Mechanism for the decomposition of iron pentacarbonyl on Pt(111): evidence for iron tetracarbonyl and iron tricarbonyl intermediates

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Received 12 December 1990; accepted for publication 2 April 1991

The surface chemistry of iron pentacarbonyl on Pt(111) was studied using reflection-absorption infrared spectroscopy (RAIRS). A small amount of molecular adsorption is observed below half saturation at 110 K, but about 70% of the iron pentacarbonyl decomposes upon chemisorption to yield atomic iron and coadsorbed carbon monoxide. Deposition at 275 K, on the other hand, results in total decomposition and in a steady state growth of iron films on the surface; only CO bonded directly to platinum atoms is seen by RAIRS. The molecular adsorption of iron pentacarbonyl is proposed to occur with a concomitant change of geometry from a trigonal bipyramid to a square pyramid as suggested by the high frequency value observed for the CO mode, around 2060 cm⁻¹. Annealing the surface to 185 K after exposures at 120 K results in desorption of the condensed multilayer and in decarbonylation of the remaining molecules to form iron tetracarbonyl, which displays a peak in the RAIRS spectrum at 2035 cm⁻¹. Further heating to 240 K yields two new bands at 1980 and 1935 cm⁻¹, which we assign to $Fe(CO)_3$. Both $Fe(CO)_4$ and $Fe(CO)_3$ desorb as iron pentacarbonyl after recombination with CO at 195 and 265 K, respectively.

1. Introduction

Chemical vapor deposition (CVD) processes are becoming increasingly important for electronic device fabrication. This technique is quite versatile and offers many advantages over more conventional technologies such as plasma and sputtering deposition, especially in applications where either isotropic film growth or substrate chemical selectivity is required.

The surface chemistry of metal carbonyls has been recently addressed by several research groups in connection with the use of those molecules as precursors for CVD [1-7]. Even though most of that research has focused on the photolytic decomposition of such compounds [1-4], some attention has been given to their thermal chemistry as well [5-7]. We have studied the details of iron film deposition from iron pentacarbonyl using thermal programmed desorption (TPD), X-ray photoelectron (XPS) and ion scattering (ISS) spectroscopies [8,9]. We found that films can be grown in a steady state fashion if the substrate is kept at temperatures above 275 K in spite of the fact that the decomposition of iron pentacarbonyl is inhibited by the resulting coadsorbed carbon monoxide, but the mechanism for such process is not yet fully understood. Photolytic studies indicate that the first step, which involves the decarbonylation of iron pentacarbonyl to the tetracarbonyl, can be induced in the gas phase, and that subsequent thermal decomposition to metallic iron takes place readily on almost any surface [10]. This would imply that the decarbonylation occurs in a stepwise manner, even though past attempts to isolate $Fe(CO)_x$ intermediates (x = 1-4) on surfaces have not been successful [6,7,11,12]. In this report we show infrared evidence for the formation of both iron tetracarbonyl and iron tricarbonyl on a Pt(111) surface, as well as data suggesting that iron pentacarbonyl isomerizes to a square pyramid configuration upon adsorption and before decomposition.

2. Experimental details

Reflection-absorption infrared spectroscopy (RAIRS) was performed in an ultra-high vacuum (UHV) chamber pumped with a cryopump to a base pressure below 1×10^{-10} Torr [13]. This chamber is equipped with instrumentation for low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and thermal programmed desorption (TPD), and has a long travel manipulator for transferring the sample to a second chamber where the RAIRS experiments were performed. The infrared beam from the Fouriertransform infrared spectrometer (Mattson Sirius 100) is focused through a sodium chloride window onto the sample (under vacuum) at an angle of $85 \pm 3^{\circ}$, passed through a polarizer after reflection, and collected by a mercury cadmium telluride (MCT) detector. The spectra shown here were taken with 4 cm^{-1} resolution and ratioed against background spectra taken for the clean surface. Each spectrum was the result of averaging 100 scans (30 s acquisition time), which resulted in a reduction of noise to below 1×10^{-4} absorbance units (a.u.).

Thermal desorption data was taken in another UHV apparatus, described in detail elsewhere [8,14]. This chamber, pumped with a turbomolecular pump to a base pressure of about 1×10^{-10} Torr, is equipped with a mass quadrupole (with a detection range up to 800 amu) used for TPD, a 50-mm radius concentric hemisphere electron energy analyzer used for ISS, AES and X-ray photoelectron (XPS) spectroscopies, an electron gun, an X-ray gun with an aluminum anode, a sputtering gun for cleaning and for ion scattering spectroscopy (ISS), gas dosing facilities, and a sample manipulator capable of cooling down to below 100 K and resistively heating to above 1200 K. TPD spectra were collected using an interfaced computer for further data processing.

