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Method to Double the Surface Concentration and Control the Orientation of Adsorbed (3-Aminopropyl)dimethylethoxysilane on Silica Powders and Glass Slides

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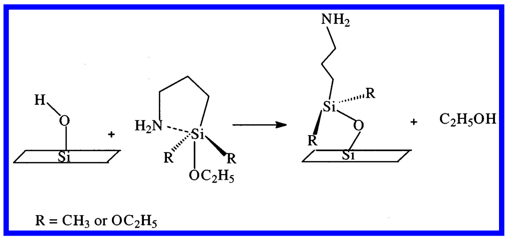
We have developed a two-step method using preadsorbed ethylenediamine (EDA) to catalyze the reaction of (3-aminopropyl)dimethylethoxysilane (APDMES) on silica surfaces. The amount of adsorbed APDMES is nearly twice the amount obtained when the same reaction is performed without the preadsorbed EDA or when monoamines such as propylamine or triethylamine are used instead of EDA. In addition, the use of preadsorbed EDA leads to an increase in the number of chemisorbed APDMES with free aminopropyl groups extending from the surface. Preadsorbed monoamines such as triethylamine, pyridine, or propylamine do not alter the adsorbed amount or change the number of free amine groups extending from the surface because they are easily displaced from the surface by APDMES. Infrared spectroscopy is used to follow the surface reactions on silica powder, and contact angle measurements show that this method also works on glass slides.

Introduction

Aminopropylethoxysilanes are popular silanating agents for modifying the surface of silica-based material. For example, aminosilanized glass slides find extensive use in areas such as biochip technology because a reaction with the amino group is the first step in the process of tethering additional molecules to the surface.[1] In the idealized picture, the aminosilane anchors to the surface by forming a covalent Si−O−Si bond with the amino group extending from the surface. However, as found for all chloro- and alkoxysilanes, the surface treatment of siliceous material with aminosilanes suffers from lack of reproducibility in film quality, and this can be traced to a competition between surface reactions and self-polymerization occurring with water.[2−5]

Among the various silanating agents, aminosilanes are also unique in surface reaction chemistry because they contain a built-in catalyst. This could be an advantage as amine-catalyzed reactions of alkoxy-[6−11] and chlorosilanes[12,13] with the surface of siliceous material may offer a potential solution to uniformity issues in film quality. In this case, the amine catalyzes a direct reaction of the chloro- or alkoxysilane with the surface hydroxyl groups at ambient temperatures. Polymerization is avoided because there is no need for water to obtain silanized coatings. In one mechanism, the aminopropyl group of the aminosilane binds to the Si atom of the same or a second aminosilane molecule (i.e., intra or inter interaction) and forms a pentacoordinate intermediate that is very reactive with nucleophiles such as the surface hydroxyl groups. This is illustrated in Scheme 1. The caveat to this approach is that in the presence of trace quantities of water, the pentacoordinate intermediate is also very reactive with water, leading to uncontrolled levels of polymerization as shown in Scheme 2.[14]

Scheme 1



Thus, the ideal case is to eliminate all possible contact with sources of water when attempting amine-catalyzed reactions. While avoidance of trace quantities of water is relatively straightforward in gas-phase reactions,[15] it is very difficult to accomplish in solution-based reactions.[4] Some success is achieved in using supercritical CO_2 as a

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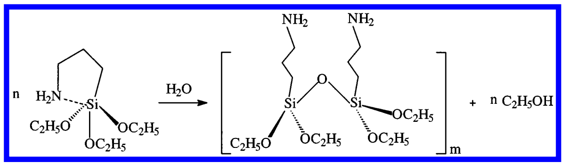
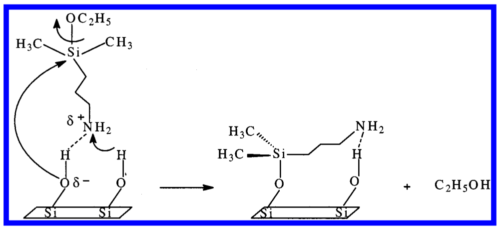
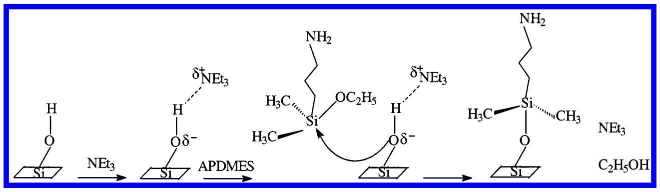
Scheme 2



