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Combined far infrared RAIRS and XPS studies of TiCl₄ adsorption and reaction on Mg films

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Abstract

In recent years there has been an increase in interest in the study of model Ziegler-Natta catalysts used for the polymerisation of ethene and propene. Particular attention has focused on catalysts consisting of TiCl₄ on activated MgCl₂ accompanied by a co-catalyst, usually triethylaluminium (AlEt₃). As part of a wider project on the characterisation of model Ziegler-Natta catalysts we have investigated the interaction of TiCl₄ with metallic Mg films grown on a Au surface using X-ray photoelectron spectroscopy (XPS) and far infrared reflection absorption infrared spectroscopy. Somewhat surprisingly, the infrared spectra show little variation as a function of exposure to TiCl₄. A very broad asymmetric vibrational band grows in with maximum intensity at 382 cm⁻¹. Three prominent low frequency shoulders are observed at approximately 360, 320, and 260 cm⁻¹. For monolayer coverages of Mg the main band at 382 cm⁻¹ is narrower, less asymmetric and accompanied by a prominent shoulder at 398 cm⁻¹, which increases with increasing exposure to TiCl₄. TiCl₄ exposure in the presence of 5×10^{-8} Torr of ethyl benzoate results in a change in line shape with low frequency broadening and a small shift in the frequency of the band. These spectra are discussed in the light of the possible constituent species making up the surface layer.

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1. Introduction

Polypropylene is one of the most industrially important polyolefins and its efficient production requires a catalyst with both high activity and good stereospecificity. The most successful catalyst to date for this system has been the MgCl₂ supported Ziegler-Natta catalyst. This consists of a pre-catalyst composed of titanium tetrachloride chemisorbed on defective magnesium chloride, which is reduced and alkylated by an alkyl aluminium co-catalyst, typically AlEt₃. Lewis bases are added to act as internal or external electron donors [1] and enable good control of the stereoselectivity of the active catalyst. This ensures that highly isotactic polypropylene is produced.

Despite the importance of these catalysts, the catalytic process remains poorly understood on a molecular level, and the reaction mechanism still needs elucidating. Characterisation of the active centres in the 'real' catalyst has been hindered by the inherent complexity of the catalyst, low concentration of active sites and its sensitivity to water and oxygen in the surrounding ambient. In order to circumvent these problems, recently there have been a number of surface science studies directed at investigating the structure and properties of the active centres using model catalysts under highly controlled conditions.

Somorjai et al. [2,3] have investigated the surface properties of model Ziegler-Natta catalysts fabricated by exposing thin films of magnesium on an inert gold foil substrate at 300 K to TiCl₄ and AlEt₃. Through this pioneering work valuable information was provided on the electronic properties and composition of these model catalysts including the Ti oxidation state distribution, adsorption site distribution, and important correlations between surface structure and polypropylene tacticity. However a molecular level understanding of the catalytic process remains elusive and furthermore there are currently conflicting theories on the role of the Lewis bases in the system [4,5].

Surface sensitive vibrational spectroscopic techniques could potentially provide further information on the nature of the catalytically active sites and the molecular components involved in the reaction mechanism. In this study we utilise far IR reflection absorption infrared spectroscopy (RAIRS) to investigate a model Ziegler-Natta catalyst system, and to determine the feasibility of the technique in providing further molecular level information. We have chosen to use a similar model catalyst to that used by Somorjai [3] i.e. thin films of magnesium deposited on an inert gold foil substrate subsequently exposed to TiCl₄. As an extension to this study we have also chosen to investigate the role of Lewis bases in the catalytic process by incorporating ethyl benzoate into our model catalyst.

2. Experimental

The far infrared RAIRS measurements were performed on the dedicated IR beamline 13.3 at the SRS, Daresbury, the basic elements of which have been described in detail elsewhere [6]. The recently modified experimental arrangement consists of a UHV chamber coupled with an independently pumped fast entry lock/preparation chamber. The main analysis chamber is equipped with an ion gun for sample cleaning, an X-ray source and hemispherical analyser for XPS, an RGA and an electron flood gun for electron irradiation of the sample. The chamber was also equipped with two leak valves for gas admittance and a shuttered evaporator to allow deposition of thin films of Mg or MgCl₂. The evaporator consists of a ceramic tube charged with the deposition material, which is heated to the desired temperature via a resistively heated filament surrounding the assembly.