The platinum single crystal was cut in the (111) direction and polished using standard procedures.

It was cleaned under vacuum by a combination of oxygen treatments and sputtering-annealing cycles until no impurities were detected using either AES or XPS. Particular care was taken to sputter the sample between experiments to make sure that no iron remained on the surface or even in the subsurface. The iron pentacarbonyl was obtained from Aldrich (99.5% purity), and was kept in a dark glass bulb and freeze-pumped daily in order to eliminate excess CO gas resulting from its decomposition. The purity was periodically checked by mass spectrometry.

3. Results

Fig. 1 shows reflection-absorption infrared (RAIRS) spectra for iron pentacarbonyl adsorbed on Pt(111) at 110 K as a function of initial exposure. A peak around 2090 cm⁻¹ grows first and shifts to higher frequencies with increasing coverage as a second feature about 2055 cm⁻¹ begins to develop; after 3 L exposure (1 L = 10^{-6} Torr \cdot s) the two peaks are centered at 2097 and 2056 cm⁻¹, respectively. Additional iron pentacarbonyl doses results in the growth of the low frequency peak only, which shifts to higher energies as it increases in intensity. The spectra for the iron pentacarbonyl multilayer consists of a main,



Fig. 1. Reflection-absorption infrared spectra for iron pentacarbonyl adsorbed on Pt(111) at 110 K as a function of initial exposure.



Fig. 2. Reflection-absorption infrared peak positions as a function of initial exposure for iron pentacarbonyl deposition on Pt(111) at 110 and 275 K. The peaks shown are those seen in the 2050-2150 cm⁻¹ region.

skewed peak with maximum at 2065 cm^{-1} and a small shoulder around 2010 cm^{-1} . The peak positions and integrated areas as a function of exposure are shown in figs. 2 and 3, respectively.

A similar series of spectra for the uptake of iron pentacarbonyl at 275 K is shown in fig. 4.



Fig. 3. Reflection-absorption infrared peak areas as a function of initial exposure for iron pentacarbonyl deposition on Pt(111) at 110 and 275 K. The peaks shown are those seen in the 2050-2150 cm⁻¹ region.



Fig. 4. Reflection-absorption infrared spectra for iron pentacarbonyl adsorbed on Pt(111) at 275 K as a function of initial exposure.

Only one peak grows above 2000 cm^{-1} in this case: a small feature at 2089 cm⁻¹ (0.2 L) grows and shifts to higher frequencies with increasing exposures until reaching a value of 2103 cm^{-1} at 4 L, after which no other significant changes are observed. Another small and broad peak appears around 1485 cm⁻¹ at 1.2 L; it grows and sharpens until reaching 3 L (when it is centered at 1854 cm⁻¹). This feature broadens again at higher exposure as it shifts back to higher frequencies. The changes in the peak maxima and peak areas with coverage for the depositions at 275 K are also shown in figs. 2 and 3.

Fig. 5 shows RAIRS spectra for a 6 L dose of iron pentacarbonyl on Pt(111) at 110 K after annealing to the indicated temperatures. The initial spectrum, which has peaks at 2095, 2062 and a shoulder at 2010 cm⁻¹, remains unchanged when annealing to temperatures up to 155 K. Above that temperature the peak intensities decrease as the maxima shift to lower frequency: the spectrum for 175 K shows two peaks at 2086 and 2058 cm^{-1} . These changes are due to molecular desorption of some of the iron pentacarbonyl. Annealing further to 185 K results in a spectrum which displays three peaks at 2090, 2035 and 1865 cm^{-1} . The additional molecular desorption that occurs around 200 K ([8] and fig. 6) is accompanied by the slow disappearance of the peak at 2035 cm^{-1} and a shift and broadening of the peak at 1865



Fig. 5. Reflection-absorption infrared spectra after a 6 L dose of iron pentacarbonyl on a Pt(111) at 110 K followed by annealing to the indicated temperatures.

cm⁻¹. The spectra after annealing to 205 K has only one major peak at 2089 cm⁻¹ and another broad feature around 1850 cm⁻¹, and at 240 K the main peak is centered at 2093 cm⁻¹ and additional small features are seen around 1980, 1935 and 1850 cm⁻¹. The peaks in the 1900–2000 cm⁻¹ range disappear by 275 K, and further heating of the sample only results in few slight changes in the spectra, mostly a sharpening of the highfrequency peak. The spectra for 325 K has a sharp peak at 2095 cm⁻¹ (FWHM of about 6 cm⁻¹), and another broader one at 1850 cm⁻¹. Annealing above 400 K leads to the desorption of carbon monoxide and the corresponding disappearance of the RAIRS signal.

