Infrared Study of the Surface Species Formed by Sequential Chemical Vapor Deposition of Dimethyl Zinc and Ethanethiol on Hydroxylated Alumina Surfaces

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The surface species formed by the reaction of gas-phase dimethylzinc with self-supported alumina pellets are examined by Fourier transform infrared spectroscopy. Dimethylzinc reacts with the surface −OH groups of alumina at room temperature evolving methane and yielding mainly surface Al−O−Zn−CH$_3$ species. A small amount of CH$_3$ species appears to bind to the Lewis acid sites of alumina as well, forming Al−CH$_3$ groups. Temperature-dependence studies reveal that these species are stable at room temperature and gradually decompose upon heating in vacuo. During the annealing process, some of the Zn-bound methyl groups also appear to migrate to free Lewis acid sites of the alumina surface. The dimethylzinc-treated alumina surface is then exposed to ethanethiol, which reacts with the surface methylzinc species at room temperature, eliminating methane and producing Zn-bound ethanethiolate surface species. These are stable in air and aqueous environments, and up to about 523 K in vacuo and may provide a possible synthetic strategy for formation of protective layers. The major gas-phase products from their thermal decomposition are found to be diethyl sulfide and ethylene. In addition, a small amount of methylzinc−thiol coordination intermediate is found on the dimethylzinc-treated alumina surface following the room-temperature reaction with ethanethiol. This intermediate decomposes with methane evolution upon annealing up to 398 K.

Introduction

Chemical vapor deposition of inorganic films formed by reaction between organometallic compounds and reagents containing active hydrogen atoms is widely used for atomic layer growth of semiconductor III−V and II−VI thin films and oxide layers[1−5] which are necessary for development of new electronic and opto-electronic devices. In this study, we use a similar approach to attach stable chains of short hydrocarbons to a model alumina surface. Such layers, if stable in air and aqueous environments, may potentially find applications not only as semiconductor precursors but also in the areas of corrosion protection, lubrication, and adsorbent modification. According to our previous IR studies,[6] *alkoxide* species adsorbed on alumina hydrolyze almost completely after exposing the modified surface to water. A more covalent Zn−S linkage to the alumina surface may provide a promising strategy for solving this problem, since ZnS and zinc thiolates

precipitate from aqueous solutions.[7−9] Thermolysis of such thiolate layers may be also used for growing ZnS and other II−VI semiconductor thin films since similar chalcogenates of Zn and Cd, as well as their complexes with amino and phosphine ligands, decompose upon heating to produce the corresponding chalcogenides.[8−11] These chalcogenolato compounds are also air-stable and have low toxicity. Epitaxial layers of ZnS have already been grown on GaAs (100) substrates using metal−organic chemical vapor deposition from dimethylzinc combined with *tert*-butylmercaptan[12] or methanethiol.[13]

Adsorption of methanethiol, CH$_3$SH, on alumina surfaces dehydroxylated at 873 and 1153 K has been studied in detail by Saur et al.[14] Two different dissociative mechanisms leading to surface thiolate species are suggested[14,15] involving reaction at strong Lewis acid sites that may be poisoned by pyridine or other bases (i) and weaker Al−O pair sites, not poisoned by bases

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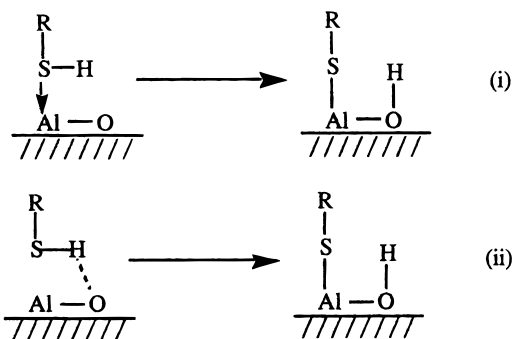(11) Bochmann, M.; Webb, K. J. *Mater. Res. Soc. Symp. Proc.* **1991,** *204,* 149.
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(ii). In addition, reversible adsorption is thought to

occur when the thiol remains molecularly coordinated to a Lewis acid site, hydrogen-bonded to surface oxygen or associated with surface −OH groups via the S atom to form Al−OH···S(H)CH$_3$ species. Dissociative adsorption is also reported for ethanethiol, CH$_3$CH$_2$SH, on alumina evacuated at 523 K.[16]

In this work, the reaction of dimethylzinc ((CH$_3$)$_2$Zn; DMZ) with alumina surface hydroxyl groups is studied using transmission infrared spectroscopy, and the resulting methylzinc species are then reacted with CH$_3$-CH$_2$SH (EtSH) to produce mainly Zn-bound ethanethiolate surface species. These are found to be stable in air and aqueous environments. Background experiments are conducted by exposing a prehydroxylated sample directly to EtSH, and the infrared spectra of the resulting surface species are collected for comparison with DMZ pretreated surface and to distinguish between the species bound to surface −OH groups and alumina Lewis acid sites and those bound to Zn following DMZ pretreatment.

Experimental Section

All spectra are recorded using a Perkin-Elmer Fourier transform infrared spectrometer at a resolution of 4 cm^{-1} employing a DTGS detector for five cycles (80 scans) for all spectra of the alumina surfaces and two cycles for the gas-phase spectra. A background spectrum is taken after each evacuation of the infrared cell (to, at least, 3×10^{-6} Torr) with the alumina pellet retracted from the beam. This spectrum is subsequently ratioed to all spectra following either thermal treatment or dosing with various reagents. Smoothing is applied to the stretching region of all spectra. The baselines of all spectra (between 1250 and 1125 cm^{-1}) displaying the temperature dependence of methylzinc species formed on alumina are fitted by interpolation and the corresponding background subtracted. Due to the extremely low intensity of the remaining broad feature, unmodified spectra in the methyl bending region (1225−1100 cm^{-1}) are presented to show the effect of thiol coordination to residual methylzinc surface species following thiol dosing. All other spectra showing the bending modes resulting from thiol dosing after DMZ pretreatment (1650−1200 cm^{-1}) are leveled by subtraction of a straight baseline. The bending region of all spectra of an alumina surface directly exposed to EtSH (1750−1200 cm^{-1}) are leveled by a multiple-point baseline correction. Baseline-corrected integration is used to evaluate the amount of surface methyl species formed on hydroxylated alumina following DMZ treatment. The baseline-corrected infrared absorbance intensity of certain modes (at 3016 cm^{-1}

for CH$_4$, 950 cm^{-1} for C$_2$H$_4$, 1260 cm^{-1} for CH$_3$CH$_2$SH and Et$_2$S) is used to evaluate the temperature-dependent distribution of these products desorbing from the DMZ/EtSH-derived alumina surface into the gas phase.

Dimethylzinc, (CH$_3$)$_2$Zn, was synthesized using a literature procedure[17,18] by reacting 0.05 mol (6.82 g) of anhydrous ZnCl$_2$ (EM Science, 98%) with 0.1 mol (9.6 mL) of trimethylaluminum (Aldrich Chemical Co., 97%) at room temperature under nitrogen atmosphere:

$$ZnCl_2 + 2Al(CH_3)_3 \rightarrow Zn(CH_3)_2 + 2Al(CH_3)_2Cl$$
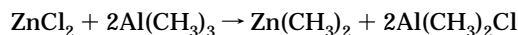
The mixture was stirred at room temperature and, after all solid ZnCl$_2$ was dissolved, the resulting dimethylzinc (bp 319 K) was distilled under nitrogen using a distillation apparatus constructed from greaseless Teflon valves and clear-seal joints. The product was transferred via a syringe into a glass vial in a nitrogen-filled glovebox and then additionally purified by four freeze−pump−thaw cycles. It was analyzed by infrared spectroscopy, and the recorded gas-phase spectra corresponded well to those already published and tabulated.[19−21] Distilled water (H$_2$O) was used for alumina rehydroxylation. Ethanethiol, CH$_3$CH$_2$SH (Acros, 97%), was used as received after purification by four freeze−pump−thaw cycles.

Alumina pellets were prepared as described earlier[6] from aluminum oxide (Baker Chemical Co.) by pressing 0.0138 g/cm^2 of the fine powder obtained after grinding by mortar and pestle, into a pellet at about 25 500 pounds per square inch (PSI). A magnetically coupled, stainless steel manipulator, mounted in the infrared cell was used to move the pellet back and forth from the infrared beam to the tube oven. The pellet was cleaned using the procedure discussed in greater detail elsewhere[6,22,23] by initially evacuating at room temperature and heating, first to 400 K and then to higher temperatures in vacuo (normally at 800 K for 6−8 h) to ensure the optimal extent of rehydroxylation upon subsequent dosing with H$_2$O at 300 K). Somewhat lower extent of rehydroxylation (judged by the intensity of −OH stretching modes centered at ∼3600 cm^{-1}) was achieved by longer annealing, still at 800 K. Since prolonged annealing of alumina samples at higher temperature in vacuo appears to severely inhibit the rehydroxylation process when relatively low hydroxyl coverages were needed, the pellet was cleaned longer at higher temperatures (e.g., 948 K for 12 h). When the cleaning was complete, the sample was exposed to saturated H$_2$O vapor (∼20 Torr) at room temperature for about 2 min. Excess molecular water was removed by annealing at 400 K in vacuo for 2 h, and water removal was verified by the complete loss of the H$_2$O bending mode at ∼1650 cm^{-1} in the infrared spectrum of the pellet.