Scheme 3



Scheme 4



solvent,[16] but for conventional nonaqueous solvents, the silica behaves as a drying agent, concentrating even minute quantities of water from the solvent to the surface of the oxide.[17] It is for the above reasons that we focus our attention on the monoalkoxysilane $(CH_3)_2Si\,OC_2H_5(CH_2)_3NH_2$ (APDMES) rather than the more commonly used trialkoxysilane $Si(OC_2H_5)_3(CH_2)_3NH_2$ (APTES). The former cannot polymerize and has sufficient vapor pressure to enable the reaction to be conducted in the gas phase.

In a recent study, the reaction of gaseous APDMES on silica was shown to anchor through formation of a surface Si−O−Si bond at room temperature.[18] While the gas-phase reaction avoided exposure to water vapor and yielded reproducible silanized silica surfaces, it was found that the amino group did not freely dangle from the surface but rather was H-bonded to a second surface silanol (see Scheme 3). In essence, each adsorbed APDMES occupied two silanol sites; one consumed in the formation of a Si−O−Si bond and the second H-bonded with the amine. In the end, the density of adsorbed APDMES is lower than conventional treatment protocols with polymerized layers of APTES on the surface.

One approach to increase the APDMES density is to first dose the surface with a second amine catalyst and then add the aminosilane sequentially in a separate step. This is a simple trick that has been used to minimize the amount of amine-catalyzed polymerization in the reaction of chlorosilanes with hydrated silica.[12] In the first step, the amine is exposed to the silica and adsorbs through formation of a strong hydrogen bond (H-bond) with the surface silanols (see Scheme 4). This is easily accomplished by exposing the silica to the vapor of the amine and then evacuating to remove the excess gaseous compound. In the second step, the incoming aminosilane (added in the gas phase or from nonaqueous solution) reacts with the H-bonded SiOH group resulting in a Si−O−Si linkage between the silane and the surface. By applying the two-step amine-catalyzed reactions to APDMES, it may be possible to increase the density of attached aminosilanes as well as the number of free aminopropyl groups extending from the surface.[18,19] In essence, the preadsorbed amine serves two purposes. First, the use of an amine that is a stronger base than the aminopropyl group would block the adsorption of the aminopropyl functionality. Second, the preadsorbed amine catalyzes the reaction of the ethoxy ends to the surface resulting in one SiOH group consumed per attached APDMES (see Scheme 4).

While the two-step process works for all chlorosilanes, to the best of our knowledge, it has yet to be demonstrated for either di- or trialkoxysilanes[20] or for APDMES.[18] This is because both alkoxysilanes and APDMES simply displace the adsorbed amine from the surface and expel it into the gas or solution phase. This refers to the initial competitive physisorption onto the surface as opposed to the liberation of the amine occurring after chemisorption of a silane molecule.

The two-step amine-catalyzed process works with chlorosilanes because they adsorb through weak van der Waals interactions with the surface silanols and do not displace the more strongly H-bonded amines from the surface. Even though alkoxysilanes absorb more strongly than chlorosilanes through H-bonds between the alkoxy group with the surface silanols, the strength of this H-bond is still weaker than that of an H-bond formed with adsorbed amines. Thus, at first glance, alkoxysilanes are also not expected to displace adsorbed amines from the surface. However, it is found that di/trialkoxysilanes[20] and APDMES[18] displace adsorbed amines from the silica surface because the overall strength of adsorption depends on two factors: the strength of the individual bonds to the surface and the number of such bonds per molecule.

