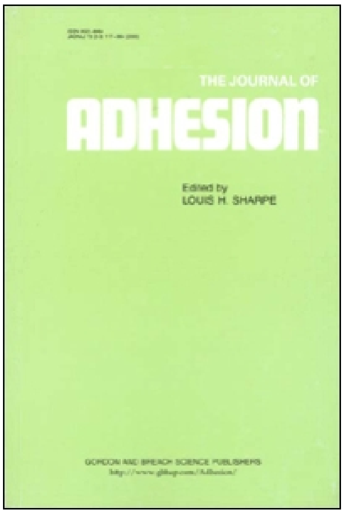

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Characterization of Poly(Aminosiloxane) Surface Chemistry on Aluminum Oxide*

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N-2-aminoethyl-3-aminopropyltrimethoxysilane (AAPS) was shown to react with aluminum oxide powder to form an amine/carbonate salt, as observed by diffuse reflectance infrared spectroscopy (DRIFT) and thermogravimetric analysis with mass spectroscopy (TGA-MS). TGA-MS, together with electron spectroscopy for chemical analysis (ESCA), reveal that the stoichiometric ratio of amine salt to free amine is higher on the surface of aluminum oxide powder than in a comparable neat film. In addition, TGA-MS shows that a nonstoichiometric ratio of CO_2/H_2O is evolved upon heating the surface-treated powder (4.5/1), whereas the neat film evolves CO_2/H_2O at a ratio near unity. The high fraction of protonated amines, together with the higher ratio of CO_2/H_2O in the presence of alumina, is consistent with a proposed bonding mechanism which involves carbonate bridging between protonated amines and hydroxyl sites on the aluminum oxide surface.

Keywords: Aminosilane; Alumina; Carbonate salt; TGA-MS; Bonding

INTRODUCTION

Trialkoxyorganosilanes are known to enhance adhesion of organic polymers to inorganic substrates such as glass and metals [1, 2]. Silanes

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[*] One of a Collection of papers honoring F. James Boerio, the recipient in February 1999 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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are also used to treat the surfaces of inorganic additives such as aluminum trihydrate [3], alumina [4, 5], and silica [6] for use in reinforced polymer systems. In addition, they can also be blended directly into the matrix of a polymer for subsequent bonding to an inorganic substrate as has been accomplished with ceramic green tapes [7], with polymeric interlayers for use in photovoltaic modules [8, 9], and with polymeric interlayers for use in automotive and architectural safety glazings [10–12].

Several review articles have been written which describe the commercial application of silanes, as well as the general chemical reactivity of these molecules [13–15]. However, very little research has been published on the actual chemical state of silanes in their end-use applications, or as a function of process history (during the fabrication of materials employing organosilanes). The mechanism of silane hydrolysis has been studied *via* solution NMR techniques [16, 17] for several silanes in both aqueous and aqueous/organic solutions. The hydrolysis of a silane in a typical end-use environment (such as within a polymer matrix) is more difficult to study because of the low concentrations that are often employed, and because the environment is often composed of a complex mixture of solid organic and inorganic materials. However, several spectroscopic techniques have been used to study the nature of silanes at the surfaces of inorganic substrates, including FTIR, XPS [18, 19], solid state NMR [20–24], and pyrolysis mass spectroscopy [25].

Trialkoxysilanes are hypothesized to promote adhesion through a combination of two general mechanisms. In the first mechanism, a "coupling" reaction may occur between the organic functional group of the silane molecule and the polymer matrix, resulting in a chemically covalent bond between the two species. This reaction is accompanied by the hydrolysis of alkoxy groups to form silanols, which can either directly condense to form covalent bonds with the inorganic surface, or can physically adsorb and bond through forces such as hydrogen bonding or electrostatic interactions. In a second mechanism, the alkoxy groups can hydrolyze to form silanols, which then condense to form silesquioxane networks that can compatibly blend and interpenetrate with the polymer matrix at the interface, while simultaneously adsorbing onto the surface of the inorganic substrate either through direct condensation, or through physical adsorption *via* secondary chemical bonding interactions.