Prehydroxylated alumina pellets prepared in this manner were exposed to ethanethiol for about 2 min (∼545 Torr) and evacuated to 3×10^{-6} Torr for background experiments. When DMZ pretreatment was needed, the prehydroxylated samples were exposed first to a saturated vapor of the organometallic reagent for 2 min at room temperature (∼344 Torr calculated using the formula given by Thompson et al.[24]) and evacuated to 3×10^{-6} Torr. The DMZ-derived alumina surface was then exposed to saturated vapor of ethanethiol (∼545 Torr calculated from reference data[25]) for about 2 min and evacuated to 3×10^{-6} Torr. Infrared spectra of the reagents and gas-phase products were recorded before each evacuation with the

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alumina pellet retracted from the beam. After evacuation at room temperature (3×10^{-6} Torr), the spectrum of the resulting surface species is recorded with the alumina pellet having been reintroduced into the beam. Next, during the temperature-dependent experimental series, the infrared cell is closed, the sample is annealed for about 30 min in the tube oven at the desired temperature, and the gas-phase spectra of products desorbing from the alumina surface are recorded at each temperature. The cell is then evacuated, and the annealing process is continued in vacuo at the same temperature for another 30 min. The infrared spectra of the surface species remaining after each anneal cycle are recorded after cooling the sample to room temperature. When the reactivity of the DMZ/EtSH-derived surface species on alumina with water is investigated, the pellet is exposed to saturated water vapor at room temperature twice for about 1 and 4 min, and after the second dosing the infrared cell is closed and the sample is held under the H_2O vapor for 3 h. These samples were also exposed to the laboratory atmosphere for up to 6 days to further evaluate the stability of these species in air. Another DMZ/EtSH-treated sample is annealed in vacuo up to 398 K and exposed to water upon cooling to 300 K, and the thermal stability of the remaining species is studied up to 748 K in vacuo.

Results

Adsorption of Ethanethiol on Prehydroxylated Alumina. The adsorption of ethanethiol on prehydroxylated alumina was studied and agreed well with the results of other workers.[14,16] The results are briefly summarized below. Fewer new surface species are formed on prehydroxylated alumina pellets exposed directly to EtSH at room temperature compared to the results of Sugioka et al.[16] for alumina that had been dehydroxylated at 523 K. On hydroxylated alumina preheated to 400 K in our experiment, a slight decrease in the overall infrared transparency is observed, which is similar to the effect seen upon adsorption of alcohols[6,26] but much less than in that case. A slight increase in infrared absorption is noted in the −OH stretching region (between ∼3300 and ∼2000 cm^{-1}, not shown), indicating a perturbation of the surface −OH groups of alumina in agreement with Saur et al.[14] Another broad feature, with low intensity, is noted superimposed on the continuous −OH absorption in the region of the C−H stretching modes between 3000 and 2800 cm^{-1} due to the −CH$_3$ and −CH$_2$− asymmetrical and symmetrical stretching modes of adsorbed species, with a very small peak at ∼2925 cm^{-1} assigned to ν_{as}(CH$_2$).[27] Other C−H stretching modes could not be clearly distinguished due to their low surface concentrations on prehydroxylated alumina and, at least partially, to the obscuring effect of the continuous adsorption arising from alumina −OH groups. Both features in the −OH and C−H stretching region are lost after annealing at 398 K, and the initial transparency of alumina is completely restored over the entire accessible spectral range.

The bending modes of the species formed on prehydroxylated alumina following ethanethiol adsorption are more clearly distinguished, even though they still appear with very low intensity (Figure 1, spectrum a). The broad absorption feature between 1550 and 1750 cm^{-1} and the peak at ∼1324 cm^{-1} are not assigned, but their
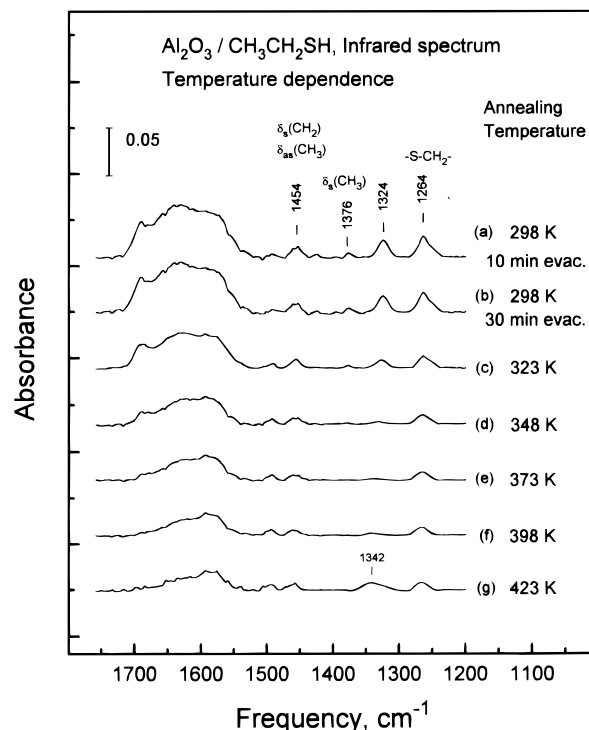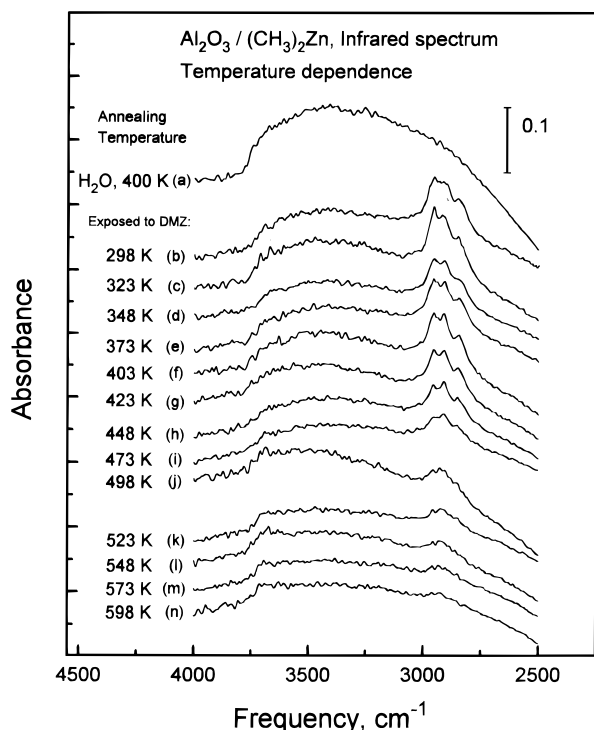

Figure 1. Temperature dependence of the infrared spectra collected following ethanethiol adsorption on an alumina sample that has been cleaned at 800 K for 6 h, rehydroxylated twice with H_2O (∼20 Torr, 2 min each exposure) at 300 K and annealed at 400 K for 2 h in vacuo to remove molecular water: (a) prehydroxylated alumina sample exposed to 545 Torr of C_2H_5SH for 10 min and evacuated for 10 min at room temperature; (b) sample evacuated for 30 min at room temperature; spectra c−g are taken after annealing for 30 min in vacuo at the temperature displayed adjacent to each spectrum and after cooling the sample to room temperature.

temperature dependence implies that they arise mainly from the interaction of weakly adsorbed species with the alumina surface. The peak at ∼1454 cm^{-1} is assigned to the δ_s(CH$_2$) scissoring mode, which typically appears near 1465 cm^{-1} [27] in the spectra of hydrocarbons and overlaps the asymmetrical bending mode of the methyl C−H bonds, δ_{as}(CH$_3$), near 1450 cm^{-1}. The band at ∼1264 cm^{-1} is assigned to the wag of −CH$_2$− groups adjacent to the sulfur atom.[28] These assignments are in reasonable agreement with the earlier study of Sugioka et al.[16] No significant changes are observed in the spectrum after evacuation at room temperature for 30 min (Figure 1, spectrum b). A decrease in intensity of all features is evident after annealing to 323 K in vacuo (Figure 1, spectrum c). This is not quite consistent with the results of Sugioka et al.,[16] where the spectrum obtained after ethanethiol adsorption is reported to disappear completely upon evacuation at 323 K. Our data are more consistent with the results of Saur et al.[14] obtained for methanethiol adsorption if the intensity decrease is attributed to the desorption of hydrogen-bonded surface species only. Following these assignments, the infrared modes seen after evacuation at 348 K (Figure 1, spectrum (d)) are characteristic of ethanethiolate surface species strongly chemisorbed on alumina Lewis acid sites. These chemi-

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Figure 2. Temperature dependence of infrared spectra of the surface species formed by reaction of DMZ (~344 Torr) with alumina that has been cleaned at 948 K for 12 h in vacuo, rehydroxylated by exposing twice to ~20 Torr of H_2O for 2 min at 300 K, and annealed at 400 K in vacuo for 2 h to remove molecular water from the surface: (a) spectrum of the prehydroxylated alumina pellet, taken after cooling to room temperature; (b) after exposure to ~344 Torr $(CH_3)_2Zn$ vapor and evacuated to 3×10^{-6} Torr at room temperature. Spectra c−n are collected after annealing the sample in vacuo at the temperature shown adjacent to each spectrum and cooling to room temperature.