While $CH_3OSi(CH_3)_3$ can adsorb through only one methoxy group, $(CH_3O)_2Si(CH_3)_2$ has two and $(CH_3O)_3SiCH_3$ has all three methoxy groups participating in H-bonding interactions with the surface SiOH groups.[20] Similarly, APDMES was found to be strongly adsorbed on silica via two H-bonds between a surface SiOH and both the amino and alkoxy groups. The net effect is that the adsorption strength per molecule of a difunctionally adsorbed APDMES is stronger than that of a singly H-bonded monoamine.[18] In the end, the nature and density of adsorbed APDMES is the same with or without preadsorbed monoamines on the surface.[18]

In this paper, we describe a general scheme that extends the operational range of the two-step amine-catalyzed reaction to include aminoalkoxysilanes such as APDMES on silica. Basically, we have identified a suitable amine catalyst that is not displaced by APDMES. In particular, ethylenediamine (EDA) is substituted for the more commonly used monoamino catalysts such as propylamine, pyridine, or triethylamine. The ethylenediamine adsorbs via two H-bonds per molecule and is more strongly bonded to the surface than APDMES. The strongly adsorbed EDA catalyzes the adsorption of APDMES, leading to a higher density of attached APDMES and a higher proportion of free aminopropyl groups extending from the surface. Infrared spectroscopy is used to follow the chemical reactions on silica powder, and contact angle measurements are used to show that there is a difference in APDMES-treated glass slides that are fabricated with or without EDA pretreatment.

Materials and Methods

The silica was Aerosil A380 from DeGussa AG and had a measured surface area (BET N_2) of 375 $m^2\ g^{-1}$. The thin film

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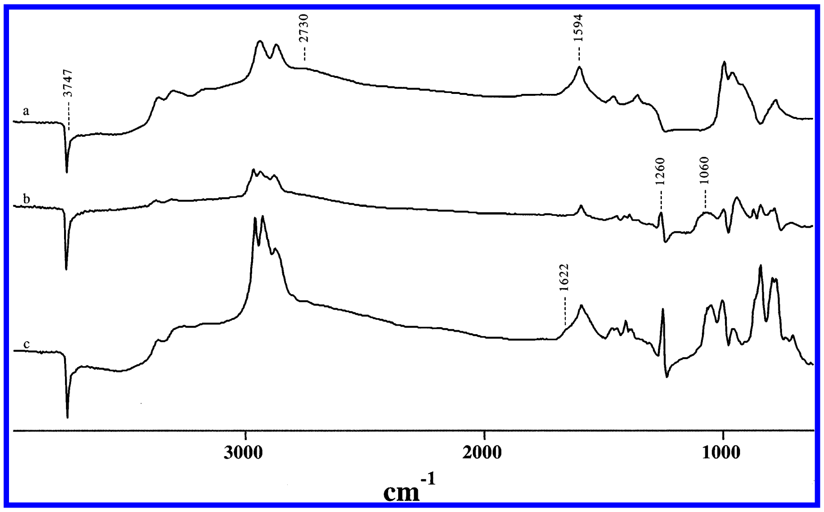

Figure 1. (a) Infrared spectra of EDA adsorbed on silica and APDMES adsorbed on (b) silica and (c) silica pretreated with EDA.

technique, infrared cells, and other experimental details are described elsewhere.[15] The silica was evacuated at 400 °C for 30 min followed by cooling to room temperature. Under these pretreatment conditions, the hydrogen-bonded surface hydroxyl groups are removed and reaction of the silanes occurs only with the isolated hydroxyl groups.

EDA was obtained from Aldrich and used as received. The APDMES was purchased from United Chemical Technologies. The reagents were transferred to evacuated glass bulbs, and delivering the gaseous compounds to the infrared cell was accomplished using standard vacuum line techniques. Gas-phase infrared spectra of the reagents were taken periodically to check for purity.

Infrared spectra are reported as difference spectra using silica as the reference. Positive bands are due to species formed on the surface, and negative bands refer to bonds removed from the surface. The 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 spectrum required approximately 10 min.