The sample used in the experiments consists of a 4 cm^2 polycrystalline gold foil attached to a sample plate with aluminium strips. The sample could be heated by electron bombardment to temperatures greater than 1000 K and rapidly cooled to below 100 K. Argon ion sputtering was used to clean the sample and surface cleanness was checked by XPS prior to each experiment. The sample was not annealed following sputtering.

Deposition of magnesium occurred at normal incidence to the gold surface at 300 K. The magnesium flux was controlled by adjustment of the

temperature of the cell and varying the time of exposure. A shutter directly in front of the source aperture allowed accurate and reproducible dosing of magnesium.

The thickness of the magnesium layer on the gold foil was calculated by monitoring the attenuation of the Au4f_{7/2} photoelectron peak. Assuming an inelastic mean free path of the Au4f_{7/2} electron in magnesium to be 22 Å [7], and the thickness of 1 monolayer (ML) of magnesium to be 2.6 Å [2] a 4 min dose at 370 K was calculated to be equivalent to a 3 ML film. XPS spectra of the grown films revealed that the magnesium layers were reproducible and there was little or no evidence of oxygen contamination. However, once the source had been calibrated, XPS spectra of the grown films were not recorded prior to the RAIRS experiment to minimise contamination of the films.

The magnesium chloride source was calibrated similarly to magnesium via the attenuation of the Au4f_{7/2} photoelectron peak. For this calculation we have assumed that the mean free path of the Au4f_{7/2} photoelectron in magnesium chloride is similar to that in magnesium i.e. 22 Å. Given that MgCl₂ grows layer by layer on polycrystalline gold [8] and a monolayer is 5.9 Å thick [9], we have calculated that evaporation for a duration of 100 s corresponds to approximately 2 ML of magnesium chloride.

TiCl₄ and ethyl benzoate were introduced into the chamber from the vapour phase above the liquid, following purification by several freeze– pump–thaw cycles. The leak valve used for dosing TiCl₄ was fitted with a doser facing the sample to enhance the partial pressure at the surface while minimising contamination of the UHV chamber. Pressures quoted in this paper are those obtained from the nude ion gauge positioned on the opposite side of the chamber from the leak valves. Therefore, doses quoted here have not been corrected for the sample pressure enhancement due to the presence of the doser or the ionisation cross sections of the gases.

The fabricated model catalysts were investigated by far infrared RAIRS, and spectra were obtained from the co-addition of 256 interferrograms at 8 cm⁻¹ resolution.

3. Results

3.1. Exposure of Mg/Au films to TiCl₄

The far infrared RAIRS spectra obtained following the exposure of a 1 ML thick film of magnesium on gold at 300 K to increasing amounts of titanium tetrachloride are shown in Fig. 1. Even at low exposure the bands are intense. The spectrum obtained following 0.025 L TiCl₄ shows a broad absorption band centred at 382 cm^{-1} . With increasing exposure the band increases in intensity and two smaller broad features develop at 0.325 L centred around 290 cm⁻¹ and 464 cm⁻¹. At higher exposure the high frequency feature shifts from



Fig. 1. RAIRS spectra of 1 ML Mg/Au at 300 K exposed to (i) 0.025 L, (ii) 0.075 L, (iii) 0.325 L, (iv) 5.8 L, (v) 30.8 L, and (vi) 125 L of TiCl₄.

464 cm⁻¹ to 450 cm⁻¹, and the main band at 382 cm^{-1} also starts to become asymmetric as a weak shoulder grows in at 398 cm^{-1} . With increasing exposure up to 125 L the 382 cm^{-1} main band and the shoulders at 290 cm⁻¹ and 464 cm⁻¹ saturate but the high frequency feature at 398 cm⁻¹ continues to grow relative to the main band.

XPS measurements performed on the sample after RAIRS revealed the presence of magnesium, titanium and chlorine on the surface. Peaks were observed at 458.3 eV, 464.0 eV, corresponding to the Ti2p_{3/2}, and Ti2p_{1/2}, levels (Fig. 2(a)) and at 1178.9 eV (K.E) due to the MgKLL Auger, Fig. 2(b). This peak can unambiguously be assigned to the MgKLL of MgCl₂ [10]. In addition, the absence of a peak at 1185.5 eV indicates that within the detection limits, all the magnesium has been converted to magnesium chloride through reaction with TiCl₄ [3]. Peaks at 271.6 eV and 200.6 eV (not shown), corresponding to the Cl2s and Cl2p, respectively, were also observed.

