

Infrared Spectroscopy of Trimethylaluminum and Dimethylaluminum chloride Adsorbed on Alumina

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The species formed by adsorption of trimethylaluminum and dimethylaluminum chloride on γ -alumina that has been dehydroxylated at 400 K are identified using infrared spectroscopy. Gas-phase trimethylaluminum dimer is proposed to adsorb via reaction of the bridging methyl groups forming adsorbed dimethylaluminum. A small amount of dimer is also found on the surface immediately following exposure to trimethylaluminum, but this is removed by prolonged evacuation at room temperature. Adsorbed mono- and dimethylaluminum species are distinguished by their corresponding peak profiles in the methyl bending region where, in the latter case, a splitting is found due to coupling between adjacent methyl species. Relative dimethyl- and monomethylaluminum coverages can be monitored as a function of annealing temperature where it is found that dimethylaluminum converts to monomethylaluminum by reaction with surface hydroxyl groups and evolving methane. The remaining methyl group in the monomethylaluminum surface species reacts in a similar manner with surface hydroxyl species to form methane but is found to be significantly less labile than the dimethylaluminum species. A similar reaction pathway is also found for dimethylaluminum chloride. The surface species formed from dimethylaluminum chloride, however, react more rapidly than those formed by trimethylaluminum adsorption.

Introduction

Metal alkyls provide an important class of volatile precursors for the growth of inorganic thin films using a method generally known as organometallic chemical vapor deposition (OMCVD).¹⁻¹² These can react with non-metal hydrides to form the inorganic layer and to eliminate methane and are most often used for growing films of III-V compounds. In addition, aluminum oxide can be grown by a variant of this chemistry by the reaction of trimethylaluminum and water.¹³ This reaction has the advantage, from the point of view of fundamental studies, that it is sufficiently fast for alumina layers to be grown by this method both in ultrahigh vacuum as well as at higher pressures (~ 1 Torr) on high-surface-area alumina substrates. It has been previously demonstrated that the chemistry in

both regimes appears to be identical and can, therefore, be followed in ultrahigh vacuum on a planar alumina substrate or alternatively using high-surface-area powders to identify surface species using infrared spectroscopy.¹³ Alumina films can be grown in a controlled manner using this strategy by sequentially exposing the surface to trimethylaluminum (TMA) and water; each cycle forming an alumina layer approximately 1 Å thick.¹³ The stoichiometry of the reaction during each cycle is consistent with the initial formation of adsorbed dimethylaluminum due to the adsorption of trimethylaluminum on hydroxylated alumina. However, the adsorption of TMA on silica leads to the formation of monomethylaluminum as well as the deposition of methyl groups on silica sites.¹⁴⁻²² This chemistry can be followed on silica since distinct methyl stretching modes due to both Al-CH₃ and Si-CH₃ can be distinguished. Such direct experimental evidence is not possible on alumina surfaces since an analogous reaction on alumina leads to two identical Al-CH₃ species. To obtain direct experimental evidence for the existence of either mono- or dimethylaluminum species following trimethylaluminum adsorption on alumina and to in-

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investigate their relative reactivities, we take advantage of the splitting in the methyl bending modes of a dimethyl species compared to monomethyl group resulting from coupling between these modes. This is a well-known effect in the infrared analysis of organic compounds where a splitting of $\sim 10\text{ cm}^{-1}$ in the bending region of the spectrum is found for terminal methyl groups in 1,1-dimethylalkanes compared to *n*-alkanes.²³⁻²⁶ This effect is used to identify the nature of the surface species formed on hydroxylated alumina following trimethylaluminum adsorption where high-quality, high-resolution infrared spectra can be collected on the high-surface-area substrate.

Experimental Section

The experimental apparatus used to obtain infrared spectra has been described in detail in a previous publication.¹³ Briefly, a pressed γ -alumina pellet is mounted to the end of a transfer rod which is enclosed in an evacuable cell which operates at a base pressure of $\sim 1 \times 10^{-6}$ Torr. The γ -alumina is degassed in vacuo for 90 min to remove molecular water. The magnetically coupled sample mounting rod can be moved so that the alumina pellet is located either between two sodium chloride windows to allow infrared spectra to be collected or to be retracted into a tube furnace where the sample can be heated up to $\sim 1200\text{ K}$ in vacuo. The infrared cell is also connected to a gas-handling line to allow reactants to be introduced into the cell. Infrared spectra were collected using a Midac Fourier transform infrared spectrometer generally using a resolution of 0.5 cm^{-1} for 1000 scans, and the spectrum due to the background was substrated from the signal due to the pellet. Initial infrared spectra showed a broad feature due to surface hydroxyl species along with small peaks between 1300 and 1700 cm^{-1} which may be due to either a small amount of surface carbonate or residual water. The spectrum of the gas-phase species could be measured using the same apparatus merely by retracting the sample from the path of the infrared beam.

