The nature of carbon monoxide adsorption on platinum group metal catalysts

Patrick John Sears

Sears, Patrick John (1996) The nature of carbon monoxide adsorption on platinum group metal catalysts. Masters thesis, Durham University.

The nature of carbon monoxide adsorption on platinum group metal catalysts

by

Patrick John Sears, B.Sc.(Hons)
(Hatfield College)

Submitted for the degree of Master of Science.

University of Durham

Department of Chemistry

September1996

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Acknowledgements

I would like to acknowledge the help of the following people during the course of this work:

Dr. K.L.Peat for technical advice, support and encouragement.
Professor K.Wade for advice and direction.
Dr. J.R.Jennings and Dr. M.Kilner for helpful discussion.
The technical staff of University College Stockton-on-Tees for expert experimental support.
Miss J.K.Cook and Mr. D.Wileman for proof reading and advice on composition.

Declaration

No part of this work has previously been submitted by the candidate for a degree in this or any other university.

Abstract

The nature of carbon monoxide adsorption on alumina supported platinum group metal catalysts was investigated using in-situ infra-red spectroscopy. Both adsorption and thermal desorption studies were made and the results combined to give a complete picture of the bonding schemes observed for each metal. In light of the conclusions drawn from this research, bimetallic samples were then investigated. The observations from these experiments were explained by comparison with the results from the constituent metals.

When attempting to study the bonding schemes in more detail using an enhanced method of data collection, anomalous results were obtained. It was proposed that the species formed would be alumina carbonates, this was proven correct by comparison with the results from a standard preparation of these groups. Standard techniques for the analysis of catalysts and the treatment of results were developed during the course of this work.

Chapter 1

Aims and Introduction

1 Aims and Introduction

The aim of this project was to design, commission and test a catalyst examination apparatus and then to use this equipment to investigate the adsorption of carbon monoxide to supported platinum group metals (PGM) under working conditions for exhaust catalysts. Catalysts of this type had previously been studied using infra-red spectroscopy (IR) and by ultra-high vacuum (UHV) surface techniques but it was normally the case that a study would concentrate on one metal. This study aimed to use the same in-situ infra-red spectroscopic method to study several different catalysts therefore producing comparative results.

This area of research was of interest because the adsorption and desorption of CO with PGM catalysts is one of the processes that occurs within an automotive catalytic converter. The adsorption of CO to a metal surface allows activation of the CO bond making it susceptible to oxidation.

The experimental conditions used for this study were designed to mirror those found within the exhaust stream of a standard car. Temperatures over 1000°C have been observed in test conditions; however under normal circumstances the temperature of the gases that pass through the catalytic converter do not exceed 500°C. The exhaust system of a car is connected directly to the atmosphere therefore most of the system remains at atmospheric pressure. The resistance caused by the addition of a catalytic converter to the exhaust system will result in a slight pressure increase though this should not exceed 4 bar.

Chapter 2

Vehicle Exhaust Catalysts

2 Vehicle Exhaust Catalysts

Every new car with a petrol engine produced in the United Kingdom has, by law, to be fitted with a catalytic converter. What is a catalytic converter, what does it do, and how does it work?

A catalytic converter is a device fitted to the exhaust system of a car. It is a block through which the gases pass en-route to the atmosphere. As the exhaust stream passes through the converter it is converted chemically reacted to produce "less harmful" gases.

Apart from air depleted in oxygen and the products of fuel combustion (CO_2 and H_2O), the exhaust from an engine contains the following pollutants:

Carbon Monoxide
Nitrogen Oxides (NO_x)
Hydrocarbons (including aromatics)
Particulate matter (e.g. soot)
Trace heavy metals

The gases are most readily dealt with by the following reactions:[1,2]

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2$$

$$C_xH_y + (x + \tfrac{y}{4})O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

$$2CO + NO_2 \longrightarrow 2CO_2 + N_2$$

Whilst the solids, particulate matter and heavy metals are best removed by filtration.

Any catalyst used must be able to cope with all of the above contaminants without any loss of activity. The catalyst must reduce the concentrations of the gases that pass over it without producing a side product that is considered more harmful. Most catalysts work by having a metal surface where gas molecules may adsorb and then desorb having first undergone some sort of reaction.

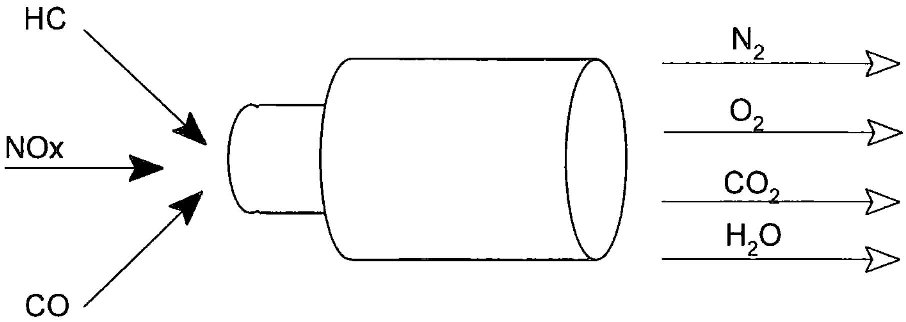

Figure 2.1 Schematic representation of a modern catalytic converter

There are many requirements of a catalytic exhaust system. The main points are listed below:

- The catalyst system must not impair the efficiency of the engine.

  Any resistance of the gas flow from the engine will cause a reduction in the efficiency of the car - even the standard exhaust system causes a slight drop in power. A catalytic system should not impair the engine efficiency and must therefore have minimal restriction to gas flow.

- The catalyst system must be able to cope with a wide range of temperatures.

  The operating temperature of an engine varies considerably from ignition to that encountered after running for a long period. The catalyst has to be able to operate between 0°C (ambient temperature on cold winter days) and temperatures up to

800°C that may be encountered after a long run. The catalyst has to be able to work at these temperatures and also has to be able to withstand the heat, and rate of heating, without physically or chemically degrading.

- The catalyst and its mounting must be strong and light.

  In day to day use a car undergoes many vibrations, the catalytic converter must be able to withstand these for a period equal to the expected lifetime of the car. The catalyst must also be light, since if it is too heavy it will reduce the operating efficiency of the car.

- The system should be recyclable.

  The number of new cars produced each year is ever increasing. The catalyst systems that are scrapped with old cars must be disposed of in some way. Therefore the system must either break down under certain conditions to give a product that can be safely disposed of, or be recyclable.

Another consideration in the design of catalysts is poison resistance. Trace elements that are found in fuel, such as sulphur and lead, can build up on the surface of the catalyst and poison it. This reduces the efficiency and in extreme cases prevents further catalytic activity.

It has been found that the best catalysts for the breakdown of these pollutant gases are the metals platinum, palladium and rhodium. The expense of these metals has led to much research into cheaper alternatives such as nickel, copper, iron and cobalt[4]. None of these latter metals have the selectivity or activity of the platinum group metals, though work continues in the search for cheaper alternatives.

The metals in the catalyst are held on a support[1,3], usually alumina, which is present not just to hold the metal in place but to form an integral part of the catalyst. Although the bulk of the support is alumina, other elements are present in varying quantities to help promote a variety of reactions. The function of the alumina is several fold:

- The alumina has a very high surface area, which allows the catalytic metal to be highly dispersed throughout the main body of the catalyst.

- Alumina can remove by absorption most of the materials that are poisonous to the catalyst, e.g. lead and sulphur.

- Alumina is used because it has similar thermal expansion properties to the active metals that are used in the catalysts. This gives the system a greater resistance to thermal shock.

There are several ways that a catalyst can be mounted within the converter:

- A powder of the catalyst could be used, but this is impractical since retention of a powder is practically impossible without restricting airflow through the engine.

- The catalyst and support could be formed under pressure into pellets. This kind of catalytic system is widely used in the chemical industry. It allows easy handling of the catalyst once produced however pellets are impractical for use in cars because of the vibration that system is subjected to which may lead to erosion of the catalytic surfaces.

- The favoured system for catalytic converters in cars is a monolith[7]. This is a large block of inert material with channels cut into it to allow the gas to flow through.

The catalytic metals and support material can be applied to the surface of the block as a washcoat.

A catalytic system that controls all three of the major pollutants (CO, NO_X, hydrocarbons) is referred to as a three way catalyst (TWC). The major factor affecting the efficiency of the catalyst system is the amount of fuel and oxygen going into the engine at any one time. This is known as the fuel/air mix. Changing the stoichiometery of combustion can alter the different relative amounts of each pollutant in the exhaust stream. This will also affect the ratios of the non-pollutant gases, e.g. oxygen, to the pollutants, which will cause a change in the operating efficiency of the catalyst. Many of the catalyst systems in use today work using the feedback from an oxygen sensor so the fuel/air mix can be constantly adjusted by an electronic fuel injection system. The ability to change the fuel/air mix enables the system to cope with the different loads placed upon an engine whilst still maintaining maximum catalyst activity. An example of this kind of system is shown in figure 2.2.

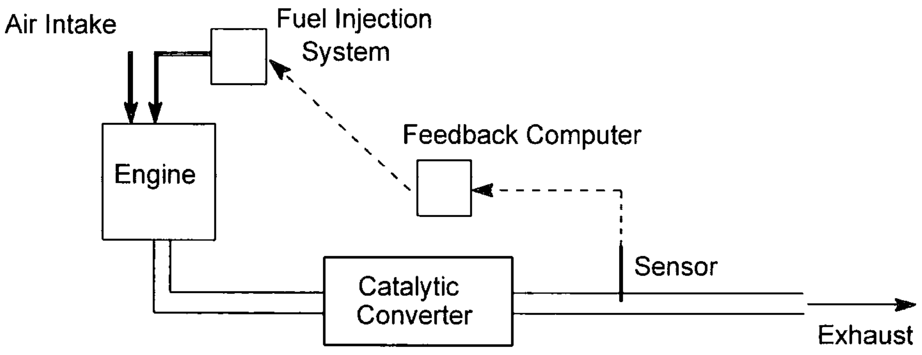

Figure 2.2 Catalytic exhaust system with automatic fuel/air mix adjustment[3]

The temperature range in which a catalyst may both adsorb and desorb reactant and product molecules is known as the "light off" region. Outside this range the catalyst is either too cold to undergo a desorption process with any detectable rate or so hot that the gaseous species cannot adsorb preventing reaction. Maintaining the operating temperature of the catalyst is a major problem as is heating of the surface, from ambient to the light off region, to prevent build-up of surface species and poisons. If too many adsorbed pollutant molecules are present there are no sites left for oxygen to attack.

The general reactions that are performed on the surface of one of these catalysts are;

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2$$

$$C_xH_y + (x + \tfrac{y}{4})O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

$$2CO + NO_2 \longrightarrow 2CO_2 + N_2$$

As can be clearly seen the first two reactions are oxidations, because of this both can be performed under similar conditions. The other reaction is the more difficult since it involves the reduction of NO_X to nitrogen. Many catalysts produce NH_3 by the reduction of NO_X but this is merely oxidised back to NO_X by the oxygen rich conditions needed for the conversion of CO to CO_2. This gives no decrease in the overall throughput of NO_X pollutants, therefore a more specific catalyst is required to promote the required reaction.

The fuel/air ratio is another critical factor in the running of the engine[1,2]. Engines are capable of running at a stoicheometry of reaction that is far less rich in fuel (leaner) than the catalysts allow. The main problem with running an engine at this, more efficient, fuel/air ratio is that the catalytic system becomes less efficient at the reduction of NO_X pollutants, as shown in figure 2.3.

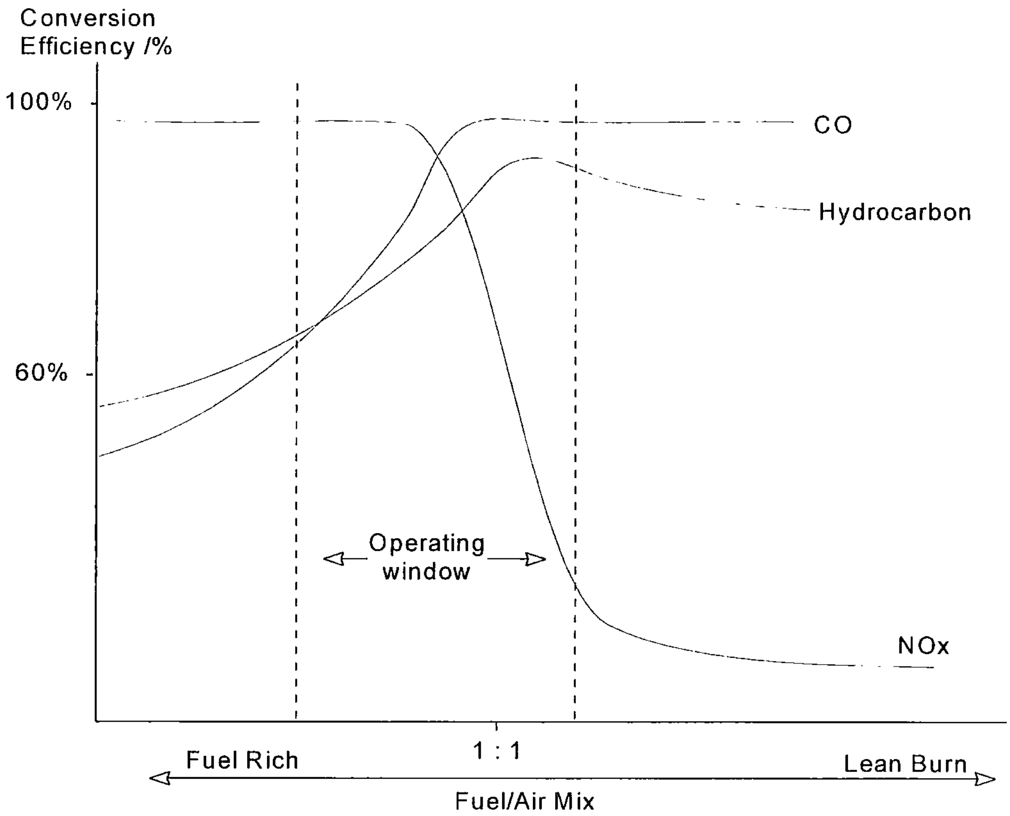

Figure 2.3 The effect of fuel/air ratio on TWC efficiency[1]

Since, by law, target reductions of NO_X pollutants have to be met, engines have to be set to use more fuel in the combustion mixture than is necessary. This means the motorist spends more on fuel and causes our limited oil reserves to be used inefficiently. The aim of much of the research into these catalyst systems is to enable the engines of modern cars to run using a lean fuel mix whilst still meeting NO_X reduction targets.

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Chapter 3

Studying Adsorbed CO By Spectroscopy

3 Studying Adsorbed CO By Spectroscopy

3.1 IR Spectroscopy of surfaces

Infra-red spectroscopy is the study of absorption or emission of energy in the IR region of the spectrum[1,2]. The majority of the transitions in this region are the stretching and bending of bonds. At room temperature it is assumed that all molecules lie in their ground vibrational state (predicted by the Boltzmann distribution) which means that the usual transition studied is that of v=0 to v=1[*1]. This is complicated by rotational transitions that may occur at the same time hence producing a spectrum that will have a rotational fine structure superimposed over the vibrational transition.

A molecule usually has 3n-6 modes of absorption (3n-5 for a linear molecule), where n is the number of atoms in the molecule. When a species is bound to a surface the rotational and translational modes change and become new modes. These are best considered as the analogues of the rotational and translational modes but hindered by attachment to the surface. This causes a shift in the frequency of surface groups when compared to free species. Any vibrations of the same symmetry can mix and will give frequencies removed from either of the two original absorptions.

The selection rule for absorptions of molecules at a surface also plays an important role in any spectroscopic study[3]. The usual requirement for absorption of IR radiation by a molecule is that the transition that occurs causes a change in the molecular electric dipole moment. For molecules adsorbed to a surface this is enhanced by the requirement that this be in a direction perpendicular to the surface. This requirement is caused by a screening of the parallel component of any electric field by the metal surface, such as the molecular dipole. The metal also produces an opposite

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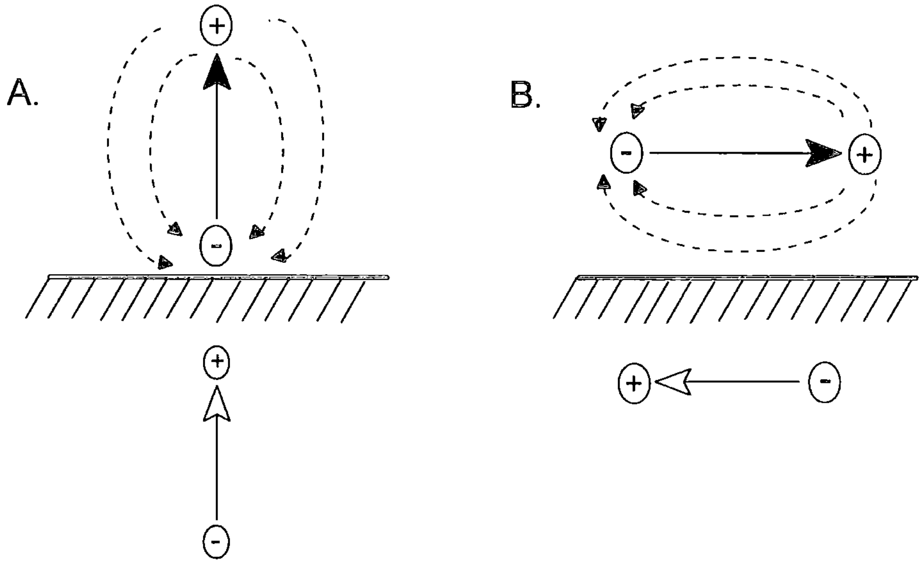
[*1] v is the vibrational quantum number

instantaneous dipole parallel to the surface. This second effect can be best explained in terms of the metal producing a mirror dipole in opposition to that belonging to an adsorbed molecule. If this is for a perpendicular molecule then the original field is reinforced by this "induced dipole". When the field is parallel, the "induced dipole" is directly opposed to the original and hence cancelled out by it. This is shown by the figure 3.1 below.



A. Perpendicular and B. Parallel arrangements

Figure 3.1 Mirror dipoles formed by an adsorbed diatomic molecule.[3]

3.2 Modes of CO adsorption

Carbon monoxide can adsorb to metal surfaces in several different ways. These, known as modes of adsorption, are shown below in figures 3.2-3.4.

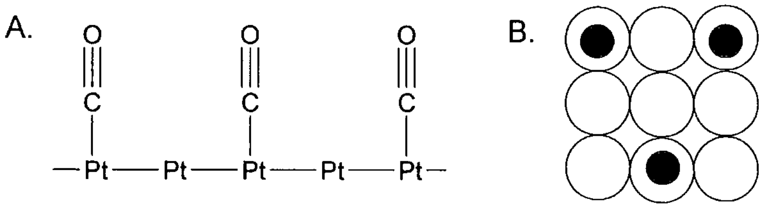


Figure 3.2 Terminal CO adsorbed on Platinum (100)[4]

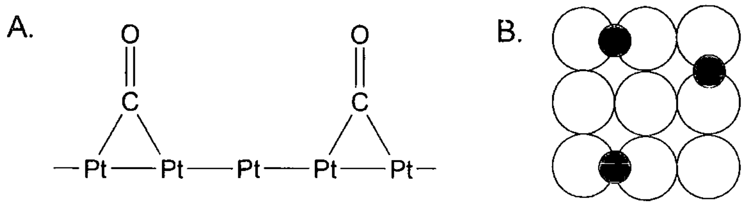


Figure 3.3 μ-2 bridging CO adsorbed on Platinum (100)[4]

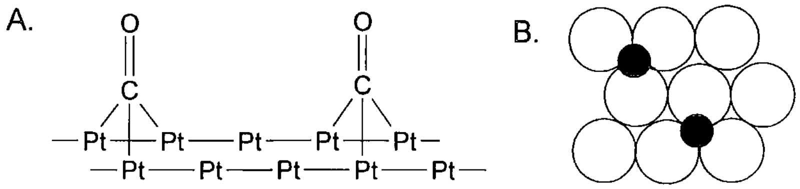


Figure 3.4 μ-3 bridging CO adsorbed on Platinum (111)[4]

3.3 Bonding in metal carbonyl clusters

Many correlations can be drawn between the adsorption of CO on metal surfaces and the bonding of carbonyl ligands to metal clusters[5]. Many of the ways in which the atoms are bound to the surfaces of metal catalysts can also be seen in the corresponding metal cluster systems. This bonding has been extensively studied and the forces which hold these groups of atoms together are well understood. The study of metal carbonyl clusters can provide an insight into CO adsorption on metal catalysts which cannot be gained through conventional analysis. Information on the bond lengths and angles within a cluster can be precisely ascertained using x-ray diffraction, a technique which is inappropriate to the study of catalysts.