Molecular thermal desorption spectra as a function of exposure has been reported before; fig. 6 shows the results for a 5 L dose. Two main peaks are seen in these traces: a peak at 195 K, which grows first and saturates around 4 L, and a second feature around 170 K due to multilayer condensation, which starts to grow about 5 L. There is also a small and broad feature around 265 K that grows after very large exposures [8]. The traces for 84, 168 and 196 amu shown in fig. 6 all display similar features within the experimental noise, and the relative intensities follow closely those corresponding to the iron pentacarbonyl mass spectrum (shown in the inset).



Fig. 6. Molecular thermal programmed desorption spectra from a 5 L dose of iron pentacarbonyl on Pt(111) at 110 K. The traces for 84, 168 and 196 amu are shown. Also shown in the inset is the mass spectrum for iron pentacarbonyl in the 50-200 amu mass range taken with the same mass quadrupole.

Partial pressures are given in arbitrary units (a.u.).

The only other desorption product from iron pentacarbonyl on Pt(111) is carbon monoxide. Fig. 7 show CO TPD after 10 L Fe(CO)₅ exposures at 120 and at 350 K. Four peaks are seen after low temperature deposition with maxima at 170, 195, 265 and 410 K (the peak below 150 K originates from Fe(CO)₅ desorption from the supports). The first three features are due to molecular desorption; the peak positions and relative intensities match those obtained for the 84, 168



Fig. 7. Carbon monoxide thermal programmed desorption spectra after a 10 L dose of iron pentacarbonyl on Pt(111) at 120 and 350 K. Partial pressures are given in arbitrary units (a.u.).



Fig. 8. Reflection-absorption infrared spectra taken after different $Fe(CO)_5$ and CO deposition sequences as explained in the figure. See details in text.

and 196 amu traces. The last peak, however, is due to a small amount of iron pentacarbonyl decomposition on the surface, as confirmed by previous XPS data. Also, the spectrum obtained after dosing at 350 K displays two peaks centered around 430 and 530 K: the first corresponds to the hightemperature feature seen in the low-temperature deposition experiments (although slightly displaced) while the the second is associated with the iron films which form under these high temperature deposition conditions [9].

Finally, additional experiments were done in order to determine the origin of the several bands seen in the RAIRS data. The two bottom traces in fig. 8 were obtained after adsorption of iron pentacarbonyl at low temperatures followed by flashing to 475 K, quenching back to low temperatures, and exposing the surface to carbon monoxide. One main peak is observed in each spectrum at 2090 and 2093 cm⁻¹ respectively. The third trace, which has one major peak at 2096 cm^{-1} , was obtained after a more severe iron deposition procedure, namely, a 20 L Fe(CO)₅ dose at 275 K followed by flashing to 475 K and CO adsorption at 110 K. Flashing to 475 K was done in all three cases in order to insure that any CO resulting from the iron pentacarbonyl deposition was desorbed, and that the iron present on the surface was in its metallic form. Finally, the two top spectra, obtained after 20 L Fe(CO)₅ dose at 275 K and after 5 L CO exposure at 110 K, respectively, are given for reference. The peak positions are as follows: 2103 and 1845 cm^{-1} for the iron pentacarbonyl, and 2101 and 1842 cm^{-1} for CO.

4. Discussion

The infrared data presented here for the chemical vapor deposition of iron using iron pentacarbonyl complement our previous XPS and TPD studies [8,9] and provides new insights into both the iron pentacarbonyl surface decomposition mechanism and the steady growth of iron films.

