under varied reaction conditions.

Experimental Section

Reagents. Cab-O-Sil MS75 (Cabot Laboratories) dried at 200 °C under 0.1 mmHg vacuum for 12 h was designated as "dry" Cab-O-Sil. A portion of this sample was equilibrated in 50% relative humidity atmosphere for at least 2 weeks to ensure reproducible water content and designated as "wet" Cab-O-Sil. Trimethoxymethylsilane (TMMS) and dimethoxydimethylsilane (DMDMS) were obtained from Dow Corning Corp. Methoxytrimethylsilane (MTMS) was obtained from Petrarch Systems Inc. All silanes were distilled under vacuum prior to use. Solution-phase ^{13}C NMR spectra of the distilled silanes showed little or no methanol, suggesting negligible hydrolysis of methoxy groups. Toluene was dried over molecular sieves for at least 24 h. All glassware used for the silylation reaction were pretreated with hexamethyldisilazane.

Ammonia Determination. Ammonia was bubbled into a slurry of Cab-O-Sil (1 g) in 25 mL of toluene. Aqueous HCl was immediately added to extract ammonia from the toluene–Cab-O-Sil slurry. The extraction was carried out overnight. After filtration, the aqueous phase was separated from toluene and was titrated with NaOH with methyl red as an indicator. The toluene–Cab-O-Sil slurry was found to contain 7.5 mmol of ammonia. The same titrimetric procedure indicated the concentration of ammonia dissolved in 25 mL of toluene in the absence of Cab-O-Sil to be 5 mmol. Unless stated otherwise, all reactions were in the presence of 7.5 mmol of ammonia.

Silica–Silane Reactions. Silylation reactions were done in a glove bag (I^2R) purged with dry nitrogen to minimize exposure to laboratory atmosphere. Aliquots of "wet" or "dry" Cab-O-Sil (1 g) were slurried with 25 mL of toluene. Ammonia from a lecture bottle was bubbled into the toluene–Cab-O-Sil slurry through a $BaCl_2$ drying tube for 5 min. Two hundred milligrams of silane were added and the reaction was allowed to proceed for 2 h in a stoppered flask with occasional swirling. The slurry was filtered, washed three times with 20 mL of toluene, and dried under 0.1 mmHg vacuum at room temperature for 4 h. Separate aliquots of the room temperature dried sample were further cured at 80, 140, and 200 °C for 4 h under 0.1 mmHg vacuum.

Gaseous ammonia was bubbled into toluene (in the absence of Cab-O-Sil) for 5 min. Different volumes of this solution were added to a slurry of Cab-O-Sil in toluene to introduce variations in the concentration of ammonia during subsequent silane reaction.

Instrumentation. A Nicolet 60SX FTIR spectrometer (Nicolet Analytical Instruments) purged with dry air and equipped with a liquid nitrogen cooled wide band mercury cadmium telluride detector was used to obtain infrared spectra. All spectra were acquired by signal averaging 100 scans at a nominal resolution of 4 cm^{-1}. The Fourier deconvolution program developed at the National Research Council of Canada[19] and available as standard software for the Nicolet 60SX was used to increase the apparent spectral resolution of overlapping bands.

Samples for diffuse reflectance were prepared in a glove bag purged with dry nitrogen. A 10% (w/w) dispersion of Cab-O-Sil in KCl (<5 μm particle size, dried at 120 °C for 8 h) was prepared by mixing in a Wig-L-Bug (Crescent Dental Manufacturing Co.) without the grinding ball for 30 s. The powder was filled into the sample cup and immediately transferred to the spectrometer. A DRA-2CN diffuse reflectance accessory (Harrick Scientific Corp.) was used. A cylindrical internal reflection cell (Spectra-Tech, Inc.) was used to obtain infrared spectra of TMMS in toluene in the absence of Cab-O-Sil.

Chromatographic results were obtained with a Sigma 2 gas chromatograph (Perkin-Elmer Corp.) equipped with a 0.25 mm diameter DB-1 column (30 m). Aliquots (1 μL) of the filtrate from the silane-Cab-O-Sil reaction were injected into the gas chromatograph. The eluting analytes were detected with use of a flame ionization detector and identified by their retention time with respect to known standards.