Five main methods of carbonyl bonding have been observed for metal clusters, these are shown below in figure 3.5.

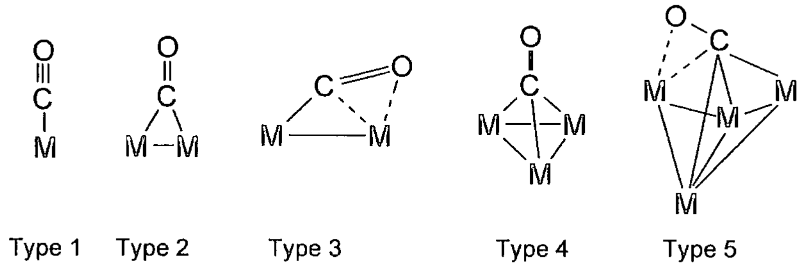


Figure 3.5 Ways in which carbonyl ligands can co-ordinate.[5]

Two of these species (type 3 and 5) include interaction of a metal centre with the CO bond, this type of bonding has been observed in the manganese cluster $Mn_2(CO)_5(Ph_2PCH_2PPH_2)_2$. In this system the carbonyl ligand is bound terminally to one of the manganese atoms whilst bonding in a dihapto fashion to the other. The dihapto bonding of metals to CO is shown below in figure 3.6.

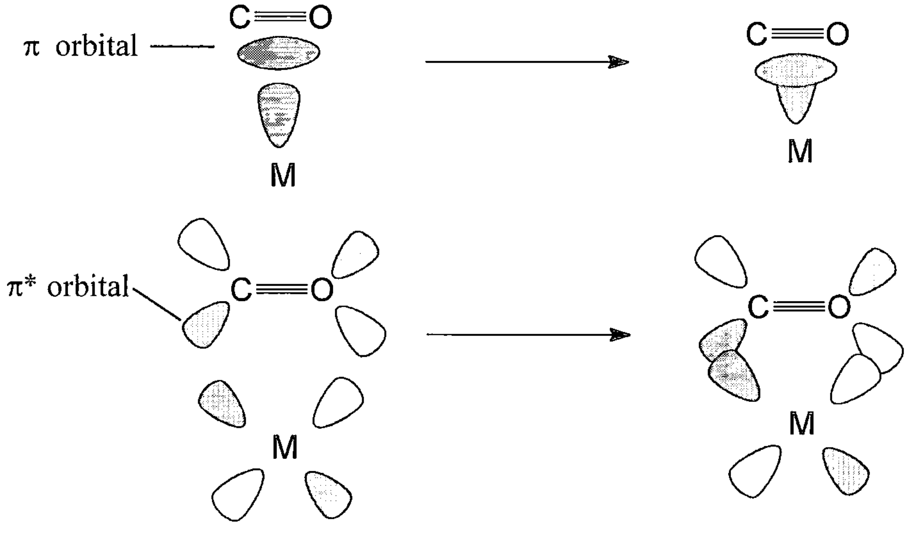


Figure 3.6 Molecular orbital diagram showing dihapto metal/CO bonding[5].

3.4 Absorption of IR by CO bound to a M/Al_2O_3 surface

The most important consideration for IR studies of alumina supported M-CO is that the absorption of the transition relating to M↔CO cannot be directly observed. The absorption of M-C occurs at 470cm^{-1}[*1] which cannot be seen as the absorption of the alumina obscures the detection of the M-C absorption. Instead the absorption corresponding to stretching of the CO bond can be seen (M-C↔O).

The stretching absorption of $CO_{(g)}$ occurs at 2143cm^{-1}. This should be shifted by the mechanical coupling of the two bands to give a value of aproximately 2200cm^{-1} when bound to platinum. The actual observed frequency for this system is aproximately 2100cm^{-1} a difference of 100cm^{-1} from what was predicted. This discrepancy arises because of two different effects. Reinforcement of the electrical dipole by the metal, as described in the previous section, causes a shift to lower frequency of approximately 50cm^{-1} for CO bound to a transition metal. However the more important effect is a bonding consideration. Carbon monoxide bonds to a metal surface by means of donation of electrons from the carbon lone pair to the surface, as shown in figure 3.7. These electrons are accepted by a hybrid metal orbital and form a σ M←C bond.

Figure 3.7 Formation of σ M←C[*2]

The donation of electron density to the surface gives it a partial negative charge and to neutralise this charge imbalance there is donation of electrons from the metal d-orbitals to CO. The only orbital of correct symmetry to accept these electrons is the C-O antibonding (π*) orbital as shown below in figure 3.8.

[*1] Figure measured using electron energy loss spectroscopy.

[*2] Shading on orbital diagrams represents the sign (±) of the wavefunction.

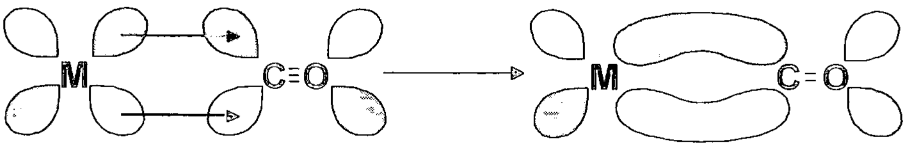


Figure 3.8 Formation of π M$\overset{\rightharpoonup}{=}$C

Donation of electrons from the metal d_{xz} or d_{yz} to the CO π^*_p forms a π M$\overset{\rightharpoonup}{=}$C bond. This new bond that is formed will strengthen the bonding between the surface and the carbon but since it populates an orbital that is CO antibonding it will weaken the bonding between the carbon and oxygen. Since the major contribution to the observed IR band results from the force constant of the C-O bond, an observed decrease in frequency will be the result of an increase in M-C bond strength. The process by which this occurs is known as synergic bonding or "back donation", and carbon monoxide, like phosphines (R_3P), alkenes ($R_2C{=}CR_2$), alkynes ($RC{\equiv}CR$) and many other ligands with suitable orbitals to receive electrons from metals in this way are referred to as π-acid ligands.

A consideration of bond order also shows the expected change in frequency with the changing co-ordination.

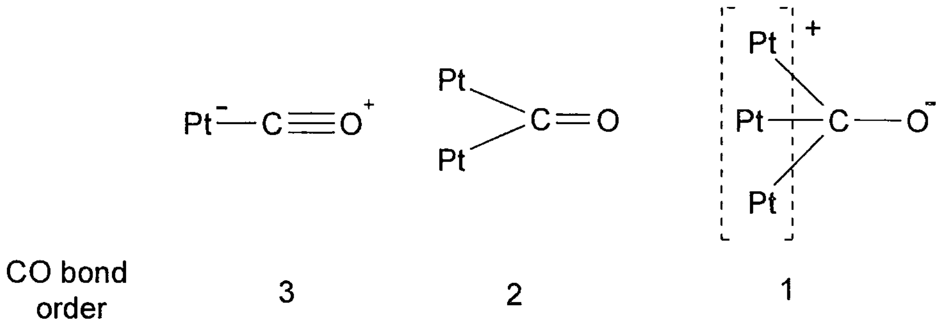


Figure 3.9 C-O bond order in platinum surface species

As can be seen from the diagram 3.9 above the bond order of CO decreases as the number of platinum atoms to which the group is bound increases. The decrease in bond order will lead to a decrease in the vibrational frequency. This is explained by Hookes Law of vibration which states that the frequency (ν) is proportional to the square root of the force constant (*k*) divided by the mass (*m*).

$$\nu \propto \sqrt{\frac{k}{m}}$$

In this case the mass remains constant and the force constant is a measure of the bond order.

3.5 Crystal faces and Miller indices

Miller indices are a method by which a crystal face can be defined. The Miller index describes the plane through which the unit cell is cut to create a surface. The arrangement of atoms within a surface can be determined if the crystal face and the bulk arrangement are known. Platinum, rhodium and palladium all have the same, face centred cubic arrangement within the bulk and so the arrangements below are correct for all of the metals considered in this thesis[4]. The faces displayed below are those on which carbon monoxide adsorption has been reported.

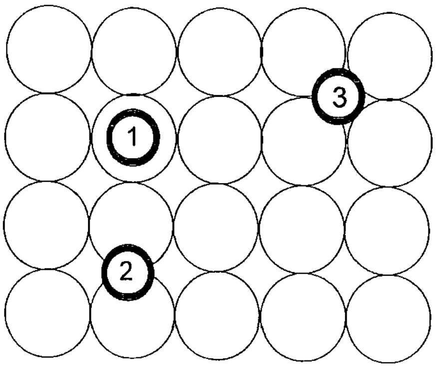


Figure 3.10 FCC (100)

The (100) surface of a face centered cubic metal possesses sites for terminal adsorption (1), μ-2 bridging (2) and μ-4 bridging (3) species.

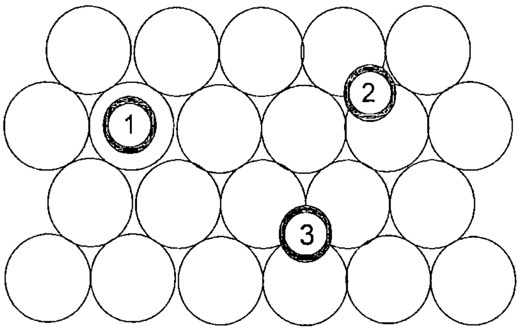


Figure 3.11 FCC (111)

The (111) surface of a face centered cubic metal possesses sites for terminal adsorption (1), μ-2 bridging (2) and μ-3 bridging (3) species.

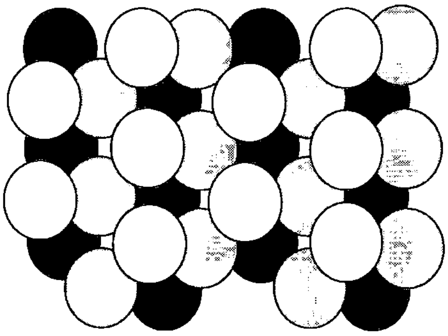


Figure 3.12 FCC (210)

As can be seen in figure 3.11, the (210) face is considerably more complex than the (100) or (111). The inter-atomic distance as measured between two atoms in the same layer (e.g. two white atoms) is aproximately 3.9Å in platinum. This distance is too great for μ-2 or μ-3 bridging to occur between atoms within the same layer.

3.6 Other spectroscopic methods of studying adsorbed CO

Other spectroscopic methods have been used in the study of carbon monoxide adsorbed to supported metal catalysts. The two main methods are detailed below.

3.6.1 Low energy electron diffraction (LEED)[6]

The wavelength that is associated with low energy electrons is of the same order of magnitude as the interatomic spacing within crystals. This means that electrons of the correct energy can be diffracted by atoms within a crystal and the resultant pattern analysed to give information on atomic position. The low energy of the electrons means that the penetration of the surface is slight and only the first few atomic layers can be studied. This technique can also be used to look at the re-arrangement of surface atoms following adsorption of gas molecules. The technique uses ultra high vacuum since the crystal surface has to be kept free of gaseous contaminants, and the scattering from electrons colliding with gas molecules needs to be minimised.

3.6.2 Infra-red reflection-absorption spectroscopy (IRAS)[6,7,8]

IRAS (or RAIRS as it is also known) is another UHV technique. It can be used to study a monolayer of adsorbate on a metal surface since it has excellent sensitivity and stability. The optical geometry of the IRAS system is shown in figure 3.13 below.

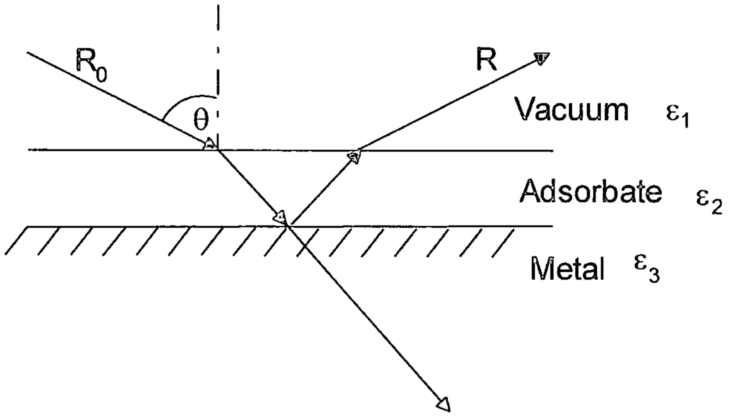


Figure 3.13 Optical geometry in IRAS exeriment

As can be seen the infra-red beam passes through three phase changes (ε_1-ε_2, ε_2-ε_3-ε_2 and ε_2-ε_1), because of this, optimisation of the geometry is important to achieve strong signals. The optimum angle (θ) for the incident beam is dependent on the wavenumber for 2100cm^{-1} this is 87°. Originally dispersive IR instruments were used with this technique but an improvement in the accuracy of interferometers has led to the use of Fourier transform spectrometers because of the signal to noise enhancement that can be achieved. IRAS is a useful technique because, when optimised, it allows detection of sub-monolayer concentrations of surface species.

3.6.3 HREELS and UPS[6,7]

High resolution electron energy loss spectroscopy (HREELS) is another technique that has been widely used to study PGM catalysts. This technique allows accurate measurement of the vibrational energy levels and hence gives spectra similar to IR spectroscopy. The main advantage of this technique is the experimental set-up which allows the probing of energy levels in the sub-800 cm^{-1} region. This allows detection of the metal-carbon bond vibration in CO adsorption studies.

Ultraviolet photoelectron spectroscopy (UPS) is a method by which the energy levels and density of states of valence level electrons can be obtained. The sample is irradiated with UV radiation, this interacts with electrons in the valence levels and an electron will be emitted. This electron can then be captured and the energy of the level from which it originated found using the final kinetic energy and the wavelength of UV radiation used.

This technique has been applied to M-CO studies because it allows measurement of the energies of bonding and anti-bonding energy levels and the populations of these levels. This is useful since the amount of π-back bonding can be determined.

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Chapter 4

Previous studies of carbon monoxide adsorbed on metal surfaces.

4 Previous studies of carbon monoxide adsorbed on metal surfaces

4.1 In-situ IR spectroscopy studies

Much of the recent work looking at the interaction of gases with surfaces under working[*3] conditions has been performed using in-situ techniques. In-situ work is based on a situation where a reaction can be studied as it proceeds without any change in the conditions. Infra red spectroscopy is especially suited to this technique because of its unintrusive nature and because the range of temperatures and pressures used for catalyst studies of this type are all within the scope of IR spectroscopy.

4.2 Platinum systems

The most comprehensive work produced on the platinum/alumina system has been done by R.Barth *et al.* A comprehensive study of the adsorption and subsequent desorption of CO with a supported platinum catalyst has been documented in two papers[1,2].

The first study was performed using a home-made cell which consisted of a sealed quartz tube with KCl windows[1]. A self supporting disc of catalyst was mounted in a quartz sample holder, heated by a resistance heater controlled via a thermocouple which was sheathed in stainless steel to prevent contamination.

The initial results were very simple: A sharp peak at 2060cm^{-1} with a shoulder on the high frequency side (2080cm^{-1}) and a second broader peak at 1845cm^{-1} which was of much lower intensity. These peaks were assigned to the terminal (2060 & 2080cm^{-1}) and μ-2 bridging (1800cm^{-1}) modes of CO adsorption discussed in chapter 3. The

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[*3] The term "working" in this context means realistic to conditions under which the catalyst would be operated.

main peak at 2060cm^{-1} was lower than had previously been observed on platinum and therefore it was suggested that this was CO bonding to small numbers of platinum atoms or to disordered surfaces whilst the higher frequency peak was a result of extended Pt-CO systems on larger platinum crystallites.

A second low frequency peak was detected at 1760-1780cm^{-1} but was not assigned due to the interference with water at this frequency[*4]. Barth continued his investigation to look at the way that the frequency of the main peak changed with temperature. This followed the general trend that frequency dropped with increasing temperature. There were however two points on the curve plotted where the frequency remained the same (c.a. 200°C & 300°C). Another experiment was carried out with a sample where the metal loading was different and this produced a different shaped graph (though the major features remained the same).

The integrated intensities of the various peaks were investigated as a function of temperature. The findings were of interest as they showed an initial increase in the intensity of the main peak. This was interpreted as either being a result of conversion from bridged CO to terminal or due to an increase in CO absorbivity at increased temperatures, but no other works have been found to corroborate this claim.

A later work by the same group[2] looked at the difference between alumina and silica as supports for platinum catalysts. A species at 2000cm^{-1} was found to be present only when the metal was supported by alumina, not with silica. This species was assigned to the interaction between terminal bound CO to platinum sites and the support. The interaction was proposed to be the transfer of electron density from CO bonding orbitals to acceptor sites on the support.

[*4] Water appears on an infra red spectrum at 1630cm^{-1}

The adsorption of CO on platinum was investigated in a paper by Anderson and Rochester[3]. The spectra included in the report were the result of subtraction of a "reduced" spectra from the original data. This method is unreliable because the IR spectrum of the alumina support changes with heating. The results from this experiment showed the presence of a species at 2080cm^{-1} as well as the main terminal peak which was reported at 2070cm^{-1}. This new species was described as an additional terminal CO complex. This species was unaffected by further heating although the main peak continued to shift to lower frequency. Bridging species were detected at about 1850cm^{-1} and were quickly desorbed upon heating to 523K. Upon cooling in CO two entirely separate peaks were visible at 1885 and 1836cm^{-1}.

A review of CO/Metal adsorption by Sheppard and Nguyen[4] compared the results of single crystal studies with those where supported catalysts were used. The frequencies for terminally adsorbed CO for both single crystal and supported metal studies are very similar. From single crystal work CO absorption on Pt (111) occurs at about 2065cm^{-1} [5,6,7] and increases with increasing coverage to about 2100cm^{-1}. Only one of these studies[7] reported a bridging species and this was found to be present at 1870cm^{-1}.

Further work on CO adsorption on single crystals of platinum have been performed since Sheppard and Nguyen's review. The adsorption of CO to Pt (100) has been described by two groups[8,9], the first of which describes the bonding of terminal CO to platinum and reports the change in absorption frequency from 2074cm^{-1} to 2094cm^{-1} with increasing coverage. This is also documented in the later work of Pirug *et al*[9], who also report the presence of a μ-2 bridging peak at 1950cm^{-1}. As can be seen there is a large variation in the frequency of the μ-2 bridging species for different crystal faces. There is also a difference in the frequency of the terminal CO but this is less well pronounced. The reason for the bigger change with bridging species is that there is a change in the Pt-Pt distance for different crystal faces, this will alter the amount of back donation from the metal and hence the vibrational frequency. This change should not affect the frequency of the terminal species though the variation of surface density of Pt atoms will alter the frequency by a small amount.

With supported metals, terminal CO absorption occurs at about 2060-2070cm^{-1} and where investigation into coverage was made it was found that the absorption frequency increased with coverage from 2050cm^{-1} to 2120cm^{-1}. Bridged species were observed in most studies at about 1820cm^{-1} (though a range from 1850-1780cm^{-1} was seen). One study[10] reported a second bridging peak at a frequency of 1605cm^{-1} this was formed on small platinum particles (10Å) though it was ill-defined. These studies were carried out either using silica or alumina as the support and the frequency of absorption appears independent of the support used.

Two of the studies are of interest because they use different experimental methods[7,11] to observe metal-CO interactions. The first used a self supporting disk of metal particles pressed with KBr and the other used a suspension of the metal in oil. In both of these studies it was possible to observe the metal-carbon bond stretch at about 470cm^{-1}. It is not possible to observe this feature in alumina or silica supported systems because of absorption by the support at this frequency.