The exact mechanism of bonding will depend on several factors including the relative acidity or basicity at the interface (pH), the thermodynamic compatibility of the polymer with the organosilane and its condensation products, the temperature dependence of hydrolysis and condensation, the temperature dependence of polymer creep compliance and chain disentanglement to facilitate interpenetration, the activation energy for achieving a covalent bond (coupling) between the polymer matrix, and the organic functionality of the silane molecule. For example, when the organic functional group is a primary amine, no external acid or base catalysts are needed for hydrolysis since the amine will catalyze auto-condensation in the presence of water [1]. This reaction has been studied by several authors, both in solutions and on surfaces. Chiang, Ishida and Koenig [26] have found that aminosilanes will hydrolyze to form stable solutions of cyclic oligomeric structures that condense further upon solvent removal during the "drying" stage on a glass surface. Pleuddemann has shown that better polymer adhesion to glass fibers is achieved when glass fibers are treated with this pre-hydrolyzed form of aminosilanes [1], most likely because the oligomeric structures contain free silanol groups which can facilitate further condensation with other surface bound oligomers, or with inorganic hydroxy groups on the surface itself.

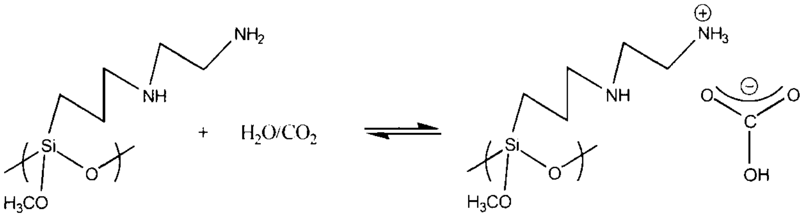
Silanes can also react with other molecules through the organofunctional group. In cases involving aminosilanes, certain condensation reactions can be employed such as ester hydrolysis and amide formation, or epoxy ring opening. Other common "reactive" functionalities include vinyl, styrenic, epoxy, acryloxy, and straight alkyl [1, 27]. When silanes are used as coupling agents for treating inorganic fillers for use in polymers, the choice of the organic functional group can affect polymer/filler interactions and, hence, will affect final macroscopic mechanical properties [28]. When the organic group is a vinyl or acrylic type, peroxides and silanes can be formulated together with polymers containing potential grafting sites such as polypropylene or poly(ethylene-covinylacetate). The results can include higher adhesion to inorganic substrates such as glass or aluminum [8].

The exact mechanism of silane reactivity with inorganic surfaces is still controversial. Although several authors have found evidence to indicate the existence of Al–O–Si bonds on silane treated aluminum substrates, the exact characteristics of such covalent bonds remain obscure. Furukawa *et al.* [29, 30] have used inelastic electron tunneling spectroscopy to study the interaction of an aminosilane with an Al_2O_3 surface. Their results indicate that Al–O–Si bond formation is unlikely since the intensity of the surface —OH group band was not diminished. Instead, the hydroxyl shift from $3580\,cm^{-1}$ to $3650\,cm^{-1}$, and complementary amine deformation shifts were attributed to amine hydrogen bonding with surface hydroxyl groups. On the other hand, Boerio *et al.*, maintain that aluminosiloxane bonds will form [11]. Naviroj *et al.*, have used FTIR to study the interaction of a model monoethoxyaminosilane on alumina to reduce the complicated overlap which may occur between Si–O–Si and Al–O–Si bands near $1000\,cm^{-1}$. Difference spectra of treated minus untreated alumina reveal a weak band at $963\,cm^{-1}$ which is attributed to the Al–O–Si bond [32].

The pursuit of an Al–O–Si bond as a discrete entity may be a moot point since dynamic equilibria may yield a "time averaged" species that could be more ionic than covalent as suggested by Pashchenko *et al.* [33]. An ionic bond would be more susceptible to ion pair separation by surface moisture or other surface species (as we will suggest in this work). Perhaps the more important bonding force would result from the summation of these individual bonding interactions (be they dynamic or static) over the spatial domain which would be occupied by a high molecular weight polysiloxane condensation polymer. The sum of these forces, coupled with the insolubility of any resulting 3-dimensional condensate, would result in a stable, non-labile surface layer. As an example, pre-hydrolyzed *n*-octyltriethoxysilane remains adsorbed on the surface of Al_2O_3 powder particles even after ethanol or toluene extraction steps [5].

The reaction of aminosilanes with glass surfaces has generally been studied at greater length in the literature than reactions with other surfaces. Chiang *et al.*, have used FTIR to assign a series of amine deformation bands at 1630, 1332, 1575 and $1488\,cm^{-1}$ to an intramolecular zwitterion of $SiO^-NH_3^+$ [26]. This "backbonding" mechanism of the amine group with the inorganic substrate surface was paralleled by Furakawa *et al.* [29, 30] on aluminum surfaces as indicated above. Also, Boerio *et al.* [34] have used XPS to show that the amine exists in both the protonated and free form on oxidic aluminum surfaces. These findings were taken as supporting evidence for the generality of the zwiterionic "backbonding" mechanism.