Table 1. Assignments of the Infrared Modes Arising on a Prehydroxylated Alumina Surface after Reaction with $(CH_3)_2Zn$ Vapor and Evacuation to 3×10^{-6} Torr at Room Temperature[a]

mode	$Al_2O_3/(CH_3)_2Zn$ (this work)	$(CH_3)_2Zn(g)$[21]
$\nu(C-H)$	2956	2970
$\nu(C-H)$	2916	2914
combn $2\nu_{10} + \nu_{13}$	2852	2846
$\delta(CH_3)$	1274	1301
$\delta(CH_3)$	1180	1183

[a] All frequencies given in cm^{-1}.

Infrared peak assignments for the surface species remaining on alumina after evacuation at room temperature are given in Table 1. These frequencies are compared to those of gas-phase $(CH_3)_2Zn$ and indicate the presence of adsorbed methylzinc surface species. A very low intensity feature is also observed at ~1210 cm^{-1} and assigned to methyl groups bound to alumina Lewis acid sites (see below).

Smoothed spectra of the −OH and C−H stretching region (from 4000 to 2500 cm^{-1}), obtained following evacuation, as a function of increasing annealing temperature from 298 K, following room-temperature adsorption of dimethylzinc (DMZ), are displayed in Figure 2. It is clear that, at higher temperatures, the characteristic C−H stretching modes between 2800 and 3000 cm^{-1} gradually decrease in intensity together with the broad −OH stretching absorption (Figure 2, spectra b−n). This may imply that secondary reactions are taking place between the surface methyl and hydroxyl groups, as observed previously with trimethylaluminum $((CH_3)_3Al)$ on alumina.[22,23] Evaluation of the intensity of the broad absorption of hydrogen-bonded surface −OH groups suggests that, upon annealing the DMZ-reacted sample in vacuo from 298 up to 598 K (Figure 2, spectra b−n), the surface −OH groups concentration decreases approximately as much as during the initial surface reaction with DMZ at room temperature (~40%). This effect is also observed for samples with different initial extents of hydroxylation (Figure 3). Note that, after annealing at 598 K, only traces of methyl species remain as evidenced by the residual intensity of the C−H stretching peak at ~2900 cm^{-1} (Figure 2, spectrum n). This suggests that almost all of the surface methyl species react with the neighboring −OH groups as the sample is heated in vacuo eliminating methane. The fact that the decrease in −OH stretching intensity caused by the initial reaction with DMZ at 298 K and the drop caused by annealing in vacuo from 298 up to 598 K are very close for pellets with different surface hydroxyl concentrations (Figure 3), indicates that almost identical surface −CH_3 and −OH concentrations are involved in the reaction at each step. Since each DMZ molecule contains two methyl groups, this implies that there is an initial rapid reaction of the first methyl group from DMZ with surface −OH groups at room temperature producing predominantly monomethylzinc surface species, CH_3−Zn−O(s). This is followed by a higher temperature reaction of the remaining Zn-bound surface methyl group with the neighboring surface −OH groups to yield further methane. The peak at the highest $\nu(CH)$ frequency (Figure 2) is more intense in spectrum (c) than in (h) or (i), which suggests the presence of two types of species. This may be due to the presence of some unreacted dimethylzinc species

sorbed ethanethiolate species seem to be relatively stable at higher temperatures (Figure 1, spectra e and f) and may be considered as a precursor in the dehydrosulfurization reaction which is initiated at around 473 K in a pulse catalytic reactor and at about 373 K in a thermal desorption experiment.[16] The fact that the methyl bending mode, $\delta_s(CH_3)$, at ~1376 cm^{-1} is not clearly seen at temperatures higher than 323 K (Figure 1, spectra e and f) can be explained by its lower initial intensity compared to the other two peaks at ~1454 and ~1264 cm^{-1} and does not necessarily mean the absence of methyl species on the surface thiolate species, since no other peaks of high-temperature products are seen at this point. The small broad feature growing near 1342 cm^{-1} after evacuation at 423 K (Figure 1, spectrum g) can be attributed to high-temperature coke products resulting from ethanethiolate surface species decomposition.

Reaction of $(CH_3)_2Zn$ with a Prehydroxylated Alumina Surface. Large amounts of methane are formed following exposure of prehydroxylated alumina at room temperature to a saturated vapor of dimethylzinc (~344 Torr) and the area of the broad infrared stretching absorption of alumina surface −OH groups centered at ~3400 cm^{-1} decreases by 40 ± 5% (Figure 2, spectra a and b). Identical relative decreases are found for two samples with different initial extent of alumina hydroxylation.

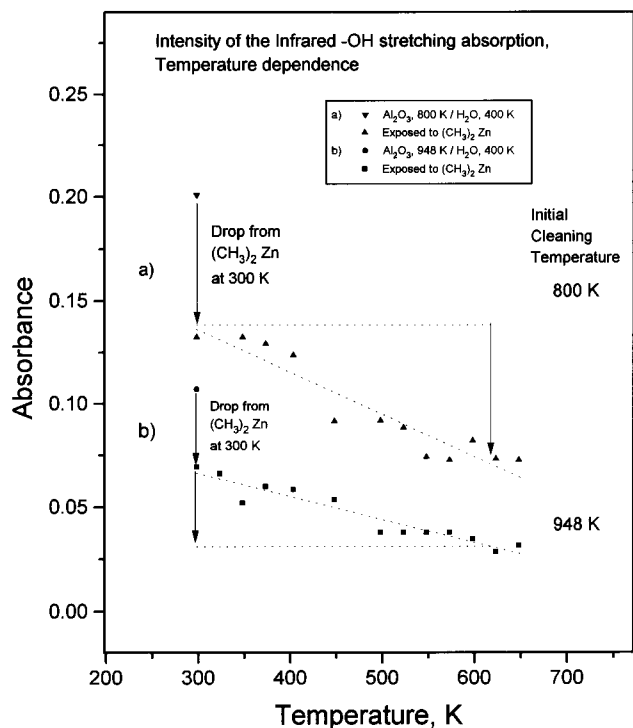**Figure 3.** Plot of the changes in the −OH stretching absorption intensity upon reaction of the prehydroxylated alumina surface with DMZ at 300 K and as a function of the in vacuo annealing temperature for two alumina samples with different initial extent of hydroxylation: (a) sample cleaned at 800 K for 8 h in vacuo, rehydroxylated by two exposures to saturated H_2O vapor (~20 Torr, ~ 2 min each) at room temperature and annealed for 2 h at 400 K in vacuo to remove molecular water before DMZ dosing; (b) cleaned at 948 K for 12 h, exposed twice to H_2O (~20 Torr, 2 min each exposure) at room temperature and annealed for 2 h at 400 K. Note that the pellet treated at 948 K for 12 h has nearly half the initial extent of hydroxylation as the sample in (a).

remaining chemisorbed on the alumina surface at lower temperatures in addition to the predominating monomethylzinc surface species.