The interaction of potassium with the CO/Pt system was studied on a single Pt (111) crystal using high vacuum (UHV) techniques[12]. A combination of low energy electron diffraction (LEED) and reflection absorption infra-red spectroscopy (RAIRS) was used to investigate adsorbed CO on platinum and the interaction of this system with potassium. The results of the study show that three bands are present when CO is adsorbed to a platinum surface, a sharp peak at 2100cm^{-1}, a shoulder on the low frequency side of the main peak (2095cm^{-1}) and a small peak at 1842cm^{-1}. The doping of a surface, that had previously been exposed to CO, with potassium results in a shift to lower frequency in the terminal peak and an increase in the peak width. Potassium doping also leads to a number of new states appearing in the range 1300-2000cm^{-1} and a drop in the intensity of the terminal peak. The study theorises that potassium doping causes a change in the favoured adsorption site from on top (terminal) to bridging and it is the interaction between the potassium and bridging CO that causes the appearance of these new states.

The LEED study compares the experimental data with theoretical data that was generated from supposed surface arrangements. Several important approximations were made in the calculation of the theoretical data but similarities can be seen between theoretical and experimental results. Explanations are offered to the surface arrangement of potassium and CO species through the combination of LEED and IR data and several possible surface configurations for these atoms are suggested. These conlusions mainly focus on the influence of the potassium which is beyond the scope of this study.

4.3 Rhodium systems

A group working on the adsorption of CO on supported rhodium catalysts have obtained spectra of CO bound to the alumina support[13]. This, they claim, is observed at 2199cm^{-1} and is carbon monoxide chemisorbed to Al^{3+} sites. This group compared the results they obtained using supported catalysts to those reported in the literature both for single crystal studies and for model supported systems[*5].

Thermal desorption results from this group showed the loss of the Al^{3+}-CO group at -100°C whilst loss from rhodium sites occurs over a very much wider range (150-400°C) with maximum desorption rate occurring at ≈ 220°C. Infra-red results for this system included 5 separate peaks as detailed in table 4.1.

Peak	Frequency	Assignment
1	1923cm^{-1}	Rh-CO (bridging)
2	2038cm^{-1}	Gem-dicarbonyl
3	2069cm^{-1}	Rh-CO (terminal)
4	2104cm^{-1}	Gem-dicarbonyl
5	2199cm^{-1}	Al^{3+}-CO

Table 4.1 Peak assignments in reference 13.

The results are very similar to those seen for the platinum system with the exception of the gem-dicarbonyl. The term gem-dicarbonyl refers to a group where there are two carbon monoxide groups bonded to a single surface metal site as shown below.

[*5] A model system in this context refers to rhodium deposited onto a single crystal of Al_2O_3 or onto a film of Al_2O_3 which had been grown on a molybdenum crystal.

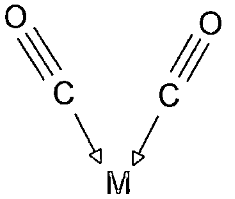


Figure 4.1 An example of a gem-dicarbonyl surface species

However, the assignment of a gem-dicarbonyl in the work by Diaz *et al.*[13] is questionable as the spectra presented in this paper show little evidence of gem-dicarbonyl species. However where IR absorption bands at 2105cm^{-1} and 2035cm^{-1} are expected, Diaz *et al.* reported the higher frequency peak (2104cm^{-1}) as a small shoulder on the side of the terminal peak (2069cm^{-1}) whilst the low frequency peak (2038cm^{-1}) was not visible on the spectra.

Gem-dicarbonyl species have been reported elsewhere[3,14]. The paper by Yates *et al.*[14] shows that the peaks relating to the gem-dicarbonyl species have a higher intensity than all the other groups present in the spectrum. The gem-dicarbonyl species are proposed to be present on rhodium sites that are sterically unhindered. i.e. on isolated rhodium atoms. Angular strain occurs in this system because of the proximity of two separate π systems, as shown below.

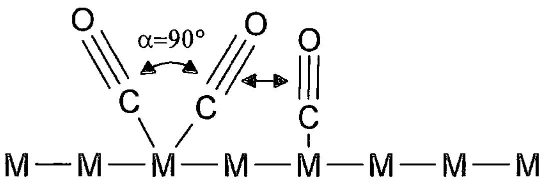


Figure 4.2 Steric interactions on metal surfaces.

Another reason for proposing that the gem-dicarbonyl exists only on highly dispersed surfaces is the stability of the associated frequencies. There is little or no change in the observed frequency of gem-dicarbonyl species when either the temperature or coverage is changed. A change in coverage would not affect the frequency of species bonded to small Rh_x clusters or isolated atoms as the coverage dependence is primarily a surface effect.

The other features reported in the paper by Yates[14] are a broad band at $1870cm^{-1}$ assigned to bridged CO (Rh_2-CO) and a sharp band at $2070cm^{-1}$ which is assigned to CO bound to a single surface site. A desorption study by this group shows that the terminal peak is lost before both the gem-dicarbonyl and bridging species.

The paper uses the integrated areas of the various peaks to estimate the proportion of isolated rhodium atoms to those contained in Rh_x groups. This calculation is based upon the assumption that the only sites capable of adsorbing two CO groups are isolated atoms. No account is taken of adsorption at edges or steps which may also be able to support $Rh(CO)_2$ groups. Another assumption is that the absorptivity of gem-dicarbonyl and bridging species is similar. There is no reason for this to be so.

A paper by Rasband *et al.*[15] claims that the nature of the gem-dicarbonyl species is very different to that proposed by Yates. The observations of this paper are that the gem-dicarbonyl is easily desorbed from the surface and that this is the first species to be lost on heating. This is contrary to the report in reference 14 where gem-dicarbonyl species were stable to temperature. The spectra produced by this group are similar to those observed for the platinum experiments though these are using silica and not alumina as a support.

The reasons for the markedly different spectra that have been observed in the papers above are explained by Rice *et al.*[16] In a series of experiments they demonstrated how the spectra of CO-Rh/Al_2O_3 were dependent on both the metal loading and the reduction temperature used prior to CO adsorption. The gem-dicarbonyl species remained constant with changing reduction temperature whilst the other species that were observed (terminal and bridging CO) showed dependence both with frequency and intensity. The general trend observed was that the higher temperatures gave higher frequencies and in most cases higher intensities. A maximum temperature was also observed beyond where the trend was reversed.

The paper by Rice suggested that the gem-dicarbonyl species were formed on the edges of small Rh_x rafts. The frequencies of Rh-CO and Rh_2-CO are justified by comparison with analogues observed in cluster studies. Species are also proposed for other bands observed as shown below.

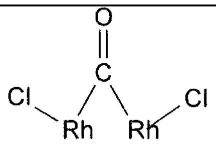
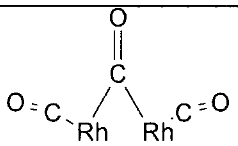
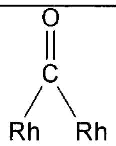
Frequency	Proposed Structure
2096-2102 cm^{-1} 2022-2032 cm^{-1}	Rh^{I}-$(CO)_2$
2080-2100 cm^{-1}	Rh^{I}-CO
2042-2076 cm^{-1}	Rh^{0}-CO
2000-2020 cm^{-1}	
1900-1920 cm^{-1}	
1845-1875 cm^{-1}	

Table 4.2 Proposed structures for adsorbed Rh/CO groups from reference 16

There has been considerable difference in the frequency of μ-2 brigding species caused by other groups bonded to surface sites. As can be seen in table 4.2 above there are three species based on the μ-2 system. The presence of either chlorine or carbonyl species has been suggested as a reason for an increase in frequency of the main carbonyl group with respect to the unsubstituted groups.

The presence of gem-dicarbonyl bands in IR is questioned in the review by Sheppard[4] because according to the surface selection rule[*6], the out of phase (anti-symmetric) vibration should be forbidden since the molecular dipole lies parallel to the surface of the molecule. This is shown in figure 4.3 below:

[*6] See section 4.1

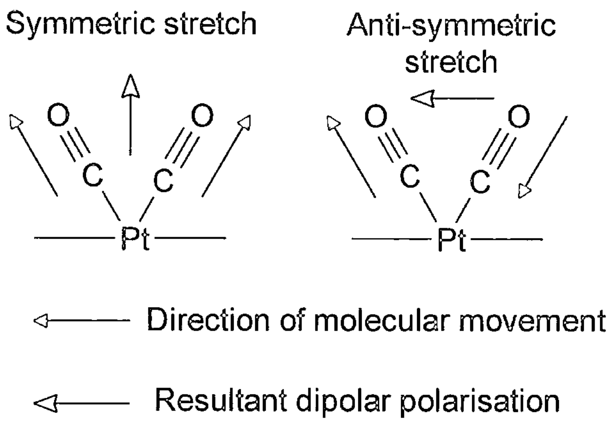


Figure 4.3 Diagram showing dipolar polarisation in symmetric and anti-symmetric stretches of gem-dicarbonyl species.

The fact that the anti-symmetric stretch would not be seen on an extended surface supports the argument that these structures are formed on isolated Rh atoms since the surface selection rule would not apply for a small group of atoms. A review on CO adsorption to various metals by Sheppard and Nguyen[4] gives an excellent comparison of many results. Some of the results detailed by the review did not include gem-dicarbonyl species[17,18].

A comparison between the results observed with single crystal, supported catalyst and cluster studies has been made by Dubois and Somorjai[8]. A summary of the data presented in this report is included below in table 4.3:

	CO bonding mode				
System	Analysis Technique	μ-3	μ-2	Terminal	Gem-dicarbonyl
Rh (111)[8]	EELS		1870cm^{-1}	2070cm^{-1}	
Rh/Al_2O_3[19]	IR		1870cm^{-1}	2070cm^{-1}	2031, 2101cm^{-1}
Rh/SiO_2[20]	IR		1890-1900cm^{-1}	2040-2065cm^{-1}	1990-2020, 2080cm^{-1}
$Rh_2(CO)_8$[21]	IR (solution)		1845, 1861cm^{-1}		2061, 2086cm^{-1}
$Rh_4(CO)_{12}$[22]	IR (solid)		1848cm^{-1}		2028-2105cm^{-1}
$Rh_6(CO)_{16}$[23]	IR (solid)	1770cm^{-1}			2016-2077cm^{-1}

Table 4.3 Comparison of Rh-CO absorption frequencies

This report shows the importance of considering the cluster studies that have been mentioned in chapter 3. Comparison of the data from cluster studies can give insights into the bonding arrangements in other systems. The gem-dicarbonyl species that are observed in the alumina supported catalyst[19] are far more similar to the gem-dicarbonyl species in $Rh_4(CO)_{12}$ than those in the other clusters listed. The advantage of drawing comparisons with clusters are that the geometries and bonding arrangements can be precisely identified using x-ray diffraction.

4.4 Palladium systems

The adsorption of carbon monoxide on supported palladium catalysts has been widely studied[23,24,25]. The survey by Palazov *et al*[23] is useful in understanding the various modes of adsorption seen on this catalyst. Palladium adsorbs carbon monoxide to give features that are not present with either platinum or rhodium. The table below shows the adsorption states reported by Palazov.

Frequency	Notes	Assignment
2075 cm-1	High coverage	CO adsorbed terminally to Pd (111) and/or Pd (100)
1980 cm-1	High coverage	CO bridging Pd (100)
1930 cm-1	High coverage	CO bridging Pd (111)
1900 cm^{-1}	Low coverage	CO bridging Pd (100)
1820 cm-1	Low coverage	μ-3 CO on Pd (111)

Table 4.4 CO species observed on Pd crystals from reference 23

The frequencies of bridging species are far higher than those previously observed for either of the other two metals examined. The shift in frequency that is seen upon a change in the coverage is explained as being dipole-dipole coupling and interaction via the metal.

The review[4] by Sheppard and Nguyen compares data obtained from single crystal studies to that measured using supported catalysts and evaporated metal films. In most cases the results show a terminal group (2060-2100cm^{-1}) and a number of bridging groups (2035-1786cm^{-1}). The appearance of terminal groups is prevalent where the metal support interaction is strongest, either in supported studies or where finely divided metal particles are used. This is suggested as being a result of the electronic influence of a strong support interaction.

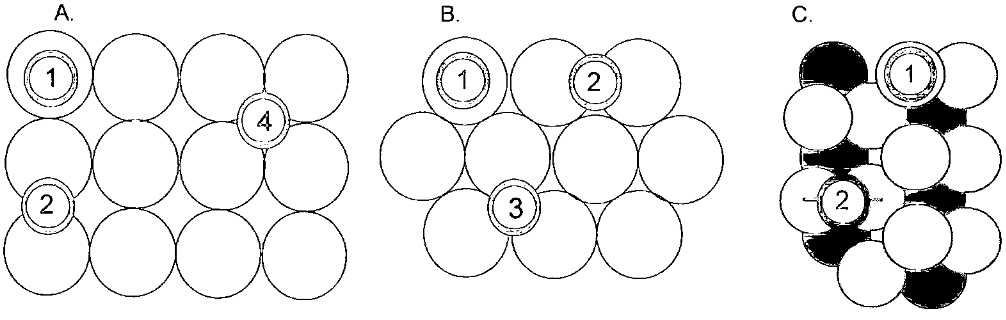
The single crystal work by Bradshaw *et al*[26] gives the best insight into the various species that have been observed on the surface of palladium. This work, performed by RAIRS, shows that the spectrum of CO/Pd is highly dependent both on the crystal face that is studied and the CO coverage achieved. The results of studies on three different faces (100), (111) and (210) are detailed in table 4.5 below and illustrated in figure 4.4.

Species	Frequency	Crystal Face
μ-3 bridge	1820-1840cm^{-1}	111
μ-2 bridge	1890-1930cm^{-1}	100
μ-2 bridge	1890-1946cm^{-1}	111
μ-2 bridge	1898-1945cm^{-1}	210
Compressed	1950-1983cm^{-1}	100
Compressed	1950-1995cm^{-1}	210

Table 4.5 CO adsorbed to Pd crystals. Data from reference 26

Compressed species are those where there is a forced interaction between one group and the next because of the high coverage. There will be a steric repulsion from the two π systems being held close together which result in angular strain and a shift to lower frequency. LEED data was used in the above experiment to produce accurate analysis for the species seen.

Pd (210) has an open top layer structure with an interatomic distance of 3.88Å. The μ -2 bridging species cannot be bridging two sites in the first layer as the inter-atomic distance is too great. Instead it is proposed that the species is bridging between atoms in the first and second layers of the open structure as shown in figure 4.4.



1. Terminal CO, 2. μ-2 bridging CO, 3. μ-3 bridging CO, 4. μ-4 bridging CO

Figure 4.4 CO bonding to a. (100), b. (111) and c. (210) crystal faces of Pd

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Chapter 5

Experimental

5 Experimental

5.1 Spectrometer

The spectrometer used for these experiments was a Mateson Genesis series spectrometer. This is a Fourier transform spectrometer controlled by computer. The principle of a Fourier transform spectrometer is that of a Michelson interferometer, which passes a broad band of frequencies through the sample. The interference pattern is observed because of the difference in path length between the main beam and the fraction of the beam split off through the moving mirror, as shown above. The laser beam is used as reference beam to allow alignment of the system since the IR beam is by definition not within the visible range of the spectrum. This type of spectrometer is illustrated in figure 5.1.

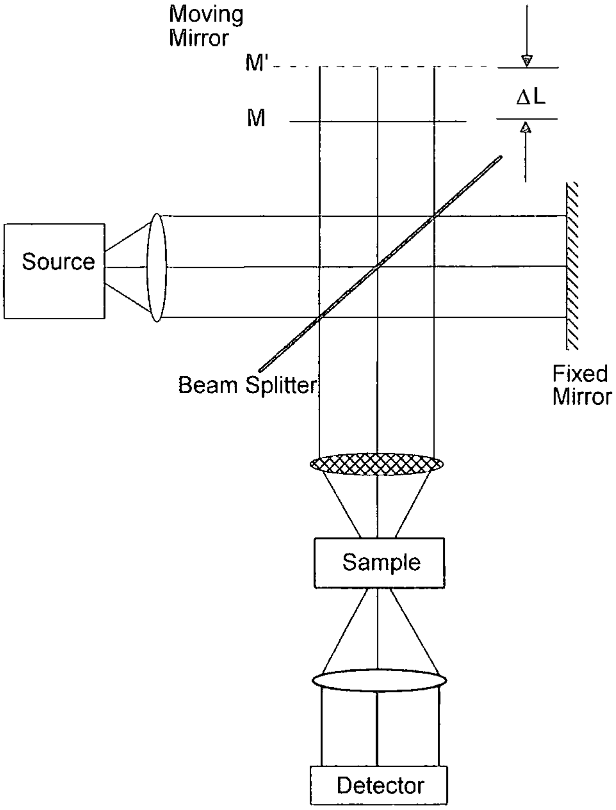

Figure 5.1 An FTIR spectrometer

The Fourier transform is a mathematical process whereby data can be collected in a 'time' domain and can be subsequently converted into a frequency. The main advantage of the Fourier transform infra-red spectrometers is that all of the data, across the whole spectrum, is collected in one pass of the mirror. This means that it is possible to quickly collect a large number of scans that can be averaged to help reduce the noise contribution. The improvement in the signal to noise ratio is defined by the following equation:

$$\Delta S.N = \sqrt{n}$$

Clearly the change in the signal to noise ratio ($\Delta S.N$) depends on the square root of the number of scans (n) taken. This will mean that by taking 100 scans there will be a 10 fold improvement over a single scan. Where samples transmit little radiation, this enhancement in resolution can be an enormous advantage since there is only a small difference between the peak intensity and the background noise.

5.2 Preparation of catalyst samples

The catalyst samples studied consisting of platinum group metals supported by alumina, were supplied by Johnson Matthey. These samples were the scrapings from a monolith after the catalytic washcoat had been applied, therefore they contained materials such as alkali metals and ceria which form an effective catalyst rather than the kind of system used for abstract studies. The samples included both unimetallic species (Pt, Pd and Rh) and mixtures of two or three of the metals. In effect the unimetallic samples formed a control for any further experiments. The samples were supplied as a powder which was pressed into a disk suitable for mounting within the sample holder in the infra-red cell.

The disks made were 13mm in diameter and were created by pressurising the powder. No external support material was needed to make the disks though the effect of adding additional alumina was investigated and found to be small in terms of the spectra produced. A small amount of the sample, usually about 25mg, was then placed between the polished surfaces of two stainless steel disks. The press assembly was then placed in a hydraulic press and approximately 3 tonnes of pressure was applied for 2 minutes.

5.3 Spectral cell

The sample cell was supplied by Greasby Specac. It was designed to sustain pressures of 50 bar and temperatures up to 800°C. The temperature was controlled by a thermocouple on the main sample holder linked to an external temperature controller. A heating element in the main body of the cell allowed the temperature of the cell body and windows to be controlled, this prevents gaseous species condensing within the apparatus.

The samples were mounted in the sample holder (pictured below in figure 5.2). 13mm disks could be placed within the mount and held in place by two keep rings. Uniform heating was ensured by the use of a block of large thermal mass which meant that the sample was heated evenly.

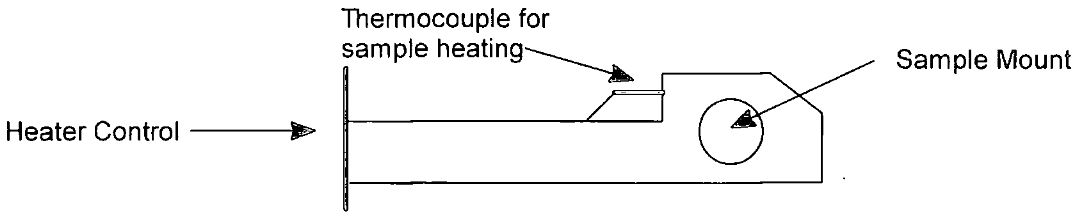

Figure 5.2 Sample holder from infra-red cell

Gas can be supplied to the cell by any or all of three inlets, the outlet has a larger bore so that only one outlet is needed for any of the inlets that are used. The outlet from the cell was connected to a valve to allow the cell to be pressurised. All gases used in the experiments were vented through a fume cupboard to the atmosphere after first being cooled by passing through a coil of 1/8" tubing. The supply system, shown below in figure 5.3, was designed and built so that any one of three gases could be supplied to the cell. The nitrogen line was fitted with a drying tube packed with 3Å molecular sieve to prevent contamination of the sample by water, this was only deemed necessary for nitrogen because of the large volumes used. Non-return valves were fitted to all of the lines to prevent cross-contamination of the supplies.