However, later studies by Culler *et al.* [35, 36] on glass surfaces suggested that N-2-aminoethyl-3-aminopropyltrimethoxysilane (AAPS) reacts reversibly with atmospheric moisture and CO_2 to form an aminebicarbonate salt on the surface of glass fibers. They also analyzed neat AAPS films that were cast under conditions identical to the conditions for glass fiber treatment (with atmospheric drying). In both cases, they found that CO_2 weight loss could be monitored gravimetrically with heating, and that subsequent free amine formation could also be spectrophotometrically monitored. The reaction was most effective at the natural aminosilane pH of 10.6, and was found to yield reversibly the free amine, free CO_2, and water after heating at elevated temperatures as shown below.



The aminebicarbonate salt mechanism was consistent with a shift in the $—NH_2$ deformation mode from $1600\,cm^{-1}$ (free amine) to $1575\,cm^{-1}$ (hydrogen bonded amine) [35, 36]. They also attributed bands at $1630\,cm^{-1}$ and $1332\,cm^{-1}$ to OCO_2 carboxylate deformations coupled with ammonium salt deformations ($—NH_3^+$ bending) between 2700 and $2100\,cm^{-1}$. These bands were also reduced in intensity after heating (corroborating with the gravimetric loss of CO_2). Thus, depending on process conditions (for either surface treatment or for polymer fabrication), it was theorized that the formation of both bicarbonate salts and imines could interfere with the overall effectiveness of an aminosilane coupling agent.

More recent ^{15}N NMR studies of aminosilane on alumina by Chu *et al.* [37] show that the amine exists in three to four environments depending on the solvent deposition medium. Taken collectively, all of these studies seem to indicate that the bonding mechanism between aminosilanes and inorganic substrates such as aluminum oxide is complex and, in many ways, still unclear. For example, the most common theme shared by these works is that protonated amines are somehow involved in the bonding between aminosilanes and inorganic oxides. On the other hand, the nature of the counterion(s) and the number of chemical environments remains in question. Also, very little work has appeared on the involvement of CO_2 or carbonate species. An understanding of these interactions is important from the industrial standpoint, since aminosilane surface treatments are often used with the intention of promoting covalent bonding with crosslinkable polymer systems. In this work, we have attempted to investigated the degree to which CO_2 is involved in the reaction of aminosilanes with Al_2O_3 by using complimentary characterization techniques, including thermogravimetric analysis with mass spectroscopy (TGA-MS), diffuse reflectance infrared spectroscopy (DRIFT) and electron spectroscopy for chemical analysis (ESCA). The emphasis, however, was placed on the TGA-MS technique since it allows for the simultaneous detection of both CO_2 and H_2O evolution during the heating of neat aminosilane films and treated alumina samples. In this way, the overall stoichiometric ratio between CO_2 and H_2O could be determined together with the fraction of protonated amines.

EXPERIMENTAL

Alumina Surface Treatment

A sample of highly calcined α-alumina powder from Alcoa (Al_2O_3, 5 µm average diameter, low porosity, low surface area of $0.8\,m^2/g$) was treated in a slurry of isopropyl alcohol from Fisher (IPA, reagent grade) with N-2-aminoethyl-3-aminopropyltrimethoxysilane (AAPS), otherwise known as Z6020 from Dow Corning. The slurries were prepared with 43% alumina solids by weight at room temperature both in the presence of 3.0% AAPS by weight alumina, and in the absence of AAPS for control purposes. The slurries were then allowed to dry into cake form under laboratory hood atmospheric conditions at 25°C.

This level of AAPS equates to approximately 0.013 moles of silane monomer per 100 g alumina or, in other words, 1.7×10^{-4} moles/m^2, which is a factor of ten greater than the level of AAPS which has been found to adsorb on α-alumina at equilibrium in solvent slurries such as IPA and ethanol [5, 7]. This level was chosen to insure both adequate surface coverage upon drying, and to help facilitate detection during subsequent TGA-mass spectroscopy experiments. A similar IPA/AAPS solution was prepared without alumina, and was then cast under identical conditions to yield a neat AAPS polymeric film for a relative comparison.