To investigate the effect of increasing the thickness of the magnesium film, a thick multilayer (>10 ML) was grown on the clean gold substrate. Fig. 3 shows the RAIRS spectra obtained following exposure of the thick magnesium film to increasing amounts of titanium tetrachloride. Upon exposure of the multilayer film to 50 L TiCl₄ an intense band with a broad line shape appears at 382 cm^{-1} . Examination of the band reveals that it is actually composed of a series of bands and is observed as several weak shoulders on the main band centred at 273, 324, 360 and 466 cm^{-1} . With increasing exposure the band at 382 cm^{-1} intensifies and the shoulders appear slightly more prominent. The intensities of the bands saturate at exposures greater than 200 L, but there is a frequency shift of the bands at 382 cm^{-1} and 466 cm^{-1} to 378 cm^{-1} and 435 cm^{-1} , respectively. (Unfortunately due to S/N problems, low exposure data on the thick Mg films was not obtained during the beamtime.)

Assignment of the absorption bands observed in the RAIRS data is problematic due to the complexity of the spectra. The XPS spectra revealed the presence of titanium and magnesium chloride



Fig. 2. XPS spectra of 1 ML of Mg exposed to 125 L TiCl₄ showing (a) the Ti2p and (b) MgKLL Auger regions.



Fig. 3. RAIRS spectra of thick multilayer Mg/Au at 300 K exposed to (i) 50 L, (ii) 100 L, (iii) 150 L, (iv) 200 L, (v) 250 L, and (vi) 300 L TiCl₄.

on the sample surface, suggesting that in agreement with Somorjai's work on Mg films [2], TiCl₄ is reacting with Mg to form magnesium chloride and reduced titanium chloride. A good starting point for the analysis would be to determine if the bands we observe in the RAIRS spectra are consistent with the presence of magnesium chloride and/or reduced titanium chloride. Unfortunately there is little vibrational data on MgCl_x and TiCl_x in the research literature.

3.2. Electron irradiation induced titanium chloride growth on gold at 300 K

Magni [11] reported that ultrathin films of titanium chloride could be grown on gold at 300 K by irradiation of the sample with 1 KeV electrons in a 5×10^{-7} Torr background pressure of TiCl₄. Detailed AES and angular resolved XPS characterisation of these films revealed them to consist of 3–4 ML of TiCl₂ with 1 ML of TiCl₄ chemisorbed on the TiCl₂ surface. To facilitate interpretation of our RAIRS spectra we have attempted to reproduce this system to enable us to obtain a vibrational spectrum for TiCl₂ and TiCl₄.

Fig. 4 shows the RAIRS spectra obtained for the gold foil irradiated with 1 KeV electrons in a 5×10^{-7} Torr background pressure of TiCl₄. Following 50 L exposure of TiCl₄ two weak bands appear in the spectrum at 398 cm⁻¹ and 470 cm⁻¹. Increased



Fig. 4. RAIRS spectra of electron irradiation induced titanium chloride growth on Au at 300 K. Exposures of (i) 50 L, (ii) 100 L, (iii) 200 L, (iv) 300 L, and (v) 400 L with 1 KeV electron energy.

exposure causes no change in the band at 470 cm^{-1} , but the 398 cm⁻¹ band continues to grow in intensity until it finally saturates at 400 L. Since the relative intensities of the bands at 398 cm^{-1} and 470 cm^{-1} change as a function of exposure it is reasonable to assign them to two different types of species. AES data from Magni [11] reveals that for similar conditions to those employed in our system, the atomic ratio of Cl:Ti is close to 4 at the start of growth but decreases as the films grow thicker. This would be in agreement with the major constituent in the film being TiCl₄ at the start of the growth process, but with the proportion of TiCl₂ increasing as growth proceeds. Given that the RAIRS band at 470 cm^{-1} saturates at low exposure and the 398 cm^{-1} band continues to grow, this would suggest that the two bands in the RAIRS spectra could potentially be due to $TiCl_4$ and $TiCl_2$, respectively.