Results

An infrared spectrum of TMMS-modified Cab-O-Sil in the absence of ammonia during reaction is shown in Figure 1A. The band at 3750 cm^{-1} is assigned to isolated silanol groups on the Cab-O-Sil surface. Bands in the 3100–2800-cm^{-1} region arise from the CH stretch modes of TMMS on the surface. The two

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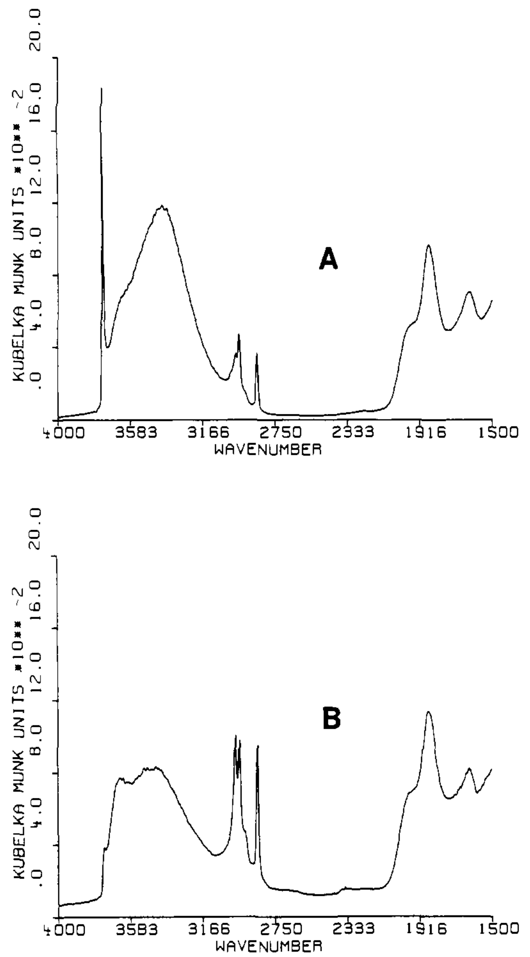

Figure 1. Diffuse reflectance FTIR spectra of TMMS-modified Cab-O-Sil in the (A) absence and (B) presence of ammonia.

partially resolved bands with maxima at 2975 and 2955 cm^{-1} are assigned to the asymmetric CH stretch mode of Si–CH_3 and Si–OCH_3, respectively.[20] The band at approximately 2835 cm^{-1} is assigned to the symmetric CH stretch modes of both groups. The Si–O–Si combination band of the Cab-O-Sil substrate appears at 1860 cm^{-1}. Murthy and Leyden[6] have demonstrated that the ratio of silane band area to the area of the silica band at 1860 cm^{-1} in the diffuse reflectance spectrum correlates well with the concentration of silane on the surface determined by elemental analysis or calorimetry. In the absence of a suitable calibration procedure, diffuse reflectance spectra can be used to obtain relative concentrations of the silane provided all precautions in sample preparation are taken.[6]

The overlapping CH stretch bands from Si–OCH_3 and Si–CH_3 groups were deconvolved.[19] The ratio of the deconvolved Si–CH_3 band area to the Si–O–Si combination band area was used to obtain relative concentrations of silanes on silica surfaces. The three silanes of interest (TMMS, DMDMS, MTMS) have different numbers of methyl groups per molecule which was taken into account when band area ratios were calculated.

The OCH_3/CH_3 band area ratio was used to give an indication of the extent of methoxy group loss. Infrared bands from methanol interfere with those of –OCH_3 groups. Methoxy groups may hydrolyze to form silanols or may act as a leaving group in the direct condensation reaction of unhydrolyzed silane with silica silanols. Both reactions produce methanol. The amount of methanol which would be produced from the loss of all methoxy groups of TMMS was added to the toluene–Cab-O-Sil–ammonia slurry in the absence of any silane. Little or no methanol was found adsorbed on the surface after drying under vacuum at room temperature for 4 h. Therefore ammonia does not catalyze the reaction of methanol with surface silanols, and methanol adsorption is not a factor in this work.

