AN INFRARED SPECTROSCOPIC STUDY OF ADSORBED SPECIES ON NICKEL AND PLATINUM

by

Lyle Edwin Moran

Thesis submitted to the School of Graduate Studies of the University of Ottawa as partial fulfillment of the requirements for the degree of Master of Science in Chemistry

UNIVERSITY OF OTTAWA
OTTAWA, CANADA, 1977

TO MARY

THE ROAD NOT TAKEN

Two roads diverged in a yellow wood,
And sorry I could not travel both
And be one traveller, long I stood
And I looked down one as far as I could
To where it bent in the undergrowth;

Then took the other, as just as fair,
And having perhaps the better claim,
Because it was grassy and wanted wear;
Though as for that the passing there
Had worn them really about the same.

And both that morning equally lay
In leaves no step had trodden black.
Oh, I kept the first for another day!
Yet knowing how way leads on to way,
I doubted if I should ever come back.

I shall be telling this with a sigh
Somewhere ages and ages hence:
Two roads diverged in a wood, and I—
I took the one less travelled by,
And that has made all the difference.

Robert Frost

ABSTRACT

In this thesis, infrared spectroscopy has been used to study adsorbed species on silica-supported nickel and platinum catalysts. The chemisorption of the oxides of nitrogen (particularly nitric oxide) was studied initially, followed by a study of the chemisorption and oxidation of pyridine on bare and oxidized nickel and platinum. The results of these studies will be described below.

Infrared spectral data have shown that nitric oxide chemisorbs on Ni/SiO_2 to form a single adsorbed species, which has been attributed to linear, neutral Ni-NO. On Pt/SiO_2 two major surface species were produced and these have been assigned to linear, neutral Pt-NO and bent Pt-NO. In addition, the spectral data have indicated that, at high surface coverage, other nitrogen-oxygen containing species are formed one of which has been tentatively identified as $PtONO_2$.

The study of nitrogen dioxide chemisorption has demonstrated that nitrogen dioxide dissociates on both Ni/SiO_2 and Pt/SiO_2 to form adsorbed nitric oxide and oxygen.

Isotopic substitution experiments have shown that carbon monoxide and nitric oxide react over Ni/SiO_2 to form a surface nickel isocyanate species and the formation of this species is independent of the order of the addition of the reactants. However, on Pt/SiO_2 a surface isocyanate species was generated only if the nitric oxide was preadsorbed at low surface coverage. In both studies, it has been concluded that very little M-NCO is produced (M = Ni or Pt).

When hydrogen was added to chemisorbed nitric oxide on Pt/SiO_2, two new surfaces species are formed and these have been identified as $Pt\text{-}NH_3$ and Pt_2O_2NH.

In addition to the above results, this thesis also contains extensive reviews of the chemisorption of nitric oxide and nitrogen dioxide and of the formation of surface isocyanate species on the transition metals.

Pyridine

Infrared spectral data have indicated that pyridine dissociatively chemisorbs on Pt/SiO_2 to form a Pt-C σ bond at the 'ortho' position and a coordinate bond with the N-atom such that the molecule lies perpendicular to the surface. On Ni/SiO_2 a different strongly adsorbed species is formed which has been identified as a simple nitrogen-coordinated pyridine which also lies perpendicular to the surface, and, as proposed by others, the coordination of this species is promoted if the nickel surface is pretreated with either CO or O_2. When oxygen is added to chemisorbed pyridine on Pt/SiO_2 two new adsorbed species are formed and these have been assigned to a surface (N=O) containing species of the type, $PtNO_x$ (x = 2 or 3) or Pt_2NO, and a cyclic C_5 derivative of unknown structure. The same species were formed on oxidized Pt/SiO_2, but, in addition, coordinated pyridine is formed.

ACKNOWLEDGMENTS

The research described in this thesis has been supported by a grant from Imperial Oil Limited to Dr. B.A. Morrow, Associate Professor of Chemistry at the University of Ottawa. I wish to thank Dr. Morrow for the inspiration that he has given me throughout this study.

Further,I would like to extend thanks to the support staff of the Department of Chemistry, University of Ottawa; without their help this study could never have been completed.

Eva Szabo deserves special thanks for assistance with the diagrams in this thesis.

I thank Sandra Childerstone for her patience, good humour, and diligence while typing this thesis.

Finally, my wife Mary deserves special credit for her patience and reassurance, and, particularly for her confidence in me.

TABLE OF CONTENTS

	Page
ABSTRACT	i
ACKNOWLEDGEMENTS	iii
LIST OF FIGURES	vii
LIST OF TABLES	ix
CHAPTER 1 - INTRODUCTION	1
Heterogeneous Catalysis: General	1
Supported Metal Catalysts	4
Purpose of Present Study	6
CHAPTER 2 - EXPERIMENTAL	8
Infrared Spectrometer	8
Mass Spectrometer	8
Vacuum Line	9
Sample Cell	9
Silica Support	11
Supported Metals	12
Background I.R. Spectra	14
Deuterated Samples	16
Chemicals	17
Calibration of Infrared Bands	18
CHAPTER 3 - NITRIC OXIDE	19
Properties and Behaviour	19
Errors in the Literature	19
Transition Metal - Nitric Oxide Complexes	20

	Page
CHAPTER 4 - A REVIEW OF THE CHEMISORPTION OF NITRIC OXIDE AND NITROGEN DIOXIDE AND OF SURFACE ISOCYANATE FORMATION ON METALS	25
General	25
Infrared Spectroscopic Studies	27
Nitric Oxide	27
Nitrogen Dioxide	32
Reaction Between NO and CO	34
CHAPTER 5 - THE CHEMISORPTION OF THE OXIDES OF NITROGEN ON NICKEL	42
Preface	42
Results	43
Nitric Oxide	43
Nitrogen Dioxide	44
Preadsorbed Nitric Oxide + Carbon Monoxide(g)	44
Preadsorbed Carbon Monoxide + Nitric Oxide	49
Discussion	52
Nitric Oxide	52
Nitrogen Dioxide	53
Nitric Oxide + Carbon Monoxide	54
Mechanisms of Isocyanate and CO_2 Formation	55
Conclusions	56
CHAPTER 6 - THE CHEMISORPTION OF THE OXIDES OF NITROGEN ON PLATINUM	57
Results	57
Nitric Oxide	57
Nitrogen Dioxide	62
Nitric Oxide + Carbon Monoxide	65

	Page
Discussion	68
Nitric Oxide	68
Nitrogen Dioxide	72
Nitric Oxide + Carbon Monoxide	73
Conclusions	75
CHAPTER 7 - PYRIDINE	77
General	77
Results	79
Platinum	79
Nickel	83
Discussion	85
Nickel	85
Platinum	88
Concluding Remarks	94
Interaction Between Adsorbed Pyridine and Oxygen on Platinum	95
Results	95
Discussion	100
Conclusions	104
"SUGGESTION FOR FURTHER RESEARCH"	106
BIBLIOGRAPHY	108

LIST OF FIGURES

Figure		Page
1	Model of Solid Surface	3
2	Sample Cell	10
3	Background Spectrum of a Silica Supported Metal Disc	15
4	The Adsorption of NO on Ni/SiO_2	45
5	The Reaction of Adsorbed NO with CO(g) on Ni/SiO_2	46
6	Hydrolysis of Adsorbed Species Formed During the Reaction of Adsorbed NO and CO(g) on Ni/SiO_2	48
7	Isotopic Study of the Reaction Between Chemisorbed NO and CO(g) on Ni/SiO_2	50
8	The Reaction of Adsorbed CO with NO(g) on Ni/SiO_2	51
9	The 'In Situ' Adsorption of NO on Pt/SiO_2	58
10	Comparison of the Infrared Absorption Spectrum of Chemisorbed ^{14}NO with that of Chemisorbed ^{15}NO on Pt/SiO_2	59
11	The Reaction of Adsorbed NO with H_2(g) on Pt/SiO_2	60
12	The Reaction of Adsorbed NO with O_2(g) on Pt/SiO_2	63
13	The Adsorption of NO_2 on Pt/SiO_2	64
14	Comparison of Adsorbed NO_2 with the Reaction Between Adsorbed NO and O_2(g) on Pt/SiO_2	66
15	The Reaction of Adsorbed NO with CO(g) on Pt/SiO_2	67
16	Pyridine on SiO_2	80
17	Pyridine on Pt/SiO_2	81
18	Pyridine vs Pyridine-d_5 on Pt/SiO_2	82
19	Pyridine on Ni/SiO_2	84

Figure		Page
20	Possible Structures for Adsorbed Pyridine on Pt/SiO_2	91
21	Addition of O_2 to Chemisorbed Pyridine on Pt/SiO_2	96
22	Addition of O_2 to Chemisorbed Pyridine-d_5 on Pt/SiO_2	97
23	Pyridine on Oxidized Pt/SiO_2	99
24	Pyridine-d_5 on Oxidized Pt/SiO_2	101

LIST OF TABLES

Table		Page
1	Types of Nitric Oxide Bonding on Chemisorption	22
2	Summary of Infrared Spectroscopic Studies of Nitric Oxide Chemisorption	28
3	Summary of Infrared Spectroscopic Studies of Nitrogen Dioxide Chemisorption	33
4	Summary of Infrared Spectroscopic Studies of Surface Isocyanate Formation	35
5	Infrared Absorption Bands due to Pyridine-h_5 and Pyridine-d_5 on Pt + O_2 and on PtO	102

CHAPTER 1

INTRODUCTION

Heterogeneous Catalysis: General

A heterogeneously catalyzed reaction starts when one or more of the reactants adsorbs on a surface. The reaction then proceeds by reaction of the adsorbed species with either a coadsorbed species or a molecule from the gas phase with subsequent desorption of the product, leaving the surface regenerated and active for further adsorption. An understanding of how a surface can catalyze a reaction can be obtained from consideration of how surface properties differ from bulk properties.

Surface atoms are in an anisotropic environment since they are surrounded by atoms on one side and vacancies on the other. Because of unbalanced interatomic forces, these atoms can relax perpendicular to the surface and hence the surface can "buckle" or reconstruct, a motion not allowed for bulk atoms. In certain temperature ranges the formation of some of these reconstructed surfaces can be energetically favoured over the formation of flat surfaces.

Spontaneous adsorption of the Van der Waals type (i.e. physical adsorption) occurs as a result of the unbalanced interatomic forces. Further, the electronic properties of the surface atoms are undoubtedly different from those of the bulk atoms and one can visualize a situation whereby electrons may be donated from a surface atom to an adsorbate or vice versa. (i.e. rearrangement of the electrons of the interacting gas and solid). This type of strong chemical interaction with the surface

is usually termed chemisorption. The distinction between chemical and physical adsorption is not always clear but the heat of adsorption in the latter case is usually less than 10 Kcal per mole.

A heterogeneous surface usually contains different exposed crystal planes or faces and as a result there are variations in the bonding affinity of the surface atoms, or sites, due to the differing metal-metal coordination of the surface atoms. Further, heterogeneous surfaces contain edges, corner atoms, lattice defects, and dislocations and these would give rise to differences in the coordination numbers and the electron densities of the surface atoms. There are several atomic sites distinguishable by the number of nearest neighbour atoms surrounding them, as shown in figure 1. Atoms in terraces have the highest coordination number while adatoms, which stand singly on top of a lower layer, have the lowest. The techniques of low energy electron diffraction (LEED) and field ion microscopy have provided experimental evidence for the presence of these surface sites. Atoms in terraces, steps, and kinks are the most numerous while the concentrations of adatom and terrace vacancy sites are about an order of magnitude smaller. The different reactivities among the active sites are reflected physically by quantities such as heats of adsorption and magnetic properties.

Various spectroscopic techniques have been used not only to analyze adsorbed species but also to characterize the active sites on solid surfaces. These include electron spectroscopy for chemical analysis (ESCA), Auger emission spectroscopy (AES), ultraviolet spectroscopy (UV.) and infrared spectroscopy (I.R.).