It should be noted that aminosilanes tend to be basic, driving the pH of aqueous solutions towards higher pH. In the presence of water or other proton sources, the basic amines will serve to autocatalyze the hydrolysis of the alkoxy silane moieties to silanols, which, in turn, can condense to form silane dimers, trimers and oligomers [7]. Although no water was added directly to these slurries, water under these conditions was available from surface-adsorbed species on the alumina and from the atmosphere during drying. Thus, a mixture of monomers and oligomers would be expected to form in both the alumina slurry and in the neat solution. As a result, condensation occurs upon drying, leading to a powdered cake as in the case of the alumina slurry, and to a flexible film as in the case of the neat AAPS solution.

Both the treated powder samples and the control samples were analyzed by thermogravimetric analysis with mass spectroscopy (TGA-MS), diffuse reflectance infrared spectroscopy (DRIFT) and electron spectroscopy for chemical analysis (ESCA). Samples were analyzed after exposure to various drying conditions including laboratory atmospheric drying at 25°C, oven drying at 110°C for 24 hours, and oven drying at 200°C for 6 hours to follow the possible evolution of labile species or degradation products.

Thermogravimetric/Mass Spectroscopy Analyses (TGA-MS)

The TA Instruments 951 Thermogravimetric Analyzer (TGA) interfaced with a VG Quadrupoles mass spectrometer (MS) was used to follow the degradation behavior of the AAPS-coated powders. The TGA heating profile was 10°C/min to 800°C under a dry nitrogen purge. The percent weight loss and derivatives were calculated and plotted *versus* temperature. The derivative curves for the coated powders were normalized to the absolute weight of the AAPS coating to facilitate data comparison between coated powders and the neat AAPS film.

The volatiles were analyzed by using the MS in multiple ion monitoring mode. Twelve masses were selected based on the expected degradation or fragmentation pattern of the silane. These included 16, 17 and 18 amu for NH_2, NH_3 and water fragments, 15 amu for the CH_3 fragment, 30 amu for the CH_2NH_2 fragment, 31 amu for CH_3O, and 44 amu for CO_2 and $C_2H_4NH_2$ fragments. The partial pressures of these masses were plotted *versus* time to provide the relative mole ratios of the degradation products. The time axis for the MS scans correlates linearly with the TGA heating rate such that 200°C corresponds to approximately 18 minutes on the MS time scale.

Diuse Reflectance Infrared Spectroscopy (DRIFT) and ESCA Analyses

Samples for DRIFT were diluted with potassium bromide to a ratio of 25 parts by weight sample to 75 parts KBr. DRIFT spectra were acquired using a Mattson Polaris spectrometer with a DTGS detector and equipped with a Spectra-Tech diffuse reflectance accessory. DRIFT spectra represent the average of 256 scans obtained at $8\,cm^{-1}$ resolution.

Treated and untreated powders were also analyzed with high resolution electron spectroscopy for chemical analysis (ESCA). The powder samples were supported on a double-sided tape substrate. Standard ultra-high vacuum cleanliness procedures were employed during sample mounting and during introduction to the chamber. Survey data were first collected (0 to 1100 eV range, 1.0 eV/channel resolution) followed by high resolution with an energy resolution of 0.08 eV/channel, both being sensitive to a depth of approximately 50 Angstroms. The sample volume from which the ESCA data were acquired was 600 mm × 1000 mm × 0.01 mm. High resolution spectra were acquired from Al(2p), Si(2p), Cl(2p), C(1s), N(1s) and O(1s). Spectra were referenced to the binding energy corresponding to the $-(CH_2)n-$ signal at 284.6 eV.

RESULTS AND DISCUSSION

Earlier studies performed by Culler *et al.* [35, 36] showed that AAPS reacts with atmospheric moisture and CO_2 to form an aminebicarbonate salt on the surface of glass fibers. They also analyzed neat AAPS films that were cast under conditions identical to the conditions for glass fiber treatment with atmospheric drying. In both cases, they found that CO_2 weight loss could be monitored gravimetrically with heating, and that subsequent free amine formation could be spectrophotometrically monitored with heating. Interestingly, a higher fraction CO_2 was evolved (by weight of AAPS) from the treated glass fibers as compared with the neat film. They estimated that 5% of the amine groups were protonated in the neat film *vs.* 54% on the glass treated fibers. No complete explanation for this behavior could be given except to note that the difference in amine reactivity may be associated with the difference in the effective pH of the glass surface environment.

