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Cyclic azasilanes: volatile coupling agents for nanotechnology

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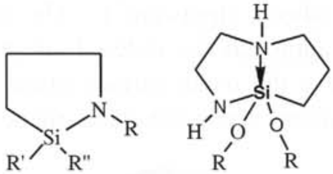
Abstract—New cyclic azasilanes have been synthesized with the purpose of developing coupling agents appropriate for a variety of nanotechnologies including surface modification of nanoparticles and chemical vapor deposition (CVD) consistent with nanoscale features. A facile method for the formation of Si–N bonds which comprises heating aminoalkoxysilanes in the presence of a neutral ammonium salt catalyst has been developed. Compounds ranging from simple azasilacyclopentanes to pentacoordinate azasilacycloctanes, as shown below, were prepared.



Preliminary data for the treatment of inorganic surfaces, including nanoparticles and oxidized silicon wafers, with cyclic azasilanes suggest high density monolayer deposition by a ring-opening reaction.

Keywords: Silane; azasilacyclopentane; coupling; nanoparticles; silica; silanol.

1. INTRODUCTION

Surface modification of hydroxyl-containing surfaces, particularly inorganic surfaces such as nanoparticles, microelectronic and optoelectronic devices with features less than 10 nm, poses challenges for conventional alkoxysilane coupling agents. Monolayer deposition with a high density of functional groups is critical. In the modification of surfaces with small or nano-scale features, it is desirable to

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effect the functionalization of surface hydroxyl groups in high yield and at low temperatures. Byproducts of substrate reactions with alkoxysilanes and chlorosilanes can remain strongly adsorbed to the surface interfering with the desired functional or chemical behavior of the modified surface. Most significantly, nano-scale feature modification is generally preferred in an environment free of water.

Organofunctional silanes remain the most versatile chemical "platform" for the modification of inorganic surfaces with organofunctional groups [1]. The most common organofunctional silanes have alkoxy groups. The reaction of surface hydroxyl groups with alkoxysilanes normally requires hydrogen bonding of hydroxyl groups with either neighboring hydroxyl groups or the addition of hydrogen-bonding additives such as amines. Alternatively, alkoxysilanes can be prehydrolyzed, but these silanol-containing species tend to self-react and polymerize, generating their own nano-scale domains, often large enough to bridge across features. Prehydrolyzed silanes are not suitable for vapor phase deposition, the method of deposition for most nano-scale applications, since they are not volatile.

The challenge of depositing monolayers with high functional group density on nano-scale features is further exacerbated when both the absolute number and the scarcity of reactive sites within the geometrical confines of nano-scale features is considered. Elaborating on the earlier discussions of Iler [2] on the theoretical concentration of surface hydroxyl groups, Figure 1 depicts a 20-nm diameter particle (a typical dimension for pyrogenic silica) which has a surface area of approx. 12.6×10^2 nm^2. The step and repeat area (Fig. 2) for SiO_2 on the surface is approx. 0.13 nm^2, giving a total population of about 10 000 silicon atoms on the surface (or about 7.8 silicon atoms/nm^2). The structure of a fumed silica nanoparticle is thought to approach the ordered structure of tridymite, with one silicon atom extending above the mean surface plane and one below it (Fig. 3). Assuming that only silicon atoms above the plane can be hydroxylated, the potential

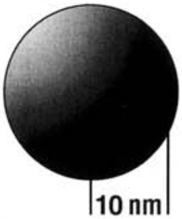


Figure 1.

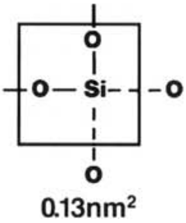


Figure 2.

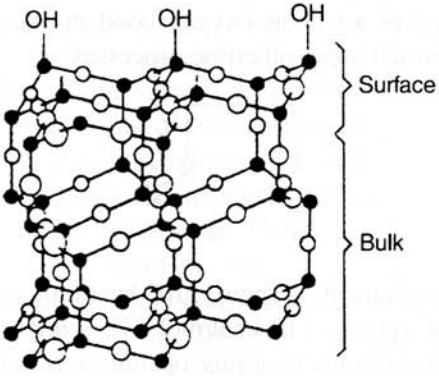


Figure 3.