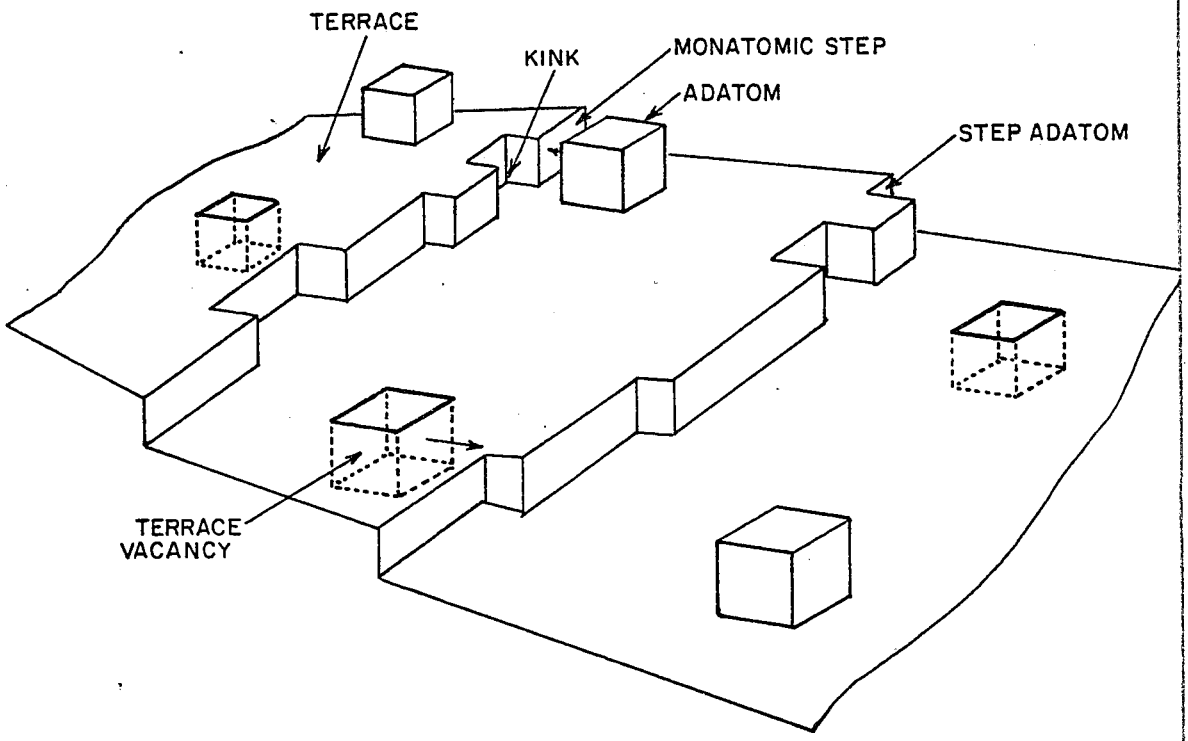


FIGURE 1

MODEL OF SOLID SURFACE

Infrared spectroscopy is a particularly useful technique with which to investigate adsorbed species on the surface of solid materials, because it can provide information with regard to the structure of the surface, it provides a means of observing the interactions and perturbations that occur at the surface during the chemisorption process, and it can be used to determine the structure of chemisorbed species or of adsorbed intermediates in a catalyzed reaction. It is recognized that the latter may have short lifetimes and exist in small concentrations during the course of a catalyzed reaction. Therefore, care must be exercised when evaluating surface species as intermediates and assigning them kinetic significance for the following reasons. Firstly, strongly chemisorbed species which might occupy most of the catalyst surface may not be involved in the catalyzed reaction as an intermediate. Secondly, if the spectrum of an adsorbed species cannot be observed due to infrared inactivity, this species may nonetheless be directly involved in the overall reaction and its omission from the kinetic data will lead to erroneous conclusions. Finally, most infrared studies are not carried out under dynamic reaction conditions (as, for example, in a flow reactor system) and the intermediates detected using infrared spectroscopy under static conditions may not be the same as those which could be generated under steady state conditions.

Supported Metal Catalysts

Finely dispersed metals offer a high concentration of surface atoms and this leads to a high specific activity. But highly dispersed metals are thermally unstable with respect to sintering into larger

crystallites, particularly at temperatures above $0^{o}C$. One method of overcoming the latter problem is to disperse these metals on high surface area supports of greater stability. Further, these supports (eg. silica, alumina) should be relatively inert to chemical attack so that any observed catalytic activity can be attributed solely to the dispersed metal. Such catalysts are widely used in industry and they are also very suitable for infrared spectroscopic studies, a point which will be discussed further in the experimental section. Another useful method of stabilizing finely dispersed metal particles for infrared work involves evaporating the metal of interest onto infrared cell windows which are coated with hydrocarbon oil to produce a mull of small metal particles. This method was developed by Blyholder[1,2,3,4] and although it provides useful spectroscopic data it has little industrial significance.

The sintering of the surface metal atoms of a supported catalyst due to prolonged heating at elevated temperatures is nonetheless a commonly encountered problem. Sintering generally leads to deactivation of the metal catalyst, a phenomenon that is complicated and not very well understood. A model for the sintering of platinum, supported on alumina, has been proposed by Flynn and Wanke[5]. They envisage that individual platinum atoms move from the metal crystallite to the surface of the support with subsequent migration of the platinum atoms across the support surface. Finally, the migrating atoms either collide with a platinum crystallite or are stabilized by a fall in the temperature of the surface.

Another common but not fully understood phenomenon is that of catalyst 'break-in' as reported by Baddour et al[6]. They investigated the break-in period for carbon monoxide oxidation over a silica supported

palladium catalyst. They postulate that the break-in phenomenon involves structural rearrangement of the palladium surface in the presence of oxygen or oxygen-carbon monoxide mixtures. The structural rearrangement is attributed to a redistribution of exposed crystallographic planes resulting from surface diffusion of palladium atoms or palladium-oxygen complexes. This type of structural rearrangement has been discussed for platinum single crystal surfaces by Somorjai[7]

Purpose of Present Study

In this thesis, infrared spectroscopy has been used to study adsorbed species on silica-supported nickel and platinum catalysts. The chemisorption of the oxides of nitrogen (particularly nitric oxide) was studied initially. Nitric oxide is a particularly interesting molecule because it is a monomer in the gaseous state and is a stable odd electron species. As such it is capable of bonding as a nitrosonium ion, NO^+, as neutral NO, and as a nitrosyl ion, NO^-. The NO stretching frequency varies considerably for each of the above and infrared spectroscopy can be used in order to determine the mode of bonding of this molecule on a catalyst surface.

The scientific impetus for this work arises because NO is a contaminant within our environment and a major source of this is from automobile emissions. Several approaches have been taken to eliminate this pollutant and the most successful of these is the reduction of the NO in "catalytic" mufflers which employ noble metal catalysts. However, little is known of the mechanism of the reduction process and the present study was undertaken in order to expand our knowledge of the adsorption

and catalytic reduction of NO on Pt and Ni.

A second aspect of this thesis was concerned with an infrared spectroscopic study of the chemisorption and oxidation of pyridine on bare and oxidized Ni and Pt. It is known that pyridine can hydrogen bond to surface hydroxyl groups, coordinate to Lewis acid sites and form pyridinium ions with Brønsted acid sites on oxide[8] catalyst surfaces and each of these species has a very characteristic infrared spectrum. The objective of this work is to determine whether this technique could also be used to probe the surfaces of metal catalysts in order to determine the conditions (if at all) under which various types of active adsorption sites would be generated.

The experimental aspect of this work will be discussed in the next chapter followed by a review of the chemisorption of NO in Chapter 3. The adsorption of pyridine will be reviewed in chapter (7).

CHAPTER 2

EXPERIMENTAL

Infrared Spectrometer

The infrared spectrometer used in this study was a Perkin Elmer 13G Filter-Grating Spectrometer. For routine use slit widths of 5-10 cm^{-1} were used over a range extending from 3800 to 1350 cm^{-1}. The instrument was used in the double beam mode with one exception. Single beam operation was employed when band frequencies between 1890 and 1350 cm^{-1} were calibrated against atmospheric water vapour. In order to minimize the latter during normal operation the spectrometer was flushed with a continuous flow of dry air from a Beckman Automatic Air drier.

The chopper was situated between the Nernst Glower source and the sample thus ensuring that the observed absorption spectrum was due to the absorption of radiation by the surface species and not to the emission of radiation from the sample due to heating in the infrared beam. Chopping the beam gives rise to an ac signal at the detector and radiation emitted by the sample will produce a dc signal which will be rejected by the ac-tuned amplifier.

The infrared spectrometer was mounted on a mobile table so that it could be moved close to any vacuum line. The sample cell (figure 2) could then be left in the infrared beam and connected to a vacuum line so that 'in situ' studies could be carried out.

Mass Spectrometer

An A.E.I-MS10 mass spectrometer was employed to analyze gas

phase products and to check the purity of reactant gases. The mass spectrometer was portable and, therefore, it could be connected directly to a vacuum line if necessary.

Vacuum Line

A standard pyrex vacuum line was used for the transfer of gases from container bulbs to a sample cell and for the degassing of the catalyst samples. A mechanical backing pump was connected to a mercury diffusion pump and pressures of about 10^{-6} torr could be obtained. A vacuum of 10^{-5} torr was considered satisfactory for the experiments in this study. Two liquid nitrogen traps were placed in the line: one between the main line and the mercury diffusion pump and the other between the oil backing pump and the mercury diffusion pump.

A mercury manometer was employed to measure pressures greater than 1.0 torr. A McLeod gauge was used to record pressures between 0.005 and 5 torr. To estimate pressures in the range from 1.0 torr to 10^{-4} torr a pirani gauge was used.

Sample Cell

The sample cell which was used is shown schematically in figure (2). A ball joint system was used for connection to the vacuum line. The design of the sample cell allowed it to be connected to a vacuum line in a horizontal position or to be left in a vertical position in the infrared spectrometer for 'in situ' studies. The cell was designed in this laboratory especially for studies of the sample at room temperature. The body of the cell and the sample holder was made of quartz and the windows were

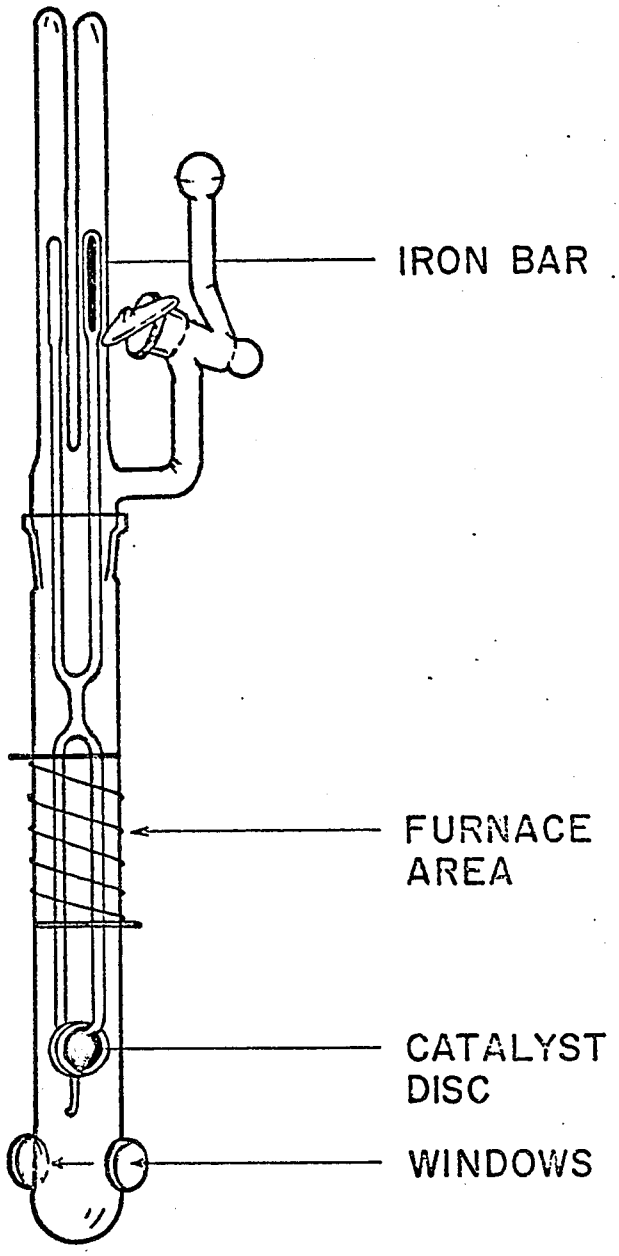


FIGURE 2

SCHEMATIC DIAGRAM OF SAMPLE CELL

either NaCl or CaF_2 (5.5 cm diameter and 5mm thickness). Glyptal was used to seal the windows to the quartz body.