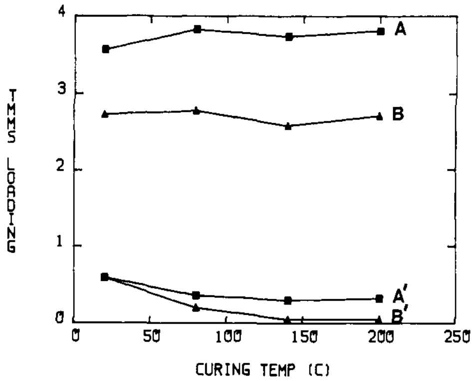

Figure 2. TMMS loading on "wet" Cab-O-Sil (A) with and (A') without ammonia and on "dry" Cab-O-Sil (B) with and (B') without ammonia.

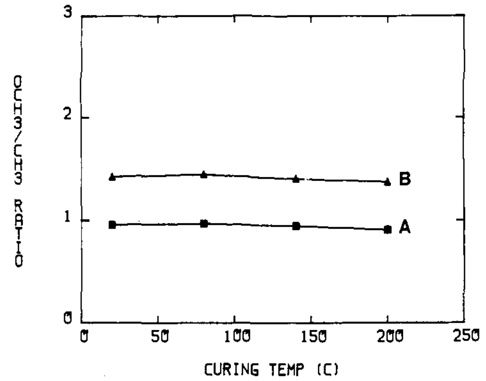

Figure 3. Methoxy to methyl band area ratio for TMMS-modified (A) "wet" and (B) "dry" Cab-O-Sil in the presence of ammonia.

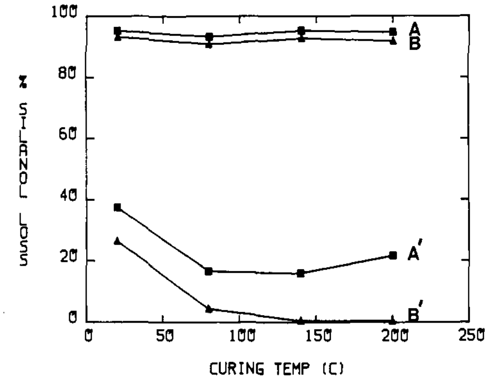

Figure 4. Percent silanol loss on Cab-O-Sil modified with TMMS. "Wet" Cab-O-Sil (A) with and (A') without ammonia and "dry" Cab-O-Sil (B) with and (B') without ammonia.

The relative concentration of isolated silanol on silica was determined from the ratio of isolated silanol band area to Si–O–Si combination band area. Because surface silanols are consumed to form siloxane bonds with the silane, the degree of isolated silanol loss is a measure of the extent of bond formation to the surface. However, some silanol loss can also be attributed to hydrogen bond formation with physisorbed water or ammonia. Blank reactions were conducted to obtain a measure of the maximum concentration of isolated silanol expected under different reaction conditions and curing temperatures. The SiOH/Si–O–Si band area ratio did not change either in the presence or absence of ammonia for the blank reactions indicating amination of surface silanols was not occurring to a significant extent. The SiOH/Si–O–Si band area ratios obtained for different samples were normalized to the corresponding blank reaction values to give the fraction of silanols remaining. Subtracting this number from 1 and multiplying by

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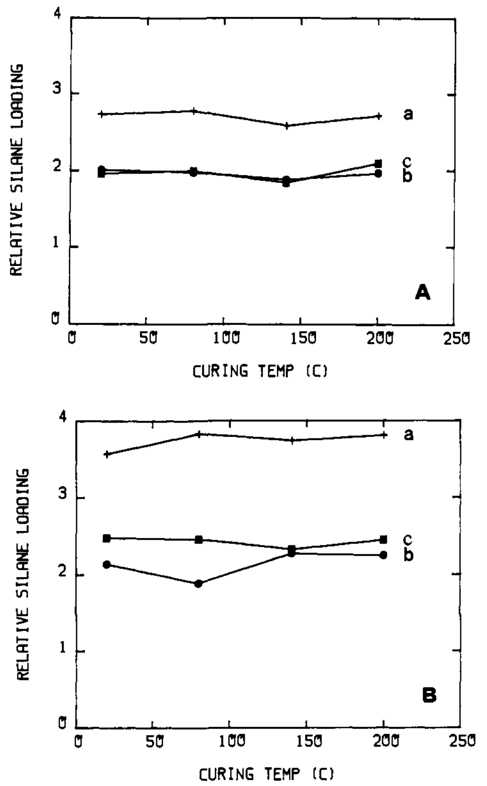

Figure 5. Relative silane loading of (a) TMMS, (b) DMDMS, (c) MTMS on (A) "dry" and (B) "wet" Cab-O-Sil.