In an attempt to determine if the 470 cm^{-1} band is due to TiCl₄ we have exposed the gold foil at 100 K to increasing amounts of TiCl₄ to form a physisorbed multilayer. The RAIRS spectrum obtained (Fig. 5) gives rise to a single absorption band due to the v_3 mode of molecular TiCl₄ at 520 cm⁻¹. The observation of a band at 470 cm^{-1} in Fig. 3 would be consistent with the v_3 mode of TiCl₄, shifted down from the multilayer frequency due to its interaction with the surface. Hastie [12] reported that TiCl₂ in a nitrogen matrix has an infrared active absorption mode at 434 cm^{-1} . It is therefore possible that the band observed in Fig. 3 at 398 cm⁻¹ is due to TiCl₂ which is shifted down in frequency from the matrix isolated value. On the basis of this information, and in conjunction with the electron spectroscopy findings of Somorjai for this system, we assign the band at 398 cm^{-1} to TiCl₂.

3.3. Multilayer films of magnesium chloride

To further aid interpretation of the RAIRS spectra obtained for the TiCl₄/Mg/Au system we have also used RAIRS to obtain a vibrational spectrum for multilayers of MgCl₂ deposited on the gold substrate. Magnesium chloride was deposited by heating the source to evaporation temperature, and opening the shutter to allow



Fig. 5. RAIRS spectrum following exposure of gold at 100 K to 8 L TiCl₄.

a flux of MgCl₂ normal to the surface while continuously collecting RAIRS spectra. Fig. 6 shows the RAIRS spectrum obtained for films of MgCl₂ of increasing thickness deposited on the gold foil at 300 K. For a film of nominally 2 ML MgCl₂ a band is observed at 389 cm^{-1} with what appears to be a weak shoulder at approximately 408 cm^{-1} . There is also a broad band of low intensity at this same coverage, at approximately 260 cm^{-1} and a weak shoulder at 245 cm^{-1} . With increasing film thickness the band at 260 cm^{-1} and its shoulder intensify. However the band at 260 cm^{-1} gradually shifts to 282 cm^{-1} while the shoulder at 245 cm^{-1} appears to stay at the same frequency. The band at 389 cm^{-1} and its shoulder at 408 cm⁻¹ also intensify with increasing thickness of the film but the relative intensity of these



Fig. 6. RAIRS spectra of multilayers of MgCl₂ grown on gold at 300 K. Coverages of MgCl₂ are (i) 2, (ii) 4, (iii) 6, (iv) 8, (v) 10, and (vi) 12 ML.

two features remains the same. The positions of these bands are consistent with transmission far infrared spectroscopy performed on α -MgCl₂ and β -MgCl₂ [13] where absorption bands have been observed at 407 cm⁻¹, 372 cm⁻¹, 329 cm⁻¹, 276 cm⁻¹ and 248 cm⁻¹.

3.4. Influence of electron donors on the model catalyst

Our study of the model catalyst was extended to investigate the influence of electron donors and therefore form a better approximation to the real industrial catalyst. Ethyl benzoate was chosen as the electron donor because of its general use in the catalyst for polypropylene production. For this preliminary investigation we look at the effect of co-dosing ethyl benzoate and titanium tetrachloride on a 2.5 ML thick magnesium film on the gold foil at room temperature. The sample was exposed to a dynamic pressure of 5×10^{-8} Torr of ethyl benzoate followed by a variable dynamic pressure of TiCl₄, and RAIRS spectra were consecutively acquired with a collection duration of 100 s each (Fig. 7). The total exposure of the sample was nominally 20 L of ethyl benzoate and 15 L TiCl₄.

The first spectrum is recorded in a background pressure of ethyl benzoate only, and no absorption bands are observed. The spectrum obtained in the background of ethyl benzoate and a constant pressure of 5×10^{-8} Torr TiCl₄ shows a strong



Fig. 7. RAIRS spectra of 2.5 ML of Mg on Au, at 300 K exposed to a background pressure of 5×10^{-8} Torr of ethyl benzoate and a dynamic pressure of (i) 0 Torr, (ii) 5×10^{-8} Torr and (iii) 1.5×10^{-7} Torr of TiCl₄. Spectrum (iv) is as for (iii) but after both leak valves have been closed and gases have been pumped away. For comparison, spectrum (v) is of 2.5 ML of Mg on Au, at 300 K exposed to 5 L of TiCl₄ only.

absorption band at 387 cm^{-1} and contains a very broad shoulder centred around 290 cm⁻¹. With increased pressure of TiCl₄ (1.5×10^{-7} Torr) there is a slight increase in intensity of the absorption band at 387 cm^{-1} and the shoulder at 290 cm⁻¹. However there is no increase in absorption band intensity below 260 cm⁻¹. The spectrum obtained after stopping admittance of TiCl₄ and ethyl benzoate into the chamber is identical to the previous spectrum indicating that the film is stable without the dynamic pressure present.