The temperature dependence of the corresponding lower-frequency methyl bending region between 1250 and 1125 cm^{-1} is presented in Figure 4. The 1180 cm^{-1} peak is assigned to a $CH_3-Zn-O(s)$ species (Table 1) and demonstrates that the majority of the surface methyl species are still bound to zinc atoms, at least up to 473 K. A corresponding higher frequency mode near 1274 cm^{-1} (Table 1, not shown) has much lower intensity but shows a very similar temperature dependence. The other feature noted at ~1210 cm^{-1} is very close to the corresponding methyl bending mode of methylaluminum surface species[22,23] formed on alumina by reaction with trimethylaluminum. On the basis of this similarity, this peak is assigned to surface methyl groups, bound directly to strong alumina Lewis acid sites. Reaction of DMZ with an alumina surface that has nearly twice as high an initial extent of hydroxylation under otherwise identical conditions gives rise to a ~1210 cm^{-1} peak with ~50% of the intensity on the more dehydroxylated surface. Such Al−CH_3 surface species also have been found on alumina following room-temperature adsorption of trimethylgallium and their surface concentration has been related to the initial concentration of the alumina Lewis acid sites.[30]
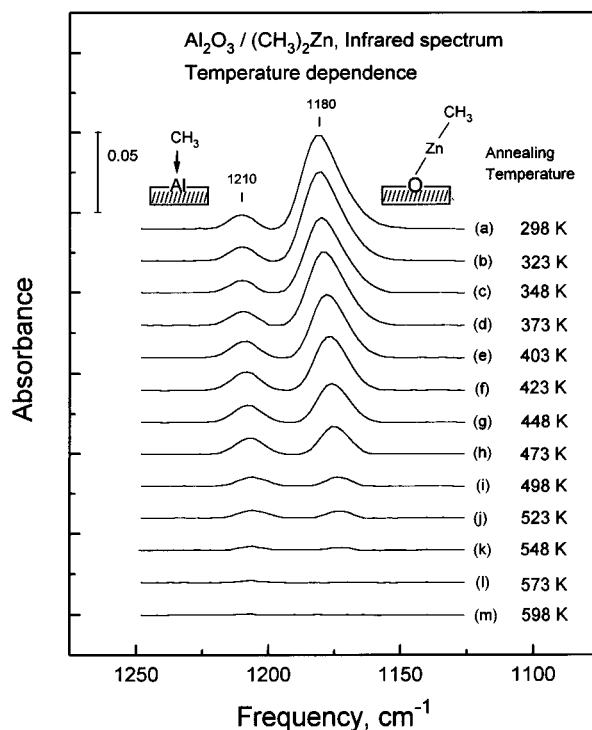

Figure 4. Baseline-corrected infrared spectra displaying the bending region between 1250 and 1125 cm^{-1} characteristic of the surface species formed on prehydroxylated alumina following DMZ dosing, displayed as a function of temperature: (a) Pellet exposed to DMZ and evacuated to 3×10^{-6} Torr at room temperature. Spectra b−m are taken after annealing the sample in vacuo at the temperature displayed adjacent to each spectrum and allowing the sample to cool to room temperature.

It has been shown previously that surface Lewis acid−base pair sites and defect sites are created during thermal dehydration of alumina.[29,30] Most of them are consumed during the reverse process of rehydroxylation at room temperature, but the completion of this process appears to depend on the pretreatment temperature (see above). Therefore, a lower extent of hydroxylation in these experiments also means a correspondingly higher number of free Lewis acid sites and vice versa. In light of this argument, the lower intensity of the ~1210 cm^{-1} methyl bending mode at higher initial extent of alumina hydroxylation is fully consistent with our assignment, since the number of available Lewis acid sites in this case is much smaller.

The temperature-dependent behavior of the intensity of this methyl mode at ~1210 cm^{-1} ($CH_3-Al(s)$) is shown in Figure 5 for aluminas dehydroxylated at different temperatures and, again, confirms this assignment. The initial increase in intensity for both samples with smaller (Figure 5, trace a) and larger (Figure 5, trace b) extents of initial hydroxylation implies that some Zn-bonded CH_3 groups are transferred from Zn to Al surface atoms upon annealing up to ~500 K in vacuo, while the intensity of ~1180 cm^{-1} mode of the surface methylzinc species decreases steadily until completely removed at 573 K (Figure 4, spectrum l). The slight shift of the methylzinc bending mode to lower frequencies may be due to the heterogeneity of the

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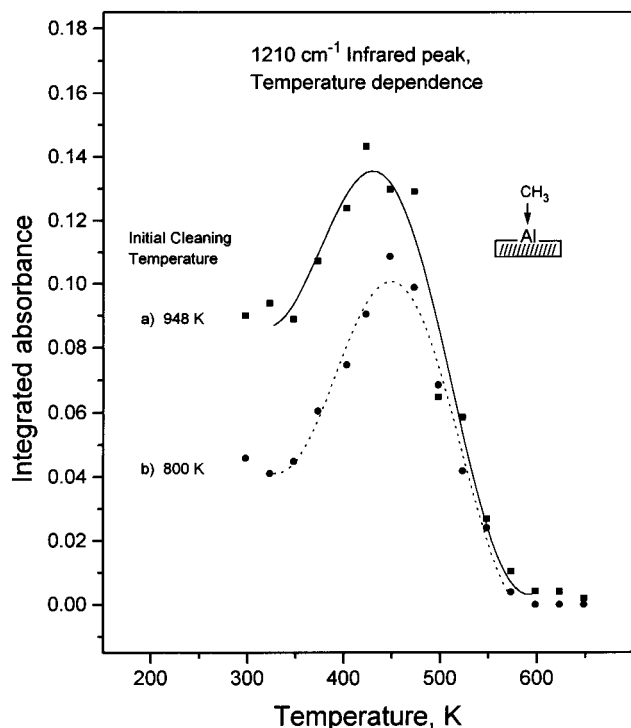
Figure 5. Plot of integrated absorbance of the 1210 cm^{-1} infrared feature as a function of the annealing temperature in vacuo for the two alumina samples with different initial extent of hydroxylation: (a) sample cleaned at 948 K for 12 h in vacuo, rehydroxylated, and exposed to DMZ at room temperature; (b) cleaned at 800 K for 8 h in vacuo, rehydroxylated, and exposed to DMZ at room temperature.

surface sites. At temperatures higher than 448 K, when 65 ± 2% of the methylzinc surface species absorbing at ~1180 cm^{-1} are already removed (Figure 4, spectrum g), the intensity at ~1210 cm^{-1} starts decreasing gradually (Figure 5), showing that the surface methyl groups bound to strong alumina Lewis acid sites disappear under these conditions. The fact that the maxima for both samples (Figure 5, traces a and b) with different extent of hydroxylation occur at approximately the same temperature implies that these Al−CH$_3$ surface species indeed involve strong, and not easily accessible, alumina Lewis acid sites. Small amounts of such unreactive methyl species are also observed in the study of methanol reaction with surface methylaluminum species,[6] where some Al−CH$_3$ species (isotopically distinguished from the resulting deuteriomethoxide species) persist on the surface even after dosing with methanol at up to 523 K. Note that the 1180 cm^{-1} methylzinc bending mode decreases by more than 80% in intensity upon annealing up to 473 K and disappears at somewhat lower temperature than the 1210 cm^{-1} Al−CH$_3$ bending mode (Figure 4, spectra k−m), emphasizing the different stabilities of these surface Al−CH$_3$ and Zn−CH$_3$ species.

Reaction of Ethanethiol, CH$_3$CH$_2$SH, with Dimethylzinc Pretreated Alumina Surfaces. Large amounts of methane, comparable to that evolved during the initial room-temperature reaction of DMZ with the prehydroxylated alumina surface, are detected in the gas-phase infrared spectra upon exposing a DMZ-treated sample to a saturated vapor of ethanethiol (~545 Torr) at room temperature. New surface species remain on the surface following subsequent evacuation at room temperature (Figure 6 A, spectrum a) and the intensity

of these features is more than an order of magnitude larger than for similar spectra found in the absence of DMZ (Figure 1, spectrum a). The overall transparency of alumina is greatly decreased over the entire accessible spectral range. This is gradually recovered at higher temperatures.