Several details on the mechanism for the iron pentacarbonyl decomposition can be obtained by close inspection of the RAIRS data. The features associated with adsorbed molecular iron pentacarbonyl at low temperatures, a skewed peak centered around 2050-2065 cm^{-1} and a small shoulder at 2010 cm^{-1} , are guite different from those previously reported for this compound. Iron pentacarbonyl has been shown to exist in a trigonal-bipyramidal form with D_{3h} symmetry [15,16] and to have two IR active bands in the C-O stretching region, an A" mode associated with the axial positions, and a E' mode corresponding to the equational locations [17-21]. The position of those peaks does not depend significantly on the environment surrounding the iron pentacarbonyl molecules (table 1), so no matrix effects can explain the blue shift of over 30 cm^{-1} seen in our case. Also, polymerization of metal carbonyls tends to shift the C-O stretching frequencies to lower values; Fe₂(CO)₉ displays its two strongest IR bands at 2034 and 1828 cm^{-1} [21]. Therefore, the discrepancy between our results and those published previously suggests that iron pentacarbonyl is highly perturbed upon chemisorption on Pt(111); we propose that a change of geometry takes place and that the molecule rearranges to a square pyramidal structure with C_{4v} symmetry. Pentacarbonyls with C4v symmetry have been observed for a variety of metals including V [24], Cr [25,26], Mo [26,27], W [26,28], Mn [24,29], and Re [30], and in fact, for the vanadium, chromium and molybdenum cases both C_{4v} and D_{3h} structures have been reported [25,27,31]. Also, although the

Table 1 Infrared active absorption bands for the C–O stretching modes of iron pentacarbonyl in different environments

Environment	$ \frac{\nu_6 (A_2'')}{(cm^{-1})} $	$v_{10} (E')$ (cm ⁻¹)	Ref.
Vapor	2034	2012-2014	[15,18,20]
Solid	2003	1982, 1977	[15]
Liquid	2002-2016	1979-1984	[15,17]
C_6H_{12} solution	2022	2000	[17]
CS ₂ solution	2019	1995	[18]
CCl ₄ solution	2020	1995	[15]
Xe matrix	2023	1996	[20]
Ar matrix	2027	2004	[20]
In PFTE polymer	2020	1998	[53]
Ads. on glass	2026	2004	[22]
Ads. on silica	2024	2002	[23]
Ads. on Si(111)-			
(7×7)	-	1893	[12]
Ads. on Pt(111)	2064 (A ₁)	2010 (A ₁)	This work

structure of iron pentacarbonyl have been determined to be a trigonal-bipyramid by using both X-ray crystallography [15] and electron diffraction [16], the rapid exchange between the axial and equational positions [32] has been explained by the so-called Berry pseudorotation mechanism [33,34] which proposes a reversible distortion of the D_{3h} structure into a C_{4v} geometry. This interconversion has an activation barrier of about 1 kcal/mol [35], and even though different theoretical calculations have yielded contradicting results regarding the relative stability of the D_{3h} and C_{4v} structures, they all agree that both geometries are very close in energy [36–39].

Metal pentacarbonyls with C_{4v} symmetry have three IR active bands in the C–O stretching region, two of A₁ symmetry and another of E symmetry. The final assignments have been traditionally made based on relative intensity arguments and have placed the A₁ apical mode around 1930 cm⁻¹, the E peak at 1965–1975, and the A₁ basal feature about 2095 cm⁻¹ [26,29]. Several calculations estimate the angle between the top and each basal CO to be between 90 and 110° [26,38]. We propose that iron pentacarbonyl adsorbs on platinum with the square base towards the surface, and that, because of the surface dipole selection rule obeyed by RAIRS [40], only the A₁ modes are seen in our spectra. We also suggest that the peak at 2065 cm^{-1} is due to the apical CO ligand, and that the basal vibration is too weak to be observed (since θ is close to 90°). Two more reported facts help understand the high frequency value observed in our case for the C-O stretch. First, extended Hückel calculations have shown that a directional a₁ orbital replaces the "missing" ligand in the $M(CO)_5$ moiety when in a C_{4v} geometry [38]. This orbital is full in the case of iron pentacarbonyl, and would interact strongly with the surface valence band in the adsorption orientation proposed here. Second, it has been shown that oxidation of the metal center in metal carbonyls results in an increase in frequency for the C-O stretching mode of about 100 cm⁻¹ per electron withdrawn [41]. Even though the A1 C-O stretching mode for the top ligand is seen at 1930 cm^{-1} for tungsten, molybdenum and chromium complexes [26], the same mode is observed at 2020 cm^{-1} for HMn(CO)₅ [29]. We suggest that the high frequency we see in our chemisorbed iron pentacarbonyl case could be due to electron donation from the $Fe(CO)_5 a_1$ orbital to the surface.