Both trimethylaluminum (Aldrich Chemicals; 97%) and dimethylaluminum chloride (Aldrich Chemical, 97%) were transferred into glass vials inside a nitrogen-filled glovebag using a syringe. Both were purified by repeated freeze/pump/thaw cycles and their purities determined using infrared spectroscopy. The major contaminant in both compounds was methane presumably arising from reaction with atmospheric water.

Results

Figure 2 displays the infrared spectra of gas-phase trimethylaluminum (TMA) and dimethylaluminum chloride (DMA) showing the methyl stretching region (between 2790 and 3000 cm^{-1}) and the methyl bending region (between 1150 and 1300 cm^{-1}). Ball-and-stick depictions of dimeric trimethylaluminum and dimethylaluminum chloride are shown in Figure 1. The general appearance of the methyl stretching regions is essentially identical, showing three peaks due to the symmetric and asymmetric methyl stretches and a Fermi resonance at lower frequencies. The asymmetric stretch for TMA is at 2944 cm^{-1} , whereas for dimethylaluminum chloride it is at a somewhat higher frequency

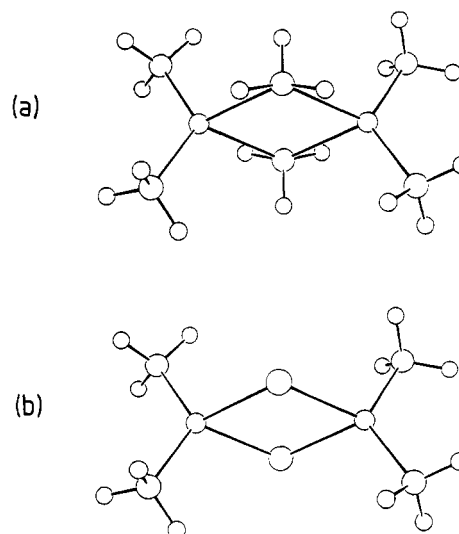


Figure 1. Ball-and-stick depictions of (a) trimethylaluminum dimer and (b) dimethylaluminum chloride dimer.

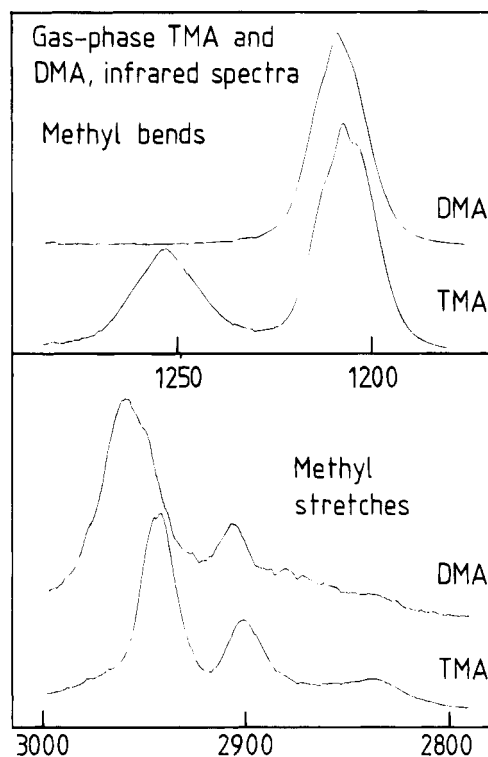


Figure 2. Infrared spectra of gas-phase trimethylaluminum (TMA) and dimethylaluminum chloride (DMA) showing the methyl bending region between 1150 and 1300 cm^{-1} and the methyl stretching region between 2790 and 3000 cm^{-1} .

of 2960 cm^{-1} . The symmetric stretch is at 2901 cm^{-1} in the case of trimethylaluminum and is at a slightly higher value of 2907 cm^{-1} for dimethylaluminum chloride. The Fermi resonances appear as a broad peak at $\sim 2835\text{ cm}^{-1}$.²⁷⁻²⁹ Shown also in this figure are the bending regions for both TMA and DMA and, in the former case, the spectrum exhibits peaks at $\sim 1254\text{ cm}^{-1}$ and a feature at $\sim 1207\text{ cm}^{-1}$ which consists of two peaks separated by $\sim 5\text{ cm}^{-1}$. This will be discussed in greater detail below. The corresponding region for DMA shows