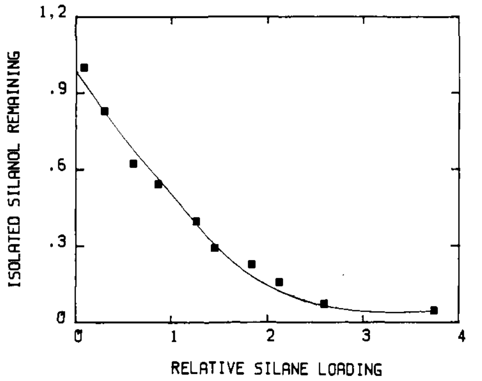

Figure 6. Fraction of isolated silanol remaining on Cab-O-Sil versus TMMS loading under various reaction conditions.

100 gives the percent silanol loss.

Figure 1B is an infrared spectrum of TMMS-modified Cab-O-Sil with ammonia present during reaction. Figure 2 is a plot of the relative concentration of TMMS on "wet" and "dry" Cab-O-Sil versus curing temperature. Figure 3 is a plot of the OCH_3/CH_3 ratio, and Figure 4 shows percent silanol loss for the same samples.

A comparison of reactivities of methoxymethylsilanes with Cab-O-Sil was made. All methoxymethylsilanes showed similar loadings with "dry" Cab-O-Sil in the presence of ammonia as shown in Figure 5A. When methoxymethylsilanes were reacted with "wet" Cab-O-Sil, TMMS showed a significantly higher relative loading than the other silanes (Figure 5B).

Studies were done to correlate isolated silanol concentration with relative TMMS loading. A series of samples were prepared with various amounts of TMMS on Cab-O-Sil by varying reaction conditions ("wet" and "dry" Cab-O-Sil, presence and absence of catalysts, varying reaction time). Figure 6 is a plot of unreacted, isolated silanol remaining versus TMMS loading for the different samples.

A series of reactions with TMMS and "wet" Cab-O-Sil were performed when the amount of ammonia present was 0.0, 0.2, 0.4, 1.1, 2.0, 4.0, or 7.5 mmol. The percent of isolated silanol loss for the corresponding Cab-O-Sil samples was 16, 88, 89, 85, 91, 95, and 95%, respectively, after curing them at 140 °C under vacuum for 4 h. Similarly, reactions with TMMS and "dry" Cab-O-Sil were performed when the amount of ammonia present was 0.0, 0.2, 0.4, and 7.5 mmol. In these cases, the percent isolated silanol loss for the corresponding Cab-O-Sil samples was 0, 76, 78, and 93%, respectively, after curing them at 140 °C under vacuum for 4 h.

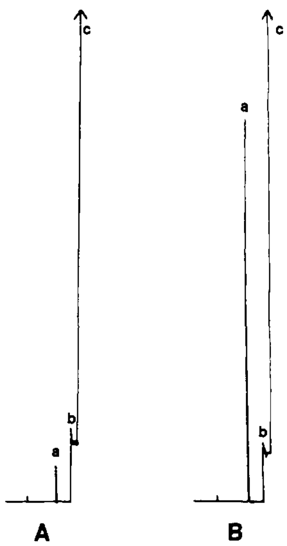

Figure 7. Chromatograms of supernatant solution of TMMS reactions with "dry" Cab-O-Sil in the (A) absence and (B) presence of ammonia: (a) methanol, (b) TMMS, and (c) toluene.

Investigations into the means by which ammonia catalyzes silylation were undertaken. The same amount of TMMS used in the reaction with Cab-O-Sil was placed in 25 mL of toluene in the presence and absence of ammonia. Solution infrared spectra were taken over time with use of a cylindrical internal reflection cell. The methoxy rock band area (with maximum at 1193 cm^{-1}) was calculated for these samples. No loss in $Si–OCH_3$ was seen either in the presence or absence of ammonia over a period of 2 h. No methanol was detected in the infrared spectrum of either sample.

TMMS was reacted with "dry" Cab-O-Sil in the presence and absence of ammonia. After 2 h, aliquots of the supernatant liquid were injected into a gas chromatograph to detect and quantify methanol. Chromatograms are shown in Figure 7.