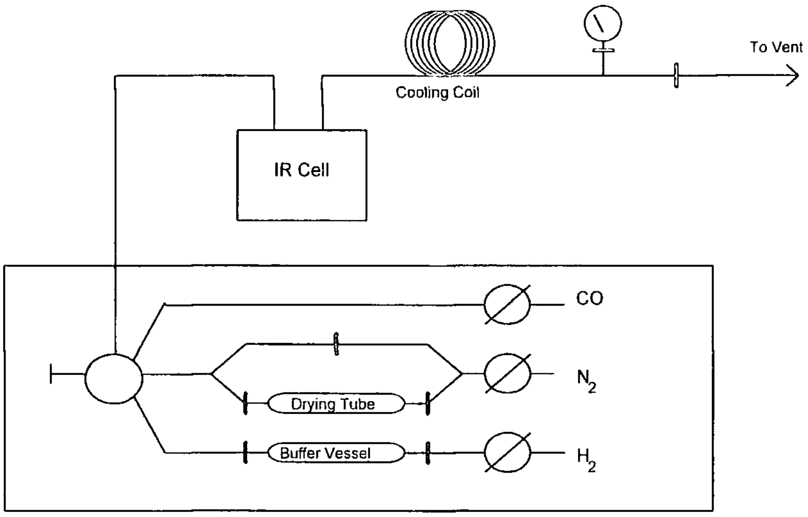

Figure 5.3 Gas flow diagram

This system was extensively pressure tested to ensure reproducibility and so that no oxygen was admitted to the cell during experiments. Loss of gas at a maximum rate of 0.1 bar in 12 hours was deemed satisfactory for these experiments[*7].

Two slight modifications were made to the system shown in figure 5.3 during experiments. Exhaust gas could be sampled using the gas vessel on the exit from the

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[*7] Compressed air at 6 bar was used to pressure test the apparatus.

cell, as shown below in figure 5.4. The bracketed section could be isolated so that the contents could later be sampled by gas chromatography or mass spectroscopy. Isolation valves were added to both the hydrogen and CO lines to eliminate any leakage through the cross valve.

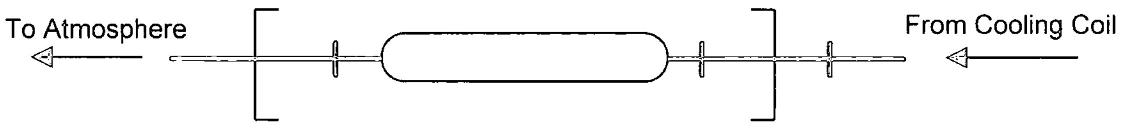

Figure 5.4 Gas sampling system

5.4 Data analysis

Using the "First" software each spectrum was smoothed using a boxcar smoothing routine*[8] and then exported from the spectral analysis software as an x,y table so that spectra could be displayed using any spreadsheet or graphics package. Microsoft Excel was used to handle the collected data. Spectra were buffered*[9], by adding a constant to the y-value of each spectrum. Buffering allows clear comparisons to be made between different spectra on the same axis when diagramatically represented.

5.5 Baseline correction

The collected data was superimposed on the absorption profile for the support. Peaks were reported at an artificial frequency and their shape was distorted by the curved baseline. The usual method to correct for this is to take spectra of the support without

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*[8] A boxcar routine weights all points in the spectrum equally when smoothing.

*[9] Stacked one on top of the other.

impregnated metals at different temperatures and to subtract these from the result with the metal. This was not possible because no sample of the support was available.

Subtraction of a spectrum from the previous one was also not possible. This method is a standard technique for showing the change between spectra. The change in frequency with changing coverage, observed in these experiments*[10], meant that spectral information became disguised. Subtraction in these cases resulted in spectra with both positive and negative components.

To overcome this problem it was decided that an artificial baseline be produced and subtracted from the original spectrum to give a corrected result. Several attempts were made using linear regression to produce a "line of best fit" to be used as the baseline. This method proved unsatisfactory since the accuracy of the correction was dependent on the fit of the line to the curve (The curvature of the baseline meant that no straight line could provide an adequate description). This method produced spectra that were distorted in both line shape and frequency.

An improvement on the previous method was devised so that an accurate artificial baseline could be produced which could then be subtracted from the original. This was done using a computer algorithm to fit a curve to a set of data points. The algorithm produced a polynomial to the fifth degree which was used to create a curve. This curve could then be subtracted from the original data to produce a "corrected" spectrum. An example of this process is shown in spectrum 5.1.

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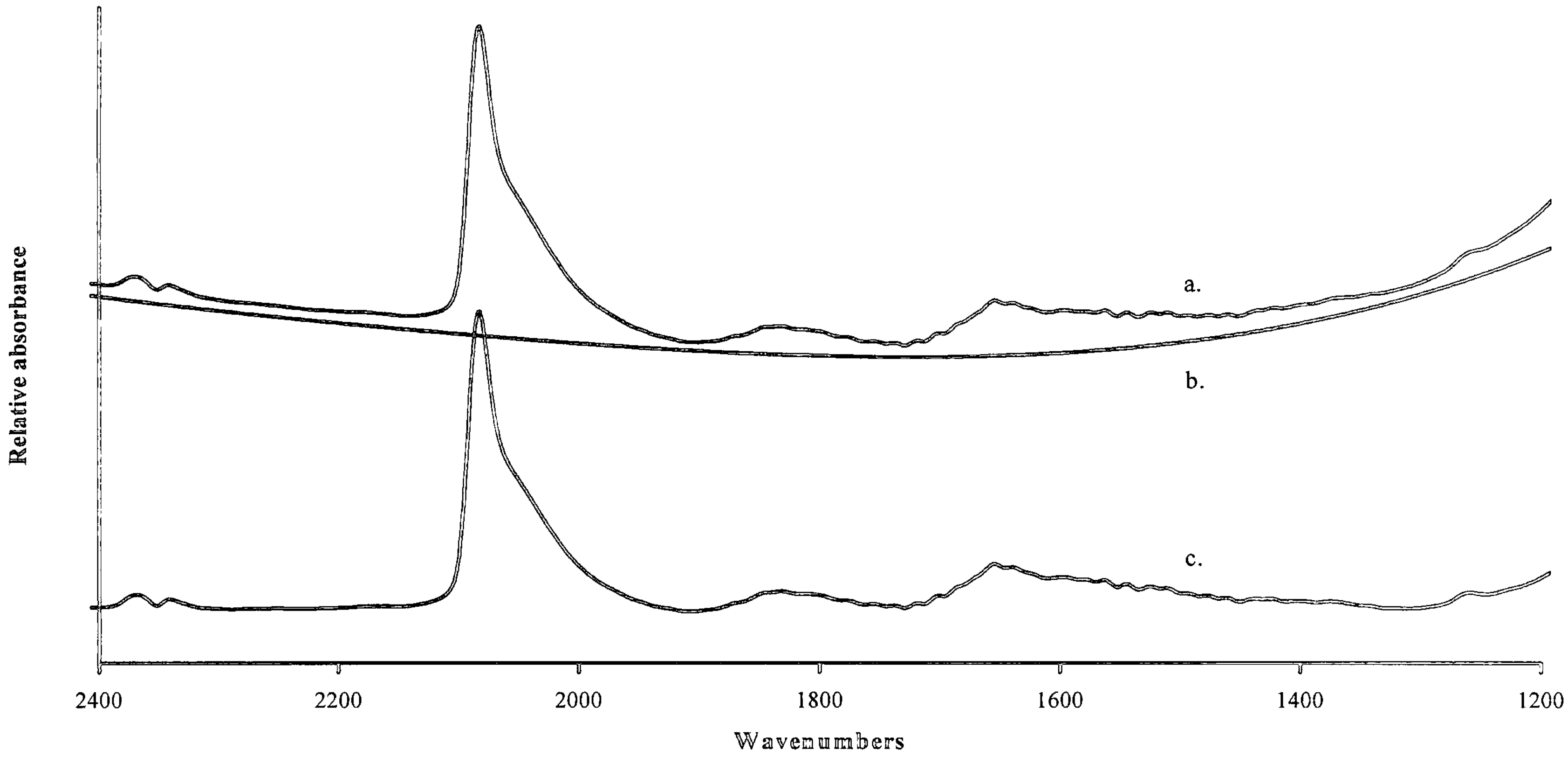
*[10] See section 6.5.2



a. Original spectrum b. Artificially generated curve c. Resultant spectrum

Spectrum 5.1 Subtraction method for baseline correction

5.6 Experimental procedure

In order to preserve integrity and reproducibility of results the first task that was undertaken was to develop a standard procedure for all experiments to follow. The basic experimental procedure is outlined below:

1. Reduction

   The catalyst was heated to 500°C. A mixture of hydrogen and nitrogen was passed over the surface (usually in the ratio of 1:10 H_2:N_2). This was maintained for 30 mins and the absence of adsorbed species is verified by IR spectroscopy.

The criterion that was used to judge if the sample had been successfully reduced was the absence of any species in the IR region 1200-2900cm^{-1}. This was used because it was easy to monitor yet many impurities would be immediately visible although many possible contaminants would be IR inactive in this region (e.g. S, Cl & C). The hydrogen percentage was judged so that there was sufficient hydrogen present to reduce the sample at the temperature used, but too little to damage either the sample or cell. If the sample was judged to be insufficiently reduced the process was repeated, if necessary at higher temperature.

2. CO adsorption

   The catalyst was cooled to a temperature around 75°C. Pure (100%) carbon monoxide was passed over the surface for 30 seconds. The atmosphere within the cell was then replaced with nitrogen.

Though 30 seconds has been the most efficient exposure time to produce a reasonable coverage at 75°C for some experiments a far longer exposure was necessary.

3. Desorption experiments

   The temperature of the catalyst was raised to 100°C and a spectrum taken. The sample was then heated at a constant rate and the temperature held every 50°C so that further spectra could be taken. This continued until a temperature of 750°C was reached (the maximum working temperature of the apparatus) or until total desorption had occurred. The gaseous atmosphere was not disturbed during desorption experiments.

The sample was heated at a constant power which means that the heating rate was not uniform. The experiment continued until either the sample temperature had reached the operating limit (750°C was judged the maximum temperature which could be safely maintained) or until total desorption. The absence of any visible species in the IR spectrum of the sample was used as the criterion for judging whether total desorption had occurred.

Chapter 6

Results and Discussion

6 Results and Discussion

6.1 CO adsorption on unimetallic catalysts

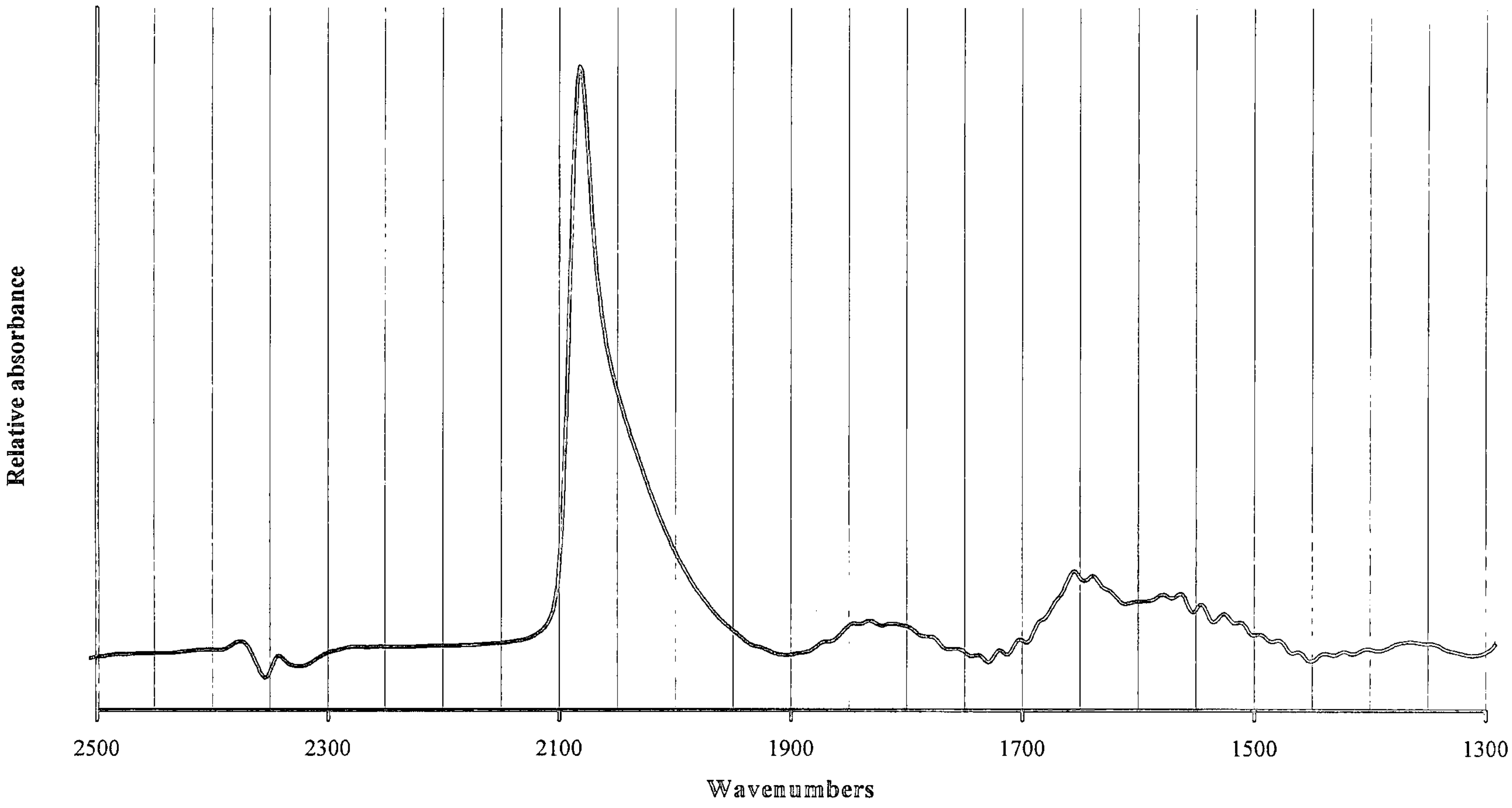
Three supported metal catalysts were used in this study: platinum, rhodium and palladium. Each catalyst was treated in the same way. The catalyst was reduced at high temperature (500°C) cooled to 75°C in a non-oxidising atmosphere (100 % nitrogen) and carbon monoxide adsorbed by passing pure CO (4-bar) over the catalyst. The spectrum taken for each of the catalysts is included below (spectra 6.1-6.3).

6.1.1 Platinum

Spectrum 6.1 shows the results from the adsorption of carbon monoxide on platinum. The frequencies of peaks shown in this spectrum are summarised in table 6.1 below.

Label	**Frequency**	**Assignment**
1	1360 cm^{-1}	
2	1655 cm^{-1}	
3	1830 cm^{-1}	Pt_2-CO
4	2080 cm^{-1}	Pt-CO
5	2170 cm^{-1}	Residual $CO_{(g)}$
6	2330-2360 cm^{-1}	$CO_{2(g)}$

Table 6.1 Frequencies of peaks shown in spectrum 6.1



Spectrum 6.1 CO adsorbed on Pt/Al_2O_3 (100°C)

Assignments that have been made in the table above are on the basis of observation (gaseous species) and on previous studies[1,2,3,4]. The major peak was that at 2080cm^{-1} which was attributed to the bonding of CO to a single Pt atom. It has been previously shown that the frequency of this state is highly dependent on the platinum particle size[1].

The narrow peak that has been implied that the distribution of particle sizes within the sample was small. This could be attributed to the high reduction temperature that was used which could induce thermal sintering of the catalyst.

The peak at 1830cm^{-1} had been previously assigned to carbon monoxide species bridging two platinum surface sites[1,2,3,4]. The peak was broad when compared to the terminal peak which suggested that the frequency of absorption was site-specific with contributions from CO bonded to several different platinum crystal sites combining to give the observed peak[*11].

The next peak was that at 1655cm^{-1}, which has not been previously reported by groups studying this system. There are several possible systems that could lead to an absorption at this frequency. One possible inference is that the peak relates to a carbon monoxide species sitting over 3 or 4 platinum surface sites. The arrangement would be dependent on the particular platinum crystal face present and may explain why this species has not been previously observed.

Another possibility is that this species is related to formate or a similar group. It has been proposed that the observed species is the result of the interaction of CO and surface OH groups which are prevalent in alumina supported catalysts. To test this hypothesis a sample of platinum catalyst was heated in ^2H_2O to promote deuterium

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[*11] Different crystal faces are shown in section 3.5

exchange with any adsorbed water or hydroxy species. The result from this experiment was then compared to samples where both ^2H_2O and ^1H_2O were present, the untreated catalyst, and a control sample where just ^1H_2O was used. All of these experiments gave identical spectra showing that any proposed species cannot contain hydrogen, otherwise an isotope shift would be observed. Further experiments with labelled $H_2{}^{18}O$ would show whether oxygen from adsorbed groups is involved in the oxidation of surface CO.

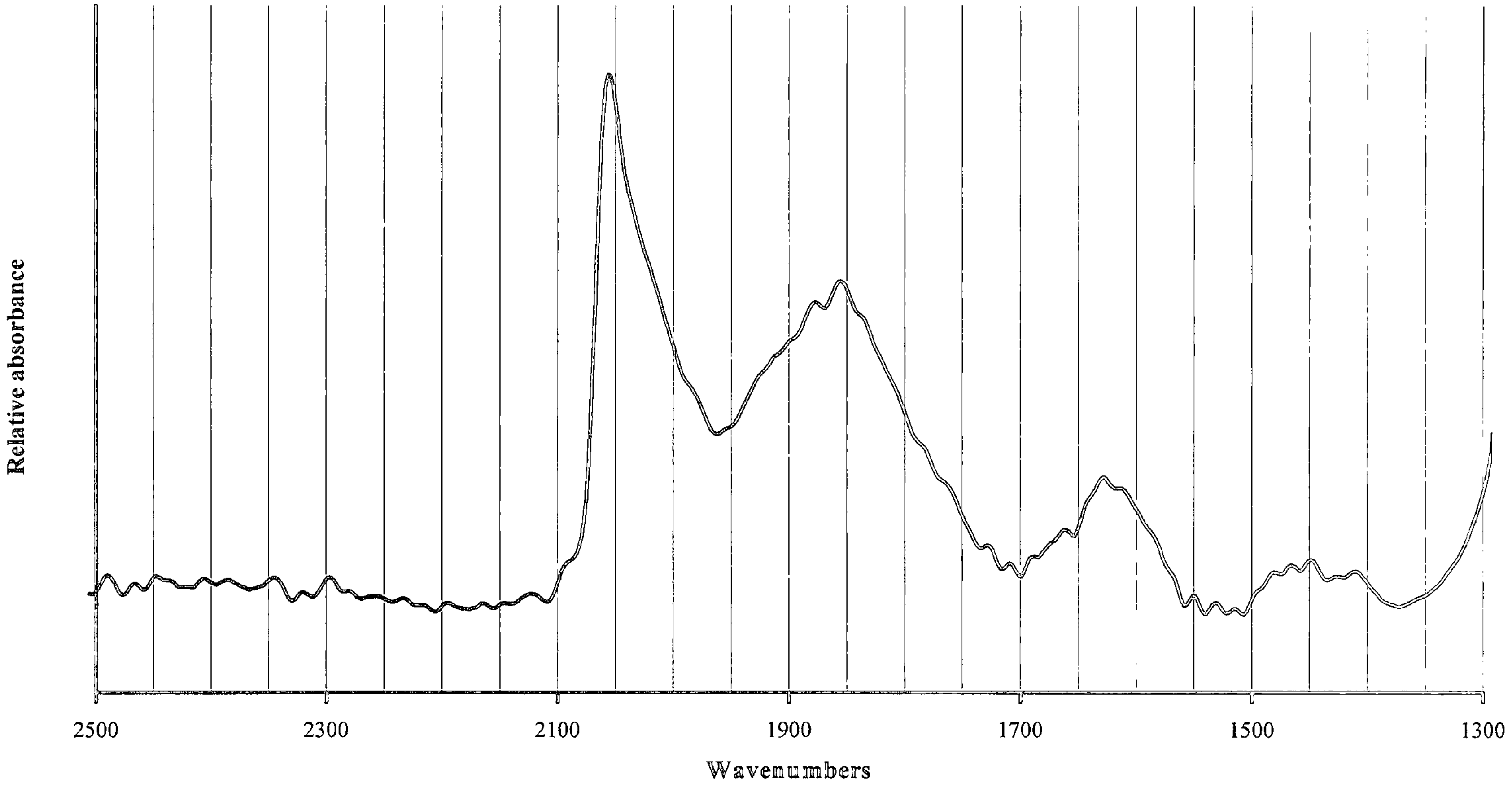
6.1.2 Rhodium

The spectrum obtained using a supported rhodium sample are shown in spectrum 6.2. Peak frequencies are given in table 6.2

Label	**Frequency**	**Assignment**
1	1413 cm^{-1}	
2	1448 cm^{-1}	
3	1627 cm^{-1}	
4	1861 cm^{-1}	Rh_2-CO
5	2057 cm^{-1}	Rh-CO

Table 6.2 Frequencies of peaks shown in spectrum 6.2

There have been several previous studies on this system and these have all made similar observations[5,6,7,8,9]. The main discrepancy between the results observed above and those made elsewhere has been the absence of gem-dicarbonyl species. Gem-dicarbonyl species produce two bands in the infra-red spectrum, a symmetric stretch at 2029cm^{-1} and an anti-symmetric at 2098cm^{-1}. It has been proposed[5] that these species are primarily formed on dispersed Rh^{1+} atoms on the surface of the



Spectrum 6.2 CO adsorbed on Rh/Al_2O_3 (100°C)

catalyst. These surface sites were either present in very low concentrations or not present at all under the conditions used above because of the absence of peaks in the correct region of the spectrum.