TGA/MS Analysis of Neat AAPS Films

Although Culler *et al.*, monitored the evolution of CO_2 and showed that it was totally evolved above 90°C, they did not simultaneously monitor the loss of H_2O. Given the proposed 1 : 1 : 1 stoichiometry of the reaction between CO_2, H_2O, and AAPS, we would expect H_2O and CO_2 to be evolved in a 1 : 1 molar ratio. Indeed, our TGA/MS results of a neat AAPS film shown in Figure 1 show an inflection on the bulk weight loss derivative curve which occurs at 90°C. The deconvolution of separate mass components shown in Figure 2 indicate that the 90°C weight loss is essentially CO_2 (m/e 44 amu) and H_2O (m/e 17 and 18 amu) at a mole ratio of 0.8, which is close to the expected theoretical value of 1.0. The loss of CO_2 and H_2O accounts for approximately 5% of the neat film weight or, in other words, approximately 0.08 moles each of CO_2 and H_2O per 0.43 moles of primary amine (the molecular weight of AAPS monomer is 220 amu). Thus, under the conditions of this study, we can estimate that approximately 18% of the primary amines exist in the form of protonated amine-bicarbonates in the neat film.

The remainder of the weight loss fragments in Figure 2 is associated with organofunctional group decomposition and silane condensation which ultimately leads to an SiO_2 type of network at 800°C [38]. Aside from the CO_2 and H_2O, the next most easily quantified weight loss occurs where the bulk derivative maximizes near 190°C. Culler *et al.* [35, 36] have shown that heating above 120°C results in the formation of an imine. The primary fragment at 190°C has an m/e of 44 amu, which would correspond to the cleavage of an amine radical cation

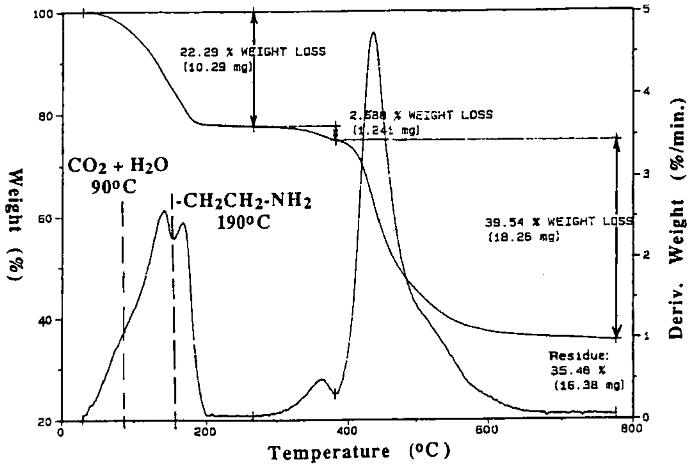


FIGURE 1 TGA weight loss scan for neat AAPS film.

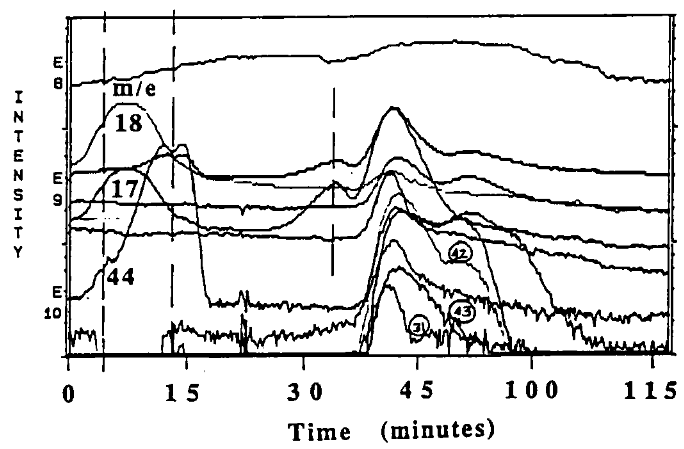
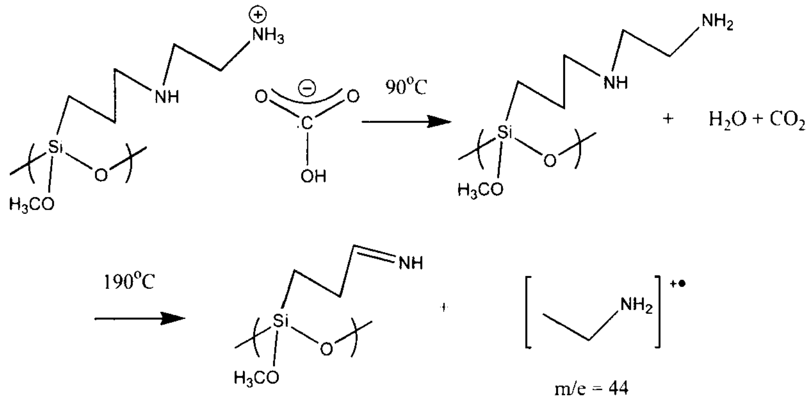