Figure 6 displays the C−H bending region of the infrared spectrum (between 1650 and 1200 cm^{-1}) for a DMZ-pretreated alumina sample exposed to ethanethiol vapor, shown as a function of in vacuo annealing temperature. The infrared modes at ~1448, ~1434, ~1374, and ~1262 cm^{-1} are assigned to the −CH$_2$− scissoring, the CH$_3$− asymmetrical bending (shoulder), the CH$_3$−symmetrical bending, and the −S−CH$_2$− waging modes respectively of the hydrocarbon skeleton of an ethanethiol molecule.[27,28] Since negligibly small amounts of EtSH adsorb directly on the prehydroxylated alumina surface under these conditions (Figure 1), the very high intensity of these bending modes (Figure 6A), together with the extensive methane evolution at both steps, indicates that thiol molecules react with the monomethylzinc surface species (originating from DMZ at the first deposition step) to form surface Zn-bound ethanethiolate species. Nevertheless, these infrared frequencies would also be characteristic of ethanethiol, molecularly coordinated to surface Zn atoms. The intensity of all bending modes remains rather constant up to 398 K (Figure 6A, spectra a−e) but decreases by nearly 50% upon annealing up to 448 K (Figure 6A, spectrum g) and diminishes further at higher temperatures until thiolate species are completely removed at 573 K (Figure 6B, spectrum l). This results in the formation of coke deposits characterized by the broad features near ~1578 and ~1466 cm^{-1} and small peaks at ~1356 and ~1270 cm^{-1}. The first two features strongly resemble those observed as high-temperature products from surface methoxy species formed from methanol on alumina,[31,6] which are attributed to surface formates. Such formate species are reported to form on alumina upon thermal decomposition of (CF$_2$H)$_2$O[32] as well. Carboxylate species have been found by infrared spectroscopy on alumina following adsorption of longer chain (C$_1$ through C$_4$) alcohols and annealing above 423 K.[33] Similar features have been observed near 1580 and 1460 cm^{-1} after exposure of alumina to acetylene at 523 K and have also been attributed to surface carboxylate species.[34] It is quite possible that the intense mode at ~1578 cm^{-1} arising from the thermal treatment of thiolate species in our experiment (Figure 6B) illustrates the formation of monothiocarboxylate species incorporating an oxygen atom from the alumina surface. This is in full agreement with the results of Lavalley et al.,[35] where thiocarbonate species (absorbing at 1570 and 1340 cm^{-1}) are observed after coadsorption of CO$_2$ and H$_2$S on alumina. According to the infrared absorption frequencies reported for the monothiobenzoates of Cr, Ni, Zn, Cd, Hg, Cu, Ag,[36,37] and Ni−thioacetate,[38] such monothiocarboxylate species in bridging or bidentate
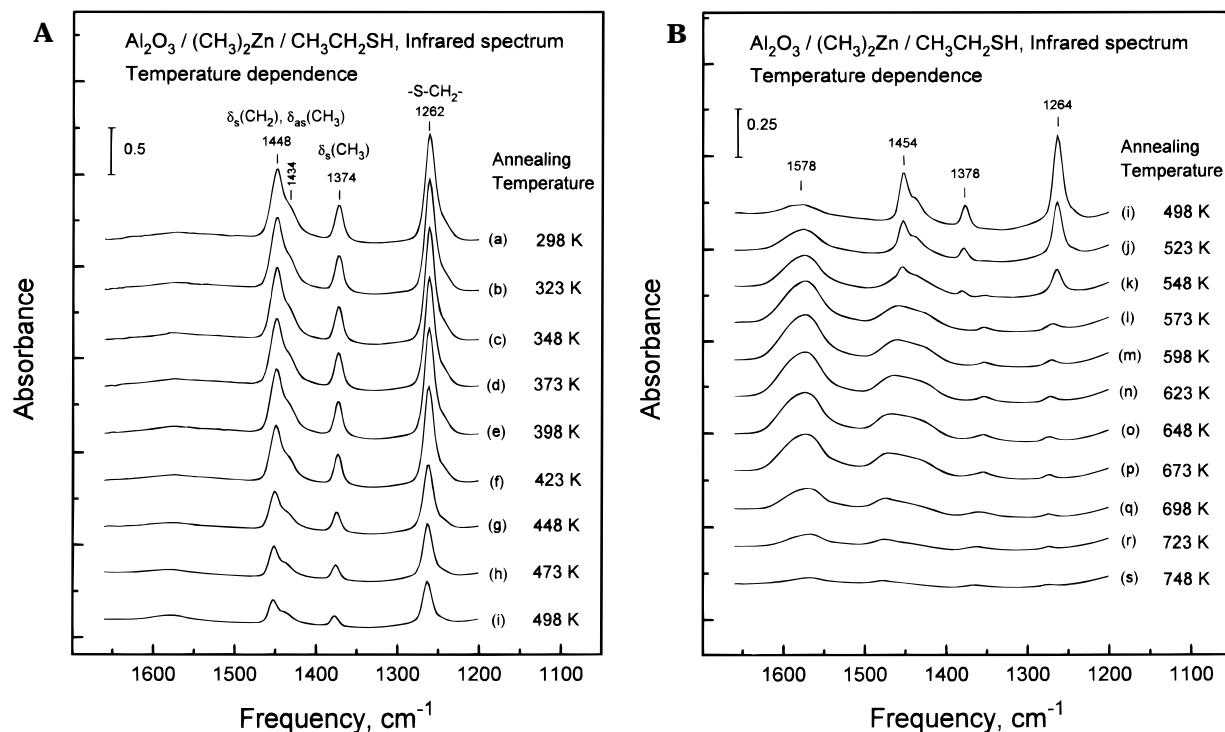
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Figure 6. Baseline-corrected infrared spectra in the bending region between 1650 and 1200 cm^{-1} of the surface species formed following the sequential reaction of DMZ and C_2H_5SH with alumina pellet cleaned at 800 K in vacuo for 4 h, rehydroxylated twice with H_2O, evacuated to 3×10^{-6} Torr at room temperature, and annealed in vacuo at 400 K, shown as a function of increasing in vacuo annealing temperature: (a) exposed to ~344 Torr of DMZ at room temperature, evacuated to 3×10^{-6} Torr, then exposed to ~545 Torr of C_2H_5SH, and evacuated to 3×10^{-6} Torr at 298 K. Spectra b–s are recorded after annealing of the pellet in a closed cell for 30 min to collect the desorbing gas-phase products and then outgassing for another 30 min at the temperature displayed adjacent to each spectrum.

coordination are likely to have the stretching mode of their C=O group near 1580 cm^{-1} if the Zn–S bond is not completely broken during this process. Of course, these modes may grow along with modes of other coke deposits. Unfortunately, the infrared absorption region of the characteristic metal–sulfur, metal–oxygen, and carbon–sulfur bonds is obscured by the alumina lattice modes, and this structure cannot be unequivocally confirmed in these experiments. Upon further annealing at higher temperatures up to 748 K in vacuo, the intense broad features at ~1570 and 1476 cm^{-1} disappear, leaving, most probably, deposits of infrared-transparent ZnS on the surface. These cannot be detected in this experiment but are reported to be the final product from thermolysis of many different zinc thiolates.[8-13]

It is known from earlier work[39,40] that the stretching (ν(Zn–Me)), rocking (ρ(Zn–CH$_3$)), and the lower-frequency methyl bending modes (δ(CH$_3$)) in the infrared spectra of solid methylzinc complexes are sensitive to coordination of different O-, N-, and S-containing ligands to the Zn center. More recent detailed matrix isolation and cryogenic thin-film spectroscopic studies[41-43] of the

interaction of DMZ with group V and VI alkyls, hydrides, methanol, and methanethiol have been able to distinguish both 1:1 and 1:2 complexes of DMZ with these ligands. Unfortunately, again due to the high-intensity alumina lattice modes below ~1000 cm^{-1}, the methyl rocking, and the ν(Zn–C) stretching modes cannot be observed in our transmission infrared experiment. The only accessible mode, which is still sensitive to coordination, is the lower frequency, methyl bending mode, δ(CH$_3$), of the Zn-bound methyl groups, which shifts to about 1164 cm^{-1} upon coordination of methanethiol to the Zn center of DMZ[43] or even further to 1156 cm^{-1} upon coordination within the structure of different polymeric and oligomeric monomethylzinc thiolates.[39]

A broad, low-intensity feature with a maximum near 1156 cm^{-1} is noted in our experiments upon reacting the DMZ-pretreated surface (Figure 7, spectrum a) with EtSH at room temperature (Figure 7, spectrum b). On the basis of the proximity of the frequency of this broad feature at ~1156 cm^{-1} to those of sulfur-coordinated Zn–CH$_3$ species observed in the previous studies, this small peak is attributed to some still unreacted methylzinc intermediates, which have Zn-coordinated EtSH molecules. The broad appearance of this feature most probably indicates a variety of 1:1 and 1:2 adducts, but the low-frequency maximum at ~1156 cm^{-139} as well as the great excess of EtSH during the self-limiting room-temperature reaction[43] suggests that the majority of these surface species are bicoordinated, 1:2 Zn–thiol complexes. The assignment of this small feature to such an intermediate complex is confirmed by the fact that

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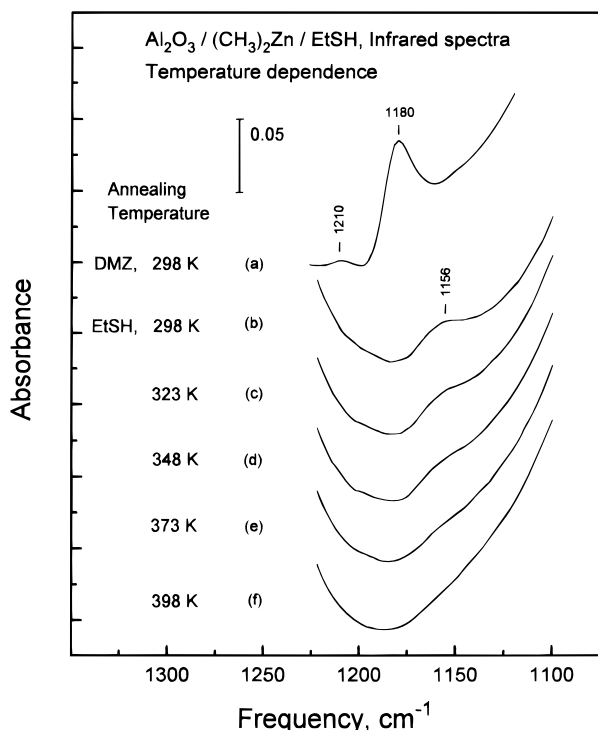(39) Coates, G. E.; Ridley, D. *J. Chem. Soc.* **1965**, 1870.
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Figure 7. Infrared spectra of the bending region between 1225 and 1100 cm^{-1} of the surface species formed following the sequential reaction of DMZ and EtSH on alumina as a function of annealing temperature: (a) exposed to DMZ and evacuated to 3×10^{-6} Torr at room temperature; (b) then exposed to C$_2$H$_5$SH and evacuated to 3×10^{-6} Torr at room temperature; Spectra c–f are taken following annealing of the sample in the closed cell for 30 min and then in vacuo for another 30 min at the temperature displayed adjacent to each spectrum.

its intensity gradually decreases with increasing temperature until it finally disappears at 398 K (Figure 7, spectra b–f) and is accompanied by significant methane evolution, illustrating the thermal decomposition of this complex up to 398 K (Figure 8, see below).