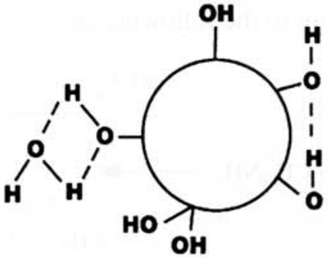
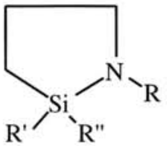


Figure 4.

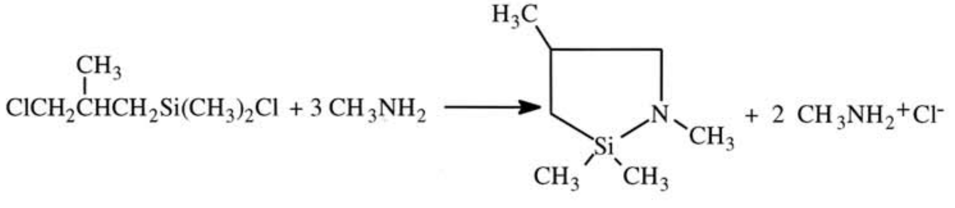
population of available hydroxyls then is 5000. This calculation correlates with reported values for rehydrated pyrogenic silica of 4.4–4.6 OH/nm^2. However, the hydroxyls are not equivalent. They include free (isolated) surface hydroxyl groups, internal hydroxyl groups, hydroxyl groups bound to molecular water, geminal hydroxyl groups (silanediols) and mutually hydrogen bonded hydroxyl pairs (Fig. 4). Mutually-bonded hydroxyl pairs, which comprise 50–70% of the silanol population, are the principal reactive species and only one member of the pair is thought to react under uncatalyzed conditions with conventional organosilanes. The final calculation is that most silane surface treatments result in only 1250–2500 modified sites on the the surface of a single particle of pyrogenic silica. Interestingly, if the radius of most organofunctional groups is considered, only about 10% of the surface area of a modified particle actually possesses functionality.

The intrinsic limitations in reactivity of conventional silanes stem from a number of factors, ranging from inadequate volatility of most silanes for vapor phase techniques, the steric restraints of bulk surfaces and, most critically, the absence of a significant thermodynamic driver for formation of oxane bonds with substrates. Exothermic formation of oxane bonds was considered the primary requirement for new coupling agents in this study. Secondarily, candidates with lower molecular weight (more volatile) and less sterically demanding structures than conventional silanes were preferred. Cyclic azasilanes with the general structure shown below emerged as theoretical candidates with appropriate structures to test this hypothesis since both the formation of a silicon–oxygen bond in place of a silicon–nitrogen bond and relief of ring strain are exothermic processes.



The silicon–nitrogen bond energy is approx. 100 kcal/mol, compared to the silicon–oxygen bond energy of approx. 110 kcal/mol [3]. Further, the cyclic azasilanes could react with hydroxyl groups by a ring-opening reaction, presumably with the loss of ring strain energy, and would not require water as a catalyst.

Cyclic azasilanes were prepared much earlier by Speier [4, 5] in a relatively inefficient synthesis according to the following equation:



There were few intermittent reports of their synthesis and no reports of their use for the treatment of inorganic surfaces. One of the reasons for the lack of interest may be that no practical, high yield syntheses have been developed for any member of this class of compounds and no method has been reported for the synthesis of the most volatile members of the series. While Speier demonstrated the formation of azasilacyclopentanes, he was not able to prepare the most volatile member of the series, namely alkoxy substituted cyclic azasilanes in which there were no methyl substituents on the hydrocarbon portion of the ring structure. Later, Pepe [6], using a different process, explicitly failed to form the 2,2-dimethoxy-1-aza-2-silacyclopentane. Again, he noted success in those cases in which the hydrocarbon portion of the ring structure had methyl substituents. It must be mentioned that evaluation of Speier's work by Ziche *et al.* [7] showed that the structure assigned to the reaction product of chloropropyltrimethoxysilane with 1,2-diaminoethane was incorrect and that it was in fact a pentacoordinate diazasilaoctane.