Standard microscope glass slides (Fisherbrand plain microscope slides, precleaned) were first cleaned under UV light at 254 nm for 30 min. The slides were transferred to an evacuated cell and subjected to the same gaseous treatment protocols as the silica powders. The contact angle of the silanized glass slides was determined using a CAHN model DCA-322 dynamic contact angle analyzer. HPLC grade water was used as the probe liquid. The glass slides were immersed into the probe liquid at a speed of 100 μm/s with an immersion depth of 2 mm. During the immersion and the subsequent withdrawing operations, the force exerted on the sample slide was automatically recorded from a balance and the contact angle value was then calculated using the Wilhelmy equation.

Results and Discussion

Competitive Adsorption of APDMES and EDA. The relative adsorption strength of the H-bonded EDA and APDMES was determined by pairwise adsorption experiments. An estimate of the relative strength of the individual H-bonds formed between functional groups of the molecule with the surface hydroxyl groups can be deduced from the shift in the infrared band due to isolated silanol groups.[21] The stronger the H-bond, the larger the shift in frequency. For example, the weak physisorption of chlorosilanes results in a shift of the SiOH band at 3747 cm^{-1} to 3690 cm^{-1}, H-bonded alkoxysilanes shift the same band to about 3350 cm^{-1}, and amines form a strong H-bond shifting the band at 3747 cm^{-1} to about 2800–2600 cm^{-1}.[12]

Figure 1a is the infrared spectrum recorded after adding an excess quantity of EDA vapor for 15 min followed by evacuation for 5 min. The key feature in this spectrum is the appearance of a single band at 1594 cm^{-1} due to the H-bonded NH_2 bending mode. There is no band at 1622 cm^{-1} due to a free amine, and this shows that each EDA molecule adsorbs through two H-bonds with both amino groups. When a silica sample pretreated with EDA is exposed to APDMES vapor for 10 s followed by evacuation, the spectrum obtained mirrors that of Figure 1a (i.e., only bands due to adsorbed EDA are detected). In the reverse experiment, when APDMES is preadsorbed on the silica, subsequent exposure to excess EDA for 10 s followed by evacuation also gives rise to a spectrum similar to that in Figure 1a. That is, the EDA completely displaces the APDMES from the surface with very short contact time. The above pairwise experiments clearly show that EDA is more strongly H-bonded to the surface than APDMES.

This is in contrast to the results obtained with pairwise competitive adsorption measurements with monoamino compounds such as propylamine and triethylamine with APDMES.[18] In this case, the APDMES displaces either propylamine or triethylamine from the surface of the silica. Therefore, we conclude that two surface H-bonds through the amine moieties of EDA are much stronger than the two H-bonds (one with the ethoxy and one with the amine) with an adsorbed APDMES molecule. In the end, pairwise experiments show that EDA does satisfy the adsorption strength requirements of an adsorbed amine for a two-step amine-catalyzed reaction of APDMES on silica.

Two-Step EDA-Catalyzed Reaction of APDMES. Short 10 s contact times were used in the competitive adsorption experiments to deduce the nature of the adsorbed species before chemisorption. Longer exposure times of an EDA-treated surface to the APDMES would lead to covalently attached silane. Therefore, to monitor the catalytic reaction, additional experiments were performed in which the EDA-treated silica was exposed to APDMES for periods of 30 s to 30 min.

Before discussing the EDA-catalyzed reaction, we first refer to Figure 1b, which is the difference spectrum obtained for the control experiment with APDMES only. This figure was generated by addition of excess APDMES to silica at room temperature for 30 min followed by evacuation for 5 min. A detailed analysis of this spectrum has been described[18] and is provided here for comparative purposes. A H-bond between the alkoxy group of the

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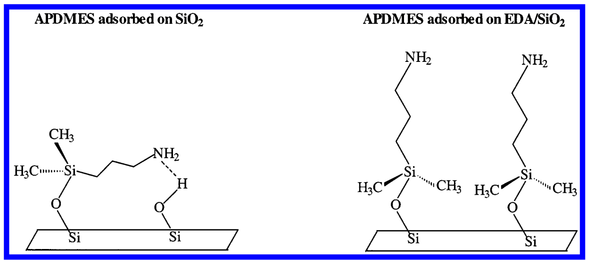
Chart 1