To monitor gas-phase products formed during the temperature-dependent study (Figure 6), the evacuated infrared cell is closed and any products desorbing from the alumina sample are collected and analyzed by infrared spectroscopy. Methane, ethanethiol, diethyl sulfide, and ethylene are the major products detected, and their relative concentrations in the gas phase are measured from the intensity of their most distinct characteristic infrared peaks at ~3016 cm^{-1} for methane,[23] ~1260 cm^{-1} for ethanethiol and diethyl sulfide,[28,44] and ~950 cm^{-1} for ethylene.[45] The intensities of these peaks are plotted as a function of the annealing temperature in Figure 8. Dashed lines below each of these curves indicate the baseline. It is difficult to distinguish between EtSH and Et$_2$S, since they both have their most intense –S–CH$_2$– waging mode near 1260 cm^{-1}. An attempt was made to use the frequency differences between their weaker skeletal modes at ~1100, ~980, ~878, and ~672 cm^{-1} for EtSH and at ~1079, ~978, ~783, and ~700 cm^{-1} for Et$_2$S. This

indicates that a very small amount of EtSH, with some traces of Et$_2$S, desorbs at 423 K (Figure 8A). At higher temperatures, only the first two modes are observed due to the intense absorption of C$_2$H$_4$ at ~950 cm^{-1}, but nevertheless the peak at ~1079 cm^{-1} is not obscured. It is clearly seen (Figure 8A) that in the low-temperature range between 300 and 400 K, only methane is evolved, most probably, as noted above, due to the completion of the reaction between monomethylzinc surface species with coordinated EtSH. The major amount of Et$_2$S desorbs between 448 and 573 K with two maxima at ~450 and 520 K together with some ethylene (Figure 8A). Et$_2$S desorption at the temperatures up to 523 K may be due to reactions between the surface zinc thiolate and possibly some molecularly adsorbed EtSH on the Zn centers and the C$_2$H$_4$ evolution (via β-hydride elimination from surface thiolate species) reaches its maximum intensity at 573 K. Some additional methane is evolved near 573 and 723 K, but much less than that formed in the temperature range 300–400 K (Figure 8A). Very small amounts of CO are also noted in the gas-phase spectra taken at these temperatures. Both CO and CH$_4$ detected at these high temperatures are likely to arise from thermal decomposition of some coke or (thio)carboxylate surface species as observed in the case of formate decomposition.[6]

To investigate the effect of water on the surface species formed on alumina from the sequential adsorption of DMZ and EtSH, another experiment is carried out on a somewhat less hydroxylated alumina (Figure 9). The sample is prepared by exposing the alumina to DMZ and ethanethiol and then annealing up to 398 K in vacuo to complete the reaction between Zn-bonded CH$_3$ groups and molecularly coordinated EtSH. The intensity of all characteristic surface modes (discussed above; Figure 9) arising from the sequential exposure to DMZ and EtSH at room temperature is somewhat lower on this alumina sample than observed during the previous experiment (Figure 6), consistent with its lower initial extent of hydroxylation. This is related to the fact that alumina samples with lower initial surface –OH concentration produce fewer intermediate monomethylzinc surface species for subsequent reaction with EtSH (see below). The sample is then exposed twice to 20 Torr of water vapor and evacuated at room temperature (Figure 9A, spectrum f). The intensity of all bending thiolate modes between 1500 and 1200 cm^{-1} is not significantly affected up to 398 K (spectra a–e) and decreases only slightly upon H$_2$O exposure and evacuation at room temperature (spectrum f). This is due, at least to some extent, to the lower alumina transparency caused by the extra adsorbed water, since both the initial peak intensity and the alumina transparency are essentially recovered by the subsequent annealing at 398 K in vacuo (spectrum g). This indicates that the resulting Zn–thiolate surface species are much more stable in an aqueous environment than the surface aluminum methoxide species formed by sequential deposition of trimethylaluminum and methanol,[6] which hydrolyze rapidly under these conditions. The first major loss of thiolate surface species occurs near 448 K (spectrum i) followed by their almost complete removal at 548 K (Figure 9B, spectrum n).

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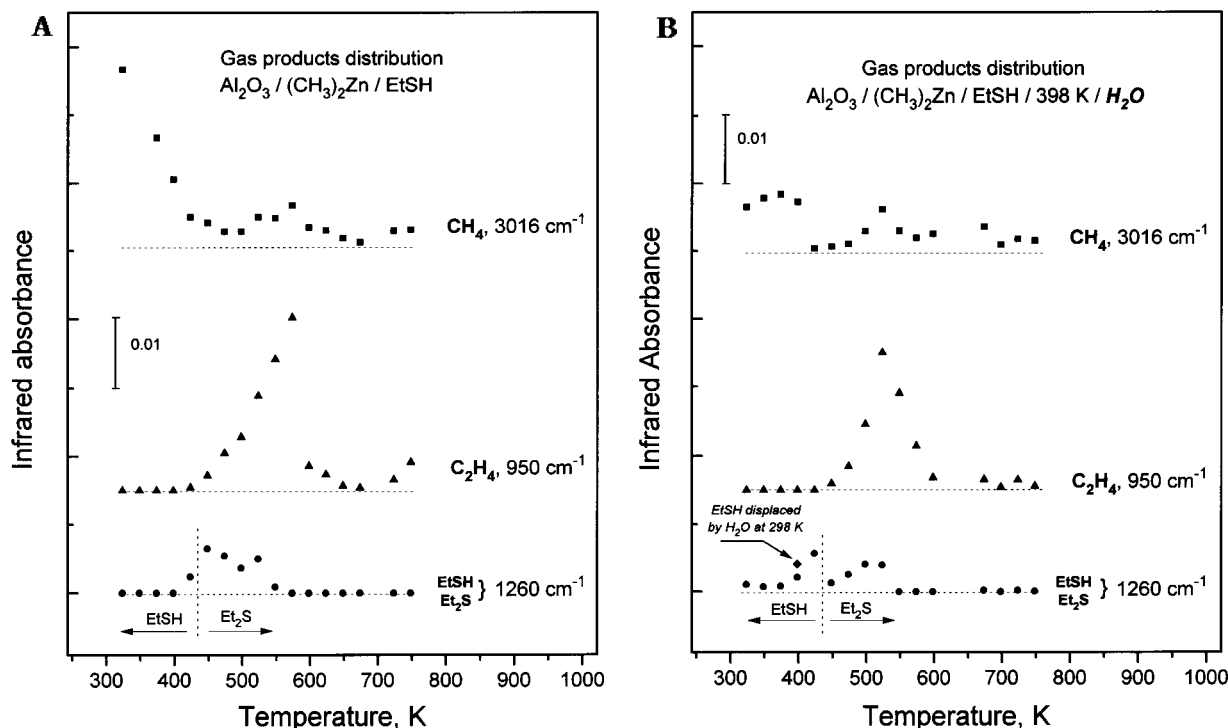
Figure 8. Thermal distribution of the major gas-phase products desorbing from the alumina pellets in the temperature range between 323 and 748 K following sequential adsorption of DMZ and EtSH at room temperature, measured by the intensity of the most distinct characteristic peak of each product as shown adjacent to each set of data points: (A) products desorbing from hydroxylated alumina sample corresponding to Figure 6 following sequential treatment with DMZ and EtSH vapor at room temperature; (B) products desorbing from less hydroxylated alumina, that has been cleaned at 800 K for 8 h, rehydroxylated with H_2O, and annealed at 400 K in vacuo, following sequential treatment with DMZ and EtSH at room temperature. After annealing in vacuo at 398 K and cooling to room temperature, the modified alumina surface has been exposed to ~20 Torr of H_2O for 1 min and held for 2 h in the closed IR cell at 300 K. The amount of EtSH desorbed into the gas phase is indicated as ◆.