The heating zone consisted of a layer of asbestos matting over which was wound approximately 3 metres of Kanthal wire such that there were approximately 4 turns per centimeter. This wire was then covered with a thick coating of powdered asbestos. A small quartz tube was placed between the windings and the asbestos mat so that the temperature could be estimated by inserting a thermocouple wire (alumel/chromel). The sample holder consisted of two concave annular discs, one on each arm of the forkpiece, which was held together by tension in the fork. To place a sample (2.5 cm diameter) inside the holder the ends of the fork could be pried apart with just light hand pressure, sufficient to allow a disc to slip in edge-ways. The upper end of the forkpiece fitted snugly into a matching sheath and contained an iron bar so that movement of the sample was possible by means of an external magnet. Therefore the disc could be moved from the furnace region to the windows while maintaining the disc in the same orientation with respect to the windows.

When temperatures of 400^{o}C were employed the ground joint reached a temperature of about 60^{o}C and this joint was lubricated with apiezon H.

Silica Support

The catalysts used in this study were supported on Cab-o-sil HS-5 silica obtained from Cabot Inc. of Boston, U.S.A. Cab-o-sil is a commercially available silica prepared by the flame hydrolysis of $SiCl_4$ in a stream of hydrogen and air at approximately 1000^{o}C.

$$SiCl_4 + H_2 + O_2 \xrightarrow{1000^{o}C} 4\ HCl + SiO_2$$

It has a B.E.T. (N_2) surface area of 320 m^2g^{-1}. This high surface area allows the metal to be highly dispersed. Therefore scattering of the electromagnetic radiation is minimized and the improved transmission leads to improved infrared spectra. Further, silica is relatively inert to chemical attack and this permits a more representative study of the dispersed metal.

Before the silica was used it was preheated in air at 600-800^{0}C for 18 hrs. to oxidize any organic contaminants.

Supported-Metals

A silica-supported Ni or Pt sample was prepared[9] by the slurrying, at room temperature, of 2 grams of silica with 1 gram of either nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] or hexachloroplatinic acid [$H_2PtCl_6 \cdot xH_2O$] in spectral quality acetone. The slurry was then left to air dry at room temperature for one week during which time the conglomerates which formed were broken up lightly with a glass rod. After this period the remaining lumps were pulverized with a mortar and pestle and ground lightly. At this stage the powder was generally light brown in colour. The sample was then stored in a desiccator for a few days and reground prior to use.

To render the sample suitable for infrared spectroscopic examination 200 mg of the dried powder was pressed into a self-supporting disc, 2.5 cm in diameter and approximately one millimeter thick, at 1000 psi for a few seconds. Circular wafers of lens cleaning paper were used to separate the powder from the die and prevent sticking. The disc was then reduced in H_2 at 400^{0}C such that by weight 9% Ni or 16% Pt was

incorporated into the catalyst. The disc contained 40 mg/cm^2 of combined material

The reduction of the sample was carried out in the sample cell (figure 2). This reduction procedure was preceded by evacuation at room temperature for several hours to remove contaminants such as acetone, water, and grease. The sample was then drawn up to the furnace zone. Ultra high purity H_2 was passed through an 'in-line' catalytic-H_2 purifier (Deoxo-Engelhard). Initially approximately 400 torr of H_2 was admitted to the cell at room temperature and, after five minutes, it was evacuated until the pressure dropped to 10^{-3} torr. This procedure was repeated twice to ensure the removal of impurities such as HCl, formed during the reduction of the salt, water, due to exposure of the sample to the atmosphere, and residual hydrocarbons, from reduction of acetone remaining in the powder. The temperature of the sample was then slowly raised to 100^{o}C in increments of 10-20^{o}C with the addition of fresh H_2 at each step. The H_2 was left in contact with the sample for 20 minute intervals, followed by degassing to 10^{-4} torr. Above 100^{o}C the increments of temperature were increased to 50^{o}C until a temperature of 400^{o}C was reached. A H_2 contact time of 15-30 minutes was generally employed. Slow raising of the temperature from room temperature to 400^{o}C was found to be necessary in order to prevent deposition of the reduction products on the cell windows. Finally the sample was heated at 400^{o}C for 18 hours. During this time the H_2 was changed several times. Experience has shown that unless the reduction process was rigidly adhered to, as outlined above, the samples would be virtually opaque in the infrared region.

After the reduction process the sample disc could then be cooled to room temperature in H_2 with subsequent degassing to 10^{-4} torr to produce a H_2-covered sample. If the catalyst was degassed at 400°C for several hours (2-3hrs) and then cooled in a vacuum a bare or H_2-free sample resulted. Unless otherwise stated H_2-free samples were used in this study.

Regeneration of a surface could be accomplished by the following procedure. Firstly, the adsorbate used in the experiment was outgassed for 30 minutes. Then, at room temperature, the sample was treated with 400 torr of H_2 for 5 minutes and degassed for 10 minutes. Then 400 torr of H_2 was admitted to the sample cell and the temperature was raised to 400°C. This temperature was maintained for about 3 hr. with frequent changes (30 min) of the H_2. The sample was then degassed at 400°C for 2-3 hr, followed by cooling to room temperature. The surface was then ready for use. Experience has shown that several 'adsorption-desorption-regeneration' cycles could be used without catalyst deactivation although the lifetime of the supported metal catalyst actually depends on the type of adsorbate used.

Background I.R. Spectra

The principal bands observed in the background spectrum of a silica-supported metal disc are shown in figure (3). These bands are due to the silica support. The broad bands between 1350-2000 cm^{-1} are SiO_2 combination and overtone modes whereas the band at 3748 cm^{-1} is due to isolated hydroxyl groups on silica. If molecular water is present or H_2-bonded hydroxyl groups exist a very broad band appears near 3500 cm^{-1}

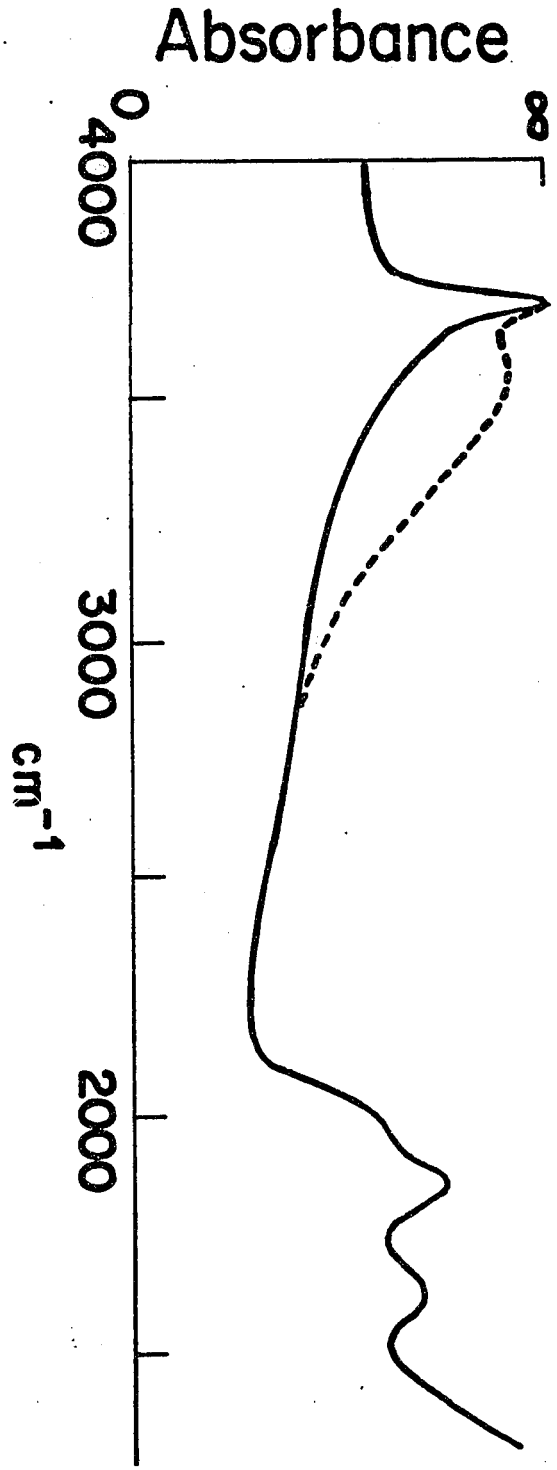


FIGURE 3

BACKGROUND SPECTRUM OF A SILICA SUPPORTED METAL DISC

as shown by the dotted curve in figure (3). Below 1350 cm^{-1} the silica support is totally adsorbing. Although this restricts the observation of vibrational modes for some adsorbed species a redeeming feature of this support is its relative inertness to chemical attack.

To render the spectral region between 2000 cm^{-1} and 1350 cm^{-1} more suitable for the observation of absorption bands attributable to adsorbed species, a silica disc was prepared containing the same quantity of silica (170 mg) as was in the supported metal disc. This disc was placed in a sample cell, degassed, and placed in the reference beam of the double beam spectrometer. An almost flat baseline was usually attainable with this silica compensation, a feature that proved to be extremely valuable for the interpretation of both adsorbed NO and pyridine.

Deuterated Samples

A rigorous procedure had to be followed to produce a deuterated sample in which complete exchange of the SiOH groups took place. (Band at 3748 cm^{-1} for SiOH shifts to 2763 cm^{-1} for SiOD). Initially a regenerated sample was degassed at 400°C for 2 hr. and then cooled to 100°C. While maintaining the temperature at 100°C, 10 torr of D_2O was admitted to the cell for 30 minutes, followed by degassing to 10^{-4} torr. This procedure was repeated four times over a period of 20 hr. Then the D_2O was outgassed for 30 minutes at 100°C. Next, 6 torr of $D_2(g)$ was admitted to the cell and the temperature was raised to 400°C. The temperature was maintained at 400°C in D_2 for 20-40 hr. with frequent changing (1-2 hr) of the D_2. Finally, the D_2 was outgassed at 400°C and the sample was then cooled to room temperature in vacuum. Complete exchange was observed to have occurred

after completion of this procedure. Experience has shown that unless the above procedure is strictly adhered to, a completely deuterated sample cannot be obtained.

Chemicals

Commercially available gases and liquids which have been used for adsorption were checked for impurities, wherever possible, by using infrared or mass spectrometry. Trap to trap distillations on the vacuum line were required for some gases (eg. NO see Chapter 3) and as well some gases such as NH_3 and NO, had to be dried by passing the gas from trap to trap, through a column of phosphorus pentoxide (P_2O_5), on the vacuum line.

Spectral grade pyridine was dried and stored over CaH_2.

A standard 'freeze-pump-thaw' cycle was used to remove air before adsorbing any condensable gas or vapour.