2. EXPERIMENTAL

2.1. Synthesis of cyclic azasilanes

2.1.1. 2,2-dimethoxy-1,6-diaza-2-silacyclooctane. A 1-l, 3-neck flask equipped with a magnetic stirrer, pot thermometer and short column with distillation head was charged with 679.08 g (3 mol) of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and 6.80 g (1 wt%) of ammonium chloride. After heating to 120–140°C for 30 min, vacuum was gradually applied and adjusted to 10 mmHg. The head temperature rose slowly to 85°C. The product mixture was collected within a temperature range of 85–105°C at 10 mmHg. At the same time, byproduct methanol that formed was removed continuously and condensed separately in a dry-ice trap. A 580 g mixture was generated in 12 h. White solids formed in the distillate and were separated. The liquid portion was predominantly the unreacted starting material. The solids were then washed with pentane and dried under vacuum for 4 h: 248 g (yield: 42.5%); mp: 61–62°C, bp 71–73°C/2.5 mmHg. The recrystallized solids were analyzed by NMR and X-ray diffraction. Data consistent with the proposed structure were obtained. ^{1}H-NMR (C_6D_6): 0.77 (m, 2H), 1.36 (m, 2H), 1.85 (m, 2H), 2.06 (m, 2H), 2.58 (m, 2H), 3.64 (s, 6H). The X-ray structure is provided (see Section 3).

The experiment was repeated with ammonium sulfate, ammonium trifluoromethanesulfonate and ammonium bromide. In all cases, identical products in similar yields were generated.

2.1.2. 2,2-dimethoxy-N-n-butyl-1-aza-2-silacyclopentane. A 1-l, 3-neck flask equipped with a magnetic stirrer, pot thermometer and short column with distillation head was charged with 478.80 g (2 mol) of N-(n-butyl)-aminopropyltrimethoxysilane and 4.80 g (1 wt%) of ammonium sulfate. After heating to 120–140°C for 30 min, vacuum was gradually applied and adjusted to 10 mmHg. The head temperature rose slowly to approx. 85°C. The distillation receiver was maintained at ambient temperature (20–24°C). Distillate was collected within a temperature range of 85–105°C at 10 mmHg. The more volatile methanol was allowed to bypass the receiver and was collected in a separate dry-ice trap. A total of 420 g of mixture, which GC analysis indicated to consist of two principal components, was generated in 12 h. The mixture was then distilled under vacuum. 2,2-dimethoxy-N-n-butyl-1-aza-2-silacyclopentane, 183 g (44.6%), was obtained with bp: 69–71°C/3 mmHg; ^{1}H-NMR (C_6D_6): 0.56 (t, 2H), 0.90 (t, 3H), 1.28 (m, 2H), 1.75 (m, 2H), 2.85 (t, H), 3.43 (s, 6H) (higher boiling distillate was identified as starting material). The effective yield was greater than 70%.

2.1.3. 2-methyl-2-methoxy-1,6-diaza-2-silacyclooctane. Conditions were similar to 2,2-dimethoxy-1,6-diaza-2-silacyclooctane. A 1-l, 3-neck flask equipped with a magnetic stirrer, pot thermometer and short column with distillation head was charged with 412.72 g (2 mol) of N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane and 4.13 g (1 wt%) of ammonium chloride. After heating to 120–140°C for 30 min, vacuum was gradually applied and adjusted to 10 mmHg. The head temperature rose slowly to approx. 85°C. The product mixture was collected within a temperature range of 85–105°C at 10 mmHg. A 370 g mixture was generated in 12 h. The mixture was then subjected to fractional vacuum distillation. 122 g (yield: 29%) of the title product, a semi-solid at room temperature, was obtained; bp: 70–72°C/3 mmHg. ^{1}H-NMR (C_6D_6): 0.21 (s, 3H), 0.72 (m, 2H), 1.76–2.55 (m, 6H), 2.67 (m, 2H), 3.54 (s, 3H).