Included in Fig. 7 is a RAIRS spectrum of 2.5 ML film of magnesium on gold exposed to approximately 5 L of TiCl₄ only. Calculation of the exposure of the sample with respect to TiCl₄ for the spectrum recorded for a dynamic pressure of 5×10^{-8} Torr titanium tetrachloride in the background of ethyl benzoate reveals it had been exposed to approximately 5 L. Comparison of

Fig. 8. XPS spectrum of 2.5 ML Mg/Au exposed to a dynamic pressure of 5×10^{-8} Torr ethyl benzoate and 15 L TiCl₄.

these two spectra allows us to investigate the effect of the ethyl benzoate on the vibrational spectrum. The spectrum obtained in the presence of ethyl benzoate and TiCl₄ is considerably broader with significantly more intensity below 350 cm^{-1} . Also noticeable is that the most intense band in the spectra obtained with dynamic pressures of TiCl₄ and ethyl benzoate occurs at 387 cm^{-1} compared to 382 cm^{-1} for the spectra obtained for Mg/Au exposed to TiCl₄ only. It is apparent that, in our model catalyst, ethyl benzoate is influencing the chemistry occurring on the surface, and this is borne out by the XPS spectrum (Fig. 8) recorded under the same conditions. The photoelectron peaks in the XPS spectrum at 286.6 and 532 eV are assigned to the C1s and O1s demonstrating that the ethyl benzoate has reacted at our model catalyst surface. The XPS spectrum is very similar to that recorded by Mori [14] where MgCl₂ was ground in a ball grinder before reaction with TiCl₄.

4. Discussion

Assignment of the bands in the RAIRS spectra obtained following exposure of magnesium films to TiCl₄ is problematic. The spectra consist of broad features and there is considerable overlap between the expected vibrational frequencies of $MgCl_2$ and $TiCl_x$. Interpretation of the infrared absorption bands observed for exposing the monolayer magnesium films to TiCl₄ is aided by comparison to the RAIRS spectra of $TiCl_x$ (Fig. 4) and MgCl₂ (Fig. 6) on gold. The band observed for low exposure of TiCl₄ at 382 cm^{-1} is in a similar position to the most intense band in the MgCl₂ spectrum at 389 cm^{-1} suggesting that it could potentially be due to the presence of magnesium chloride on the surface. At larger exposure of TiCl₄ a second band is observed at 290 cm^{-1} , and this would also be consistent with MgCl₂ formation since it occurred in the multilayer MgCl₂ films at 282 cm^{-1} . The absorption band at 464 cm^{-1} can be assigned by comparison to the spectrum we obtained for electron induced titanium chloride growth on gold (Fig. 4). On this system a weak band was observed at 474 cm^{-1} which



saturated at low exposures of TiCl₄. We assigned this band to TiCl₄ interacting strongly with the surface. Since the band at 464 cm^{-1} is in close proximity to this, it is likely that it is due to TiCl₄—either within or at the surface of the film. It is difficult to determine the origin of the shift with increased exposure of TiCl₄ in the 464 cm^{-1} band to 450 cm⁻¹. Somorjai [3] used XPS to demonstrate that exposure of thin magnesium films on gold to TiCl₄ resulted in titanium oxidation states of 4, 3, 2 and 0. Since no magnesium chloride bands occur in this region of the infrared spectrum we could speculate that the shift in the band could potentially be due to the formation of increasing amounts of TiCl₃ although we currently have no evidence for this.

There is some uncertainty into the origin of the band at 398 cm⁻¹ observed following high exposure of monolayer Mg/Au to TiCl₄. Multilayer MgCl₂ has an intense band at 389 cm^{-1} with a weaker shoulder at 408 cm⁻¹, and they both grow at the same rate as the MgCl₂ film thickness increases. The 408 cm⁻¹ feature shifted down in frequency could potentially be the origin of the band we observe at 398 cm^{-1} . The other possibility comes from the spectrum obtained for the electron induced growth of titanium chloride (Fig. 4), which featured a strong band at 398 cm^{-1} which we assigned to TiCl₂. Given that this absorption frequency exactly matches that observed in the spectrum the band could potentially be TiCl₂. Furthermore evidence for this is provided by the band at 398 cm⁻¹ growing in at a different rate to the bands we assigned to MgCl₂. Different rates of band growth are expected to occur if they are due to different types of species.