Chemicals Used	Supplier and Purity
NO	Matheson
NO_2	Matheson
CO_{16}	Matheson (Assayed)
O_2	Matheson
D_2	Matheson
H_2	Matheson (U.H.P.)
^{15}NO	Merck, Sharp, & Dohme (98.8 atom % N-15)
^{13}CO	Merck, Sharp & Dohme (90 atom %)
D_2O	Merck, Sharp & Dohme (min.purity 99.7% D)
Pyridine-d_5	Merck, Sharp & Dohme (99 atom % D)

Chemicals Used cont'd	Supplier and Purity cont'd
$C^{18}O$	Prochem (99 atom %)
O^{18}	Prochem (99 atom %)
Pyridine	Fisher Spectral grade (dried)
$Ni(NO_3)_2 \cdot 6H_2O$	B & A Reagent Grade
$H_2PtCl_6 \cdot xH_2O$	Johnson,Matthey Chemicals Ltd.

Calibration of Infrared Bands

Spectral Region	Calibrated Against
2224-1905 cm^{-1}	DCl(g)
1890-1350 cm^{-1}	water vapour
all other regions	polystyrene

CHAPTER 3

NITRIC OXIDE

Properties and Behaviour

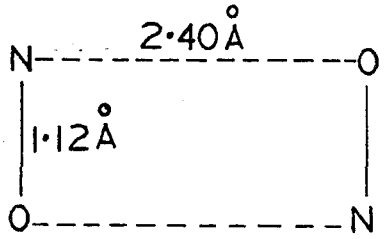
The chemical and physical properties of the nitric oxide molecule have been well documented in the literature. Comprehensive reviews of these properties, particularly with respect to heterogeneous catalysis, have been published by Shelef and Kummer[10] and by Klimisch and Larson[11]. A review of the infrared spectroscopic investigations of nitric oxide on supported metal catalysts will be presented in Chapter 4 of this thesis.

Errors in the Literature

There are discrepancies in the literature regarding the colour and structure of liquid and solid nitric oxide. Mason[12] has shown that the blue colour commonly attributed to liquid and solid nitric oxide is actually due to the presence of dinitrogen trioxide, which exists in the solid state when condensed nitric oxide and nitrogen dioxide are in equilibrium. This has special significance with respect to the present study since the nitric oxide as supplied by the manufacturer condensed into a bluish solid. However, a colourless solid was obtained after drying and distilling the nitric oxide under vacuum. Mason[12] also established that the structure of the nitric oxide molecule in the solid state (at low temperatures) does not have the rectangular structure, as shown in diagram 1-A, but has the cis-dimer structure of diagram 1-B.

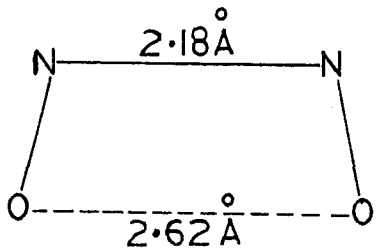
Diagram 1

A



Rectangular Structure

B



Cis-Dimer Structure

The former structure is found in the current literature even though the cis-dimer structure has been reported[13] and verified[14] for fifteen years.

Transition Metal-Nitric Oxide Complexes

An understanding of the bonding of nitric oxide to the surface of transition metal catalysts can be obtained from a consideration of the bonding and structure of transition metal-nitric oxide complexes. In the past, the following four Lewis structures were envisaged:

Diagram 2.

I II III IV

I, II, and III are terminal structures and IV is a bridging species. Structures I and II are called linear or NO^+ whereas III is called bent or NO^-. The latter designation is based on the formalism used in coordination chemistry in which the electron pair in the metal-nitrogen sigma bond is associated entirely with the ligand for the purpose of assigning ligand charge and metal oxidation state. Although the above structural arrangements were all considered to be possible, most researchers in the past postulated only linear structures in order to explain their observations.

The first structurally documented bent nitrosyl (NO^-) species was reported by Ibers and Hodgson[15]. Later Ibers[16] and coworkers advanced the understanding of nitrosyl chemistry by considering the interaction between the antibonding π orbitals of the nitric oxide molecule and low-energy d-orbitals of the metal. They postulated that if an empty low-energy d-orbital existed on the metal, the pair of electrons forming the bond would be localized on the metal, giving rise to nitrosonium ligand (NO^+). If an empty d-orbital was not present the bonding electrons would then fill the antibonding π-orbital of the nitrosyl ligand and a bent NO^- species would result. A linear species with some NO triple bond character is correlated with the nitrosonium ligand (MNO^+) whereas a bent species with double bond character is prevalent when the nitrosyl ligand (MNO^-) is formed. The latter species is characterized by a M-N-O bond angle of approximately 120^0-140^0. The N-O bond strength of the nitrosyl ligand (NO^-) is weaker than that of the nitrosonium ligand (NO^+), indicating that the bent (NO^-) species would be more likely to dissociate than NO^+.

The expected frequency ranges of the N-O stretching vibration, depending on the type of bonding involved between the NO and the transition metal, are given in table 1.

Table I:

Types of Nitric Oxide Bonding on Chemisorption

Type of bonding	Structural Arrangement	Range of NO frequency (cm^{-1})
purely ionic	NO^+ salts	2100-2400
coordinated, linear, NO^+	$\bar{\bar{M}}—N\equiv\overset{+}{O}:$, $M=\overset{-}{N}=\overset{+}{O}$	1800-2100
coordinated, linear neutral NO	$M—\dot{N}=\ddot{O}$	1700-1900
coordinated, bent, NO^-	$M—\ddot{N}=O:$	1500-1700
Coordinated, bridging,	$M\diagdown\diagup M>N=\ddot{O}$	1300-1550
purely ionic	NO^- salts	1100-1000
gaseous NO		1876

A mechanism whereby a linear nitrosyl ligand can be converted into a bent nitrosyl group has been postulated by Adams[17] et al. In a complex a metal attains a stable electronic state with a ligand when its low energy molecular and atomic orbitals are filled. If the metal bonded to a nitrosyl ligand very nearly or just reaches a closed-shell configuration with the nitrosyl ligand acting as a three electron donor, Adams[17] et al suggest that the metal-nitrosyl ligand will be essentially linear. But if the nitrosyl ligands provide more electrons than needed to fill the low energy orbitals, with the nitrosyl ligand acting as a three electron donor, they propose that the nitrosyl ligand will become a one electron donor and will be bent. Therefore, by placing additional electron density on the metal, say in the form of additional ligands, there would be an increase in back-donation to the nitrosyl ligand with a concomitant reduction in the infrared stretching frequency.

Finn and Jolly[18] have studied several nitrosyl complexes of cobalt and rhodium containing the bent M-N-O group. These complexes are characterized by M-N-O bond angles of about 120^{o} and exhibit infrared absorption bands in the range of 1500-1700 cm^{-1}.

A ruthenium complex containing both linear and bent nitrosyl ligands attached to the same ruthenium ion was first reported by Eisenberg[19] et al. The complex $RuCl(NO)_2[P(C_6H_5)_3]_2$, exhibits two infrared absorption peaks at 1845 and 1687 cm^{-1}. The linear nitrosyl ligand has a Ru-N-O bond angle of 179^{o} and a relatively short ruthenium-nitrogen bond distance. The infrared band at 1845 cm^{-1} was attributed to this ligand. The bent nitrosyl ligand has a Ru-N-O bond angle of 136^{o} with a longer ruthenium-nitrogen distance and the 1687 cm^{-1} band was assigned to this species.

An extraordinary example of a platinum-nitrosyl complex which contains both bridging and terminal nitrosyl groups has been reported by Epstein[20] et al. In this complex the terminal NO bond length is quite long and the M-N-O bond angle is 122^{o}. They therefore concluded that this ligand was a NO^{-} species. Only one other platinum complex containing a bridging nitrosyl ligand has been reported.[21]

CHAPTER 4

A REVIEW OF THE CHEMISORPTION OF NITRIC OXIDE AND NITROGEN DIOXIDE AND OF SURFACE ISOCYANATE FORMATION ON METALS

General

Nitric oxide is believed to chemisorb on surfaces via the nitrogen end of the molecule. Evidence to support this claim has been obtained[22] by analogy with inorganic nitrosyl complexes. As well, infrared spectroscopic confirmation has been reported for nitric oxide adsorbed on nickel by Blyholder and Allen[2]. They attributed bands at 1840, 650, and 625 cm^{-1} to N-O stretch, Ni-N stretch, and Ni-N-O bending, respectively.

Recently Hightower and Van Leirsburg[23] presented a review of the current status of the catalytic decomposition of nitric oxide. In their paper, and in the discussion that followed, several reaction schemes were proposed in order to explain nitric oxide decomposition. These schemes implied that the oxygen-end of the molecule reacted with the surface. Voorhoeve[24] suggested that most of the NO might adsorb on the catalyst surface via the N-atom and that this species would be identified with infrared spectroscopy, whereas the reactive species might be adsorbed, in a small concentration, via the O-atom. Intermediates that exist in small concentrations, and are, as a result, not detected with infrared spectroscopy, were discussed in chapter 1.

Primet et al[25] have related the particle size of platinum in an alumina supported platinum catalyst to the infrared stretching frequency of chemisorbed nitric oxide. They observed that the NO stretching frequency decreased as the platinum particle size increased, which was interpreted as an increase in back-donation corresponding to an increase in electron density on the platinum surface.

A number of studies have been undertaken in order to determine whether or not nitric oxide dissociates on the surface of metal catalysts. Conrad and co-workers[26], using flash desorption and ultraviolet photoelectron spectroscopy, studied the reaction of nitric oxide on a Ni (111) surface and concluded that nitric oxide dissociates on the surface even at temperatures as low as -120°C. Recently, Batra et al[27] combined photoemission studies with theoretical calculations to study nitric oxide adsorbed on nickel. They claim that partial dissociation of the nitric oxide occurs at 27°C and to obtain only molecular adsorption the nitric oxide must be adsorbed at low temperatures.

In Blyholder and Allen's[2] study of the chemisorption of nitric oxide on nickel and iron, infrared bands which were attributed to surface oxides, were observed after the adsorption of the nitric oxide. They interpreted this as evidence for the partial dissociation of the nitric oxide. The dissociation of nitric oxide on nickel has also been asserted, by Batychko and co-workers[28].

Lambert and Comrie[29] studied the adsorption of nitric oxide on Pt (110) and Pt (111) surfaces using flash desorption techniques. They claim that nitric oxide adsorbs non-dissociatively on both surfaces at 27°C, but, that when the surface is heated, dissociation occurs

producing nitric oxide, nitrogen, and oxygen as desorption products.

In a study of nitric oxide on platinum black, Otto and Shelef[30] concluded from adsorption isotherm measurements that partial oxidation of a reduced catalyst by nitric oxide is not important at 0°C but may occur at higher temperatures.

Infrared Spectroscopic Studies

There have been numerous infrared spectroscopic studies of the adsorption of the nitrogen oxides on Group VIII transition metal surfaces. For convenience all observed band positions and assignments are shown in tables 2, 3 and 4 which follow the appropriate section, and in most of the discussion which follows no specific reference to observed band positions will be made.