2.1.4. 2,2-diethoxy-1-aza-2-silacyclopentane. A 1-l 3-neck flask equipped with magnetic stirrer, pot thermometer and short column with distillation head was charged with 442.74 g (2 mol) of aminopropyltriethoxysilane and 4.80 g (1 wt%) of ammonium chloride. After heating to 120–140°C for 30 min, vacuum was gradually applied and adjusted to 10 mmHg. The head temperature rose above 75°C. Product mixture was collected within a temperature range of 85–105°C at 10 mmHg; 380 g of mixture was generated in 12 h. The mixture was then subjected to vacuum distillation: 14.2 g (yield: 8%) of liquids were obtained; bp: 69–71°C/2.5 mmHg. The product was less than 90% pure. Addition of ethanol gave an exothermic reaction and a single product, aminopropyltriethoxysilane, the starting material, was formed.

2.1.5. 2,2-dimethoxy-N-t-butyl-1-aza-2-silacyclopentane. A 1-l, 3-neck flask equipped with a magnetic stirrer, pot thermometer and short column with distillation head was charged with 239.40 g (2 mol) of N-(t-butyl)aminopropyltrimethoxysilane and 4.80 g (1 wt%) of ammonium sulfate. After heating to 100–120°C, vacuum was applied and gradually adjusted to 10 mmHg. The head temperature rose slowly to 80–100°C. The distillation receiver was maintained at ambient temperature (20–24°C). The distillate was collected within a temperature range of 85–105°C at 10 mmHg. The more volatile methanol was allowed to bypass the receiver and was collected in a separate dry-ice trap. The distillate was then redistilled under vacuum. 205.0 g of 2,2-dimethoxy-N-t-butyl-1-aza-2-silacyclopentane was obtained; bp: 58–60°C/3 mmHg. ^{1}H-NMR (C_6D_6): 0.55 (t, 2H), 1.21 (s, 9H), 1,63 (m, 2H), 2.73 (t, 2H), 3.45 (s, 6H).

2.1.6. 2,2-dimethoxy-N-methyl-1-aza-2-silacyclopentane. Under conditions similar to example (Section 2.1.2), 2,2-dimethoxy-N-methyl-1-aza-2-silacyclopentane was prepared, but in lower (14.2%) yield; bp: 48–49°C/3 mmHg; ^{1}H-NMR (C_6D_6): 0.51 (t, 2H), 1.72 (m, 2H), 2.51 (s, 3H), 2.68 (t, 2H), 3.43 (s, 6H).

2.1.7. 2,2-dimethoxy-N-allyl-1-aza-2-silacyclopentane. Under conditions similar to example (Section 2.1.2), 2,2-dimethoxy-N-allyl-1-aza-2-silacyclopentane was prepared in 31.1% yield with bp 46–48°C/3 mmHg; ^{1}H-NMR (C_6D_6): 0.54 (t, 2H), 1.70 (m, 2H), 2.72 (t, 2H), 3.45 (s, 6H), 5.06 (d, 3H), 5.84 (m, 2H).

2.1.8. N-aminoethyl-aza-2,2,4-trimethylsilacyclopentane. Under conditions similar to those used by Speier [4, 5], 3-chloroisobutyl-dimethylchlorosilane was reacted with ethylenediamine to produce N-aminoethyl-aza-2,2,4-trimethylsilacyclopentane in 54% yield, bp 54–56°C/2 mmHg; density: 0.905 g/m^3.

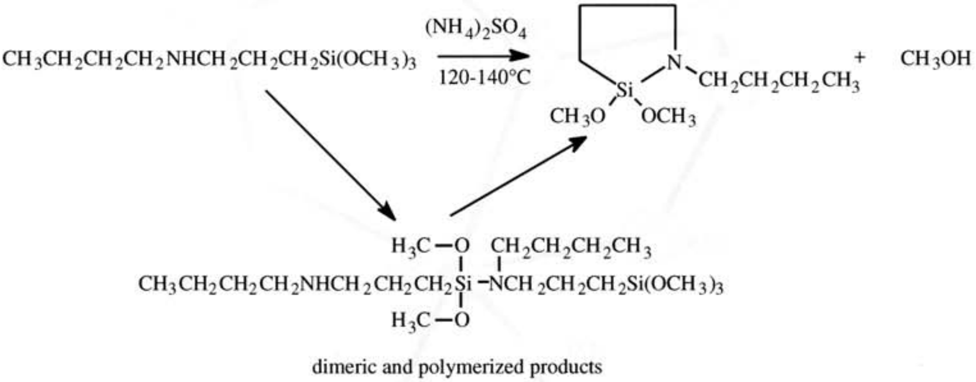
2.2. Preliminary deposition efficiency screening