An alternative hypothesis is that the gem di-carbonyl species have not been formed in this study because of the high surface concentrations of CO that are present. Most work by other groups has used very small amounts of gaseous CO adsorbed to the surface of their catalyst in order to study the effect of monolayer formation and the bonding modes associated with low surface coverages. Here, however, monoxide coverage has been made deliberately high in order to mimic the conditions found in real catalytic converters. A high surface concentration of CO would prevent the formation of di-carbonyl species because of steric interactions due to surface crowding.

A clear comparison can be made between the rhodium and platinum spectra. Both have bands in the region 1800-2100cm^{-1} which can assigned to similar species. The immediately noticeable difference between the two spectra is the ratios of the height of the two main peaks. With platinum the terminal peak was 6 times greater in height than the bridging peak, whereas with the rhodium the ratio is very much reduced. A greater importance should be attached to the difference in the areas of the two peaks[*12]. With platinum the area of the terminal peak is again roughly 6 times greater than that of the bridging peak, but with rhodium the areas of the two peaks are roughly equal. The change in relative intensities represented by these observations shows that different metals have different characteristics with regards to the adsorption of CO. Platinum has a clear preference for the adsorption of CO in a terminal mode whilst rhodium adsorbs a far greater proportion of CO in a bridging

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[*12] The area of the peak is proportional to the concentration of the species in IR spectroscopy.

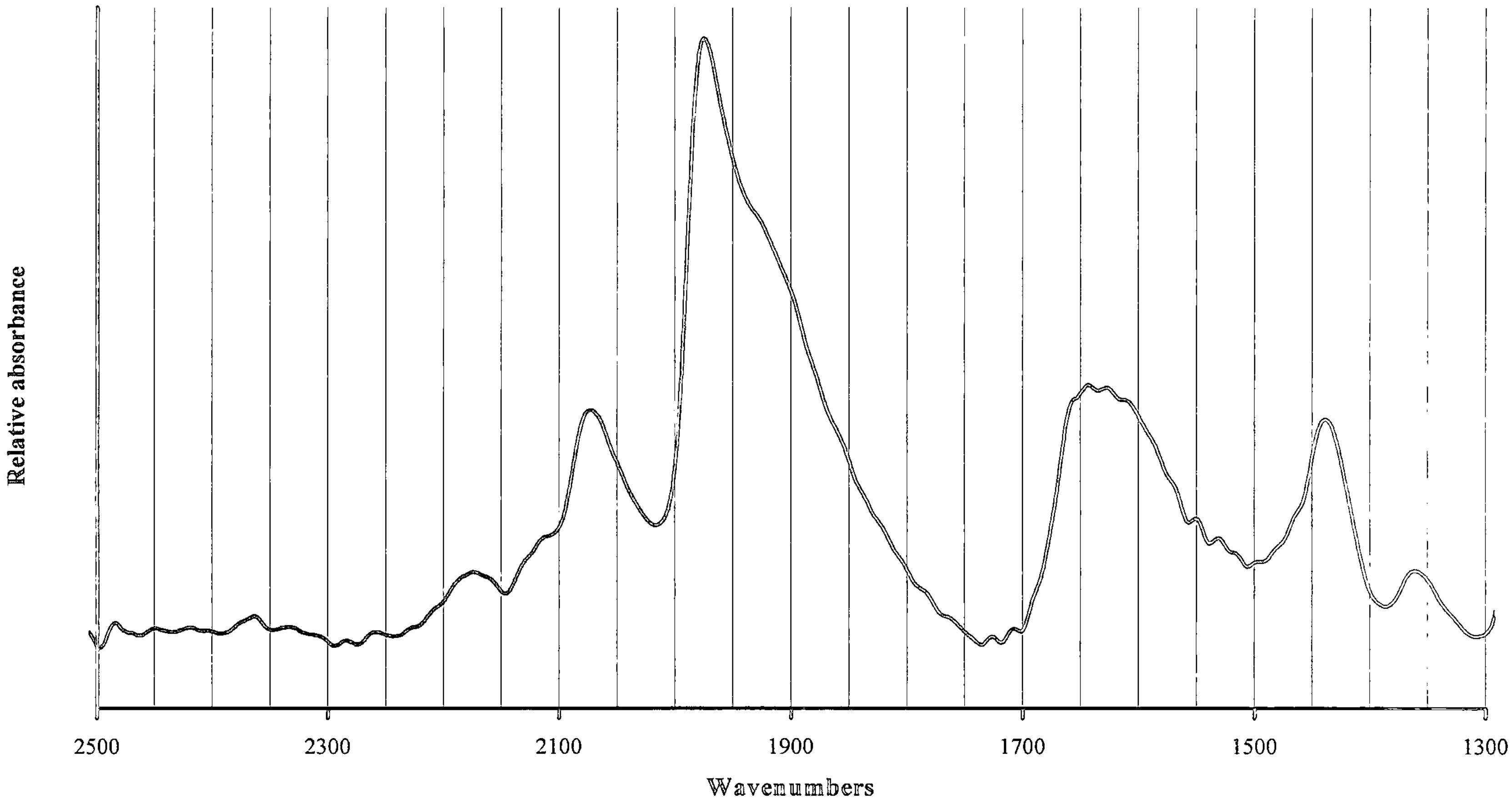
mode. Observations such as these highlight the possible uses of CO adsorption as a tool for surface analysis.

Again several of the peaks that have been seen in this experiment have not been previously mentioned in the literature. The frequencies of the two peaks (1413 & 1448cm^{-1}) are not comparable to those of the species seen for platinum. There are possible explanations for why these peaks should exist, as there are with similar peaks in the experiment with platinum, such as the formation of carbonate or formate-like species, as well as multiple bonded CO species (though species below 1600cm^{-1} are too low in frequency for this possibility).

Formate ($-CO_2H$) carbonate ($-CO_3$) and carboxylate ($-CO_2$) have been previously observed adsorbed to metal oxides[10]. Formate absorbs infra-red radiation at 2841, 1567,1377 and 1366cm^{-1} when adsorbed on alumina. Carbonate absorbs in the region 3610, 1700 and 1350cm^{-1}.

6.1.3 Palladium

Spectrum 6.3 shows the results from the adsorption of carbon monoxide on a alumina supported palladium catalyst. Table 6.3 below shows the frequencies of the peaks in spectrum 6.3.



Spectrum 6.3 CO adsorbed on Pd/Al_2O_3 (100°C)

Label	Frequency	Assignment
1	1368 cm^{-1}	
2	1442 cm^{-1}	
3	1632 cm^{-1}	
4	1925 cm^{-1}	$Pd(111)_2$-CO
5	1975 cm^{-1}	$Pd(100)_2$-CO
6	2073 cm^{-1}	Pd-CO
7	2170 cm^{-1}	Residual $CO_{(g)}$

Table 6.3 Frequencies of peaks shown in spectrum 6.3

There are 8 clearly visible peaks on spectrum 6.3 resulting from CO adsorption on palladium. The last peak (2170cm^{-1}) is residual gaseous CO, which has either not been completely displaced by nitrogen or has been regenerated after evacuation from the system.

Previous studies[11,12,13,14] have assigned the main peak (1975cm^{-1}) to CO bridging two atoms on the (100) face of palladium. The shoulder that is visible (1925cm^{-1}) on the main peak has also been assigned in the literature as bridging species on the Pd(111) face. The peak at higher frequency (2073cm^{-1}) has been assigned to terminally adsorbed CO. This peak has a very much reduced intensity when compared to the corresponding peaks for both platinum and rhodium.

Baddour *et al.*[11,12] have previously shown that palladium only adsorbs carbon monoxide in a terminal mode when the surface coverage is very high. In general the bonding in the terminal mode only occurs when CO is adsorbed to a site where there are no vacant adjacent sites.

The peak at 1632cm^{-1} can be related to bonding between CO and palladium atoms in a μ-3 (or higher) mode. The shape of the peak suggests that it consists of contributions from several states, perhaps those of differing crystal faces as well as those where there is interaction with the CO bond rather than the carbon atom as had been previously seen.

6.2 Thermal desorption experiments

A thermal desorption of adsorbed species was carried out on the catalysts. CO was adsorbed to the surface as in the previous experiment and was then removed by heating. Spectra were taken at regular intervals so desorption could be monitored. The results are summarised below.

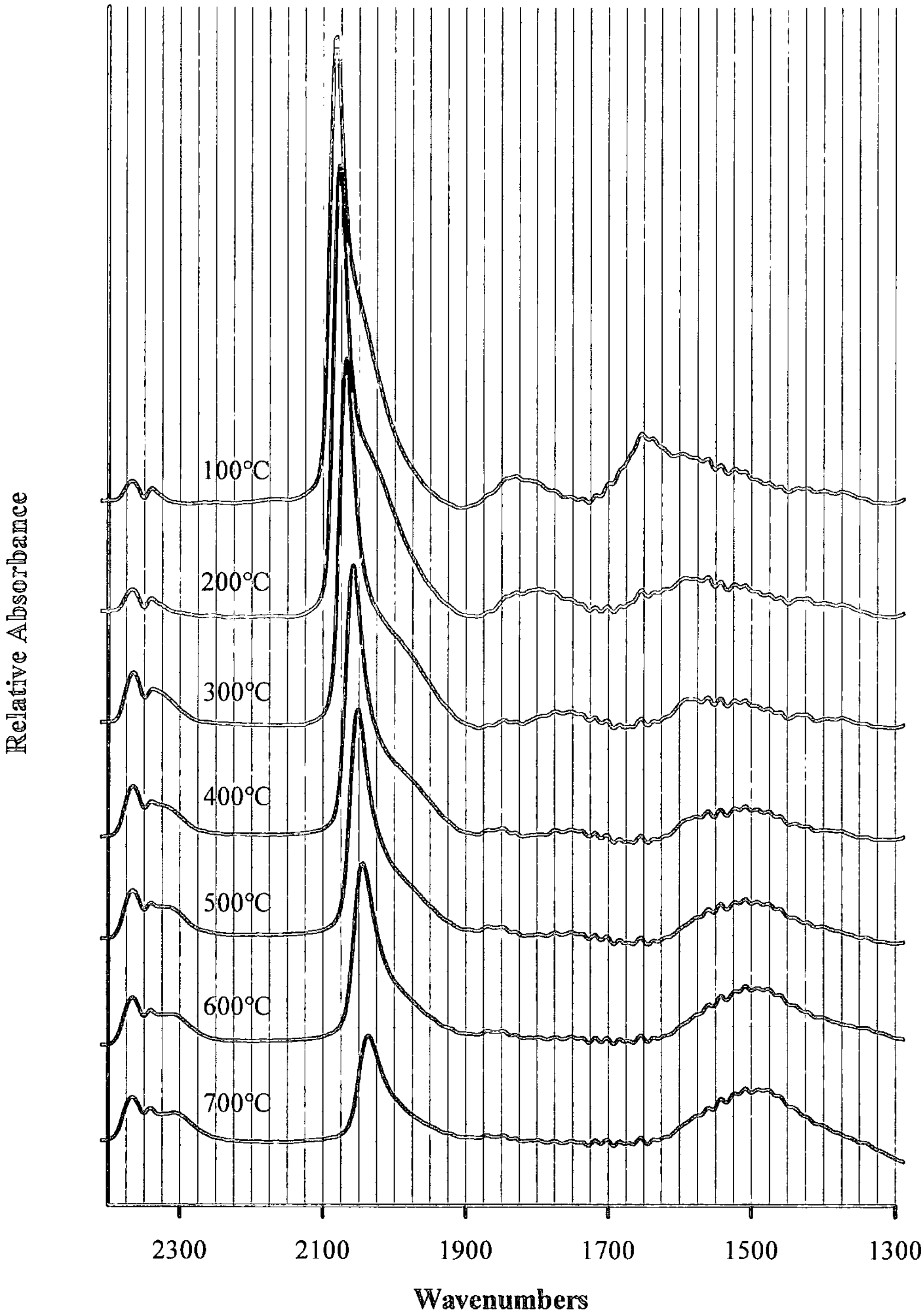
6.2.1 Platinum

The thermal desorption of carbon monoxide from platinum reveals new information about the states that have been previously identified and also shows the location of some new states. The general trend that can be seen is the reduction in intensity of states previously attributed to being CO-Pt (see section 4.2.1) and an increase in the intensity of the carbon dioxide peak. This is consistent with the observation that platinum is catalytically active in the reaction:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

The main question posed by this reaction is where the oxygen comes from. This reaction was observed in this study, yet efforts were made to isolate all possible sources of oxygen. One explanation that has been offered[13] is that the oxygen comes from adsorbed OH groups on the alumina support as shown:

$$CO_{(ads)} + OH_{(support)} \rightarrow CO_{2(g)} + \frac{1}{2}H_{2(g)}$$



Thermal desorption spectrum 6.1 CO-Pt/Al_2O_3

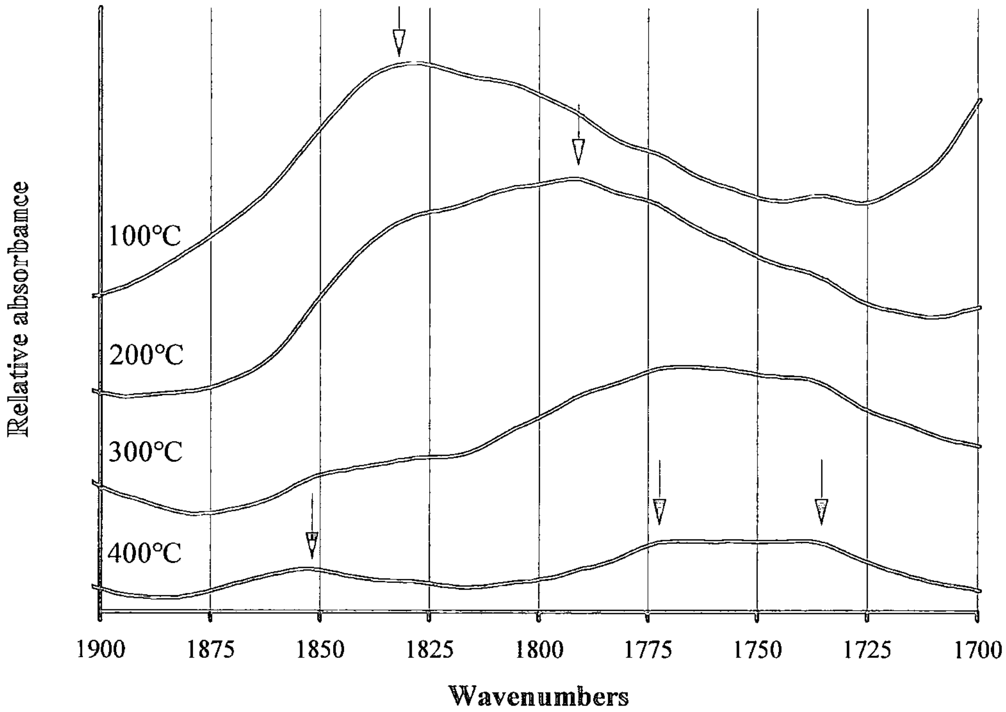
Jackson *et al*[13] also suggested that the oxidation of CO over this type of catalyst was possible without the evolution of dihydrogen. No explanation of this mechanism was offered though dissolution of hydrogen within the metal lattice is possible.

Another change that was visible when the sample was heated was to a shoulder on the low frequency side of the main peak. The shoulder became more prominent as the temperature was increased, because the desorption temperature of this species was higher than that attributable to the main peak. At 200°C the shoulder is most obvious but this desorbs and at 400°C this peak was hardly visible. A further change could be seen at 1500cm^{-1}. At this frequency a peak appeared at 300°C which grew as the temperature was increased. The species which this peak relates to was one of the few species present at very high temperatures (700°C)

The peak at 1655cm^{-1} is attributable to the first species to desorb. The species showed almost complete desorption over the temperature range 100-200°C. Another peak was revealed, which began as a barely visible shoulder on the low frequency side of the main peak, at 1580cm^{-1}. As the temperature was increased to 400°C this became hidden by a peak at 1512cm^{-1} which was absent at low temperature but increases in intensity with temperature from about 300°C.

One of the most interesting and important changes was to the peak at 1830cm^{-1}. This peak has been previously assigned as a CO species bridging two platinum atoms[1,2,3,4]. In this study, careful analysis showed that this peak was attributable to two separate species. At 100°C the observed peak was that of a single species with an absorption at 1830cm^{-1}. Upon heating this peak was observed to shift to lower frequency, broaden and then split, so that two peaks could be seen. Between 300°C and 400°C it was seen that both peaks shifted in frequency, the higher frequency peak (1855cm^{-1} at 400°C) to a higher frequency and the lower frequency peak (1767cm^{-1}

at 300°C) to a lower frequency. This can be best seen on the expanded view of spectrum 6.4.



Arrows denote positions of possible peaks.

Spectrum 6.4 Expanded view of CO-Pt/Al_2O_3

It is possible that the lower frequency of these two peaks could itself consist of two states. The spectrum at 400°C suggested that there were two peaks one at 1770cm^{-1} and another at 1730cm^{-1}.

The consideration of what these peaks may represent allows their importance to be recognised. In previous studies the single peak at 1830cm^{-1} has been assigned as CO bonded, in a bridging mode, to two surface platinum sites. The sensible conclusion to be drawn from the close proximity of these two states is that these are similar in nature. This would imply that these are both double-bonded sites with the difference in frequency being caused by the bonding distances Pt_2–CO. Different crystal faces of a metal have different interatomic bonding distances and the distance between the metal atoms on the surface will affect the amount of π^* back donation that will occur. The rapid loss of the state at the higher frequency could be due to the thermal instability of the face to which it is bonded.