The iron-surface interaction can also explain the iron pentacarbonyl reactivity observed, since electron withdrawal from the a_1 orbital results in weakening of the Fe-C basal bonds [38]. Molecular orbital calculations indicate that the iron center losses 0.11 electrons in the transition from $Fe(CO)_5$ to $Fe(CO)_4$ [42]. We have seen that about 70% of the first 2 L of iron pentacarbonyl decomposes on the surface at 100 K upon adsorption, and additional surface chemistry is observed upon thermal activation. After annealing to 185 K the vibrational spectrum changes dramatically, and a new peak centered at 2035 cm^{-1} appears which we assign to the formation of iron tetracarbonyl on the surface. $Fe(CO)_4$ has been isolated and characterized both in low-temperature matrices [43,44] and in the gas phase [45]. The IR bands in the C-O stretching region for this fragment shift by about 30 cm^{-1} to lower frequencies from those for $Fe(CO)_5$, to 2000 and 1985 cm⁻¹. In our case we do observe a red shift of about 23 cm^{-1} in going from 175 to 185 K. As in the case of $Fe(CO)_5$, we only see one peak for this species even though up to four bands are expected for this moiety. This can again be explained by the surface selection rule for RAIRS: for instance, if this fragment has C_{2v} symmetry [44] and one of its major axis is aligned with the surface normal, only the mode with a dynamic dipole in that direction will be IR active (if such axis is the z-axis of the molecule, the peak to be observed is the one corresponding to the A_1 mode, the highest in frequency). In the case of a C_{3v} arrangement [43] again only the apical A_1 mode would be seen on the surface if it is assumed that the base is parallel to the surface and θ is close to 90°.

Surface Fe(CO)₄ can either decompose further or desorb upon sample heating. TPD spectra show a molecular desorption peak at 195 K. Upon careful inspection of the traces for the different molecular fragments we conclude that the desorbing gas at that temperature is pure $Fe(CO)_5$; the $Fe(CO)_4^+$ signal detected in the TPD originates from cracking of the molecular ion exclusively. This implies that some of the surface iron tetracarbonyl recombines with chemisorbed carbon monoxide to form iron pentacarbonyl, a reaction which has been reported to take place both in low-temperature inert matrices and in gas phase [43,45–47]. The remaining $Fe(CO)_4$ undergoes yet another decarbonylation step: the RAIRS spectrum after annealing to 240 K shows some new features around 1980 and 1935 cm⁻¹, which, using similar arguments as those given above for Fe $(CO)_4$, we assign to Fe(CO)₃ moieties. The energy for the dissociation of a carbon monoxide fragment from iron tetracarbonyl has been estimated to be quite low, on the order of 5 kcal/mol (the value for the same reaction in iron pentacarbonyl is about 40-55 kcal/mol) [48,49]; the resulting iron tricarbonyl from photolytic activation of iron pentacarbonyl has been detected both in cold matrices and in gas phase [45,48]. Fe(CO)₃ is believed to be in a configuration of C_{3v} symmetry and to have IR active peaks at around 2042 (A_1) and 1935 (E) cm^{-1} . We believe that on Pt(111) this fragment recombines with carbon monoxide to form iron pentacarbonyl, which desorbs in a small peak at 265 K. Gas-phase kinetic data have shown that the formation of iron tetracarbonyl starting from iron tricarbonyl is about two orders of magnitude faster than the following reaction from $Fe(CO)_4$ to $Fe(CO)_5$ [45]; in our experiments

once $Fe(CO)_3$ is formed on the surface no $Fe(CO)_4$ can be isolated for long enough time to be characterized by RAIRS.

No other iron-containing intermediates were detected beyond 240 K, and only CO desorbs above that temperature in a peak centered around 410 K. This desorption is accompanied by the disappearance of the IR peak around 2100 cm⁻¹, indicating that the process occurring under those conditions is the molecular desorption of carbon monoxide [50]. The CO TPD after iron pentacarbonyl deposition at 350 K, on the other hand, displays an extra peak around 530 K that can be due to carbon and oxygen recombination after CO dissociation; AES and ISS results have shown that dissociation does take place in high temperature iron film deposition [9].

The assignments for the RAIRS spectra given above are tentative and will need to be further confirmed by additional experiments. An alternative interpretation of the data could be suggested in which the peak at 2035 cm⁻¹ after heating to 185 K is proposed to be due to the A''_2 peak of D_{3h} iron pentacarbonyl while the spectrum seen at 240 K would correspond to Fe(CO)₄. In any case the data show that iron tetracarbonyl does form on the surface, even though the evidence for the detection of iron tricarbonyl is less convincing.