APDMES with the surface silanol would result in a shift of the SiO−H stretching mode from 3747 cm^{-1} downward to 3350 cm^{-1}. However, there is no such broad band at 3350 cm^{-1} in Figure 1b and there are no bands due to ethoxy modes at 1118 and 1087 cm^{-1}. This information combined with the appearance of a negative band at 3747 cm^{-1} and a positive band at 1060 cm^{-1} (Si−O−Si) shows that the ethoxy group is removed by formation of a Si−O−Si covalent bond with the surface silanol. A shift in the SiO−H band at 3747 cm^{-1} to about 2730 cm^{-1} accompanied by an N−H bending mode at 1594 cm^{-1} shows that all the aminopropyl groups are H-bonded to the surface silanols. A free amine produces a band at 1622 cm^{-1}, and this is not observed. Therefore, the aminopropyl group of each covalently attached APDMES molecule is H-bonded by the amino group to a second surface silanol group. In essence, there is one adsorbed APDMES molecule per two isolated silanol groups. One silanol is H-bonded 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.

Figure 1c shows the infrared spectrum of APDMES exposed for 5 min to silica pretreated with EDA. There is no evidence of adsorbed EDA remaining on the surface, and the spectrum obtained is similar to that in Figure 1b with two notable exceptions. First, the NH$_2$ bending mode at around 1594 cm^{-1} shows a pronounced shoulder near 1622 cm^{-1} indicating the presence of free amines on the surface. Second, the number of bound APDMES molecules per surface silanol is a factor of 1.7 ± 0.1 times higher. This is calculated from a ratio of the band intensity at 1260 cm^{-1} (Si−CH$_3$ of APDMES) to the intensity of the negative band at 3747 cm^{-1} (SiOH surface groups consumed) for each spectrum. Thus, the use of preadsorbed EDA results in the desired outcome of increased APDMES density and at the same time generates adsorbed species with free aminopropyl groups extending out from the surface (see Chart 1). In contrast, a silica surface containing preadsorbed triethylamine or propylamine do not lead to an increase in either free amine or the amount of adsorbed APDMES.

It is also important to note that there is a difference in the rate of reaction occurring with and without preadsorbed EDA on the surface. We recall that with preadsorbed EDA the reaction is complete in 5 min with no evidence of adsorbed EDA remaining on the surface. In contrast, the reaction using only APDMES is complete after approximately 2 h of contact time at room temperature. This shows that the amino group of an adsorbed or gaseous APDMES molecule is a poorer catalyst for Si−O−Si surface bond formation than the H-bonded amine groups of adsorbed EDA. Moreover, it was shown that the catalytic reaction of APDMES with silica ocurrs primarily between the amino group of a gaseous APDMES molecule and the H-bonded alkoxy end of an adsorbed APDMES molecule.[18] The H-bonded aminopropyl groups are less reactive, and only a small number of these groups participate in Si−O−Si bond formation. However, with preadsorbed EDA, the APDMES does not displace the EDA from the surface and a fast reaction could occur simultaneously with both H-bonded ends of EDA and two gaseous APDMES molecules.

Table 1. Average and Standard Deviations (in Parentheses) of the Contact Angles Formed at the Glass/Water Interface

treatment	advancing angle (deg)	receding angle (deg)
glass slides	29.4 (1.9)	0
EDA only	28.4 (1.8)	0
APDMES only	62.5 (1.6)	38.7 (1.6)
EDA/APDMES	68.4 (1.9)	45.2 (1.4)

While a silica surface containing preadsorbed propylamine does not lead to an increase in either free amine or the amount of adsorbed APDMES, the reaction also proceeds rapidly, requiring only 10 min.[18] However, in this case the APDMES immediately displaces the adsorbed propylamine from the surface, and thus the catalytic reaction occurs with gaseous propylamine and the H-bonded alkoxy end of an adsorbed APDMES molecule and the H-bonded aminopropyl end remains untouched. The above explanation would account for the higher density and increased free amines when using EDA compared to the use of propylamine as a catalyst or the reaction of APDMES alone.