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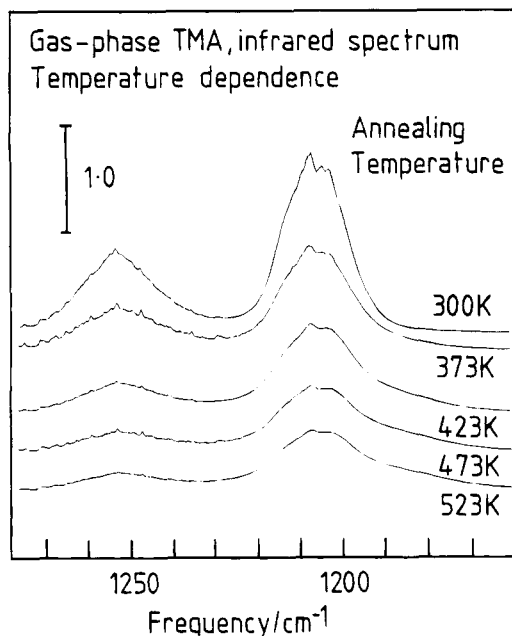


Figure 3. Infrared spectra of the bending region of gas-phase trimethylaluminum (TMA) displayed between 1160 and 1280 cm^{-1} as a function of temperature. The sample temperature is displayed adjacent to the corresponding spectrum.

only a single feature at a frequency of $\sim 1209 \text{ cm}^{-1}$; the 1254 cm^{-1} feature is completely absent. Since TMA exists as a dimer in the gas phase at room temperature, it contains two chemically distinct methyl species, the terminal methyl groups and the bridging methyl groups. Chlorine is the bridging group in DMA so that the peak at 1254 cm^{-1} is assigned to the bending modes of the bridging methyl group and the 1200 cm^{-1} modes to the terminal groups. This serves to point out the relative sensitivity of these bending modes to changes in the nature of the methyl groups. This assignment is further confirmed since the integrated intensity under the 1254 cm^{-1} peak is 0.51 ± 0.03 of the integrated intensity of the 1207 cm^{-1} state and therefore scales well with their relative abundances. The differences in methyl stretching frequencies for TMA and DMA (Figure 2) also suggest that the terminal methyl groups are modified by the presence of a bridging chlorine species. The bending modes appear to be less sensitive to this effect.

Features due to the terminal methyl groups at $\sim 1200 \text{ cm}^{-1}$, in fact, consist of two states at 1207 and 1203 cm^{-1} (split by $\sim 5 \text{ cm}^{-1}$). It is proposed that this splitting is due to coupling between adjacent methyl groups consistent with the existence of aluminum dimethyl species. To ensure that this splitting is not due to the combination of low-frequency skeletal modes with the bending modes (i.e., "hot bands"), the gas-phase TMA spectrum was recorded, using exactly identical spectrometer settings, as a function of temperature and the results are displayed in Figure 3. Here, both the 1254 and 1207 cm^{-1} peaks decrease in intensity as the temperature increases but the spectral profile remains essentially constant, with perhaps some loss in fine structure. These results indicate that the peak splitting is not due to "hot bands" and clearly indicates the existence of two states.

Figure 4 shows the methyl stretching region (between 2700 and 3300 cm^{-1}) for TMA adsorbed on alumina that has been pretreated at 400 K showing the characteristic

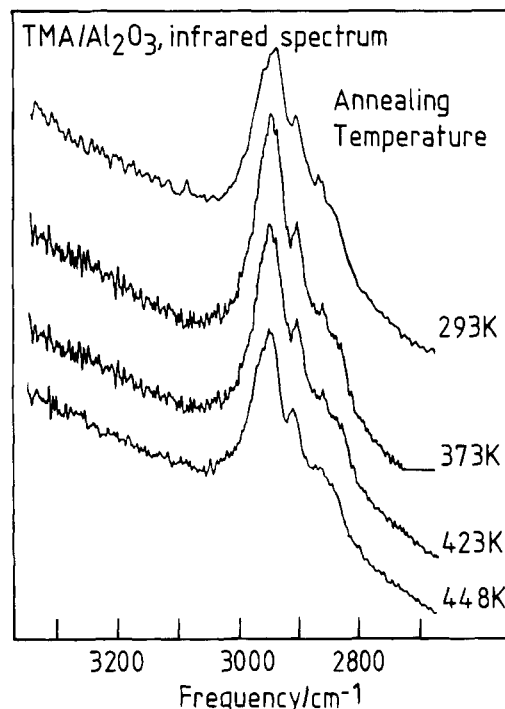


Figure 4. Infrared spectra between 2700 and 3300 cm^{-1} obtained following adsorption of trimethylaluminum (TMA) on alumina that has been pretreated at 400 K displayed as a function of annealing temperature. The annealing temperature is displayed adjacent to the corresponding spectrum.