Another possibility is that the absorption bands at 382 cm^{-1} and 398 cm^{-1} are due to different forms of TiCl_x. Somorjai revealed that exposure of thin magnesium films on polycrystalline gold produced TiCl_x with x = 0, 2, 3 and 4. Studies of the infrared active modes of TiCl_x clusters in an argon matrix [12] revealed that TiCl₄, TiCl₃, and TiCl₂ have absorption bands at 503 cm⁻¹, 497.1 cm⁻¹, and 458.2 cm⁻¹, respectively, while TiCl₂ in a nitrogen matrix has a band at 434.5 cm⁻¹. Therefore given the difference between the infrared absorption frequency in the clusters and the RAIRS bands at 382 cm^{-1} and 398 cm^{-1} , it is unlikely that either of these are due to TiCl₄ or TiCl₃. However we cannot rule out the possibility of these two bands being due to TiCl₂ in different molecular environments.

The spectra obtained from exposing a thick film of magnesium to increasing amounts of TiCl₄ showed bands in similar positions to those in the 1 ML Mg/Au system. Bands were observed at 273 cm⁻¹, 382 cm⁻¹ which is possibly due to MgCl₂ and 466 cm⁻¹ which we assign to TiCl₄. We cannot be certain of the phenomenon responsible for the shifting of the TiCl₄ band from 466 cm⁻¹ to 435 cm⁻¹. However it is possible that the shift is due to the same effect observed for the monolayer Mg/Au system where the band was observed to shift from 464 cm⁻¹ to 450 cm⁻¹.

In the monolayer Mg/Au system exposed to TiCl₄ we observed a band at 398 cm⁻¹ and assigned it to TiCl₂. For the thick films of magnesium on gold exposed to TiCl₄ it is difficult to determine if there is a band at this position due to the strong absorption band from MgCl₂ at 382 cm⁻¹. Interestingly a band was observed at 324 cm⁻¹ for exposure of the multilayer magnesium film to TiCl₄, but this band was not observed in the multilayer magnesium film. However this band has been observed for far infrared transmission spectra of solid MgCl₂ at 329 cm⁻¹ [13]. It is therefore possible that the MgCl₂ band only occurs for considerably thick films.

The preliminary RAIRS investigation of the influence of the ethyl benzoate on the model catalyst produced some interesting results. Perhaps the most striking observation was the increased absorption intensity at 250–350 cm⁻¹. TiCl_x vibrational modes generally occur above 350 cm^{-1} so it is unlikely that a titanium-chlorine species is responsible for the increased intensity in this region of the spectrum. However a magnesiumchlorine related species would be expected to have vibrational modes in the $250-350 \text{ cm}^{-1}$ region. In addition to the increased absorption intensity, a shift in vibrational frequency to 387 cm^{-1} from 382 cm^{-1} (which was assigned to MgCl₂). If the ethyl benzoate is causing a shift in the vibrational frequency of magnesium chloride then this would be interesting. There has recently been confusion over the role of the ethyl benzoate and whether it coordinates with only magnesium chloride, only on a vacancy on the titanium compound, or both. The XPS spectrum obtained for the ethyl benzoate modified model catalyst provided evidence of carbon and oxygen on the surface. However due to the low resolution of the spectrum it is impossible to determine if there has been any chemical shifts in the titanium or magnesium peaks. Further work is required to attempt to understand the influence of the ethyl benzoate on the model catalyst.

5. Conclusions

We have utilised far infrared RAIRS to investigate model catalysts fabricated from the reaction of titanium chloride with thin films of magnesium on gold. In this study we have demonstrated the difficulties in using RAIRS to investigate complex catalytic systems. However through an analysis of the complex spectra obtained we have managed to provisionally assign the spectral features to the presence of MgCl₂, TiCl₄, TiCl₂ and possibly TiCl₃ in agreement with Somorjai's studies [3]. The influence of ethyl benzoate on the model catalyst was also investigated with RAIRS. Significant differences in the vibrational spectra were observed due to the presence of ethyl benzoate, suggesting that far infrared RAIRS is a highly sensitive technique for investigating the effect of electron donors on these model catalysts.

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