Discussion

The infrared spectra shown in Figure 1 provide an excellent illustration of the effect of ammonia on the silylation reaction. The silane CH stretch band is more intense when the reaction is carried out in the presence of ammonia, and the isolated silanol band from Cab-O-Sil is severely attenuated. These results indicate a significant enhancement in silane loading due to the presence of ammonia.

The word catalyst assumes a kinetic effect, but it has been used loosely in the literature to describe the role played by an amine during silylation. To investigate whether ammonia is a catalyst and hence is not consumed, a series of samples were made in which various amounts of ammonia were present during reaction. The smallest amount of ammonia used (0.2 mmol) results in a significant loss (88%) of isolated silanol groups on the surface. Further increase in ammonia concentration has negligible effect. Calculations assuming 5 silanols/nm^2 on Cab-O-Sil (a generally accepted literature value[21]) and a surface area of 250 m^2/g (value provided by the manufacturer) indicate approximately 2 mmol/g of isolated silanol on Cab-O-Sil. If 0.2 mmol of ammonia are added and all of it is consumed during reaction, 0.2 mmol or approximately 10% of isolated silanol will be lost (not 88% as experimentally observed on "wet" Cab-O-Sil, or 76% on "dry" Cab-O-Sil). We have shown in a previous study[9] that approximately 20% of isolated silanols are lost on "wet" Cab-O-Sil, and isolated silanols are not lost on "dry" Cab-O-Sil in the absence of ammonia. These results indicate that ammonia is not consumed.

Amination of the surface is not an explanation for the ammonia effect because (i) silica silanols are not lost when exposed to ammonia and (ii) ammonia is reusable in the reaction. These results contradict a mechanism proposed by Koenig and Shih.[18] The reaction conditions used by them, however, were very different from ours. To further satisfy the last requirements of a catalyst, ammonia must exhibit a kinetic and not an equilibrium effect on the reaction. It was discussed earlier that the use of an amine for silylation of silica surfaces with chlorosilanes shifts the equilibrium by binding the acid formed in the reaction. An analogous equilibrium shift should not occur for methoxymethylsilanes because the reaction product, methanol, is not bound by ammonia. Furthermore, stoichiometric amounts of ammonia would be required if it were bonding to a reaction product in direct contrast to our experimental results. Hence, ammonia is reusable and exerts a kinetic effect on the silylation reaction. However, it may not be a very efficient catalyst because of its limited solubility in toluene. Once ammonia is adsorbed on Cab-O-Sil, its mobility is restricted and can participate in only a few reactions.

Results shown in Figures 2–4 provide a more quantitative understanding of the catalytic effect of ammonia. The first conclusion drawn from Figures 2–4 is that TMMS loading, OCH_3/CH_3 ratio, and isolated silanol loss are independent of curing temperature. An increase in post-reaction curing temperature causes no loss of TMMS from "wet" or "dry" Cab-O-Sil, in contrast to results in the absence of ammonia.[9] The OCH_3/CH_3 ratio is near 1 after room temperature curing for both samples indicating significant methoxy group loss. No further loss in methoxy groups is seen after curing the samples at higher temperatures. These results, along with the greater than 90% loss in isolated silanol (Figure 4), lead us to believe that ammonia catalyzes silylation during or prior to room temperature curing. Post-reaction curing at high temperatures to ensure bonding with surface silanols would therefore be unnecessary for reactions carried out in the presence of ammonia. Furthermore, ammonia seems to catalyze silylation in the absence of water. Surface-adsorbed water has only a small effect on ammonia-catalyzed reactions, a situation very different from uncatalyzed reactions.[9]