three peaks due to the symmetric and asymmetric stretches and the Fermi resonance. The remaining spectra show the effect of heating the TMA-covered surface to various temperatures in vacuo. These spectra were collected by heating the sample to the temperature indicated adjacent to each spectrum for 30 min and then allowing the sample to cool to room temperature (still in vacuo) after which the spectrum was recorded. These methyl stretching features merely decrease in intensity uniformly as the temperature increases, indicating thermal decomposition of the surface species, but offer no indication as to the nature of any chemical changes occurring at the surface. Note that methane evolution is detected by infrared spectroscopy over the whole annealing range.

In contrast, similar spectra obtained in the methyl bending region (Figure 5) show significant changes in shape as a function of annealing temperature. Figure 5 displays the methyl bending region following TMA exposure to alumina that has been pretreated at 400 K as a function of annealing temperature. As with the spectra displayed in Figure 3, these spectra were obtained by annealing the sample at the indicated temperature for a period of 30 min in vacuo, then allowing the sample to cool, following which the spectrum was recorded. The top two spectra are both due to TMA adsorbed on alumina at 293 K . However, the top spectrum was recorded after 10 min of evacuation following TMA exposure and the second spectrum after 30 min of evacuation. The top spectrum exhibits a broad feature centered at $\sim 1200 \text{ cm}^{-1}$ and a much smaller feature at $\sim 1250 \text{ cm}^{-1}$. The latter peak is due to bridging methyl groups (see Figures 1 and 2) and indicates the existence of some TMA dimer on the surface. The presence of dimeric TMA following adsorption on alumina has been inferred previously using

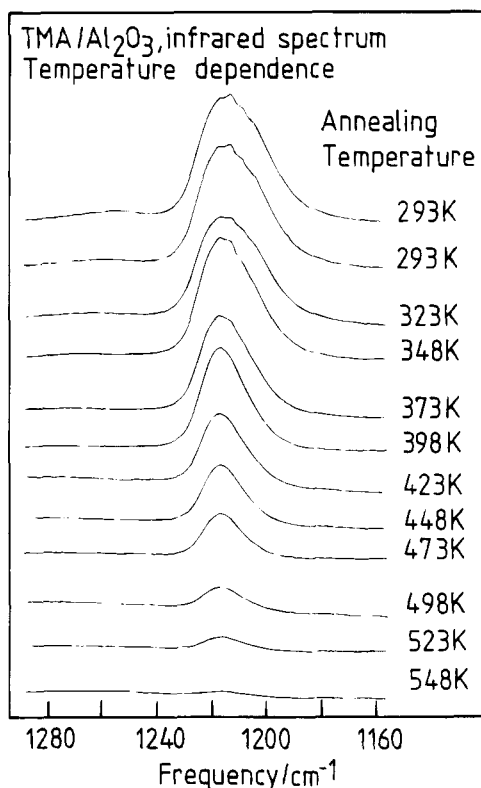


Figure 5. Infrared spectra between 1150 and 1300 cm^{-1} obtained following adsorption of trimethylaluminum (TMA) on alumina that has been pretreated at 400 K displayed as a function of annealing temperature. The annealing temperature is displayed adjacent to the corresponding spectrum. The top spectrum (293 K) is collected after 10 min evacuation following exposure to TMA and the second spectrum (at 293 K) after 30 min evacuation.

XPS.³⁰ This species is, however, relatively weakly bound since further evacuation at room temperature (the second spectrum in Figure 5) leads to a further diminution in intensity of this state without any noticeable decrease in intensity of the 1200 cm^{-1} peak. In any case, the contribution of intensity to the 1200 cm^{-1} feature from dimeric TMA is likely to be very small, since its integrated intensity is only twice that of the 1250 cm^{-1} peak. The infrared data indicate that a monomeric aluminum methyl species is present on the surface at room temperature.