FIGURE 2 MS scan of TGA volatiles from neat AAPS film.

leaving the more thermally stable imine functionality behind. The amine radical cation has a molecular weight which corresponds to approximately 20% of the overall silane molecular weight. Indeed, the total weight loss at 190°C (from the bulk TGA curve) equates to about 20% of the neat AAPS film weight. Thus, the AAPS neat film degradation behavior up to 200°C can be described as follows:



TGA/MS DRIFT and ESCA Analyses of AAPS Treated Powder

The AAPS amine groups appear to form more carbonate species when on the surface of alumina powder than in the neat film. This parallels the glass fiber results of Culler *et al.* [35, 36]. Figure 3 shows the TGA/MS scans for the treated alumina powder. Although the signal-to-noise is worse than that of the neat film (since the AAPS represents only 3% of the total sample weight), the mass fragments at 44 and 18 amu clearly dominate the weight loss spectrum. Again, we can see that CO_2 and H_2O species are being evolved near 90°C, but this time they account for 15% of the silane weight loss, with a mole ratio of CO_2 to H_2O of about 4.5/1. If all the CO_2 molecules originate from an aminebicarbonate species, this would correspond to 0.009 moles of CO_2 per 0.014 moles of primary amine, or about 60% of the primary amines are protonated on the treated powder.

Figure 4 shows the bulk derivative curves of the neat film, the powder that was treated at room temperature, and the same powder that was heated at 110°C prior to analysis. These curves are weight corrected to account for the total weight of AAPS in the treated powder samples. The heat-treated sample exhibits a decrease in the weight loss rate at 90°C which indicates that a large portion of CO_2 and H_2O were evolved during the heat treatment stage. The room-temperature-dried powder exhibits a reduced rate of imine fragment weight loss as compared with the neat film. This suggests

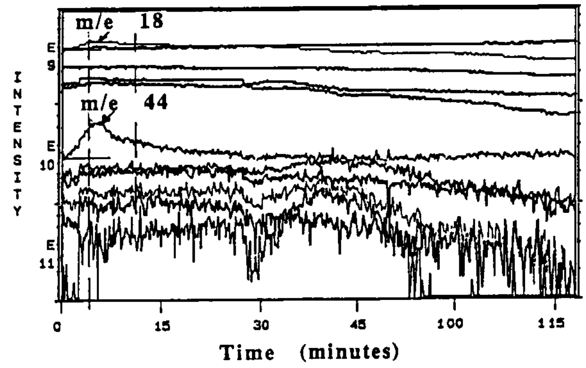


FIGURE 3 MS scan of TGA volatiles from AAPS-treated alumina powder.

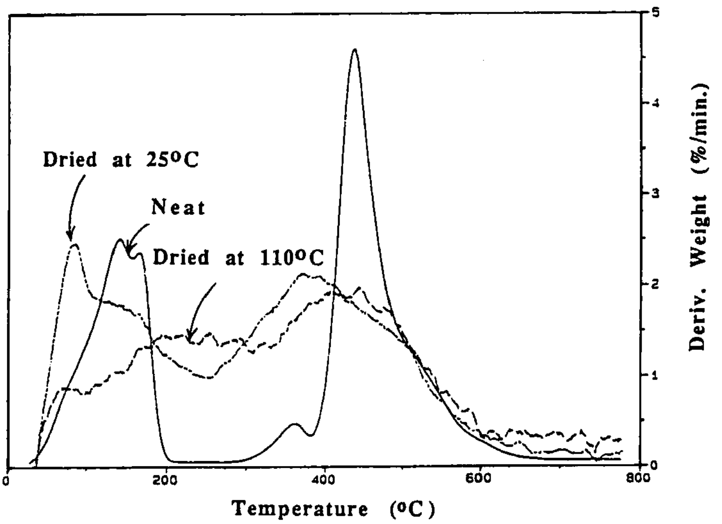


FIGURE 4 TGA weight loss derivative curves for neat AAPS film, AAPS-treated powder dried at 25°C, and AAPS-treated powder dried at 110°C for 24 hours.

that an interaction with the alumina surface may be interfering with amine fragment evolution. The rate of amine fragment evolution is reduced even further with the heat-treated powder. This is because a large portion of amine fragments were evolved during the heat treatment stage to yield imines (as DRIFT measurements will also show).