It is also important to note that one of the few species visible at 700°C is the terminal Pt-CO (2080cm^{-1} at 100°C). In chapter 3 it was discussed that the frequency of CO absorption was inversely related to the strength of metal carbon bonding. Here it is apparent that the Pt-CO species with highest frequency is the one that persists at highest temperature. No explanation for this apparent inconsistency has been offered.

An explanation to the identity of peaks in the 1700-1900cm^{-1} region has been offered elsewhere[7] with reference to rhodium. The suggested structure that could relate to both of these states is that shown below in figure 6.1. The presence of both μ-1 and μ -2 sites on the same surface site would affect the frequency of absorption for both groups. This theory would also tie in with the shoulder that is seen on the low frequency side of the peak related to the single bonded CO. What has been observed here would suggest that some of the electron density usually donated to the bridging group is instead being given to the terminally adsorbed groups.

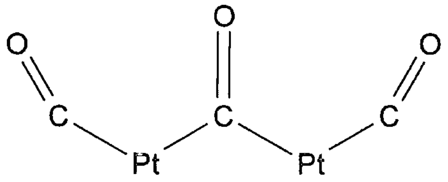


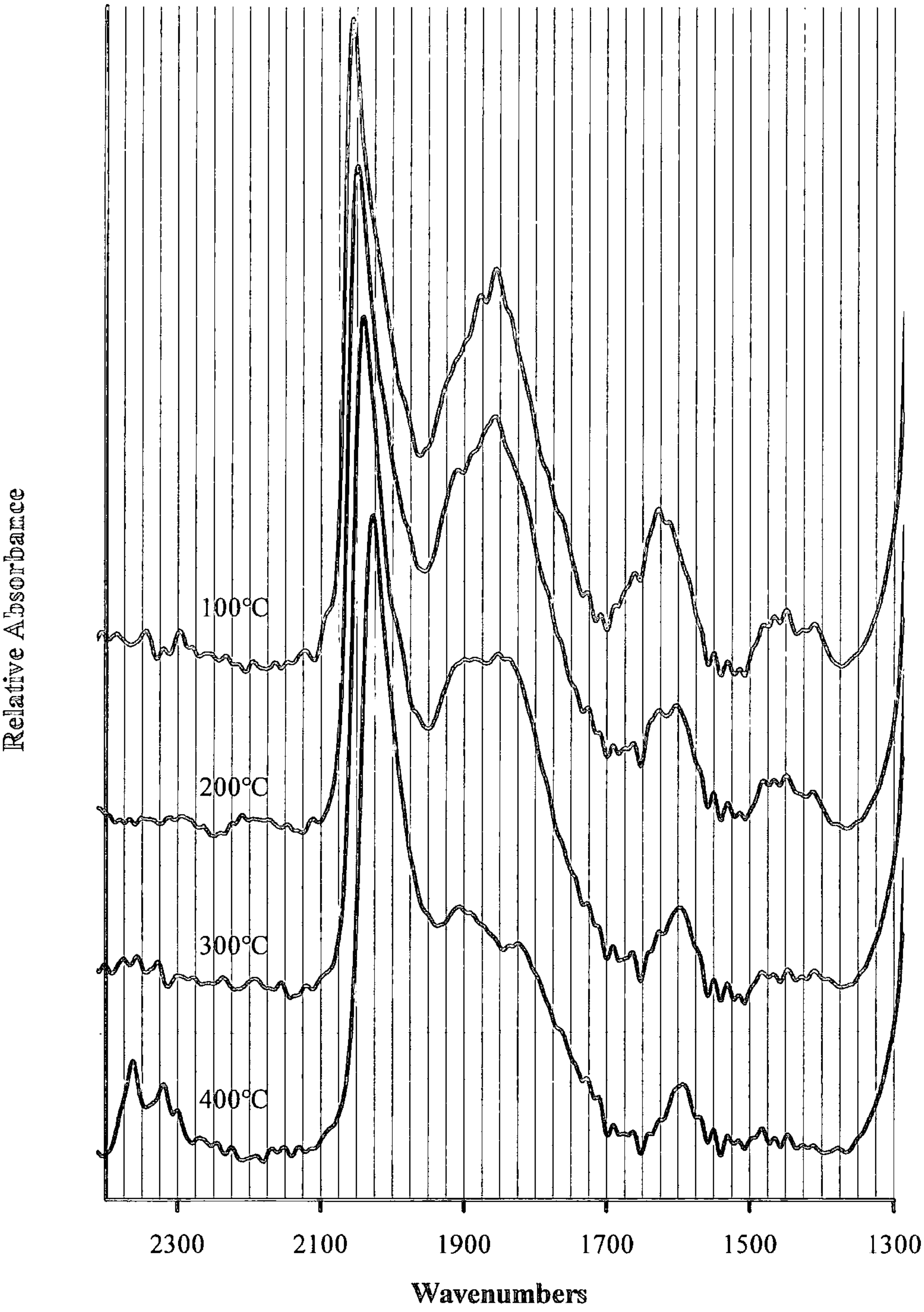
Figure 6.1 Extended CO/Pt structure

6.2.2 Rhodium

The thermal desorption spectra of CO from a rhodium catalyst revealed the presence of two new states. The general trend, observed with the platinum catalyst, could be seen here, with a gradual increase in the amount of CO_2 present as the temperature was raised. In the first spectrum there was a disturbance at the frequency where CO_2 would be expected to absorb which was caused by the presence of a negative amount of CO_2 in comparison to the background spectrum. In the second there was no detectable dioxide. The third spectrum showed a detectable amount and the final trace showed a large amount showing that in the region 300-400°C there had been significant desorption from the surface.

The peak at the lowest frequency (1380-1500cm^{-1}) was easily removed, with a substantial reduction in intensity over the first temperature increment(100-200°C) and total desorption by 400°C. The desorption of the peak at 1627cm^{-1} revealed the presence of a further species when heated. The species that was originally attributed to a peak at 1627cm^{-1} desorbed at low temperature (100-300°C) and a further species, seen as a peak on the low frequency side of the original, became visible. This species (1600cm^{-1} at 200°C) was far more thermally stable showing only a slight reduction in intensity over the range 300-400°C.

The species that was originally assigned as being the peak 1861cm^{-1} and relating to Rh_2-CO also revealed a further peak on heating. The main peak was substantially reduced in intensity over the range 200-300°C and a second peak became visible. This new species is present as a peak observed at 1910cm^{-1} and was thermally unstable with visible desorption occuring in the range 300-400°C. This peak has been previously observed by Rice *et al*[7] and is the same as that proposed above for platinum. There would need to be a corresponding peak for the terminally bound species involved in this extended carbonyl structure. This could be accounted for by a



Thermal desorption spectrum 6.2 CO-Rh/Al_2O_3

shoulder that was present on the low frequency side of the main, μ-1, peak. The shoulder, which was best seen on the spectrum at 300°C could be seen to decrease in intensity over the range 300-400°C the same temperature as the 1910cm^{-1} peak, suggested that the loss of this group occurred by loss of the Rh_2-CO converting the other groups within the original species to normal terminal carbonyl as shown below:

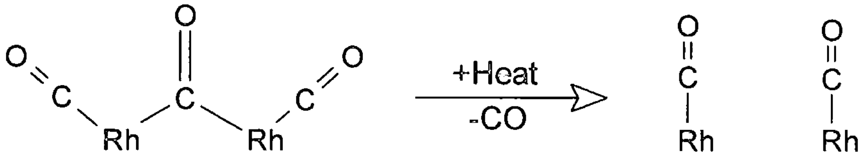


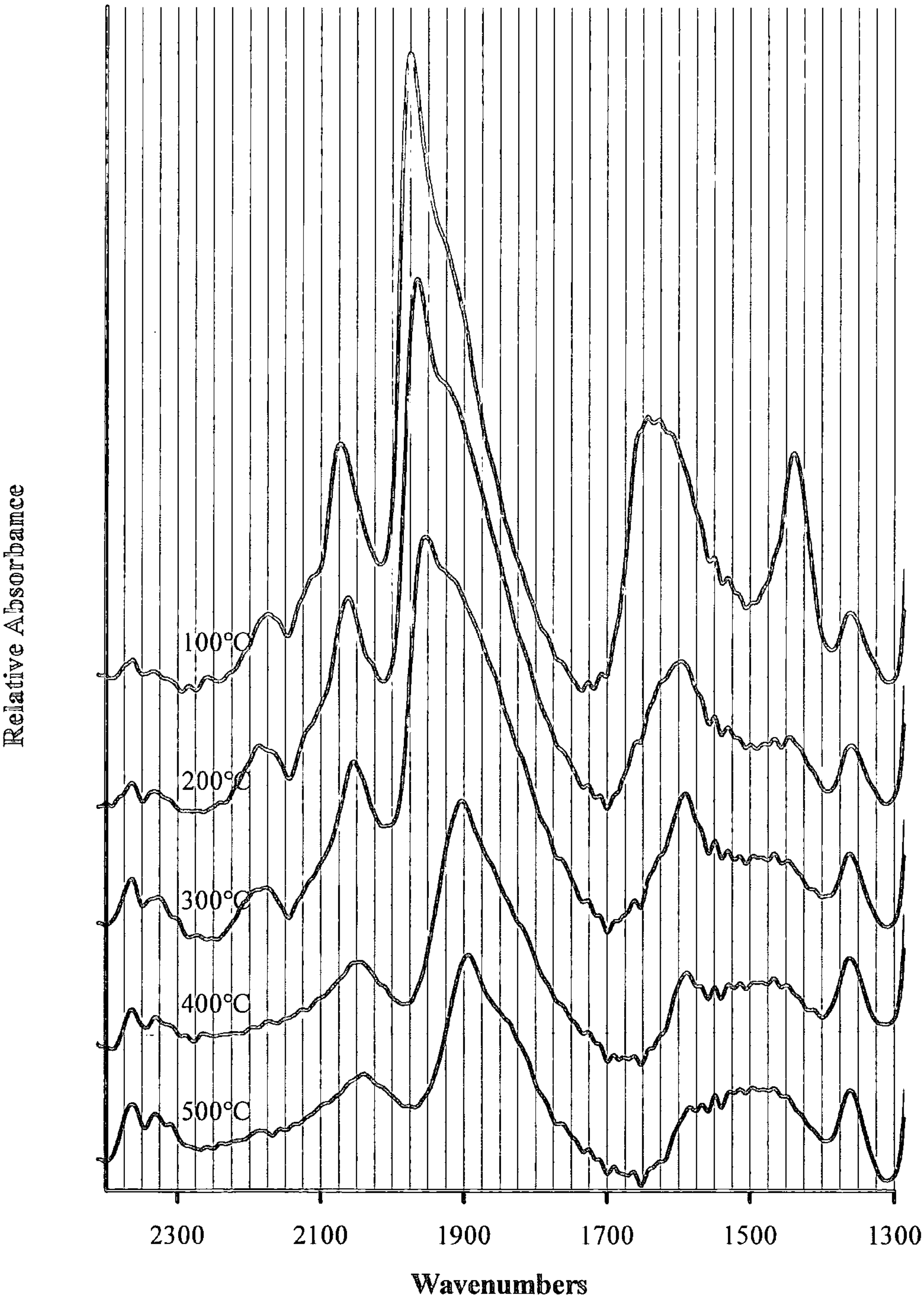
Figure 6.2 Conversion of extended carbonyl structure to terminal CO

6.2.3 Palladium

Of all the desorption spectra contained in this report the palladium spectra contain the most information in terms of the hidden states and low temperature reaction. The scope of variation is so great that the easiest place to start the description is with the species that show the smallest change.

The lowest frequency peak shown (1368cm^{-1}) is strange in that it shows no change in frequency as the temperature is increased, unlike most other adsorbed species observed in this study. It also shows no sign of desorption at temperatures up to 500° C. This would suggest that this species was unaffected by a change in the coverage of the surface. Species adsorbed on sites that were on edges or steps would have this property as would species adsorbed to isolated atoms of Pd. The peak at 2073cm^{-1} slowly desorbs with increasing temperature, accompanied by a shift to lower frequency.

The largest peak on the spectrum (1975cm^{-1}) showed the most distinct change. This peak shifted to lower frequency and slowly desorbed up to a temperature of 300°C.



Thermal desorption spectrum 6.3 CO-Pd/Al_2O_3

When the temperature was increased further this state disappeared. A further peak became visible on the low frequency side of the main peak as it desorbed (1902cm^{-1} at 400°C). This new peak was visible as a shoulder on the original spectra at 100°C but from 400°C this was the only peak present in this region with the exception of a shoulder on the low frequency side (1830cm^{-1}) which was only apparent at 500°C.

In the previous section (section 6.1.3) the higher frequency peak (1975cm^{-1}) was assigned to CO adsorption to Pd(100) and the lower was assigned to adsorption on Pd(111). This was of interest since it showed that CO was adsorbed to one crystal face stronger than another. The rapid change between 300°C and 400°C could be symptomatic of a surface rearrangement.

The most dramatic changes can be seen in the peaks at 1632cm^{-1} and 1442cm^{-1}. Both of these showed a large change at the lowest temperature increment (100-200°C). There was almost total desorption of the species generating the lower frequency of the two peaks and the other revealed a second peak on its low frequency side (1590cm^{-1} at 300°C) and this species was totally desorbed by 300°C. This new peak was related to a species that was desorbed in the region 300-500°C.

6.3 Studies of bi-metallic catalysts

Along with the standard unimetallic samples, two bi-metallic catalysts were supplied by Johnson Matthey. These samples were mixtures of two of the platinum group metals that had been previously studied. Due to industrial confidentiality, the dispersion of metals within the sample, the metal loading and relative proportions was unknown.

6.3.1 Studies of platinum/rhodium catalyst

The result obtained from the platinum/rhodium catalyst is shown overleaf as spectrum 6.5 and the peak frequencies from this spectrum are listed below in table 6.4.

Label	Frequency	Assignment
1	1409 cm^{-1}	
2	1470 cm^{-1}	
3	1643 cm^{-1}	
4	1837 cm^{-1}	
5	2064 cm^{-1}	
6	2115 cm^{-1}	Residual $CO_{(g)}$
7	2175 cm^{-1}	Residual $CO_{(g)}$

Table 6.4 Frequencies of peaks shown in spectrum 6.5

The results from this catalyst are similar to those observed for the unimetallic catalysts that have been previously tested. There is a single main peak which at 100°C absorbs at 2064cm^{-1}. At this temperature terminal CO on platinum absorbs at 2080cm^{-1} whilst on rhodium it absorbed at 2057cm^{-1}. The peak that was seen here lay between the values observed for the constituent metals. This result was partly consistent with the observations of Anderson and Rochester[3] who reported a peak which shifted from 2070cm^{-1} at 50°C, to 2060cm^{-1} at 150°C. The study of Anderson *et al* also observed two very strong bands either side of the main peak that were attributed to gem-dicarbonyl species . These twin bands were not of equal intensity, which could be a result of the forbidden nature of the anti-symmetric stretch[*13], and as

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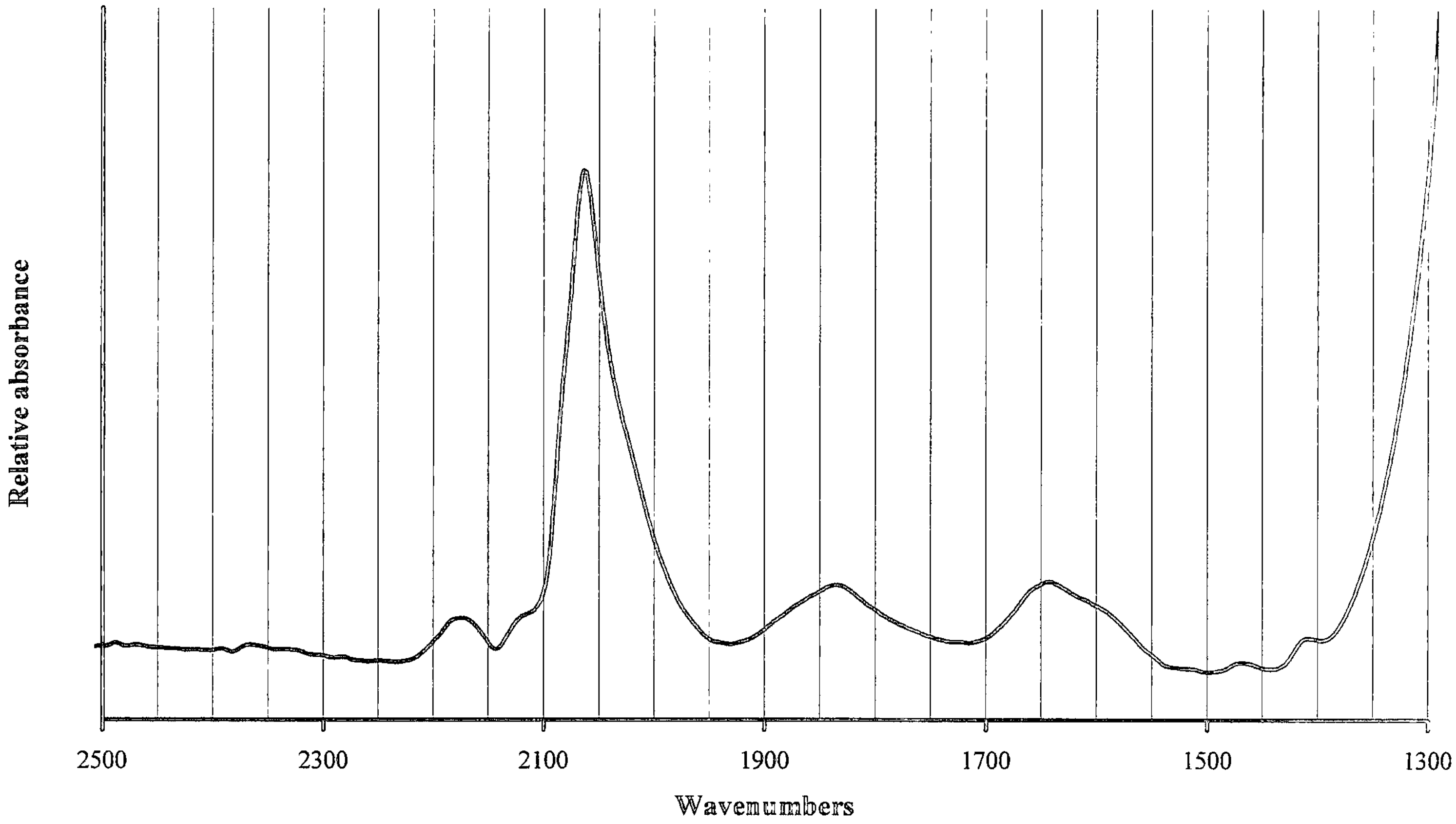
[*13] See figure 4.3



Spectrum 6.5 CO-Pt/Rh/Al_2O_3 (100°C)

desorption occurred the peak intensities did not reduce at the same rate. This would suggest that these peaks are not due to different stretches of the same surface group.

The paper by Anderson and Rochester[3] referred to the presence of a bridging state which was visible on their spectra, the frequency of this species was not quoted. This species was unusual because as the temperature was increased from 50°C to 300°C the peak could be seen to increase in intensity.

The peak at 1837cm^{-1} observed above, lies within a similar region of the spectrum to the bridging peak observed by Anderson. The frequency of 1837cm^{-1} again lies between the frequencies observed for the two constituent metals: platinum absorbs at 1830cm^{-1} and rhodium at 1861cm^{-1}.

The peak at 1643cm^{-1} is perhaps comparable to the species observed at 1655cm^{-1} and 1627cm^{-1} for the unimetallic samples. There was an obvious shoulder present on the low frequency side of this peak at 1590cm^{-1}. It is possible that the peaks at 2064cm^{-1} and 1837cm^{-1} are the bonding of CO in the terminal and μ-2 bridging modes. The question of which metal these species are bonded to remains unanswered.

A possible explanation could be that the peaks observed relate to carbon monoxide bonding to either of the metals. The frequencies of the observed peaks and the absence of any double peaks would suggest that there is significant alloying and synergy between atoms of the two metals. It could be that one metal had migrated to the surface of any alloy particles and that the energy of this metal had been altered by the close proximity of the other metal. In this case only bonding with one of the metal would be observed. The alternative is that the two metals have formed an alloyed surface. This would mean that there would be CO bonding to both metals but there would only be one observed frequency because of the synergy within the surface.