The 1200 cm^{-1} feature is rather broad following adsorption at 293 K (Figure 5) with a peak maximum located at 1208 cm^{-1} . As the sample temperature is raised, the peak shifts slightly to higher frequencies and becomes narrower, so that, after annealing to 423 K the peak maximum is at 1218 cm^{-1} . Further heating to 548 K merely leads to a diminution in intensity, so that all methyl species are essentially completely thermally removed by heating to 570 K. This temperature range for the removal of surface methyl species agrees with the attenuation noted from spectra of the methyl stretching region (Figure 4), and this will be discussed in greater detail below. A similar change in spectral profile has also been noted for TMA adsorption on dehydroxylated alumina.^{31,32}

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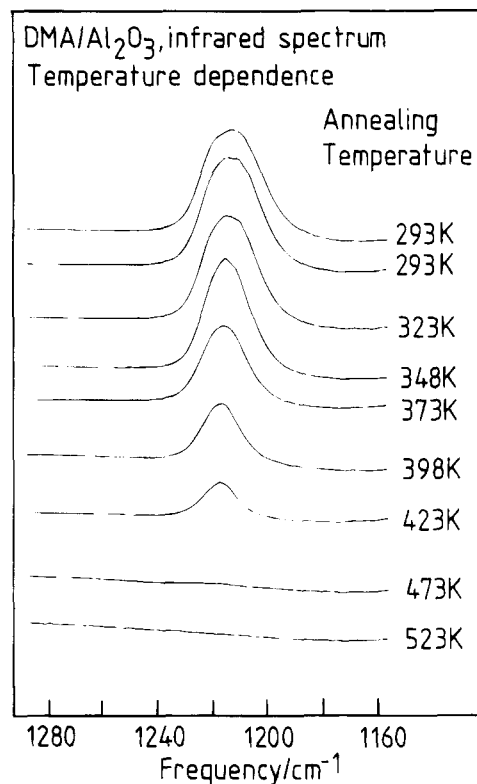


Figure 6. Infrared spectra between 1150 and 1300 cm^{-1} obtained following adsorption of dimethylaluminum chloride (DMA) on alumina that has been pretreated at 400 K displayed as a function of annealing temperature. The annealing temperature is displayed adjacent to the corresponding spectrum.

Very similar results are obtained for the adsorption of DMA on alumina which has been pretreated at 400 K. The bending region of the spectrum is displayed as a function of temperature (Figure 6). However, in this case all methyl groups are completely thermally removed by heating to above 423 K, whereas when the surface is exposed to TMA, a significant number of methyl groups remain on the surface at this temperature (Figure 5). The spectrum, however, consists of a single peak at 1218 cm^{-1} above an annealing temperature of ~ 350 K identical to the high-temperature state observed following TMA adsorption. Since there are no bridging methyl groups in the precursor to the surface species, there is no intensity at ~ 1250 cm^{-1} due to the bridging methyl species.

Discussion

The spectra shown in Figure 2 indicate that there is a detectable splitting of the terminal methyl bending modes at ~ 1200 cm^{-1} due to a coupling between them that gives rise to a separation between the modes of ~ 5 cm^{-1} . This effect is analogous to that commonly observed for methyl groups in alkanes.²³⁻²⁶ The shape of this peak in gas-phase TMA does not change substantially as the sample temperature is raised (Figure 3).

The infrared spectra of TMA adsorbed at room temperature on alumina pretreated at 400 K are shown in Figure 5. The species present at room temperature giving rise to the peak at 1200 cm^{-1} is assigned to an

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adsorbed monomeric species. This could therefore either be Al(CH₃)₃, Al(CH₃)₂, or Al(CH₃). The trimethylaluminum monomer (Al(CH₃)₃) does exist in the gas phase but only at high temperatures and is therefore unlikely to be present on the alumina at room temperature. In addition, significant methane evolution is noted at room temperature whereas none would be expected for a surface consisting entirely of Al(CH₃)₃. The surface species therefore could either be mono- or dimethylaluminum groups. The methyl stretching feature shifts from 1208 to 1218 cm⁻¹ on heating the surface from room temperature to ~398 K and becomes significantly narrower as well as decreasing substantially in intensity. Since the final removal of all methyl groups from the surface is immediately preceded by the formation of a Al(CH₃) species, the narrow peak centered at 1218 cm⁻¹ (Figure 5) is assigned to this monomethyl species. This is consistent with assignments made elsewhere.^{31,32} The broader feature centered at 1208 cm⁻¹ found after adsorbing TMA at room temperature (Figure 5) is therefore assigned to an aluminum dimethyl species. As shown by the gas-phase TMA and DMA data (Figure 2), the presence of two methyl groups bonded to the same aluminum causes a splitting of ~5 cm⁻¹ between the two modes. This splitting is not well resolved in the spectra for TMA adsorbed on alumina (Figure 5) and merely results in a broadening of the peak. Nevertheless, the observation of a broad asymmetric feature is consistent with this assignment. The spectra of Figure 5 therefore indicate the initial formation of a dimethyl surface species which converts to a monomethyl species on heating. This process will be addressed in greater detail below. Other explanations for this shift, such as adsorbate-adsorbate interactions, are precluded since solvent shifts for even very polar groups like C≡N are only ~10 cm⁻¹ between the gas and liquid phases.³³