Our data also provide new information on the details of iron film growth from iron pentacarbonyl. XPS results have shown that iron pentacarbonyl chemisorption at 140 K results in a small amount of decomposition at low coverages, but that increasing doses only produce a condensed multilayer that desorbs molecularly below 180 K [8]. Steady deposition of metallic iron on platinum can only be achieved if the surface temperature is kept above 275 K during the iron pentacarbonyl dosing. Our RAIRS data corroborates these conclusions: the iron pentacarbonyl uptake curves at 110 K indicate that the peak around 2100 cm⁻¹, which is associated with carbon monoxide chemisorbed on a top site on Pt(111) [51] resulting from iron pentacarbonyl dissociation at these temperatures, grows first. The signal intensity for this 2100 cm^{-1} peak increases until reaching a maximum around 2 L and then decreases slowly with increasing doses, probably because the incoming

iron pentacarbonyl molecules displace some of the chemisorbed CO. The second peak seen around 2050 cm^{-1} correspond to molecular iron pentacarbonyl. The signal intensity for this feature increases linearly up to about 3 L and changes its slope beyond that point by a factor of 2.3. Assuming a constant sticking coefficient for iron pentacarbonyl (as suggested by the linearity of the uptake curve below and above 3 L), the slope change would imply that initially about 70% of the carbonyl adsorbed decomposes on the surface while 30% adsorbs molecularly.

The absolute coverage for the resulting iron monolayer can be estimated by two independent methods. First, the Fe 2p_{3/2} XPS signal obtained after a 5 L Fe(CO)₅ exposure followed by flashing to 280 K corresponds to 5% iron atoms (relative to the number of surface platinum atoms) [9]. On the other hand, the CO RAIRS signal is about 45% as intense as that from a 5 L CO dose on clean Pt(111), and knowing that this latter case results in the formation of a $c(4 \times 2)$ LEED pattern corresponding to $\theta = 0.5$ [50], we calculate our CO coverage to be about 23% of a monolayer. Accounting for the fact that one iron pentacarbonyl molecule yields five CO moieties, there is good agreement between the Fe XPS and the RAIRS results; we estimate the first monolayer to be saturated after the chemisorption of about 7.5 $\times 10^{13}$ iron pentacarbonyl molecules on the surface.

Deposition of iron pentacarbonyl at 275 K vielded RAIRS spectra in which only carbon monoxide chemisorbed on platinum is observed. The main peak grows and shifts to higher frequencies with increasing doses, until reaching a value of about 2104 cm⁻¹ and a coverage of about $\theta = 0.35$ around 2 L. This peak does not shift any further upon additional iron pentacarbonyl exposures, but the overall intensity decreases slowly as CO is displaced by the new incoming molecules. A small feature is also observed around 1850 cm⁻¹ which corresponds to CO adsorbed on a bridge site, but no peaks corresponding to molecular iron pentacarbonyl are seen under these conditions, even though a steady growth of iron films is observed by XPS. We believe that at these temperatures iron pentacarbonyl dissociates almost immediately upon chemisorption to produce metallic iron and carbon monoxide [9]. Additionally, no CO adsorption on iron is detected by RAIRS, which is understandable since molecular CO desorption from iron surfaces is known to occur below room temperature [52]. We believe that the carbon monoxide adsorbed on the platinum poisons that surface towards further iron pentacarbonyl decomposition, and that the film growth takes place on "nucleation" sites where the initial decomposition had taken place [8]. This may be the reason why we have observed three dimensional island formation during the film growth [9].

5. Conclusions

The infrared data obtained here for the chemisorption and thermal decomposition of iron pentacarbonyl on Pt(111) had shed some light onto the mechanism for $Fe(CO)_5$ decomposition on this surface. We propose that the molecule changes geometry upon adsorption from a trigonal bipyramid with D_{3h} symmetry (which is the stable configuration of the pure compound) to a square planar structure where the surface becomes a sixth ligand for the central iron metal. Most of the pentacarbonyl desorbs molecularly as the sample is heated, but a small fraction decomposes in a stepwise fashion to sequentially form iron tetracarbonyl and iron tricarbonyl. Both of these moieties are stable on the surface in a narrow range of temperatures, but upon heating of the substrate they recombine with coadsorbed CO to form Fe(CO)₅, which then desorbs.

Acknowledgement

Acknowledgement is made to the Donors of The Petroleum Research Fund, administrated by the American Chemical Society, for support of this research.

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