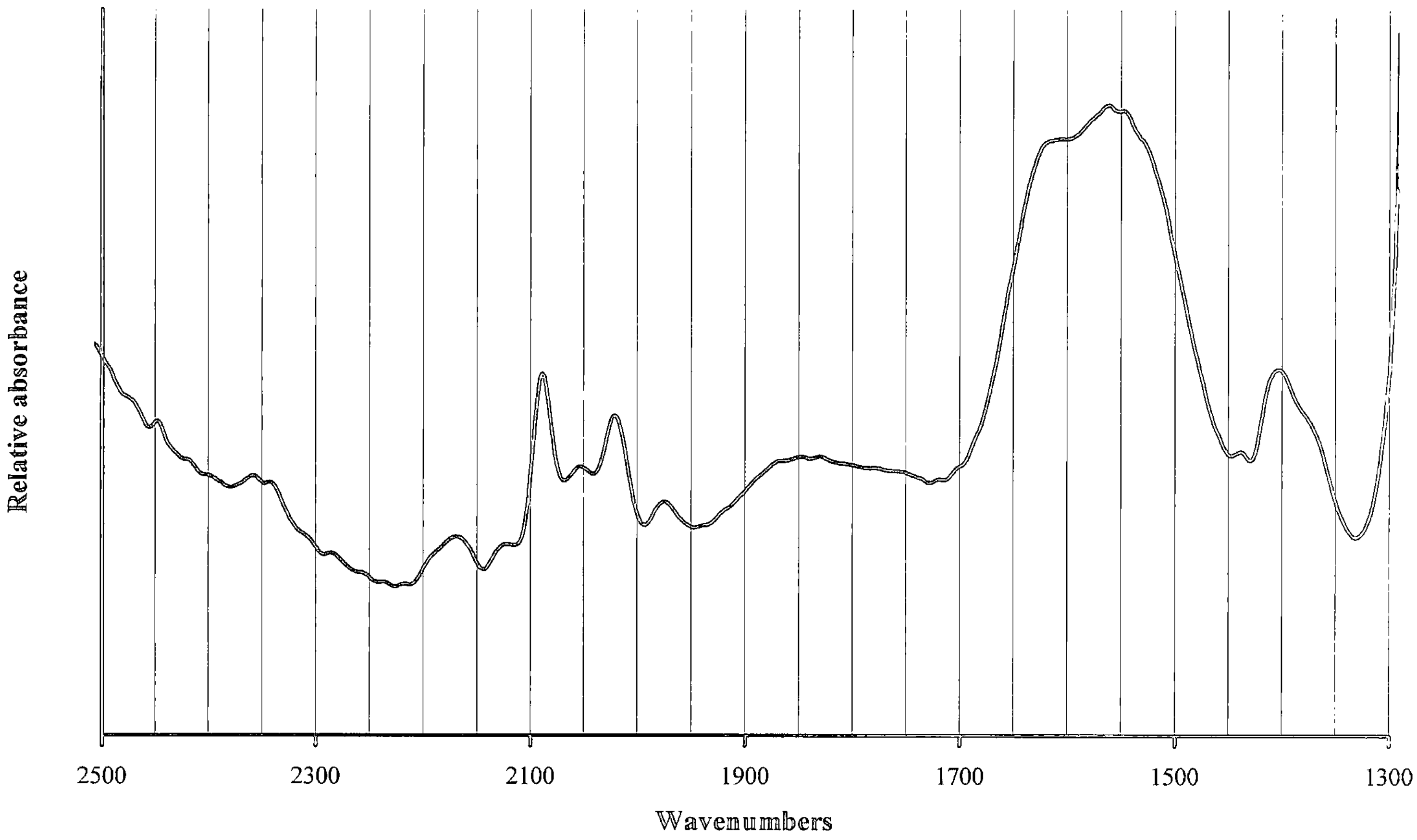
6.3.2 Studies of palladium/rhodium catalyst

The result obtained from the palladium/rhodium catalyst is shown overleaf as spectrum 6.6 and the peak frequencies from this spectrum are listed below in table 6.5.

Label	Frequency	Assignment
1	1404 cm^{-1}	
2	1439 cm^{-1}	
3	1563 cm^{-1}	
4	1850 cm^{-1}	
5	1977 cm^{-1}	
6	2022 cm^{-1}	
7	2054 cm^{-1}	
8	2089 cm^{-1}	
9	2123 cm^{-1}	Residual $CO_{(g)}$
10	2173 cm^{-1}	
11	2340 cm^{-1}	Residual $CO_{2(g)}$
12	2360 cm^{-1}	

Table 6.5 Frequencies of peaks shown in spectrum 6.6

The major difference between this system and those previously observed in this study was the considerably smaller amount of CO that was adsorbed here. Spectrum 6.6 is at a larger scale than has been previously used and even then the peaks that relate to CO adsorption are quite small. The small peaks within this system have meant that baseline correction was very difficult and the spectrum obtained has not been totally



Spectrum 6.6 CO-Pd/Rh/Al_2O_3 (100°C)

corrected. The failure to correct this spectrum could result in the distortion of reported frequencies by up to 10cm^{-1}.

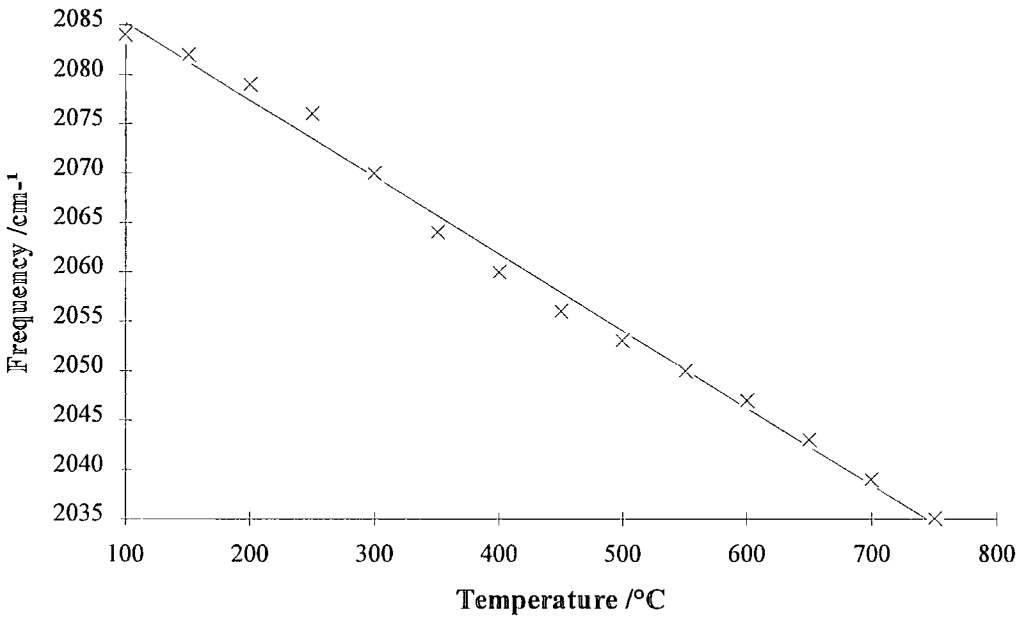
The twin peaks at 2022cm^{-1} and 2089cm^{-1} can perhaps be related to the gem-dicarbonyl species described by other groups looking at rhodium and rhodium containing systems. The amount of CO adsorbed to this sample was too small for a thermal desorption experiment to be carried out, this could have provided better evidence for the existence of gem-dicarbonyl species since these have, in most instances, been seen to desorb at low temperatures (under 300°C).

The peak that lies between the two gem-dicarbonyl peaks can be assigned as a terminal CO species. The peak frequency of 2054cm^{-1} observed for this species is very close to that observed for terminal CO adsorbed to rhodium (2057cm^{-1}). The peak at 1977cm^{-1} lies near that which has been previously assigned to μ-2 bridging species on the Pd (100) surface (1975cm^{-1}).

The next peak is at 1850cm^{-1}. There have been no species of comparable frequency observed in the study of palladium therefore the closest peak frequency that has been previously seen is the species observed at 1861cm^{-1} which was assigned to μ-2 bridging on a rhodium catalyst. The discrepancy between the frequencies observed for the unimetallic and bimetallic systems could either be due to the interaction of the second metal or the inaccuracy of spectral correction (see above).

6.4 Study of peak area and position

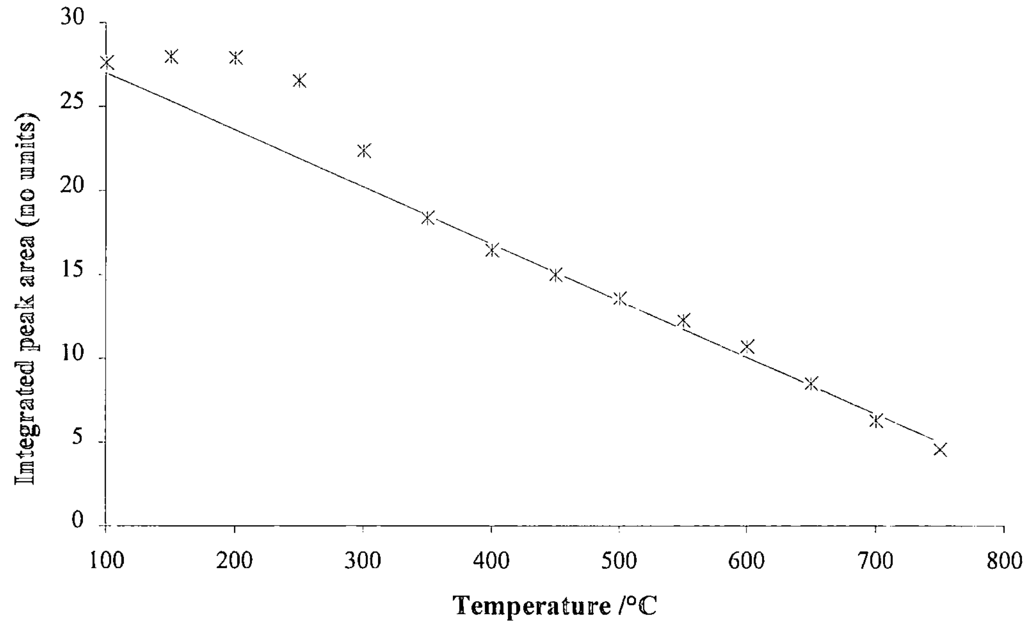
Previously[1] studies have been carried out to determine how the frequencies peaks attributed to adsorbed species change with temperature. Since the temperatures where adsorbed CO was observed differed greatly in this study to the literature values this type of investigation has been repeated. The frequency of the terminal Pt-CO peak was used to generate the results below in graph 6.1. The data used to produce this graph was collected from the results shown in section 6.2.1



Graph 6.1 Peak position vs temperature for terminal CO-Pt/Al_2O_3

It can be seen from the graph above that the frequency does not change in a linear fashion. The line of best fit which has been included purely as a guide to the eye, highlights the deviation of the relationship from linear. As can be seen the deviation is both above and below the line. There are two regions (250-300°C) and (600-650° C) where the change in peak frequency occurs at the largest rate.

It was also possible to plot the integrated peak area against temperature. The integrated area of a peak is proportional to the number of species that are absorbing the infra-red radiation, and hence the surface coverage by CO. Integration using the Simpsons rule approximation*[14] was performed between 1900cm^{-1} and 2150cm^{-1} and the results displayed in graph 6.2. The frequency range used ensured that the whole of the terminal peak was contained within the integration.



Line of best fit has been included as a guide for the eye

Graph 6.2 Peak area vs temperature for terminal CO-Pt/Al_2O_3

The maximum area of the peak can be seen to occur between 100 and 150°C, this is in accordance with the results of Barth *et al.*[1] who reported the maximum at 120°C. There are two possible explanations for the increase in peak area with temperature.

- It is possible that the absorption of IR increases with temperature. This may be related to the enhancement in absorbtivity caused by adsorption to step sites, this would also be caused by the limited surface mobility of CO at low temperatures

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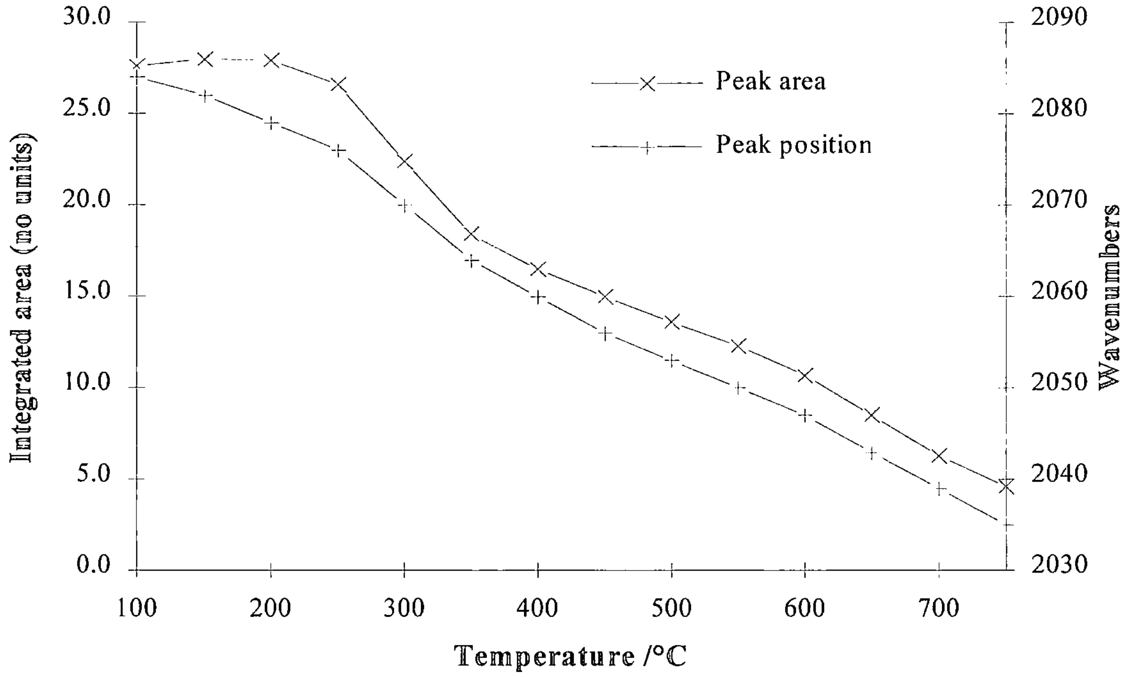
*[14] Simpsons rule is a mathematical device which can be used to accurately estimate the area under a curve by using the vertical height at set points above a baseline.

resulting in CO island formation. Raising the temperature would allow CO migration to form a surface more uniformly covered.

- The increase may also be caused by the conversion of CO adsorbed in other modes to terminal (e.g. bridging to terminal). This has been proposed[13] as being a conversion of support adsorbed CO to surface CO. Changing the support material would affect the results if this proposal were correct. The results do not show any significant changes when different support materials are used[1,2,14]. This would imply that the proposal of Jackson *et al.* is incorrect.

There is a further deviation from the best fit line that can be seen at 600°C. This correlates nicely with that seen in graph 6.1. It could be suggested that these maxima could be the temperatures where the rate of desorption is at a maximum. Placing both of the above graphs on the same axis showed the clear correlation:



Graph 6.3 Peak area and position vs temperature for terminal CO-Pt/Al_2O_3

There are two possible explanations for this correlation. Either of these could be the major factor though it is more likely that both of these affect the observed frequency of adsorbed carbon monoxide:

- The surface has to donate electron density into the CO anti-bonding orbital to decrease the bond energy. This will become less pronounced if there are more molecules present and hence there will be an observed increase in the vibrational frequency.

- If there are many molecules present on the surface then the molecules cannot get as close to the surface as when there are few. Less back donation can be made to the CO π^* orbital if the distance is great. This is known as surface crowding.

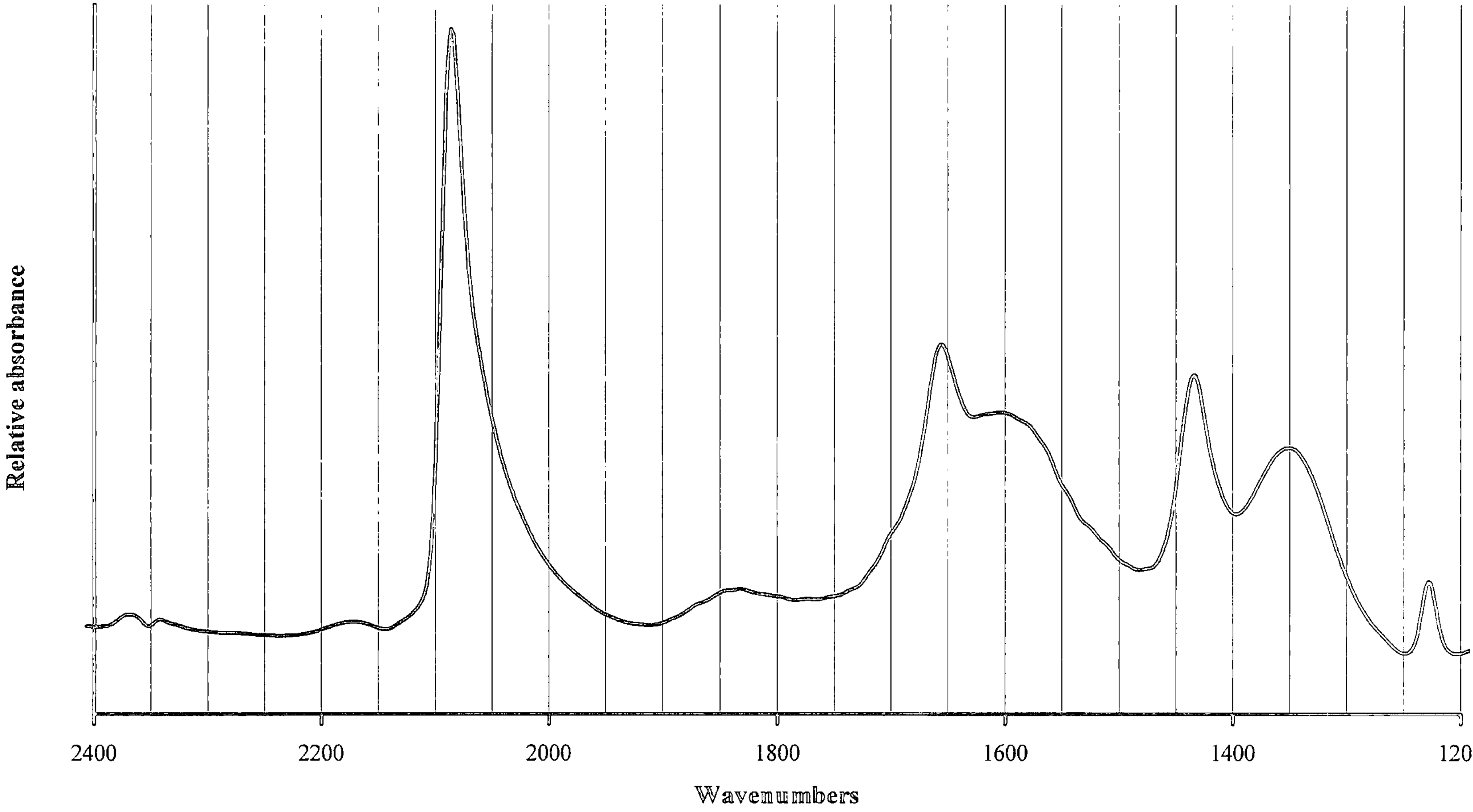
These results agree well with the results of Wade *et al.*[15] who showed that in clusters the bond energy of metal CO bonds decreases with increasing substitution.