It is proposed that the TMA dimer initially adsorbs on hydroxylated alumina preferentially by reaction with the bridging methyl groups (evolving methane) to yield two adjacent (CH₃)₂Al= species. The aluminum coordination environment in this species is currently being examined using magic-angle spinning nuclear magnetic resonance spectroscopy. One of the methyl species reacts further with surface hydroxyl groups eliminating further methane to yield a monomethyl species. It is clear from the data of Figure 5 that the dimethyl species is more reactive than the monomethyl species since monomethylaluminum remains on the surface at higher annealing temperatures. A similar difference between the reactivity of the first and second methyl group has been observed previously in studies of the reaction of the surface dimethyl species with water.¹³ The formation of monomethyl species from the dimethyl group could occur in two possible ways. First, one of the methyl species could react directly with an adjacent hydroxyl group and evolve methane to leave the monomethylaluminum on the surface. Alternatively, it could react in a manner analogous to that seen on silica where a dimethyl group rapidly decomposes yielding both Al(CH₃) and Si(CH₃) surface species. To distinguish between these possibilities, the spectra in Figure 5 are fit to the profiles due to a dimethyl and a monomethyl species. The aluminum dimethyl fingerprint is taken

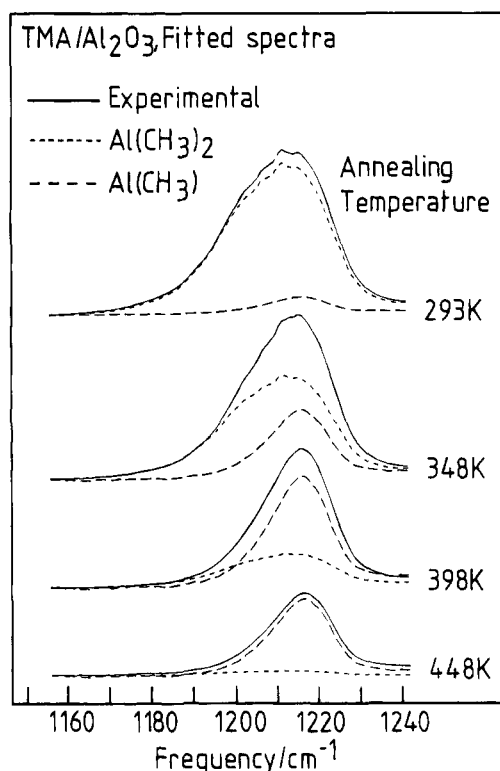


Figure 7. Fits of infrared profiles of (CH₃)₂Al_(ads) and (CH₃)Al_(ads) to the spectra of the bending regions shown in Figure 5.

to be the profile shown at the top of Figure 5 (for a sample that has been evacuated for 10 min following TMA exposure), and for the monomethyl species, the profile shown in Figure 5 for a surface heated to 398 K. The integrated area of the monomethyl profile is taken to be 50% of the dimethyl species, reflecting the relative methyl stoichiometries. The relative contributions of the component species were determined using multi-component linear regression.³⁴ In this technique, the experimental spectrum is modeled as a linear combination of the component spectra and correlation coefficients in excess 0.99 were obtained for the fits in all cases. Typical fits to the spectral profiles are displayed in Figure 7 and the resulting relative coverages (Θ) are shown plotted in Figure 8 as a function of the annealing temperature. Note that the 293 K point in this curve is for the spectrum taken following TMA adsorption and evacuation for 30 min (Figure 5; second spectrum) and indicates some Al(CH₃) formation even at room temperature. If a single surface dimethyl species decomposes to yield two surface monomethyl species, the coverage of monomethyl groups should substantially exceed that of the original dimethyl groups as the sample temperature is raised. Alternatively, if the dimethyl species react with surface hydroxyl groups forming monomethyl species and evolving methane, the monomethyl coverage should never exceed that of the initial dimethyl species. The data in Figure 8 indicate that the relative coverage of the monomethyl species never exceeds unity and the total relative coverage, in fact, remains constant at ~1.0 up to an annealing temperature of ~400 K. This indicates that the dimethyl species react with surface hydroxyl groups to