Since the AAPS amines should react at a 1/1/1 stoichiometric ratio with H_2O and CO_2, the evolution of excess CO_2 in the room-temperature-treated powder indicates that other mechanisms of carbonate formation and decomposition must be taken into account. Based on these data, there seems to be two likely possibilities.

1. The alumina itself has adsorbed more CO_2 than stoichiometrically required for aminebicarbonate formation. (However, note that neither CO_2 nor water evolution was observed for control alumina samples that were also analyzed by TGA/MS.)
2. Atmospheric H_2O is not the sole proton source during powder drying. Additional proton sources could include surface water or surface hydroxyl groups from the alumina.

ESCA Analysis of AAPS Treated Alumina

The high degree of amine protonation is also confirmed by ESCA data as shown in Figure 5, where the bands at 400.8 and 398.4 eV correspond to the protonated and free amine species, respectively [34]. Atomic percentages at various energies for treated and untreated alumina are given in Table I. Integration of the fitted amine bands indicates that about 40% of the amines are protonated. However,

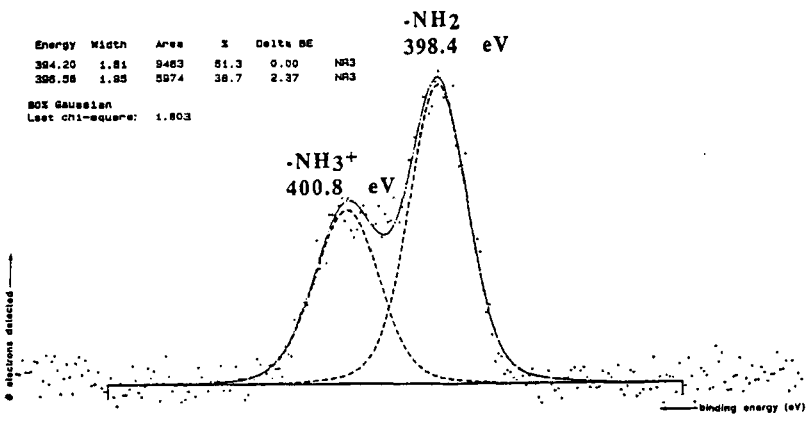


FIGURE 5 High resolution ESCA Spectrum of N(1s) band from AAPS-treated alumina.

TABLE I High resolution ESCA data: atomic percentages for alumina and AAPS-treated alumina. Binding energies are referenced to 284.6 eV

Atomic species	*Al_2O_3 surface % abundance*	*AAPS/Al_2O_3 surface % abundance*
Al (2p)	20	6.0
Si (2p)	–	8.6
Cl (2p)	0.3	4.7
C (1s)	37	46
N (1s)	0.8	12
O (1s)	40	22
Na (1s)	1.7	–

there was no evidence of a carbonyl carbon energy that would correspond to the carbonate species. Instead, a Cl^- counterion was detected at a level approximately equal to the level of protonated amines. This suggests that the vacuum preparation procedure and spot heating during measurements may have resulted in premature carbonate counterion decomposition. Similar results were reported by Boerio *et al.* [34], where the source of the Cl^- ion may have been a surface impurity that was introduced either prior to, or during, ESCA sample preparation. Surface impurities are likely, since Cl^- and Na^+ are detected on the untreated alumina sample as shown in Table I.

Although ESCA does not give direct evidence for the existence of the carbonate species, it generally shows (like the TGA/MS results) that a large fraction of the free amines are protonated. On the other hand, the DRIFT spectra in Figure 6 provide more evidence to verify the presence of a carbonate. The AAPS-treated alumina at room temperature shows the characteristic bands that were previously observed by Culler *et al.*, on glass fibers [35, 36]. The NH_3^+ stretching mode (2100 to 2800 cm^{-1}), which corresponds to a bicarbonate salt, decreases in intensity upon heating. Similarly, the free amine near 1596 cm^{-1} increases in intensity as does the C=N imine stretch at 1661 cm^{-1}. This confirms the previously-discussed TGA/MS fragment assignments.