6.5 Anomalous results

More recent studies of the platinum/CO system produced different results. Spectrum 6.8, obtained after CO adsorption on a sample of the platinum catalyst, gives an example of these findings. No changes had been made to experimental procedure yet the results were visibly different. There were 7 peaks present in spectrum 6.7, the frequencies of these are shown in table 6.6 below:

Peak Table (frequencies in cm^{-1})						
1	2	3	4	5	6	7
1228	1346	1434	1607	1655	1841	2084

Table 6.6 Peak frequencies for states observed in CO-Pt/Al_2O_3



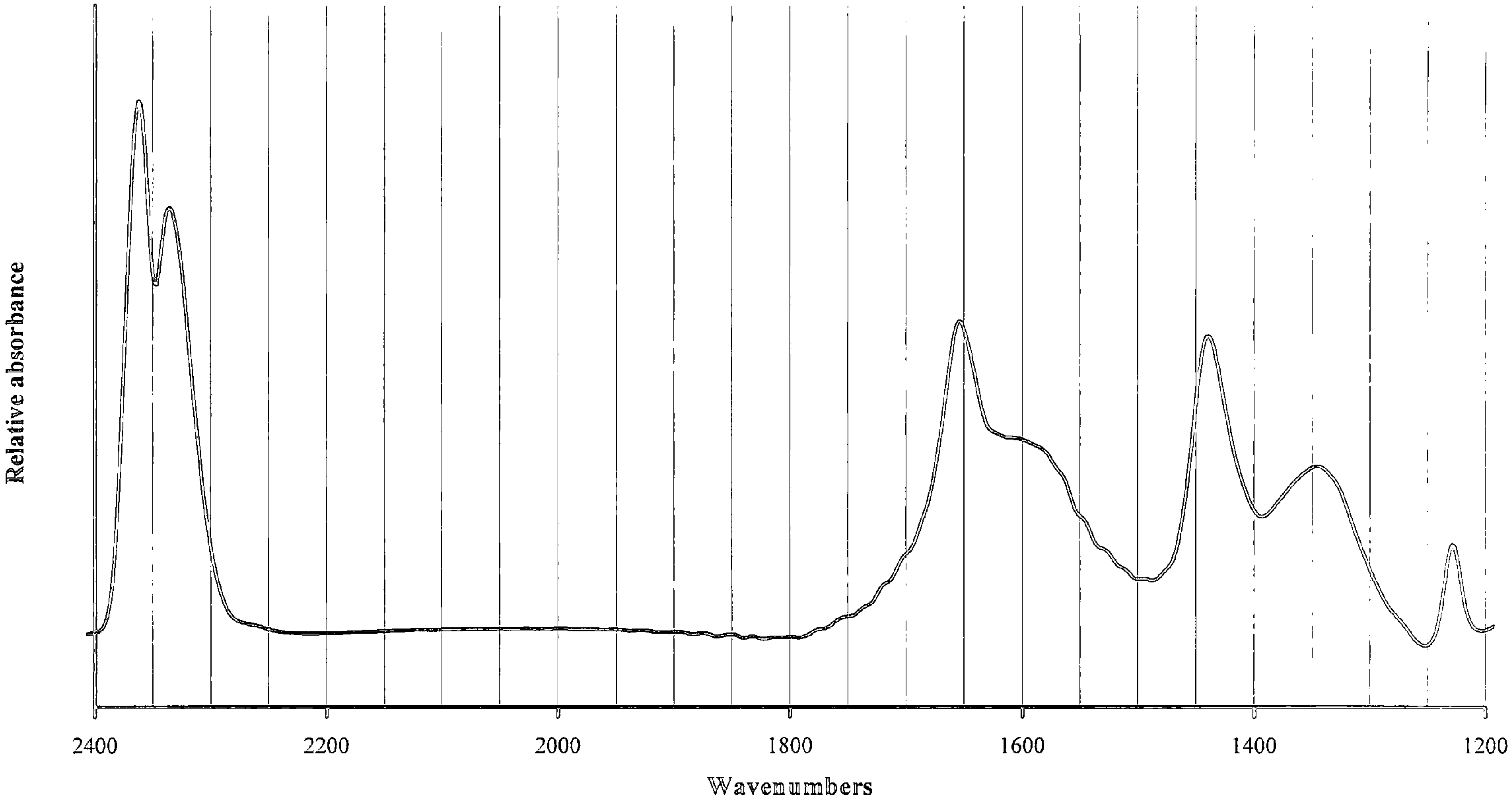
Spectrum 6.7 Recent results from CO-Pt/Al_2O_3 (100°C)

The spectrum was obviously very different to that previously observed for this system. The ratio of peak areas for the terminal and bridging species was very much increased with a greater preference shown for the terminal state. There are also 5 other, previously unobserved, states present. From the IR spectra it was difficult to form any definite conclusions for the identity of any of these species.

In an attempt to determine the identities of these species the exhaust gas from the cell was analysed following a desorption experiment. This was done using the gas collection and sampling equipment shown in figure 5.4. The analysis was performed using a gas chromatograph with a column which would allow detection of many common gases including CO and N_2, which are normally difficult to separate using chromatography. The detection of CO would suggest that these species were some sort of adsorbed CO, it was also possible that these species were a result of hydrocarbon contamination which would also be detected using a gas chromatograph. The results of this experiment were surprisingly simple with the only gases that were detected being CO_2 and N_2.

This gas analysis would suggest that the unidentified species were carbonates. In an attempt to verify this proposal, an experiment was performed using carbon dioxide instead of carbon monoxide. Carbonate species have previously been prepared on metal oxide surfaces by simple adsorption[16].

This experiment was conducted using the same method as had previously used. The catalyst was first reduced at 600°C in 15% H_2/N_2. The sample was then cooled in a stream of N_2 to 75°C (flow rate 10 l/hr). CO_2 was then passed over the surface at a pressure of 4 bar and the atmosphere retained for 5 minutes. Spectrum 6.8 was then taken immediately.



Spectrum 6.8 CO_2-Pt/Al_2O_3 (100°C)

The similarities between spectra 6.7 and 6.8 were striking. Table 6.7 contains the peak frequencies for both the above spectra as well as that for the directly analogous spectrum for CO (i.e. where $CO_{(g)}$ was still present).

Gas Present	Frequency of absorption (cm^{-1})								
None (ex CO)	1228	1346	1433	1607	1655	1840	2084	2336	2360
CO	1228	1341	1434	*	1655	1844	2093-2167**	2335	2362
CO_2	1228	1344	1439	*	1654			2336	2362
Peak description	s/w	m/m	s/m	b/m	s/m	b/l	s/h	-	-

* This state was present as a shoulder of the peak at $1655cm^{-1}$ and was not detected as a peak.

** This is an area of high absorption associated with $CO_{(g)}$

Table 6.7 Peak frequencies for CO/CO_2 adsorption to platinum

The last row row of table 6.7 describes the visual appearance of the peaks. The first letter describes the shape of the peak (s) sharp, (m) medium and (b) broad whilst the second letter describes the relative absorbance (w) weak, (l) low, (m) medium and (h) high.

From the table it can clearly be seen that the first 5 states present in both spectra are so similar that it can be suggested be suggested they are from the same surface species. The absence of the corresponding peaks at $1607cm^{-1}$ for the two samples is merely a result of being unable to assign a precise frequency to a broad shoulder.

The experimental procedure did not change from the time when the results were collected for section 6.1.1 nor was any contamination detected in either the gases, the cell and pipework or the catalyst. This means that the obvious change which has occurred has to be caused by something else. The logical explanation is that the catalyst has changed with time.

A review of CO_2 adsorption to metal oxides by Lorenzelli *et al*[10] gives an excellent account of the different carbon and oxygen surface species that may be formed by reactive adsorption to the surface of a metal oxide surface. The section detailing the results of alumina/CO_2 is reproduced below:

Sample	**α-alumina**	**γ-alumina**	**η-alumina**	**κ-alumina**
Symmetrical	-	-	-	1460 cm^{-1}
Unidentate	1610-1570 cm^{-1} 1385-1350 cm^{-1}	1530 cm^{-1} 1370 cm^{-1}	1630-1600 cm^{-1} 1515-1470 cm^{-1}	-
Bidentate	1710 cm^{-1} 1310 cm^{-1} 1675-1660 cm^{-1} 1345 cm^{-1}	1730-1660 cm^{-1} 1270-1230 cm^{-1}	1710 cm^{-1} 1315 cm^{-1}	1652 cm^{-1} 1234 cm^{-1}
Bridged	1810 cm^{-1} 1730 cm^{-1} 1310 cm^{-1}	1900-1750 cm^{-1} 1180 cm^{-1}	1900-1750 cm^{-1} 1180 cm^{-1}	-
Bicarbonate	3627 cm^{-1} 1655 cm^{-1} 1440 cm^{-1} 1227 cm^{-1}	3610-3605 cm^{-1} 1650-1639 cm^{-1} 1490-1440 cm^{-1} 1236-1225 cm^{-1}	3618-3612 cm^{-1} 1650-1636 cm^{-1} 1480-1440 cm^{-1} 1235-1230 cm^{-1}	-

Table 6.8 Results of CO_2 adsorption to alumina samples[10]

The table above shows the results for 4 phases of alumina (α,γ,η and κ). As can be seen from this table there are several different modes of coordination that carbonate can employ to bond with alumina, these are shown below in figure 6.3. Species A is the symmetrical configuration, this relates to surface states where the spectroscopic data is identical to free carbonate. Species B and C are both unidentate carbonate, IR spectroscopy will show the difference between the two forms because species C contains two identical groups. This will therefore give two peaks (symmetric and anti symmetric stretches) whereas with species B the two groups are non-degenerate so will not split in this manner.

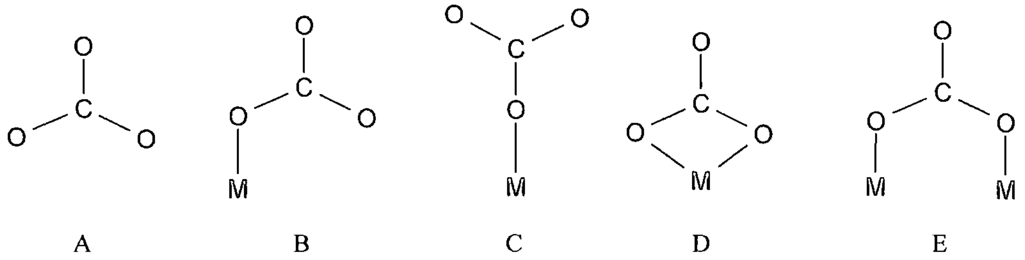


Figure 6.3 Simplified models of carbonate species

Species D is the bidentate bonding of two oxygen groups to a single surface site whilst species E is the bonding of two oxygen groups to two seperate metal sites. Bicarbonate species have also been observed, usually present as a dimer (shown in figure 6.4) though the monomeric form has been isolated.

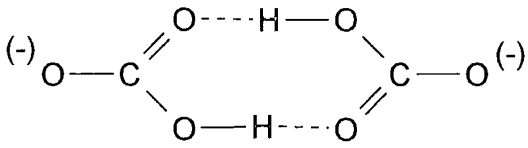


Figure 6.4 Bicarbonate dimer

The data in table 6.8 shows that there is good correlation between the results observed elsewhere[10] and those in spectrum 6.8. This correlation can be better seen in table 6.9 which gives a direct comparison between the data for α-alumina and that in table 6.6. The figures for α-alumina have been used here since this gives the best correlation (5 matches and one possible).

	CO_2 adsorption to α-Al_2O_3	CO_2 adsorption data from table 6.6
Bicarbonate	3627 cm^{-1}	
	1655 cm^{-1}	1654 cm^{-1}
	1440 cm^{-1}	1439 cm^{-1}
	1227 cm^{-1}	1228 cm^{-1}
Bidentate	1710 cm^{-1}	
	1310 cm^{-1}	
	1675-1660 cm^{-1}	1654 cm^{-1}
	1345 cm^{-1}	1344 cm^{-1}
Unidentate	1610-1570 cm^{-1}	1607 cm^{-1}
	1385-1350 cm^{-1}	

Table 6.9 Comparison between results from tables 6.8 and 6.6

Upon inspection of the data for spectrum 6.8, no species can be detected in the region above 3000cm^{-1}, because of the strong absorption of the catalyst in this area. Previously[4] it had been supposed that this was absorption by alumina, however it must relate to a different component of the support since the absorption of carbonates on alumina has been observed in this region[14,15].

It was proposed that these species could be related to the formate suggested in section 6.1.1. The frequencies of absorption observed here do not in any way match those seen elsewhere[10] for the adsorption of formate to supports or the M-CO_2 group as can be seen in table 6.10.

Mode of absorption	**M-CO_2H**
$\nu_{(CH)}$	2841 cm^{-1}
antisymmetric $\nu_{(CO)}$	1567 cm^{-1}
$\delta_{(CH)}$	1377 cm^{-1}
symmetric $\nu_{(CO)}$	1366 cm^{-1}

Table 6.10 Absorption frequencies for M-CO_2H

The obvious correlation between the two sets of data in table 6.9, immediately suggests that the species observed on the surface of the catalyst are unidentate and bidentate carbonate as well as bicarbonate bound to α-alumina. It is unknown if the alumina has changed phase to produce this result or whether it is a change in the function of the metal which has allowed the alumina to adsorb molecules when it had not been able to previously.

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Chapter 7

Conclusions

7. Summary and Conclusions

This study has achieved all of the aims laid out in chapter one:

1. To design, commission and test a catalyst examination apparatus.

   The design of the system was seen as an extremely important stage in this project. In order to encompass future work the apparatus was designed with a degree of flexibility, avoiding the need for significant reconstruction at a later date.

   The gas supply system functioned as it had been designed, by allowing flexible delivery of all the required gases without risk of contamination of the supply or safety hazard. It was tested to a pressure of 6 bar which exceeded by 50% any planned working conditions.

2. To use the catalyst testing system to investigate the adsorption of CO to supported PGM catalysts.

   All of the experiments with unimetallic catalysts produced results that broadly agreed with the literature whilst providing additional material for discussion. All of the species that were observed were achieved in a reproducible manner and the possibility of contamination of either samples or gas supply was eliminated by careful handling and rigorous testing.

   The results for platinum included terminally bound CO (2080cm^{-1}) and μ-2 bridge species (1830cm^{-1}) as well as two other states (1655cm^{-1} and 1360cm^{-1}). It is proposed that these species are the result of higher bonding interactions. Thermal desorption studies showed a thermal stability of adsorbed CO in excess of that which had been previously observed.

Similar results were seen for the rhodium catalyst sample. Both terminal ($2057cm^{-1}$) and μ-2 bridging ($1861cm^{-1}$) species were observed. The absence of gem-dicarbonyl species which had been previously reported was a feature of note as was the presence of a species in the region of $1600cm^{-1}$. This could be a μ-3 bonding interaction similar to the type that has been observed in the $Rh_6(CO)_{16}$ cluster.

The palladium system had been extensively investigated but species were still identified, in the 1300-$1650cm^{-1}$ region, that had not been previously reported. Terminal ($2073cm^{-1}$) and μ-2 bridging ($1975cm^{-1}$ and $1925cm^{-1}$) CO species were again identified, however the μ-2 species could be resolved into those bound to the (100) and (111) metal faces respectively.

3. To investigate novel catalysts using the techniques previously developed for existing systems.
   Two bimetallic catalysts of markedly different character have been examined. The nature of CO adsorption to these catalysts has been explained and suggestions for the structure of these catalysts have been made in light of these results. This study highlights the possible use of CO adsorption as a tool for structure determination.

Two other important achievements have been made during the course of this study:

1. A novel spectral preparation has been developed.
   The baseline subtraction method that has been developed during the course of this investigation has allowed the identification of species that would otherwise have gone unnoticed. This method has been extensively tested and delivers reproducible results that are accurate in both shape of spectral features and frequency.

2. Conditions for catalyst testing have been investigated.

   It is important when using catalysts of this type that a balance be achieved between adequate reduction and damage to the sample. Thermal sintering can occur at temperatures that are not far removed from those used for reduction and care needs to be used to prevent unwanted reaction. The conditions necessary for reduction were investigated and those that were used in this study were the minimum required to achieve complete reaction.

   The conditions required for CO adsorption were investigated. The temperature of 75°C that was used for this study, is a compromise between the time taken for the sample to cool and the requirement for complete adsorption. The time constraint is important because a reduced sample cannot be maintained in that state indefinitely. Species gradually adsorb to the clean surface of the catalyst following reduction, these will affect the results of adsorption.

Several of the observations of this study remain unexplained:

1. The appearance of species assigned as alumina carbonates.

   The alumina carbonates that were observed in the later experiments had been unprecedented in the results observed in the course of this study. No cause was found to precipitate the prominent change despite rigorous testing of all contamination sources. The only variable that cannot be controlled is time and it is the ageing of the catalyst which has been proposed as the cause of these results. Further experiments using the other catalysts could further elucidate the cause of this difference.

2. Rapid re-adsorption of contaminant molecules

   On many occasions during the course of this investigation samples were judged to have been reduced and where then cooled to allow for adsorption of CO. The samples adsorbed some gaseous species during the cooling which was detected when a spectrum was taken prior to adsorption. These samples required a further reduction cycle before adsorption could proceed. This process usually took about 3 hours which confounded all further practical work on several occasions. The identity of these re-adsorbed contaminants has not been identified though this could be a source of further interest within this system.

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1ST DRAFT

Board of Studies in Chemistry

POST GRADUATE COLLOQUIA, LECTURES AND SEMINARS FROM INVITED SPEAKERS

1995 - 1996 (August 1 - July 31)

1995

October 11	Prof. P. Lugar, Frei Univ Berlin, FRG Low Temperature Crystallography	*
October 13	Prof. R. Schmultzer, Univ Braunschwieg, FRG. Calixarene-Phosphorus Chemistry: A New Dimension in Phosphorus Chemistry	
October 18	Prof. A. Alexakis, Univ. Pierre et Marie Curie, Paris, Synthetic and Analytical Uses of Chiral Diamines	
October 25	Dr.D.Martin Davies, University of Northumbria Chemical reactions in organised systems.	
November 1	Prof. W. Motherwell, UCL London New Reactions for Organic Synthesis	
November 3	Dr B. Langlois, University Claude Bernard-Lyon Radical Anionic and Psuedo Cationic Trifluoromethylation	
November 8	Dr. D. Craig, Imperial College, London New Stategies for the Assembly of Heterocyclic Systems	
November 15	Dr Andrea Sella, UCL, London Chemistry of Lanthanides with Polypyrazoylborate Ligands	
November 17	Prof. David Bergbreiter, Texas A&M, USA Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers	*
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November 29	Prof. Dennis Tuck, University of Windsor, Ontario, Canada New Indium Coordination Chemistry	
December 8	Professor M.T. Reetz, Max Planck Institut, Mulheim Perkin Regional Meeting	

1996

January 10	Dr Bill Henderson, Waikato University, NZ Electrospray Mass Spectrometry - a new sporting technique	*
January 17	Prof. J. W. Emsley , Southampton University Liquid Crystals: More than Meets the Eye	*
January 24	Dr Alan Armstrong, Nottingham Univesity Alkene Oxidation and Natural Product Synthesis	

January 31	Dr J. Penfold, Rutherford Appleton Laboratory, Soft Soap and Surfaces *
February 7	Dr R.B. Moody, Exeter University Nitrosations, Nitrations and Oxidations with Nitrous Acid
February 12	Dr Paul Pringle, University of Bristol Catalytic Self-Replication of Phosphines on Platinum(O)
February 14	Dr J. Rohr, Univ Gottingen, FRG Goals and Aspects of Biosynthetic Studies on Low Molecular Weight Natural Products
February 21	Dr C R Pulham , Univ. Edinburgh Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes
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March 6	Dr Richard Whitby, Univ of Southampton New approaches to chiral catalysts: Induction of planar and metal centred asymmetry *
March 7	Dr D.S. Wright, University of Cambridge Synthetic Applications of Me_2N-p-Block Metal Reagents
March 12	RSC Endowed Lecture - Prof. V. Balzani, Univ of Bologna Supramolecular Photochemistry
March 13	Prof. Dave Garner, Manchester University Mushrooming in Chemistry
April 30	Dr L.D.Pettit, Chairman, IUPAC Commission of Equilibrium Data pH-metric studies using very small quantities of uncertain purity