2.2.1. Nanoparticle method — mixed liquid vapor deposition. A tared 100-ml flask was charged with approx. 2 g of carefuly weighed pyrogenic fumed silica with a nominal surface area of 200 m^2/g (Aerosil 200). The flask was slowly evacuated to <0.1 mmHg and then heated to 200°C for 2 h (or to constant weight). The flask was returned to room temperature. The vacuum was broken with approx. 1 g of silane. The mixture was shaken vigorously by hand for 100 s and then re-evacuated and heated to 180°C for 1 h, and the weight increase was recorded. Silanes evaluated were n-butyltrimethoxysilane, N-n-butylaminopropyltrimethoxysilane, and N-n-butyl-aza-dimethoxysilacyclopentane which gave weight gains of 6.4%, 22.5% and 38.0%, respectively.

2.2.2. Substrate reactivity by spin-on deposition. Oxidized silicon wafers were treated with a 1 : 1 mixture of 50% aqueous sulfuric acid and 30% hydrogen peroxide for 30 min and then rinsed with deionized water and dried at 110°C. Silanes were prepared in 5 wt% concentrations in diglyme and then applied to the wafers at 2000 rpm. Ellipsometric thickness was then calculated. For N-n-butylaminopropyl-trimethoxysilane and N-n-butyl-aza-dimethoxysilacyclopentane the thicknesses were 110 nm and 130 nm, respectively.

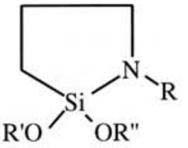
3. RESULTS AND DISCUSSION

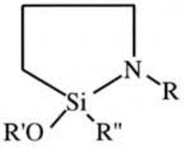
In the course of these investigations it was discovered that volatile cyclic azasilanes with or without alkoxy substituents on the silicon could be produced from alkoxysilanes by treating them with simple ammonium salts, preferably ammonium sulfate, removing the alcohol as it formed. A mixture containing the cyclic azasilane, polymeric azasilanes and alkoxysilane starting materials initially forms. The pure cyclic azasilane can be distilled in high yield from the equilibrating mixture, indicated below for the example of N-n-butyl-aza-2,2-dimethoxysilacyclopentane.

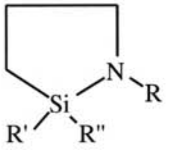


The ring-opening reaction of the cyclic azasilanes with the appropriate alcohol in the absence of a catalyst proceeds rapidly and quantitatively to form the starting material.

Cyclic azasilanes of several different general structures were synthesized by this method. Azasilacyclopentanes without substituents on the hydrocarbon portion of the ring can be prepared with or without alkoxy substitution. They have the following representative structures:

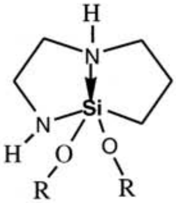






Specific examples of compounds produced include 2,2-dimethoxy-N-n-butyl-1-aza-2-silacyclopentane and 2,2-diethoxy-N-(2-aminoethyl)-1-aza-2-silacyclopentane.

The method yields silicon compounds with the following typical structure from the ring closure of 3-(2-aminoethyl)aminopropylsilanes when there are two alkoxy groups bound to silicon:



A specific example of a compound produced is 2,2-dimethoxy-1,6-diaza-2-silacyclooctane. This particular compound shows strong coordination of one nitrogen with silicon and may be regarded as a bicyclic compound with a pentacoordinate silicon. The pure pentacoordinate compounds are generally low melting crystalline solids. The X-ray structure of 2,2-dimethoxy-1,6-diaza-2-silacyclooctane is depicted in Fig. 5.