All methoxymethylsilanes reacted with "dry" Cab-O-Sil show approximately the same amount of surface loading (Figure 5A). Results from Figure 5, A and B, show no change in the extent of surface modification for DMDMS or MTMS when reacted with "wet" Cab-O-Sil. All of these samples exhibited greater than 90% isolated silanol loss so that at least close to a monolayer of surface coverage occurred. TMMS-modified "wet" Cab-O-Sil shows much higher loading values than for all other reactions (Figure 5B). However, results in Figure 4 show approximately the same amount of isolated silanol loss for this sample. This seemingly anomalous result can be explained with the data in Figure 6. A linear decrease in isolated silanol is seen as TMMS loading is increased except for the sample with highest loading. It is understandable that as TMMS loading increases, isolated silanol concentration decreases. If more than monolayer coverage is obtained, however, increase in silane loading will not cause a further decrease in isolated silanol. The sample with highest loading in Figure 6 is TMMS reacted with "wet" Cab-O-Sil in the presence of ammonia. This result along with results previously discussed indicate that all reactions of DMDMS and MTMS with Cab-O-Sil in the presence of ammonia show monolayer coverage. TMMS reaction with "dry" Cab-O-Sil also shows monolayer coverage. TMMS reaction with "wet" Cab-O-Sil and ammonia shows evidence of greater than monolayer of surface coverage, or vertical polymerization. The three hydrolyzable methoxy groups of TMMS make vertical polymerization likely whereas for DMDMS it would be less probable, and impossible for MTMS.

It has been shown that ammonia has significant effect on the silylation reaction. Solution infrared spectra of TMMS in toluene with and without ammonia (in the absence of Cab-O-Sil) indicate that ammonia has no detectable effect on TMMS in toluene for a period of 2 h. If ammonia has no effect in solution, it must affect the silylation reaction at the Cab-O-Sil surface. Chromatograms of the supernatant solutions from two TMMS reactions with "dry" Cab-O-Sil with and without ammonia are shown in Figure 7. These results show that much more methanol was produced when the reaction was carried out in the presence of ammonia than in its absence. Since these reactions were done on "dry" Cab-O-Sil, and the solution infrared spectra showed that ammonia does not catalyze hydrolysis in toluene, we conclude that ammonia catalyzes direct condensation of unhydrolyzed TMMS to silica silanols.

Since ammonia catalyzes direct condensation of TMMS with silica silanols, it is possible to infer the structure of the modified surface. When silylation occurs via direct condensation, all siloxane bonds must be formed with the silica surface. It is therefore possible to tailor a surface such that little or no cross-linking (horizontal or vertical polymerization) occurs. This knowledge provides the capability to chemically modify a surface extensively with controlled surface structure. Results in Figure 3 indicate that an average of nearly two methoxy groups have been lost on TMMS when reacted with "dry" Cab-O-Sil. TMMS-modified "dry" Cab-O-Sil likely contains predominantly structure II and a small amount of structure I. Similar structure assignment cannot be made for ammonia-catalyzed silylation reactions with a "wet" Cab-O-Sil surface. Although we have found that ammonia catalyzes direct condensation in the absence of water, we have not ruled out the possibility of ammonia-catalyzing hydrolysis and/or condensation of the hydrolyzed silane in the presence of water. Since TMMS shows evidence of vertical polymerization in the presence of surface-adsorbed water, we believe that ammonia catalyzes one or both of these reactions. TMMS-modified "wet" Cab-O-Sil likely contains some of all structures I–V, but results indicate structures similar to IV and V are favored. If stringent controls are placed on the presence of water in the system, a silylated surface which is extensively modified but well defined is obtained.

Conclusions

Ammonia catalyzes the silylation of Cab-O-Sil with methoxymethylsilanes. Surface loading enhancements of up to twelve times the uncatalyzed reactions have been found. Post-reaction curing is unnecessary for reactions carried out in the presence of ammonia. Monolayer coverage was found for all reactions except for TMMS reacted with "wet" Cab-O-Sil which showed evidence of vertical polymerization. Ammonia was found to catalyze the direct condensation reaction in the absence of water permitting detailed structure of the modified surface to be inferred. A silylated surface with nearly all surface silanols reacted with a minimum of cross-linking between adjacent silane molecules was found.

The results from these studies open up new applications and directions for further work. Since post-reaction curing is unnecessary in the presence of an amine catalyst, the possibility of performing gas-phase silylation reactions followed by flushing out the catalyst and reaction products exists. The possibility of using ammonia to catalyze the reaction of long-chain alkylsilanes in nonaqueous medium to form bonded stationary phases for HPLC also exists. Further work on the amine catalytic effect is now under way in our laboratory. Investigations into amine structure/catalytic activity relationships and the effect of amines on silylation by different organosilanes are now being done.

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Registry No. DMDMS, 1112-39-6; NH_3, 7664-41-7; Cab-O-Sil, 7631-86-9; $CH_3\text{-Si-}(OCH_3)_3$, 1185-55-3; hexamethyldisilazane, 999-97-3.