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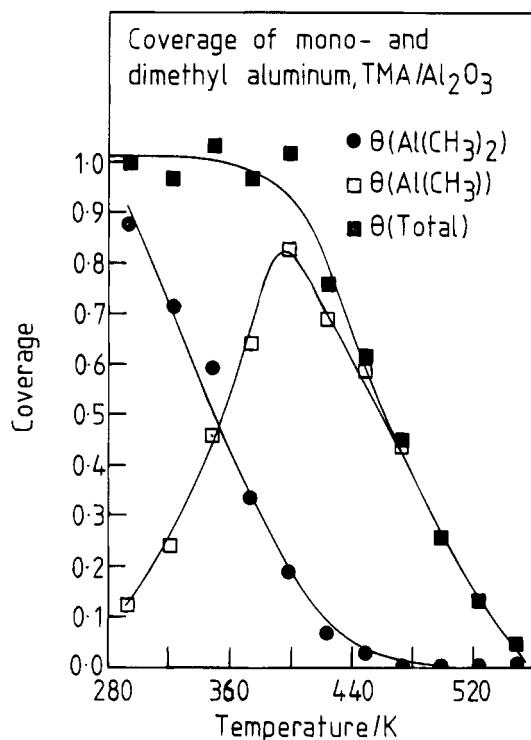


Figure 8. Plots of the coverages of $(\text{CH}_3)_2\text{Al}_{(\text{ads})}$ and $(\text{CH}_3)\text{Al}_{(\text{ads})}$ on alumina that has been pretreated at 400 K following trimethylaluminum (TMA) adsorption at 300 K as a function of annealing temperature.

form the monomethyl group. The monomethyl group is significantly less labile than dimethyl since it remains on the surface up to ~ 550 K.

A similar plot of relative surface coverages is displayed in Figure 9 for dimethylaluminum chloride adsorbed on alumina (Figure 6). An analogous effect is observed in this case since the total coverage does not exceed unity. The major difference is that both the dimethyl- and monomethylaluminum species react more rapidly when formed from dimethylaluminum chloride than when formed from trimethylaluminum.

Note that no significant change is observed in the shape of the spectrum due to the methyl stretching modes (Figure 4), in particular, for spectra taken at 300 K where the surface is predominantly covered with dimethylaluminum and at ~ 400 K where the surface is covered predominantly with monomethyl species (Figure 8). The plot in Figure 10 indicates that the data for the methyl stretching and bending regions are consistent. This figure displays the relative integrated area of the methyl stretching modes versus sample annealing temperature (\blacksquare) as well as the corresponding coverages calculated from the data shown in Figure 8 (\bullet). These show an almost linear decrease in total methyl coverage as a function of sample temperature derived from both the methyl stretching and bending modes. The agreement between the two sets of data suggests that the relative mono- and dimethyl coverages plotted in Figure 8 are reasonable.

Finally, shown in Figure 11 are the proposed structures for both the mono- and dimethylaluminum surface species. This proposed aluminum dimethyl structure provides an indication why it is more reactive than the monomethyl species. Clearly, the dimethyl species is more flexible and a methyl group in this species can