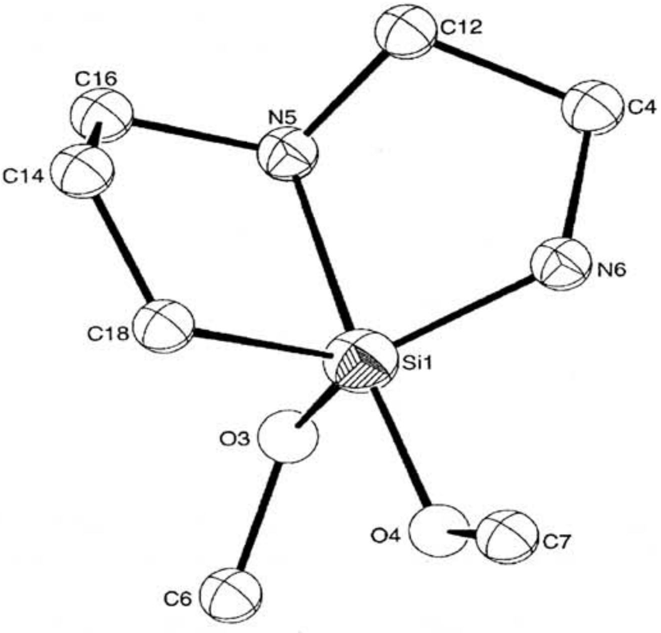
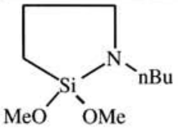
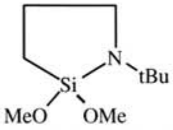
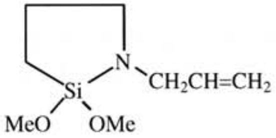
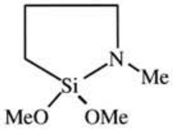
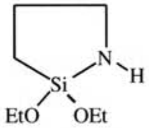
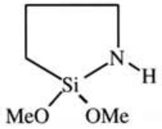
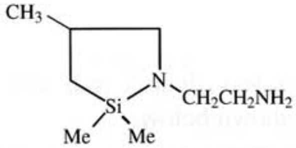


Figure 5.

Table 1.
Properties of azasilacyclopentanes

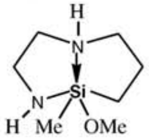
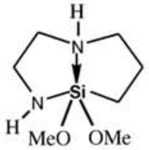
Compound	Yield	Bp	Density (g/cm^3)
	47%	69–71°C/3 mmHg	0.941
	42%	58–60°C/3 mmHg	0.932
	40%	52–54°C/3 mmHg	0.938
	19%	48–49°C/3 mmHg	1.008
	5–7%	Not isolated	
	0%	Not observed	
	*	54–56°C/3 mmHg	0.905

* New compound prepared by method of Speier in 54% yield; all others by ring closure with loss of alcohol.

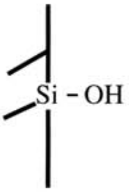
When there are less than two alkoxy substituents, the azasilacyclopentane is preferred. At room temperature these compounds are usually liquids. The cyclic azasilanes prepared in this study are summarized in Tables 1 and 2.

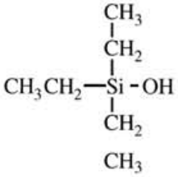
Prior to studying the comparative reactions of the azasilacyclopentane and alkoxysilanes with silica, a model compound for isolated hydroxyl groups was exam-

Table 2.
Properties of diazasilacyclooctanes

Compound	Yield	Bp	Mp
	29%	70–72°C/3 mmHg	Semi-solid
	42%	71–73°C/2.5 mmHg	61–62°C

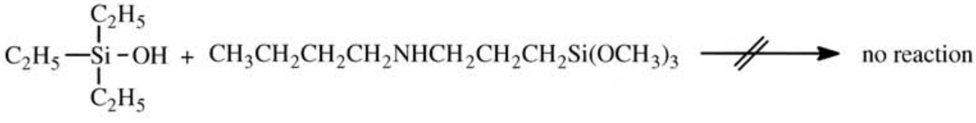
ined. The hydroxyl group of triethylsilanol can be likened to an isolated hydroxyl group on a surface. The model reaction, shown below, can be performed and followed in homogeneous liquid phase.