Nitric Oxide (See Table 2)

An infrared and temperature programmed desorption study of nitric oxide adsorbed on a silica supported cobalt catalyst was carried out by Nijyama and Echigoya[31]. Two absorption bands were observed, at 1850 and 1790 cm^{-1}, which were attributed to linear and bent species respectively. However, Nijyama and Echigoya[31] could not resolve whether the two bands involved different modes of bonding or if one mode of bonding occurred on two different sites, as proposed by Blyholder[32] for carbon monoxide which is adsorbed on nickel. Blyholder[32] observed two infrared bands at 2060 and 1940 cm^{-1} if carbon monoxide was chemisorbed on nickel. These bands were attributed to carbon

TABLE 2

Summary of Infrared Spectroscopic Studies of Nitric Oxide Chemisorption

Surface	Observed I.R. Bands (cm^{-1})	Assignment	Interpretation	Reference
Ni/Al_2O_3	1735(s) 1850(s)	NO NO	NO covalently bonded to metal cation	A.Terenin, L.Roev.[34]
Pt/SiO_2	1950(wsh) 1865(s) 1825(s)	not assigned	-	Dunken,H; Hobert,H.[35]
Pd/SiO_2	1925(m) 1845(s) 1820(w) 1765(m) 1865(s)	not assigned	-	Dunken H., Hobert H.[35]
Ni/hydrocarbon oil	2205(w)	NO^+	adsorption on plane sites.	
	1840(s)	linear Ni-N-O	adsorption on edges, corners, etc.	
	650(w)	Ni-N	evidence of NO dissociation.	Blyholder & Allen[2].
	625(m)	Ni-N-O bending	in linear species	
	460(sb)	chemisorbed oxygen	evidence of NO dissociation.	
Ni/SiO_2	2220(w) 1840(vs)	NO^+ linear Ni-N-O	adsorption on edges, corners, etc.	Blyholder & Allen[2].
Fe/Hydrocarbon oil	1810(s)	linear Fe-N-O	adsorption on plane sites.	Blyholder & Allen[2].
	1720(m)	linear Fe-N-O	adsorption on edges, corners, etc.	
	600 (vb)	chemisorbed oxygen	evidence of NO dissociation	

cont'd

TABLE 2 cont'd

Surface	Observed I.R. Bands (cm^{-1})	Assignment	Interpretation	Reference
Fe/SiO_2	1820(s)	linear Fe-N-O	adsorption on plane sites.	Blyholder & Allen[2]
	1720(w)	linear Fe-N-O	adsorption on edges, corners, etc.	
Ni/SiO_2	1860(s)	$NO^{\delta-}$	adsorption on closely packed surfaces.	Batychko[28]
	1820(m)	NO on NiO	NiO formation attributed to dissociation of NO.	
Co/SiO_2	1850(s) 1790(s)	linear Co-N-O bent Co-N-O	Two modes of adsorption or one mode of adsorption on two sites (e.g. planes or edges).	Nijyama[31]
Rh/Al_2O_3	1830(s)	Rh-NO	electron donation to π^* of NO from metal d-orbital.	Arai[36]
	1740(s)	$Rh-NO^-$		
	1910(w)	$Rh-NO^+$	electron donation from π^* of NO to metal d-orbital.	
Pt/Al_2O_3	1780(s)	NO	three electron donation to the metal plus back donation to the π^* orbital of NO.	Ghorbel & Primet[37]
Ru/SiO_2	1800 cm^{-1}(s) (1815 at high coverage)	linear Ru-NO	-	Gonzalez & Brown[38]
Pt/SiO_2	1760 cm^{-1}(b) (at high coverage)	Pt-NO	-	

(vs) very strong, (s) strong, (m) moderate, (w) weak, (sb) strong broad, (vb) very broad, (b) broad, (sh) shoulder, (wsh) weak shoulder.

monoxide adsorbed on plane sites and on edges, corners, or dislocations, respectively. Because the edges, corners, and dislocations have a higher electron density than the plane sites, Blyholder[32] hypothesized that these sites would provide more electrons for π-bonding and consequently the infrared stretching frequency would be at a lower wavenumber. Yates[33] disagrees with Blyholder's[32] argument. Yates[33] contends that the observations can be understood by considering linear and bridged CO species. Blyholder[32] does not completely rule out linear and bridged species but he concludes that there is no evidence that requires their postulation.

Nitric oxide adsorption on transition metal catalysts (supported on alumina gel) was first studied by Terenin and Roev[34] using infrared spectroscopy. They observed two infrared absorption peaks when nitric oxide was adsorbed onto nickel and assigned these bands to one species which was coordinately bonded to the surface.

Dunken and Hobert[35] used infrared spectroscopy to study the adsorption of nitric oxide on silica supported platinum and palladium. Unfortunately they did not interpret the observed bands. Blyholder and Allen[2] studied the chemisorption of nitric oxide on nickel and iron. As discussed in chapter 1, they stabilized the metal particles by depositing the evapourated metal in an oil film on the salt windows of an infrared cell. With nickel they obtained infrared evidence for a linear nitric oxide species and attributed this species to nitric oxide bonded to sites such as edges and corners, as Blyholder[32] proposed for adsorbed CO. As well,they assigned a weak band to nitric oxide chemisorbed on plane

sites. To determine the effect of the oil film on their infrared spectral data, Blyholder and Allen[2] performed comparative experiments on silica supported nickel. The only observed difference was that the infrared adsorption band, attributed to the weakly adsorbed species, shifted slightly to higher wavenumber. According to these authors two bands were observed for nitric oxide adsorbed on iron. These were assigned to two linear species, one attached to plane sites and the other to edges and corners. They claim that analogous species were formed on silica supported iron.

Batychko et al[28] investigated the infrared spectrum of nitric oxide adsorbed on silica supported nickel. At room temperature they observed a single infrared band which they attributed to adsorbed nitric oxide bearing a small negative charge.

Arai and Tominaga[36] have reported that nitric oxide, chemisorbed to an alumina supported rhodium catalyst, forms two surface species; one a nitrosonium and the other a nitrosyl species.

Recently, an infrared study of the adsorption of nitric oxide on alumina supported platinum was carried out by Ghorbel and Primet[37]. They reported that rapid adsorption of nitric oxide leads to a nitrosyl complex, whereas prolonged exposure of the surface to nitric oxide in the gas phase results in decomposition of the NO, at room temperature, with subsequent oxidation of the platinum surface.

At the time of the writing of this thesis, Gonzalez and Brown[38] reported an infrared study of the interaction between adsorbed NO and adsorbed CO on supported ruthenium and platinum. As there was no recent study of NO adsorption on supported platinum they included,

in their report, the spectrum obtained when NO was chemisorbed on silica-supported platinum. They observed a single broad band and attributed this band to the NO stretching vibration of NO adsorbed on a platinum surface atom, Pt-NO. On ruthenium they observed a single strong band which they assigned to NO linearly adsorbed on the ruthenium surface.

Nitrogen Dioxide (see Table 3).

Blyholder and Allen[3] have studied the surface species formed by the adsorption of nitrogen dioxide on oil and on silica-supported nickel and iron. At low pressures, infrared bands were observed on nickel/hydrocarbon oil that were attributed to chemisorbed nitric oxide and chemisorbed oxygen. This observation was interpreted as indicating the dissociation of nitrogen dioxide into nitric oxide and oxygen. The adsorption of nitrogen dioxide at higher pressures or onto silica supported nickel produced bands that were assigned to nitrogen-oxygen complexes containing two and three oxygen atoms. The authors also concluded that a bidentate nitrato complex, $M<^{O}_{O}>NO$, was the predominant species formed. Analogous results were reported for iron/SiO_2 and iron/hydrocarbon oil samples. In a more recent study by Ghorbel et al[37], nitrogen dioxide was adsorbed onto an alumina supported platinum catalyst. A single strong infrared band was observed, which was similar to a band produced when nitric oxide and oxygen reacted together, over the platinum surface. Therefore, the authors concluded that the nitrogen dioxide had dissociated, followed by the subsequent adsorption of nitric oxide onto platinum oxide sites. As well, two weaker bands were observed. These were

TABLE 3

Summary of Infrared Spectroscopic Studies of Nitrogen Dioxide Chemisorption

Surface	Observed I.R. bands (cm^{-1})	Assignments	Interpretation	Reference
Ni/hydrocarbon oil	1840(s) 1555(m) 1330(vw) 1090(vw) 610(wb)	adsorbed NO. nitrogen-oxygen complexes containing two or three oxygen atoms. due to adsorbed NO.	Overall behaviour: NO_2 on Ni/oil and Fe/oil, at low pressures, decomposes into NO and O_2. At higher pressures over Ni/oil and Fe/oil or over Ni/SiO_2 adsorption of NO_2 predominantly forms more complex nitrogen-oxygen species.	Blyholder[3] & Allen
Ni/SiO_2	1850(w) 1555(vs) 1440(vs)	adsorbed NO. bidentate nitrato complex. nitro complex.		
Fe/hydrocarbon oil	2005(vw) 1805(s) 1720(m) 600(vb)	adsorbed NO adsorbed oxygen.		
Fe/SiO_2	1610(s) 1525(s)	covalent nitrate. bidentate nitrato complex $Fe<^{O}_{O}>NO$		
Pt/Al_2O_3	1845(s) 1600(m) 1300(m)	NO adsorbed on PtO Nitrate ions	NO_2 dissociation NO_2 interaction with oxygen atoms of Al_2O_3 support.	Primet & Ghorbel[37]

(s) strong, (m) moderate, (w) weak, (b) broad, (v) very

ascribed to nitrate ions, formed as a result of the interaction between nitrogen dioxide and the oxygen atoms of the alumina support.

Reaction Between NO and CO. (See Table 4)

Several infrared studies have been reported for the reaction of nitric oxide and carbon monoxide over metal catalysts. The purpose of these studies was to look for intermediates or product species formed during the reduction reaction.

Undland[39,40,41] has reported the formation of isocyanate intermediates (with ν NCO bands in the range 2200-2300 cm^{-1}) in the catalytic reduction of nitric oxide by carbon monoxide. His first study[39,40] was over alumina supported noble metal catalysts whereas his second[41] was a more detailed study over Pt. Over the noble metal catalysts he observed that the isocyanate species did not form unless the reaction mixture contained excess carbon monoxide and, then, not until a temperature of 300°C was reached. In his separate study using Pt[41] he found that if stoichiometric quantities of nitric oxide and carbon monoxide were used, weak isocyanate bands appeared whereas with an excess of carbon monoxide strong bands were formed. Again, the isocyanate species was not observed until a reaction temperature of 300°C was attained. Further, bands attributable to isocyanate species were not observed if an excess of nitric oxide was used. Of the noble metal catalysts studied, Undland[39] observed that the isocyanate band was weakest for ruthenium.

Ghorbel and Primet[37] have studied the reaction of nitric oxide and carbon monoxide over an alumina supported platinum catalyst.

TABLE 4

Summary of Infrared Spectroscopic Studies of Surface Isocyanate Formation; a(NO + CO), b(CO + NH_3), c(CO + N_2H_4)

Surface	Observed I.R. bands (cm^{-1})	Assignment	Comments	Reference
[a] Ru/Al_2O_3	2259	covalently bonded NCO	The species is not formed until 300°C. No infrared bands were observed when mixtures with equimolar or excess NO were used.	Undland[39,40]
	2238	$(NCO)^-$		
[a] Rh/Al_2O_3	2269	covalently bonded NCO		
	2175	$(NCO)^-$		
[a] Pd/Al_2O_3	2264	covalently bonded NCO		
[a] Ir/Al_2O_3	2267	covalently bonded NCO		
	2239	$(NCO)^-$		
[a] Pt/Al_2O_3	2267	covalently bonded NCO		
	2148	$(NCO)^-$		
[a] Pt/Al_2O_3	2267	covalently bonded NCO	The 2267 band does not appear until 300°C. The 2148 band does not appear until 400°C. When NO is in excess over the CO, the bands do not appear. When stoichiometric amounts of NO and CO are used the bands appear, but are weaker than when CO is in excess.	Undland[41]
	2148	$(NCO)^-$		

cont'd

TABLE 4 cont'd

Surface	Observed I.R. Bands (cm^{-1})	Assignment	Comments	Reference
Rh/Al_2O_3	2235	NCO	The NCO species appeared at 200°C when a mixture of CO (100 torr) and NO (50 torr) was used and at 300°C when NO was preadsorbed. No band appeared when NO in the mixture was in excess.	Arai[36]
[a]Rh/Al_2O_3	2250(s)	Rh-NCO	Flow reactor used. (antisymmetric stretching).	
[a]Pt/Al_2O_3	approximately 2250(w) (not stated exactly)	Pt-NCO	The NCO species was formed at 300°C with a mixture of NO and CO (excess CO). Amount of NCO decreased as NO to CO ratio increased. No NCO was produced if reaction was carried out at R.T. and then heated up to 300°C.	Tanaka et al[42]
[a]Pt/Al_2O_3	Preadsorbed NO for short duration + CO 2075 1840	 adsorbed CO adsorbed CO	EXCESS NO USED. No NCO species formed. CO displaced adsorbed NO.	Ghorbel[37] & Primet
	Preadsorbed NO for prolonged duration + CO or after heating at 150°C 2130 2090	 $Pt<^{O}_{CO}$ complex not assigned	Concluded that NO dissociates with prolonged contact or heating. Pt/Al_2O_3 surface is therefore oxidized by NO decomposition; No NCO species is observed.	