The main effect of treating with water (compare Figure 8A and B) is found in the composition of the gas-phase products formed immediately after water exposure at room temperature. The fact that some EtSH desorbs at 400 K in Figure 8B but not in Figure 8A suggests that some extra EtSH may be molecularly adsorbed on the surface acid–base pairs of the less hydroxylated sample. The EtSH desorbed upon annealing at 423 K, following the H_2O exposure and evacuation (Figure 8B), is twice as much as that desorbed at the same temperature from the sample that has not been treated with H_2O (Figure 8A). The relatively small difference in the amounts of thiol desorbed at 423 K with and without water treatment suggests that water mostly displaces some EtSH, weakly bound to the surface, rather than hydrolyzing the anchored Zn–thiolate species under these conditions. From the water-treated alumina (Figure 8B), Et_2S desorbs mostly at 498–523 K and only a negligible amount of Et_2S is observed at 448 K, in contrast to the results from the more hydroxylated alumina sample (Figure 8A) which has *not* been exposed to H_2O. This will be discussed in greater detail below. The remaining gas-phase products show similar temperature-dependent distribution in both experiments.

Significant changes in the overall shape and some frequency shifts of the C–H stretching modes are observed when the DMZ-reacted alumina surface is exposed to EtSH (Figure 10, spectra a and b). New C–H stretching modes appear with nearly equal intensity at ~2960, ~2922, and ~2864 cm^{-1} (Figure 10b) and shift very slightly to higher frequencies (~2964, ~2928

and ~2872 cm^{-1}) upon annealing up to 398 K. At higher temperatures the mode at ~2872 cm^{-1} disappears first (at 523 K) followed by the other two modes at 548 K.

In addition, two very broad features appear partially superimposed on the C–H stretching modes in this region following DMZ/EtSH exposure (Figure 10b), but their intensity is at least an order of magnitude higher than that observed without DMZ dosing. The first continuous absorption, starting at about 3460 cm^{-1} with increasing intensity toward the lower frequencies is attributed (by analogy with that observed upon direct thiol adsorption on alumina[14]) to the existing surface −OH groups of alumina, perturbed by extensive surface hydrogen bonding with the sulfur atoms of adsorbed thiol molecules. The other feature (below ~2600 cm^{-1}) is proposed to be due to the S–H stretching mode observed at ~2592 cm^{-1} in the gas-phase spectrum of EtSH. Its broad appearance with increasing absorbance to lower frequencies may be caused by extensive surface hydrogen bonding between Zn-coordinated EtSH molecules and surface −OH groups of alumina. With increasing temperature up to 373 K (Figure 10, spectra b–e), the broad surface −OH stretching absorption does not change significantly in intensity, while a decrease in the intensity of the proposed surface hydrogen-bonded S–H groups is clearly noticeable. This may be related to the decomposition of the remaining methylzinc−thiol intermediate by methane elimination to form zinc thiolate surface species. This process selectively decreases the surface concentration of S–H groups. Some desorption of the extra, molecularly coordinated
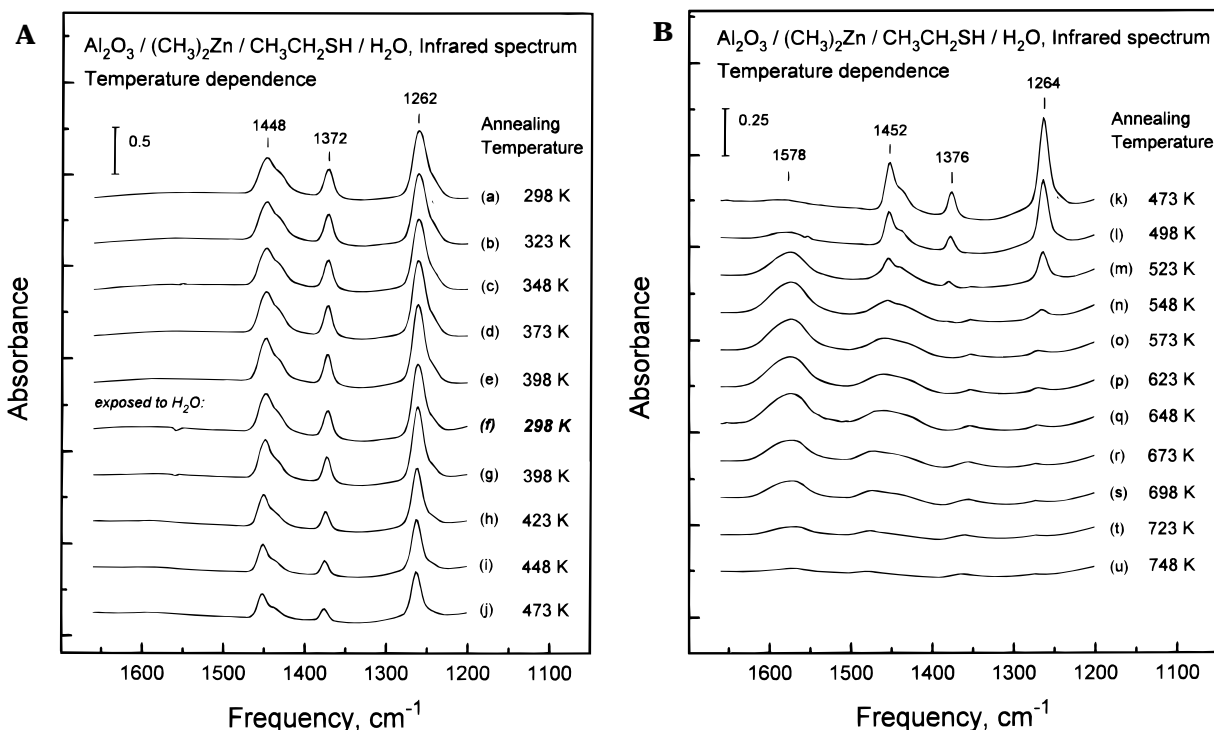
Figure 9. Baseline-corrected infrared spectra in the bending region between 1650 and 1200 cm^{-1} of surface species formed following sequential reaction of DMZ and EtSH at room temperature on alumina substrate, shown as a function of increasing temperature (spectra a–e); (f) sample exposed twice to saturated H$_2$O vapor (~20 Torr for 1 min and held in the closed IR cell for 2 h following each exposure) and then evacuated to 3 × 10^{-6} Torr at room temperature. Spectra g–u are collected after annealing the sample in a closed cell for ~30 min and then for another 30 min in vacuo at the temperature displayed adjacent to each spectrum and cooling to room temperature.

EtSH is also noted in the gas-phase spectra at 398 K (Figure 8B) which slightly changes the surface −OH stretching intensity as well. As a result of these processes, the C−H stretching modes appear with much higher intensity at 398 K (Figure 10f) compared to the initial spectrum at room temperature (Figure 10b), even though the pellet is exposed to no additional ethanethiol. Adsorption of water at room temperature following annealing at 398 K significantly increases the broadness and overall intensity of both −OH and −SH stretching absorptions almost completely obscuring the C−H stretching modes (Figure 10g). These gradually recover their initial intensity upon annealing in vacuo up to 423 K (Figure 10h and i) while some more molecular EtSH and H$_2$O desorb into the gas phase (Figure 8B). This indicates the formation of new surface hydrogen bonds upon H$_2$O exposure which are broken at higher temperatures. In addition, a broad feature is noted at 1940 cm^{-1} (not shown), but without additional evidence no firm assignment of this feature can be made to perturbed SH groups because of the extremely low frequency of this mode.

To test the stability of the surface species formed by sequential reaction of DMZ and EtSH on alumina at 300 K, a DMZ/EtSH-treated sample was exposed to air at room temperature, first for about 17 h following dosing with water and evacuation at room temperature. *No* significant decrease of the characteristic bending modes was observed. Another sample was annealed in vacuo to 423 K following the DMZ/EtSH deposition cycle and then exposed to air for 6 days. Some organic impurities adsorbed on the surface and obscured the ~1450 and ~1374 cm^{-1} bending modes, but the −S−

CH$_2$− wagging mode was still clearly seen, indicating a relatively small loss of intensity. Despite the different exposure times in these two experiments, this result illustrates the importance of the EtSH additionally coordinated to the surface zinc centers for providing a denser protective layer on the surface. A clearly evident low-intensity feature at ~1650 cm^{-1} indicated some molecular water adsorption in both cases. It disappeared on heating to 398 K, and the characteristic thiolate IR pattern was recovered upon further annealing in vacuo to 473 K with some slight loss in intensity.

Discussion

A comparison of the amount of methane evolved at each step of the DMZ/EtSH deposition cycle (Figure 3) along with the infrared spectra (Figures 1, 4, and 6) indicate that (CH$_3$)$_2$Zn adsorbs on hydroxylated alumina, predominantly by reaction with surface hydroxyl groups, to evolve methane and anchor a Zn−CH$_3$ species to the surface. The second methyl species appears to be less reactive and must be heated to ~600 K before all remaining methyl species are removed. This behavior is directly analogous to that found for trimethylaluminum on alumina[22,23] where the first methyl group was found to react significantly more rapidly than the rest. In addition, the methyl migration from zinc to aluminum sites is found (Figures 4 and 5).