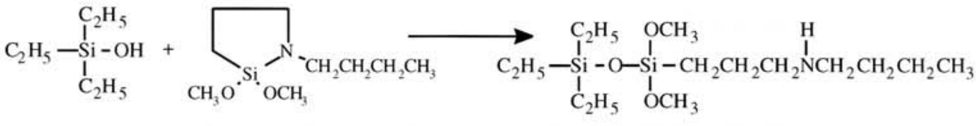
$$\mathrm{CH_3CH_2-\overset{\displaystyle CH_3 \atop \displaystyle CH_2}{\underset{\displaystyle CH_2 \atop \displaystyle CH_3}{Si}}-OH}$$

The reactions of N-n-butylaminopropyltrimethoxysilane and its cyclic analog, 2,2-dimethoxy-N-n-butyl-1-aza-2-silacyclopentane, were compared in room temperature reactions with molar equivalents of triethylsilanol. The alkoxysilane (below) showed less than 1% reaction over 24 h.

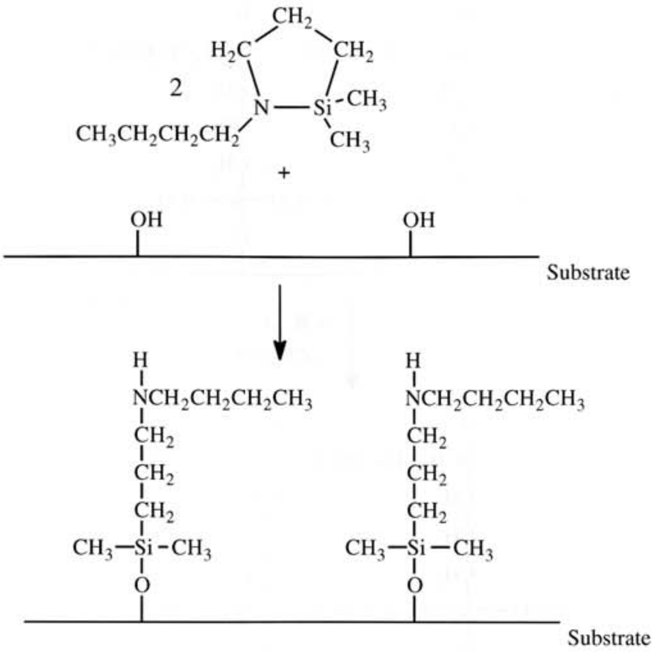


$$\mathrm{C_2H_5-\overset{\displaystyle C_2H_5}{\underset{\displaystyle C_2H_5}{Si}}-OH + CH_3CH_2CH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3 \;\not\longrightarrow\; no\ reaction}$$

The reaction of the cyclic azasilane was quantitative in less than 5 min and demonstrated a strong exotherm according to the equation shown below.



The cyclic 1-aza-2-silanes rapidly react with a variety of hydroxylic substrates, particularly siliceous and inorganic structures in vapor, liquid or solution state without the formation of byproducts. Depicted below is the ring-opening deposition of an N-alkyl-2,2-dimethylaza-2-silacyclopentane.