cont'd

TABLE 4 cont'd

Surface	Observed I.R. Bands (cm^{-1})	Assignment	Comments	Reference
[a] Ru/SiO_2	2180(w)	$Ru^{\delta+}$—$NCO^{\delta-}$	NCO formed at R.T. regardless of the order in which the reactants (NO & CO) were adsorbed. Reaction proceeds between adsorbed NO adjacent to each other.	Gonzalez & Brown[38]
[a] Pt/SiO_2	no band observed	—	EXCESS NO USED	
[a] Ni/Hydrocarbon oil	2180(w)	NO^+	adsorption on plane sites i.e. attributed to same species formed when NO interacts with Ni/ Hydrocarbon oil (at 2205 cm^{-1}).	Blyholder & Allen[2]
Fe/Hydrocarbon oil	no bands observed	-	-	
[a] CuO/SiO_2	2200	$Cu^+(NCO)^-$	Not formed until 135°C.	London & Bell[43]
[b] Vanadium/ hydrocarbon oil	2180	NCO	NCO species formed with preadsorbed NH_3 + CO; NCO species not formed when CO is pre-adsorbed. NCO species formed at room temperature.	Blyholder & Sheets[4]
[b] Fe/hydrocarbon oil	2170	NCO		
[b] Ni/hydrocarbon oil	no bands observed	-		
[b] Pd/hydrocarbon oil	no bands observed	-		

cont'd

TABLE 4 cont'd

Surface	Observed I.R. Bands (cm^{-1})	Assignment	Comments	References
^{c}V/hydrocarbon oil	2180	NCO	NCO species formed with both pre-adsorbed N_2H_4 + CO and pre-adsorbed CO + N_2H_4	Blyholder & Sheets[4]
^{c}Fe/hydrocarbon oil	2170	NCO		
^{c}Ni/hydrocarbon oil	no bands observed	-		

They observed no isocyanate formation. However they concluded that the nitric oxide dissociates on the surface after prolonged contact or after heating the surface to a temperature of 150°C and that then the carbon monoxide coadsorbs with oxygen on the platinum surface to form complexes such as Pt$\lessgtr^{O}_{CO}$. If the nitric oxide is preadsorbed for a short time, followed by the addition of carbon monoxide they claim that the carbon monoxide simply displaces the adsorbed nitric oxide.

More recently, Arai and Tominaga[36] observed that carbon monoxide reacts with nitric oxide on an alumina supported rhodium catalyst to form a surface isocyanate species. With a mixture of carbon monoxide (100 torr) and nitric oxide (50 torr) a temperature of 200°C was required before the isocyanate species appeared, whereas if pre-adsorbed nitric oxide reacted with carbon monoxide, a temperature of 300°C was necessary. No isocyanate band appeared if nitric oxide was in excess in the reaction mixture.

Recently Tanaka et al[42] conducted an infrared study of the isocyanate species formed during the reaction of NO with CO over alumina supported Rh and Pt. In this investigation they used a flow reactor to study the dynamic behaviour of the surface isocyanate species that formed on the Rh and Pt catalysts. This study was conducted to confirm whether or not the isocyanate species is a reaction intermediate as concluded by Undland[41]. Tanaka et al[42] observed that an isocyanate species was produced if a mixture of NO and CO (26 torr NO/59 torr CO) was reacted over the Rh/Al_2O_3 catalyst at 300°C. If a mixture with a higher NO to CO ratio was used a much smaller amount of the isocyanate species was formed. Further, no isocyanate species was produced when the

mixture was introduced to the sample cell at room temperature and then heated up to 300°C. These authors stated that for the reaction of NO with CO over Pt/Al_2O_3 the spectrum above 2000 cm^{-1} was similar to that obtained for the Rh sample, but that below 2000 cm^{-1} the spectrum had poor reproducibility and was very complex. Unfortunately the exact position(s) of the band(s) for the isocyanate species on the Pt/Al_2O_3 sample was not reported. Tanaka et al[42] concluded that, for both Rh and Pt, the isocyanate species is not an intermediate but is an inhibitor produced under the reaction conditions. Caution should be exercised when evaluating the results of these authors because they reported that their flow system was not completely isolated from the atmosphere. Obviously this could lead to the introduction of impurities, such as water and O_2, to their samples which would surely complicate their spectra.

Gonzalez and Brown[38] investigated the interaction between adsorbed CO and adsorbed NO on silica-supported Ru and Pt. They found that an isocyanate surface species was formed on Ru/SiO_2 at room temperature if either the CO or NO was preadsorbed at full coverage. Further they concluded that both the NO and CO must be adsorbed on the ruthenium surface before the isocyanate species will form in appreciable amounts and,also,the coadsorbed reactants must be adjacent to each other on the surface. Gonzalez and Brown[38] did not observe the formation of an isocyanate surface species on Pt/SiO_2.

Blyholder and Allen[2] adsorbed CO on a nickel/hydrocarbon oil sample that had been previously exposed to NO. They observed a new, weak, band at 2180 cm^{-1} which was assigned to nitric oxide (NO^+) adsorbed on

plane sites. However, it would seem more likely that this new band would be due to an isocyanate species, a point which will be discussed in more detail in chapter 5.

In another study, London and Bell[43] reported the formation of an isocyanate surface species during the reaction of nitric oxide and carbon monoxide over silica supported copper oxide. From infrared spectroscopic data, it was observed that the isocyanate species formed only if the reaction temperature was increased to 135^{o}C.

Only one other infrared investigation has been found in which an isocyanate surface species has been postulated. In this study, Blyholder and Sheets[4] investigated the reaction of carbon monoxide individually with both ammonia and hydrazine over vanadium, iron and nickel. The authors concluded that an isocyanate species was produced on both vanadium and iron at room temperature, if carbon monoxide reacted with preadsorbed ammonia but was not formed if the carbon monoxide was preadsorbed. No isocyanate band was observed on nickel. If carbon monoxide and hydrazine were reacted together over vanadium and iron, an isocyanate species was observed, at room temperature, regardless of which reactant was preadsorbed. Again, no surface species formed on nickel.

CHAPTER 5

THE CHEMISORPTION OF THE OXIDES OF NITROGEN ON NICKEL

Preface:

Before discussing the results of the adsorption studies of the oxides of nitrogen on Ni and Pt, some mention should be made of their adsorption on the silica support alone. A silica sample, containing the same quantity of silica as was used in the supported metal samples, was prepared by the same procedure used for the preparation of the silica supported metals. (See Chapter 2, experimental). Nitric oxide did not chemisorb on this silica sample. A similar observation was noted by London and Bell[43]. In independent studies[44] of the adsorption of nitrogen dioxide on silica, carried out in this laboratory, it has been established that nitrogen dioxide does not chemisorb on the silica support provided vacuum degassing temperatures less than 400^{o}C are employed. Therefore, any adsorption of these gases that was observed must be due to adsorption on the metal. This is an important point to be considered if unambiguous results are to be obtained. For example, in Ghorbel and Primet's[37] study of the adsorption of NO on Pt/Al_2O_3, NO was observed to interact with the Al_2O_3 support producing three weak bands at 1600, 1320 and 1220 cm^{-1} which were attributed to nitrate ions formed as a result of the interaction between a NO_2 species and the oxygen atoms of alumina. Bands similar to these have been observed by Parkyns[45] when NO_2 was adsorbed on alumina alone. He assigned these bands to nitrate ions coordinated to aluminum atoms. Therefore, in Ghorbel and Primet's[37] work, there is the possibility

that absorption in the spectral range 1200-1600 cm^{-1} attributable to NO on Pt may not be observed because of the bands produced by the adsorption of the NO_2 on the Al_2O_3. The choice of Al_2O_3 as a support was unfortunate since any interference from the alumina support could have been prevented by using an inert support such as silica.

London and Bell[43] have studied the adsorption of nitrous oxide on silica between 30 and 230°C. Infrared bands at 2220, 1290, and 590 cm^{-1} were observed only in the presence of the nitrous oxide and,therefore,were attributed to gaseous nitrous oxide which has infrared bands at 2224, 1286 and 589 cm^{-1}. No other bands were observed.

In the present work when nitrous oxide was adsorbed on Pt/SiO_2, no infrared bands were observed which could be attributed to a chemisorbed species. Griffiths et al[46] reported a similar observation when they studied the adsorption of nitrous oxide on Pt/SiO_2 between 25 and 200°C, as did Undland[40] for nitrous oxide on Pt/Al_2O_3 at 400°C.

Finally, the adsorption of nitrous oxide on Ni/SiO_2 was not studied in the present work and, to this author's knowledge, no such studies have been reported in the literature. However, a proposed study of the decomposition of nitrous oxide over nickel will be discussed later in this thesis under the heading. "Suggestion for Further Research".

Results

Nitric Oxide

The infrared spectrum of nitric oxide chemisorbed, at room temperature, on silica supported nickel showed a single, strong band at 1864 cm^{-1}. This is slightly lower than that for the free nitric oxide molecule which absorbs at 1876 cm^{-1}. No other bands were observed, even

with high surface coverage. The spectra which were obtained after adding successive doses of nitric oxide to a Ni/SiO_2 sample are shown in Figure 4.

The intensity of the band at 1864 cm^{-1} slowly diminished upon heating the sample under vacuum at 170°C and the band disappeared rapidly if evacuated at 220°C.

The intensity of the 1864 cm^{-1} band was not affected if 10 torr of H_2 was added to the sample at 20°C but the band disappeared if this was carried out at 60°C. The band disappeared if 1·4 torr of oxygen was added to the adsorbed nitric oxide, at 20°C.

Nitrogen Dioxide

When nitrogen dioxide was adsorbed on a $NiSiO_2$ sample, at low surface coverage (1 torr), a spectrum, identical to that obtained for chemisorbed nitric oxide on nickel, was produced with a strong band centred at 1864 cm^{-1}. No other bands were observed.