Such migration of surface CH$_3$ groups from Zn surface atoms to Al Lewis acid sites is not surprising since it is well-known that DMZ is easily dissociated by ultraviolet radiation (193 nm)[46,47] generating free CH$_3$ radicals or by a pulsed electrical discharge[48] giving rise to ZnCH$_3$
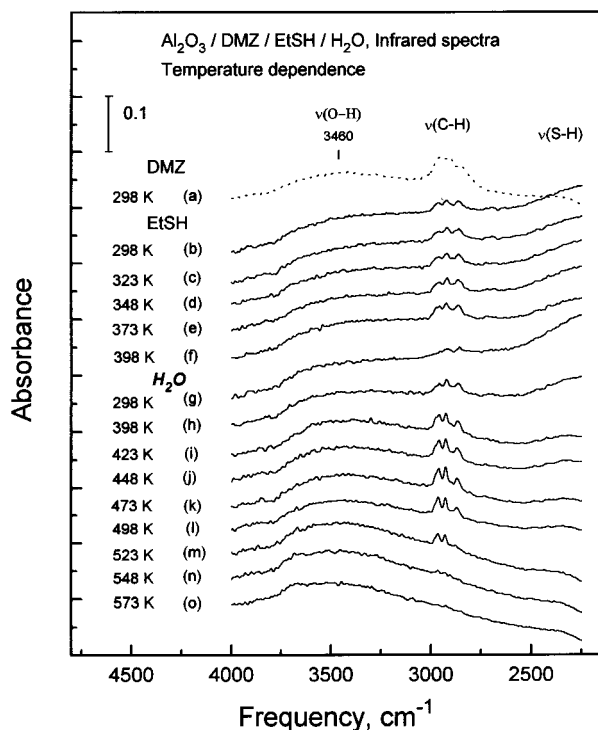
Figure 10. Stretching region of the infrared spectra of the surface species formed on a prehydroxylated alumina surface following sequential adsorption of DMZ and EtSH at room temperature: (a) exposed to DMZ (~344 Torr) at room temperature and evacuated to 3×10^{-6} Torr; (b) then exposed to EtSH (~545 Torr) at room temperature and evacuated to 3×10^{-6} Torr. Spectra c–o are collected following annealing of the sample in the closed IR cell for ~30 min and evacuation for another 30 min at the same temperature, displayed adjacent to each spectrum.

radicals. DMZ has been found to adsorb molecularly only at very low temperatures (80–100 K) on surfaces such as Si, GaAs, and Pt[49–54] and decomposes at about 200–275 K (450 K for Si substrate), giving rise to surface Zn and CH3 species. On alumina, a large proportion of the resulting surface methyl species remains bound to Zn atoms as evidenced by the intensity of the bending feature at ~1180 cm^{-1} (Figure 4). In the case of Pt (111), an adlayer of Zn–CH3 surface species is formed by dissociative adsorption at 300 K,[53] and these species are found to be stable up to around 350 K. The main thermal decomposition pathway for surface methyl groups formed by dissociative adsorption of DMZ on an As-rich, GaAs (100)-c(4 × 4) surface was recently reported[54] to be mainly via desorption as methyl radicals between 500 and 720 K.

Such weakly bound methyl species on the alumina surface are much more likely to encounter an acidic surface –OH group and react evolving methane before being "trapped" at strong Lewis acid sites due to the

high initial extent of hydroxylation. This is reflected by the fact that the increase in the area of Al–CH3 bending mode at ~1210 cm^{-1} is at least an order of magnitude smaller than the corresponding decrease in the area of the Zn–CH3 bending mode at ~1180 cm^{-1} caused by the decomposition of these surface species (Figure 4). The significant decrease in the –OH stretching absorbance of a DMZ-reacted alumina surface at relatively low temperatures (Figure 2) strongly suggests such a secondary reaction of a surface monomethylzinc species with the neighboring –OH groups. The Al–CH3 surface species are more stable than Zn–CH3 groups and disappear at higher temperature (548 K), similarly to those species formed from trimethylaluminum on alumina.[22,23] Note that metal alkyls are also used as cocatalysts in olefin metathesis reactions where carbene species (CH2)(ads) are proposed to form the active catalytic sites. Such methyl group transfer as observed here and subsequent dehydrogenation is likely responsible for their activity.

Following the analysis of our data, the major pathway for the reaction of DMZ on prehydroxylated alumina surface may be illustrated by the following scheme:
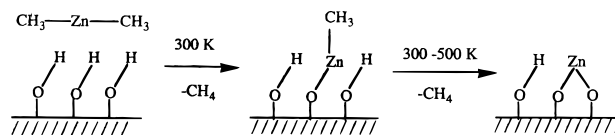
Even though the majority of the CH3–Zn–O(s) species react with EtSH at room temperature, as evidenced by the disappearance of their characteristic peak at ~1180 cm^{-1} (Figure 7, spectra a and b), a small amount of methylzinc–thiol coordination intermediate remains on the surface at 300 K as evidenced by the 1156 cm^{-1} feature (Figure 7). These species further decomposes at temperatures up to 398 K. Its relatively low-frequency infrared mode at ~1156 cm^{-1} suggests the presence of a methylzinc surface species with two thiol molecules coordinated to the Zn atom, even though the breadth of this feature indicates that not only are a variety of surface sites with different strengths involved, but also monocoordinated CH3–Zn–O(s) species may exist under these conditions, as well. It is also quite possible that the CH3–Zn–O(s) surface species, which have reacted with EtSH at 300 K evolving methane and forming a surface Zn–thiolate, can coordinate one or two EtSH molecules. Both coordinated thiol molecules may form hydrogen bonds with the neighboring surface –OH groups as evidenced by the broad –OH and –SH stretching absorptions (Figure 10).

From the temperature-dependent spectra of the alumina samples (e.g., Figure 7) and the products collected in the gas phase (Figure 8), it can be concluded that over the 298–373 K temperature range, mainly methylzinc–thiol coordination intermediates thermally decompose together with some hydrogen bond cleavage, since methane is the only gas-phase product detected, and the remaining Zn-bound methyl species (Figure 7) are completely removed at 398 K, while the intensity

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of the perturbed ν(S−H) feature in the surface spectra is significantly lowered, as expected from the Zn−thiolate formation reaction. This suggests that dense layers of thiolate species may be formed on samples with high initial hydroxyl concentrations upon annealing the DMZ-treated surface at ~373 K under saturated EtSH vapor and cooling the sample to 300 K in the EtSH environment.

Upon annealing at 398 K in vacuo, hydrogen bonds between Zn-coordinated thiol molecules and surface −OH groups undergo further cleavage, and in the case of less hydroxylated samples, some thiol desorbs into the gas phase (Figure 8B and Figure 10). Additional thiol evolution is noted following H_2O dosing at room temperature and annealing up to 423 K (Figure 8B), which suggests that some EtSH is displaced from the surface by water. This result is in agreement with a matrix isolation study[43] that suggests that methanethiol in a DMZ−CH_3SH complex is relatively weakly bound, compared to similar DMZ−CH_3OH complexes.

Significant amounts of Et_2S are evolved from the sample that was not treated with H_2O over the entire 448−523 K temperature region (Figure 8A), with two maxima at 448 and 523 K, in contrast to the H_2O-exposed sample with a reduced surface concentration of molecularly coordinated thiol, where only one maximum is observed near 500 K (Figure 8B). This suggests that at lower temperatures (448 K), when the sample is not exposed to H_2O, Et_2S may form by reaction between Zn−thiolate species and molecularly coordinated thiol, while a reaction between two neighboring Zn−thiolate species is likely to be responsible for the Et_2S evolution near 523 K. Similar effects are reported

in a recent catalytic study[55] of methanol dehydration on alumina where the methanol−methoxy and methoxy−methoxy reaction channels are activated at different temperatures.

The C_2H_4 evolution near 550 K is likely to result from thermal decomposition of isolated Zn−thiolate species by β-hydride elimination.

Conclusion

Dimethylzinc reacts with surface hydroxyl species on alumina to form CH_3−Zn−O species and evolve methane into the gas phase. This is similar to results found previously for the adsorption of trimethylaluminum on hydroxylated alumina, where subsequent reaction of the methyl groups requires higher temperatures than initial reaction. The remaining methyl group can react with the active hydrogen of C_2H_5SH to evolve methane and graft a C_2H_5−S−Zn−O species to the alumina surface. This reaction is similar to that found previously for alcohols. The *alkoxy* species formed in this way were found to react with water. In contrast, the R−S−Zn−O species formed in this work are much less reactive with water or air and may provide a possible synthetic strategy for the formation of protective layers.

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