As to the general applicability of the use of EDA, we find that the two-step method also works with both di- and trialkoxysilanes. In pairwise adsorption experiments, di- and trialkoxysilanes displace monoamines from silica but do not displace EDA. The desorption of EDA from the surface occurs only when the di- or trimethoxysilane forms a surface Si−O−Si linkage.

EDA/APDMES on Glass Slides. There is always the question as to how transferable are the recipes developed for high surface area silica powders to other siliceous-based materials such as glass slides. While it is not possible to perform the same infrared studies on the low surface area aminosilanized slides, the clear differences in APDMES density and free aminopropyl groups obtained with preadsorbed EDA could translate to a difference in other measurable properties such as contact angle.

We have measured the contact angles for four different sets of slides with a minimum of six slides per set. One set was an untreated glass slide, and the other sets were glass slides exposed to EDA vapor only, APDMES vapor only, and EDA followed by APDMES vapor. Both the untreated and EDA only treated glass slides gave statistically identical advancing contact angles of about 29° and receding contact angles of 0° (Table 1). Glass slides treated only with APDMES exhibit an average advancing angle of 62° and receding angle of 38°, whereas in EDA then APDMES treated slides the corresponding values are 68° and 45°, respectively. The average advancing and receding contact angle is 6° higher for EDA-pretreated slides than for samples treated merely with APDMES (Table 1). This 6° difference is statistically significant at the 98% confidence level (see Table 2).

From our perspective, the key point is that the same molecular differences in APDMES density and structure obtained on the silica powder using preadsorbed EDA are most likely duplicated on glass slides because there is a difference in contact angles. Beyond this level of analysis, determining the relation between differences in molecular structure and surface density to contact angle is difficult at best. Nevertheless, a lower number of H-bonded amine groups with surface SiOH may be the dominant factor

Table 2. Some Comparisons of Contact Angles Summarized from One-Sided *t*-Tests

contact angle	treatments	mean difference	*P*-value (%)[a]	remark
advancing	glass versus EDA only glass sildes	1.0	35	not significantly different
advancing	APDMES only versus EDA/APDMES	5.9	2	significantly different
receding	APDMES only versus EDA/APDMES	6.5	1	significantly different

[a] *P*-Values represent the probability of being wrong in concluding that there is a significant difference between two sample means.

contributing to the higher contact angle of EDA/APDMES compared to APDMES only treated slides. Clearly, adsorbed EDA does not change the contact angle relative to untreated glass slides despite the presence of two hydrophobic CH_2 groups in EDA. In this case, the silanol density remains unchanged relative to bare silica but now each isolated silanol is H-bonded with the amino group of the EDA. For an EDA/APDMES glass slide, there is almost twice the density of amine groups but there are also fewer isolated silanols remaining on the surface and therefore fewer H-bonded amines when compared to an APDMES only treated slide.

Conclusion

A diamine such as EDA was found to be a suitable catalyst for the two-step reaction of APDMES with silica. The key attributes of EDA that distinguish it from other amine catalysts such as propylamine and triethylamine are that it forms two strong H-bonds between the two NH_2 functionalities and the free silanols on the surface and it is not displaced by APDMES. Displacement of the EDA occurs only when the silane chemisorbs through the formation of a Si−O−Si bond between the silane and the surface.

The adsorption of APDMES on silica involves two surface SiOH groups per adsorbed APDMES molecule. One SiOH group is consumed in forming a covalent Si−O−Si bond, and the second is H-bonded with the aminopropyl end of the chemisorbed APDMES. The use of preadsorbed EDA leads to a doubling of the density of adsorbed APDMES on the surface and also to the generation of free aminopropyl groups extending outward from the surface. This difference in density and structure of adsorbed APDMES leads to a difference in water contact angles on glass slides.

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