Preadsorbed Nitric Oxide + Carbon Monoxide (g)

Nitric oxide was adsorbed, at low coverage, onto a Ni/SiO_2 sample producing a strong band at 1864 cm^{-1}, as shown in figure 5, curve 2. When a small dose of carbon monoxide was added to the adsorbed nitric oxide, at room temperature, the intensity of the band at 1864 cm^{-1} immediately decreased by more than fifty percent and, simultaneously, a new absorption band was generated at 2201 cm^{-1}. The carbon monoxide gas was left in the sample cell for 17 hours and, after this period of time, the band at 2201 cm^{-1} had intensified and the 1864 cm^{-1} band had disappeared. In

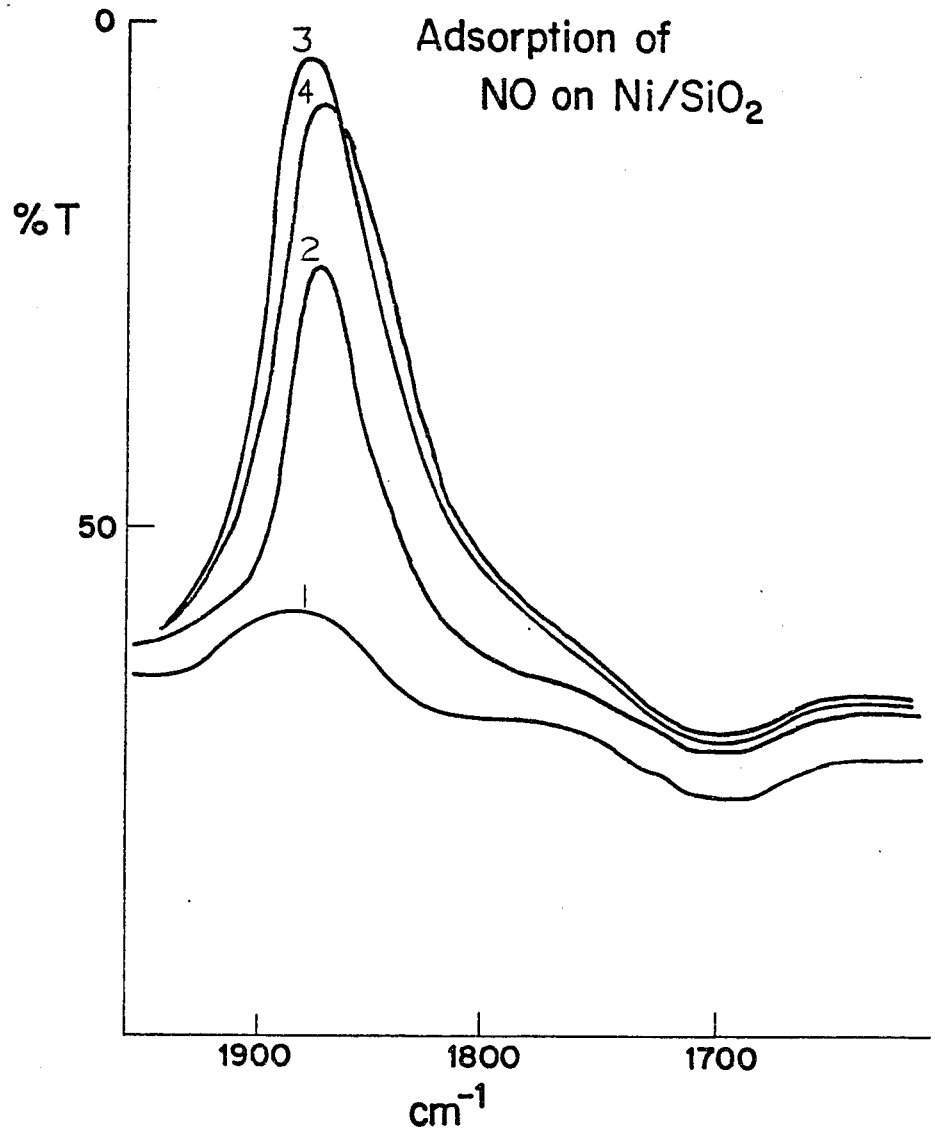


FIGURE 4

ADSORPTION OF NO on Ni/SiO_2

1. Background infrared spectrum of a compensated Ni/SiO_2 sample.
2. After adding 0.60 torr of NO to (1) for 10 minutes followed by degassing for 20 minutes at 20°C.
3. After adding 1.6 torr of NO to (2) for 5 minutes, followed by degassing for 5 min. at 20°C.
4. After adding 10 torr of NO to (3) for 5 min., followed by degassing for 17 h. at 20°C.

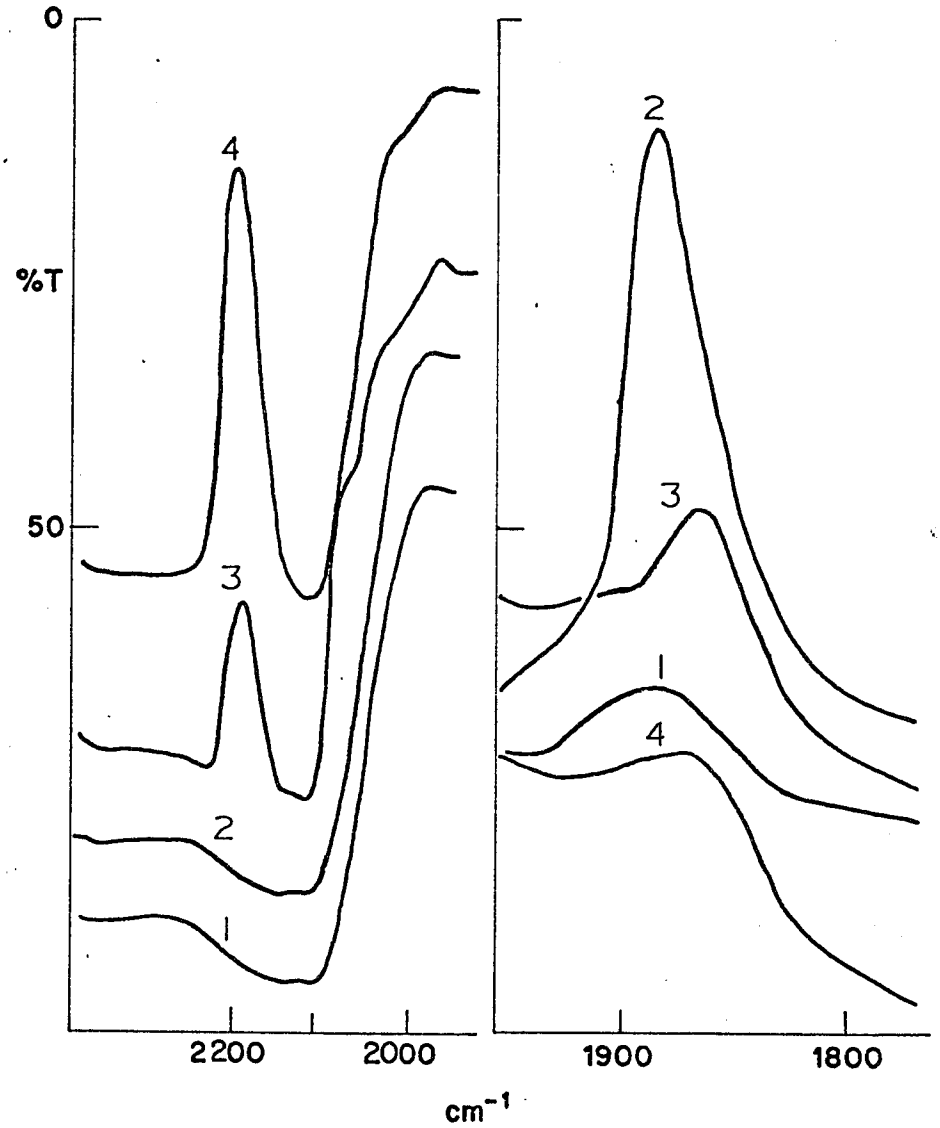


FIGURE 5

REACTION OF ADSORBED NO WITH CO(g) ON Ni/SiO_2

1. Background infrared spectrum of a Ni/SiO_2 sample. [compensated in the 2000-1800 cm^{-1} spectral region].
2. After adding 0.90 torr of NO to (1) for 10 min., followed by degassing for 10 min. at 20°C.
3. After adding 1.1 torr of CO to (2) for 1 h. at 20°C.
4. As for (3), but for 17 h. at 20°C., followed by degassing for 20 min. at 20°C. The % T scale refers to curve (1).

subsequent experiments, a reaction time of two hours was found to be sufficient for the band at 2201 cm^{-1} to attain its maximum intensity and for the band at 1864 cm^{-1} to disappear.

The intensity of the band at 2201 cm^{-1} was not affected by evacuation at room temperature for 18 hours but if the sample was degassed at 60°C for 30 minutes, it intensified slightly.

When 5 torr of water was added to the sample cell for 4.5 hr. the intensity of the 2201 cm^{-1} band slowly diminished by 50 percent, as shown in figure 6.

The addition of 4 torr of oxygen, at room temperature, had no effect on the intensity of the band at 2201 cm^{-1}.

The intensity of the 2201 cm^{-1} band was not influenced by the addition of 430 torr of hydrogen, at room temperature.

As shown in figure 5, there are some additional very weak bands between 2100 and 2000 cm^{-1}. No attempt was made to characterize these bands observed in the studies of the reaction of NO and CO over Ni/SiO_2 (or Pt/SiO_2, see chapter 6). The spectrum of carbon monoxide adsorbed on Ni/SiO_2, exhibits[47,48] a strong infrared absorption band between 2000 and 2100 cm^{-1}. Unfortunately the cyanide[9,49] group can also show strong absorption in this spectral region and cyanides are possible products formed during the reaction of NO and CO over Ni/SiO_2. Indeed, in the latter studies, often two or more bands were observed between 2000 and 2100 cm^{-1}. Also, both the CO and CN groups are extremely sensitive to their electronic environments and bands due to ν (CO) and ν(CN) modes would therefore be expected to shift because of the presence of several adsorbed species (e.g. adsorbed NO) on the Ni surface. Further, bands

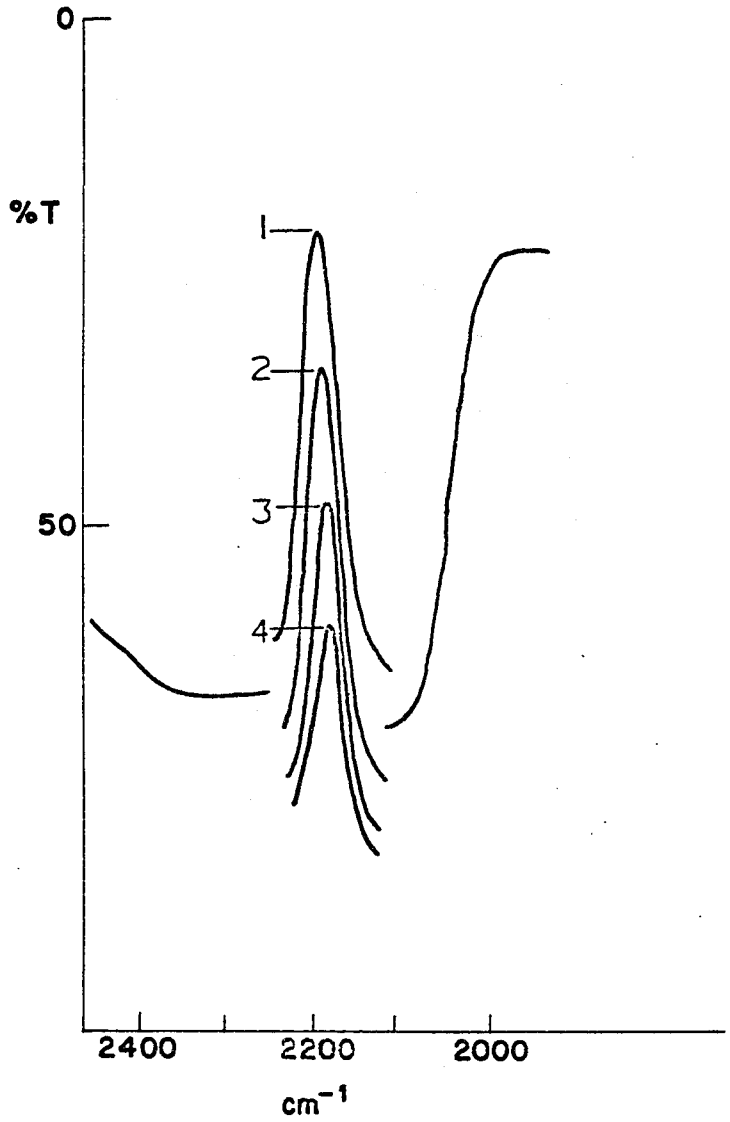


FIGURE 6

HYDROLYSIS OF ADSORBED SPECIES FORMED DURING THE REACTION OF ADSORBED NO AND CO(g) ON Ni/SiO_2

1. Infrared absorption band formed after adding 1·1 torr of CO to chemisorbed NO on a Ni/SiO_2 sample for 19 h., followed by degassing for 20 min. at 20°C.
2. After adding 5 torr of H_2O to (1) at 20°C. (immediate scan).
3. As for (2), but for 25 min.
4. As for (2), but for 4.5 h.