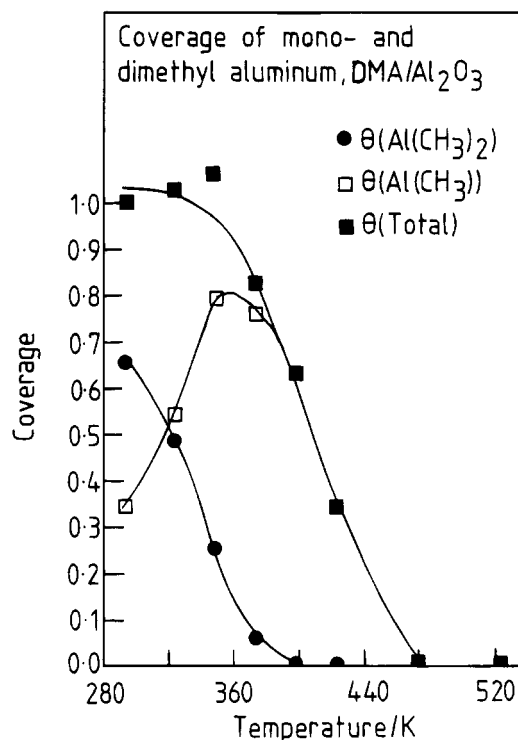


Figure 9. Plots of the coverages of $(\text{CH}_3)_2\text{Al}_{(\text{ads})}$ and $(\text{CH}_3)\text{Al}_{(\text{ads})}$ on alumina that has been pretreated at 400 K following dimethylaluminum chloride (DMA) adsorption at 300 K as a function of annealing temperature.

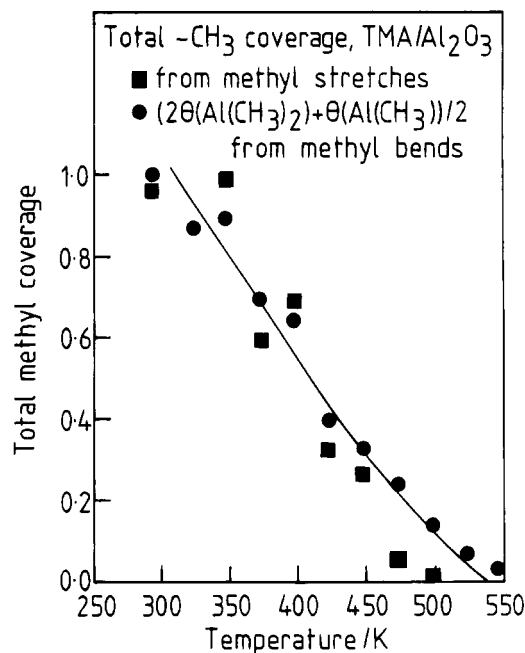


Figure 10. Comparison of the total methyl coverage following adsorption of trimethyl aluminum on alumina that has been pretreated at 400 K as a function of annealing temperature, (\blacksquare) obtained from the area under the methyl stretching modes, (\bullet) obtained from the data of Figure 8 from $(2\theta((\text{CH}_3)_2\text{Al}_{(\text{ads})}) + \theta((\text{CH}_3)\text{Al}_{(\text{ads})}))/2$.

access adjacent surface hydroxyl groups relatively easily. On the other hand, the monomethyl species is significantly more rigid and also further away from the surface so that reaction with an adjacent surface hydroxyl group is more difficult.

There may be two possible explanations for the greater reactivity of the surface species derived from

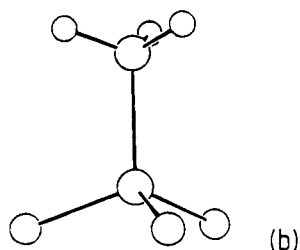
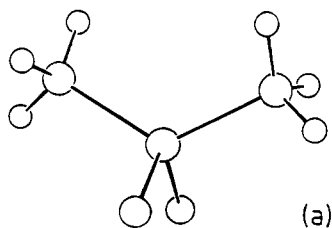


Figure 11. Schematic depictions of the adsorbed dimethylaluminum and monomethylaluminum surface species.

DMA than TMA. First, the reaction of trimethylaluminum to form the surface dimethylaluminum species involves reaction of the bridging methyl group with surface hydroxyl groups to evolve methane. This implies that the local surface hydroxyl concentration is

lower in this case than for surface species derived from DMA. In the latter case, the bridging species are chlorines which will react with surface Lewis sites and therefore not deplete the surface of surface hydroxyls. Alternatively, the reactivity may be affected due to electronic interactions because of adjacent chemisorbed chlorine.

Conclusions

Trimethylaluminum reacts with alumina that has been dehydroxylated at 400 K to yield an adsorbed dimethylaluminum species in which the aluminum is 4-fold coordinated immediately following adsorption. This suggests that the TMA dimer reacts preferentially via the bridging methyl species and evolves methane. A small amount of adsorbed TMA dimer is found on the surface immediately after adsorption, although this is removed by prolonged evacuation at room temperature. The surface dimethylaluminum species further react rather rapidly with surface hydroxyls forming monomethylaluminums. These also react with surface hydroxyls so that all surface methyl species are eventually removed, although significantly more slowly than does dimethylaluminum. This behavior can be rationalized on the basis of their corresponding surface structures.