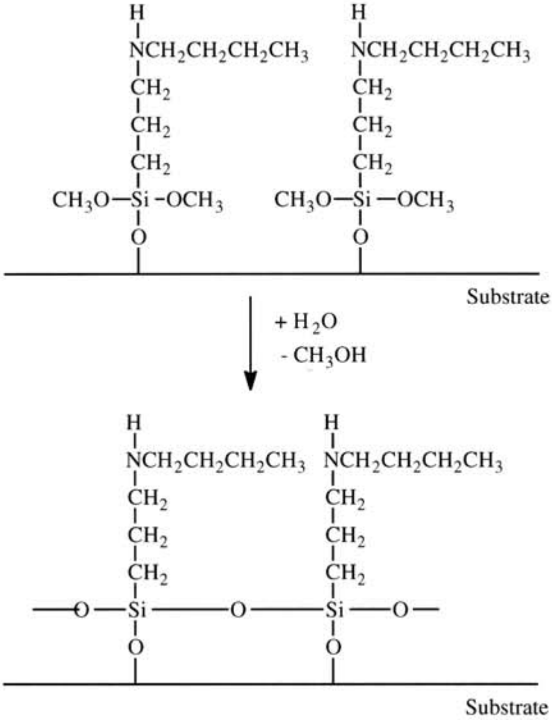


When dried pyrogenic (fumed) silica is treated with cyclic azasilanes, a strong exotherm is observed while no exotherm is observed for the alkoxysilane.

When alkyl groups (typically methyl) are substituted on the silicon, a crosslinked film will not form. In many applications these monolayers are sufficiently robust. If the substitutions on the silicon are alkoxy groups (typically methoxy), the deposition still leads to monolayers, but subsequent hydrolytic condensation of the monolayer after the excess (unreacted) silane is removed from the substrate results in formation of a more durable monolayer as shown below (see Scheme 1).

The extent of reaction of silanes with hydroxylic substrates, i.e. the effectiveness in reacting with the different types of hydroxyl groups, can be measured by a number of different techniques. The earlier discussion on silica nanoparticles can be applied directly to commercial pyrogenic silicas. A typical commercial grade has a surface area of 325 m^2/g or 3.25×10^{20} nm^2/g. If the hypothetical number of 4.5 hydroxyls/nm^2 (i.e., 1 m^2 of silica contains 7.5 μM of hydroxyl) is accepted, then one gram of silica contains 1.5×10^{21} hydroxyls or $1.5 \times 10^{21}/6 \times 10^{23}$ or 2.4×10^{-3} mol. Monolayer bonding of a silane with a molecular weight of 200 would deposit 0.5 g silane per gram of silica. In fact, most monolayer depositions of silanes result in less than 0.05 g per gram of silica.

An interesting practical experiment is to measure the weight increase of dried fumed silica after treatment with silanes followed by vacuum devolatization after a 100-s silane exposure. While more accurate and representational data can be obtained by IR [8] or solid state ^{29}Si-NMR [9] studies, simple weight gain can provide a quick screening method for effectiveness of silane surface modification. A series of n-butyl functional silanes were selected for the study. The n-butyltrimethoxysilane is comparable to typical coupling agents. N-(n-butyl)-



Scheme 1.

aminopropyltrimethoxysilane contains an amine which is expected to have a catalytic effect in promoting surface reaction [10]. Finally, 2,2-dimethoxy-N-n-butyl-1-aza-2-silacyclopentane, the cyclic analog, was evaluated. The ratio of weight gain was 1 : 3.5 : 5.9. This clearly indicates that, although there is a significant catalytic effect by the amine, the surface reaction is driven even further by the ring-opening reaction.

Modification of fillers with cyclic azasilanes without hydrolyzable groups has recently been reported [11]. However, solution deposition conditions utilized were such that adsorbed silanes probably reacted after formal contact times. Nevertheless, the one example of a cyclic azasilane demonstrated higher bonding efficiency than a non-analogous linear silane at ratios similar to the screening experiment reported here.

Spin-on deposition of 2,2-dimethoxy-N-n-butyl-1-aza-2-silacyclopentane on oxidized silicon wafers provided about 20% greater deposition than the linear analog as measured by ellipsometry, a result comparable to the vapor phase deposition.

4. CONCLUSIONS

New cyclic azasilanes have been synthesized for the purpose of developing coupling agents appropriate for a variety of nanotechnologies including surface modification of nanoparticles and chemical vapor deposition (CVD) consistent with nanoscale features. Cyclic azasilanes appear to be ideal candidates for these applications since they undergo a ring-opening reaction with hydroxyl groups driven thermodynamically by the formation of an oxane bond with silicon without byproduct formation. Preliminary data for the treatment of inorganic surfaces, including silica nanoparticles and oxidized silicon wafers, with cyclic azasilanes suggest that high density monolayer deposition is achieved.

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