All of our data on treated alumina powder and prior data on treated glass fibers indicate that the general phenomenon of carbonate adsorption and desorption is analogous to the phenomenon observed with the neat AAPS film. However, there must be mechanistic differences to account for both the non-stoichiometric CO_2/H_2O evolution, and the overall high fraction of complexed amines in the AAPS-treated alumina powder.

Prior to this study, the stoichiometric ratio of CO_2/H_2O evolution was not followed (this is the advantage of TGA-MS). Given that no

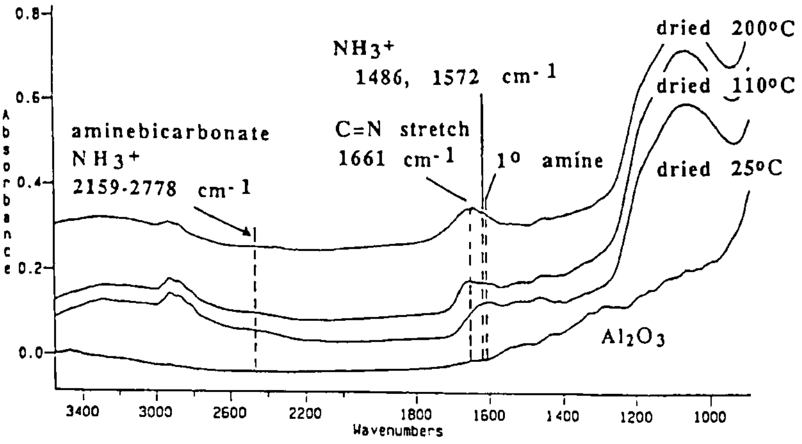
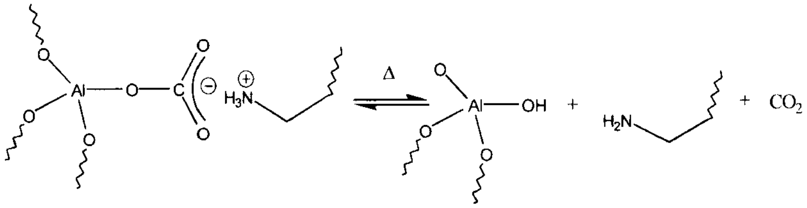


FIGURE 6 DRIFT spectra from alumina powder, AAPS-treated alumina dried at 25°C, treated alumina dried at 110°C for 24 hours, and treated powder that was dried at 200°C for 6 hours.

CO_2 was detected upon heating untreated alumina, and given that the CO_2/H_2O ratio is near unity for the neat film, it follows that a second proton/hydroxy source must be involved to account for the excess level of CO_2 that is evolved from the treated alumina, as well as the high fraction of protonated amines.

It is well established that the aluminum oxide surface will be partially hydroxylated under these conditions, and that the surface can contain both Lewis acid and Bronsted acid sites [39]. Thus, it is conceivable that some of the amines could be protonated by the Bronsted acid sites, while the resultant Bronsted base sites (O^-) could react with CO_2 to form a carbonate. The carbonate, in turn, could balance the charge and "bridge" the cationic amine with the Bronsted base. Upon heating, CO_2 could be reversibly evolved as hypothesized below.



This proposed mechanism would be consistent with the high level of CO_2 and the relatively low level of H_2O that are evolved during the heating of AAPS-treated aluminum oxide powder. Also, the labile nature of this "bridge" could explain why it is generally not detected by other analytical methods.

Several additional experiments could be conducted to test this hypothesis further. For example, it was suggested by one of the reviewers that other alumina powders having well-characterized levels of Bronsted or Lewis acid/base sites could be used in testing the above mechanism. Perhaps a more direct experiment would be to use AAPS labeled with ^{15}N in the primary position, and to study its chemical environment in the presence and absence of alumina *via* solid state NMR. This experiment could be performed first near room temperature, and then upon heating, to determine the effect of CO_2 evolution on the ^{15}N chemical shift environment(s).

CONCLUSIONS

Although another potential mechanism for aminosilane interaction with aluminum oxide surfaces has been presented here, it is important to recognize that the nature of the aminosilane/alumina interaction cannot be described by any one specific mechanism. Instead, the interaction between aminosilanes and aluminum oxide occurs through multiple pathways, many of which involve protonated amino groups together with a number of potential counterions as discussed throughout the literature. However, in this case, the experimental data suggest that one of the potential counterions is a carbonate anion which, under some conditions, may "bridge" protonated amines with the aluminum oxide surface.

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