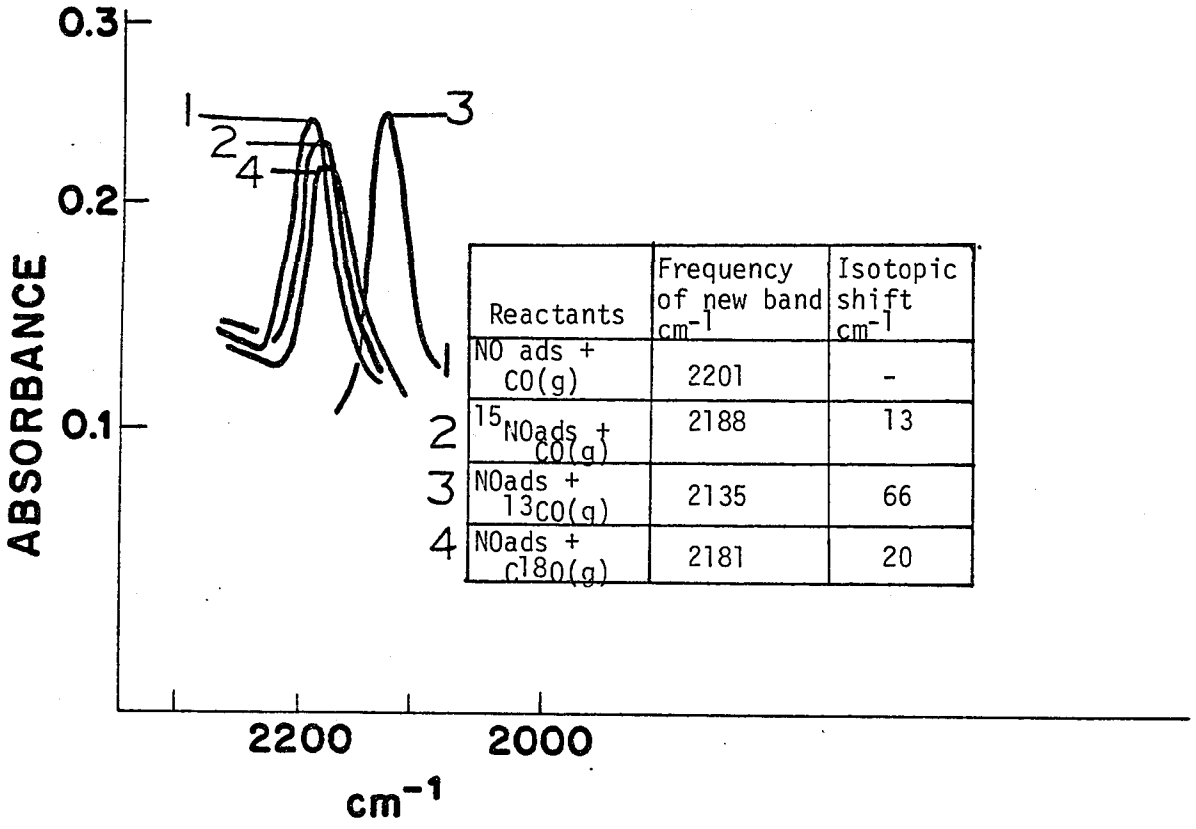
observed in this spectral region are difficult to distinctly resolve because of the strong absorption there due to the silica support. Finally, small quantities (1 torr) of CO were used in the present experiments and, as a consequence, the ν (CO) or ν (CN) bands were not always observed to be very strong.

When nitric oxide N-15 was adsorbed onto the nickel surface a strong band appeared at 1829 cm^{-1} (1864 cm^{-1} for ^{14}NO). The subsequent addition of carbon monoxide, for 2 hours, produced a band at 2188 cm^{-1}, which corresponded to the band obtained with nitric oxide N-14 at 2201 cm^{-1}. Similarly, when carbon monoxide C-13 or carbon monoxide O-18 was added to the nitric oxide N-14, which was adsorbed on the nickel surface, a band appeared at 2135 cm^{-1}, or 2181 cm^{-1}, respectively. The results of the isotopic studies are summarized in figure 7.

The gas phase reaction products from each of the isotopic experiments were analyzed with a mass spectrometer. These studies showed that only carbon dioxide was produced when carbon monoxide was added to adsorbed nitric oxide, or vice versa. Further, the gas phase products for the reaction involving $C^{18}O$ were found to contain a mixture of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$.

Preadsorbed Carbon Monoxide and Nitric Oxide

When carbon monoxide was adsorbed, at low coverage, on the nickel surface, a band appeared at about 2020 cm^{-1}. Following the addition of a small dose of nitric oxide, the spectrum initially showed a moderate band at 1864 cm^{-1} and a weak band at about 2190 cm^{-1}, as shown in figure 8, curve 3.



	Reactants	Frequency of new band cm^{-1}	Isotopic shift cm^{-1}
1	NO ads + CO(g)	2201	-
2	^{15}NOads + CO(g)	2188	13
3	NOads + ^{13}CO(g)	2135	66
4	NOads + C^{18}O(g)	2181	20

FIGURE 7

ISOTOPIC STUDY OF THE REACTION BETWEEN CHEMISORBED NO AND CO(g) ON Ni/SiO_2

1. Infrared absorption band formed after adding 1.1 torr of CO to chemisorbed NO on a Ni/SiO_2 sample for 2 h. at 20^0C.
2. As for (1), with ^{15}NOads and CO(g).
3. As for (1), with NOads and ^{13}CO(g).
4. As for (1), with NOads and C^{18}O(g).

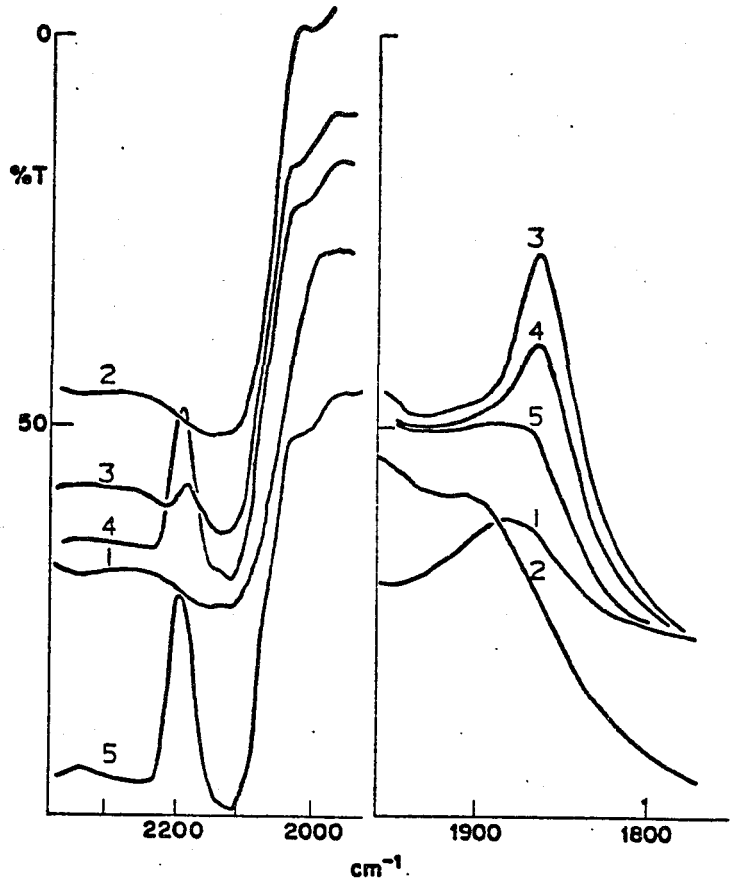


FIGURE 8

REACTION OF ADSORBED CO WITH NO(g) ON Ni/SiO_2.

1. Background infrared spectrum of a Ni/SiO_2 sample [compensated in the 2000-1800 cm^{-1} spectral region].
2. After adding 0.90 torr CO to (1) for 10 min., followed by degassing for 10 min. at 20°C.
3. After adding 1.1 torr NO to (2) at 20°C (immediate scan).
4. As for (3), but for 20 min.
5. As for (3), but for 1 h.

The % T scale refers to curve (1).

After a one hour reaction at room temperature, the band at 1864 cm^{-1} disappeared and the new band had intensified. The latter band was calibrated and found to be centred at 2195 cm^{-1}, as shown in figure 8, curve 5.

Discussion

Nitric Oxide

The band that was produced at 1864 cm^{-1} when NO was adsorbed on Ni did not alter in intensity when hydrogen was added to the sample at room temperature. This observation can be explained by considering Eischen and Pliskin's[50] studies of hydrogen adsorption. These authors observed no infrared absorption bands when H was adsorbed onto Ni/SiO_2, even though weakly bonded H is known to occur on Ni. They reasoned that the H-atoms are associated with three or four surface nickel atoms, that no discrete bond is formed, and, therefore, that no characteristic M-H absorption bands would be expected. The latter were observed on Pt/Al_2O_3, using a similar quantity of hydrogen. Further, in studies of H and CO coadsorption they reported[50] that H-adsorption was accompanied by charge donation to the surface, as evidenced by a shift of $\bar{\nu}$ (CO) to lower wavenumber upon adsorption of the hydrogen. If charge donation does occur in the present study when H_2 is added to the sample, then the Pt-N bond would be weakened and the dipole moment and the change in the dipole moment would be expected to decrease. Such effects are known to occur in metal coordination compounds of NH_3 where infrared bands due to ν (N-H) modes both decrease in intensity and shift to higher frequency as the degree of negative charge on the

metal increases. Morrow and Cody[51] observed a similar effect when H_2 and NH_3 were coadsorbed on Pt and they concluded that a Pt-H bond, with some partial ionic character, was formed, i.e. $Pt^- - H^+$. Since a similar effect was not observed when H_2 and NO were coadsorbed on Ni, such a bond is probably not formed. Therefore, it must be concluded that H_2 is only weakly associated with the Ni surface (as concluded by Eischens and Pliskin[50]) and, as a result, no interaction occurs between H_2 and NO over the Ni surface at room temperature.

The single band at 1864 cm^{-1}, formed when NO is chemisorbed on Ni, is attributed to a linear, neutral NO species, Ni-NO. Such species typically have N-O stretching vibrations that have frequencies in the spectral range 1700-1900 cm^{-1}, a point that was discussed in Chapter 3.

Nitrogen Dioxide

Since a single band was produced at 1864 cm^{-1} when NO_2 was adsorbed, at low coverage (1.0 torr), on a Ni/SiO_2 sample, this can also be attributed to a linear, neutral,NO species. It is concluded that the formation of this adsorbed NO species is evidence for the dissociation of NO_2 into NO and O. NO_2 dissociation (discussed in Chapter 4) has been observed over Ni/hydrocarbon oil samples by Blyholder and Allen[3]. The same authors[3] observed that NO_2, at low coverage, not only dissociated over Ni/SiO_2 but also produced complex nitrogen-oxygen species, as evidenced by the simultaneous formation of two strong bands at 1550 and 1440 cm^{-1}. The latter bands were not observed in the present work. moreover, the reaction between adsorbed NO and oxygen (g) produced no new bands. It should be noted that Blyholder and Allen[3] used ten times as much NO_2 in their study and, consequently, caution should be exercised

when making a direct comparison between their work and the present study.

Nitric Oxide + Carbon Monoxide

When carbon monoxide was added to nitric oxide which was adsorbed on Ni, the band at 1864 cm^{-1} disappeared slowly with the simultaneous growth of a 'new' band at 2201 cm^{-1}. This latter band shifted to lower wavenumber by 13 cm^{-1} with ^{15}NO, 66 cm^{-1} with ^{13}CO, and 20 cm^{-1} with $C^{18}O$, indicating that the surface species contained N, C, and O. The magnitude of these shifts is consistent with the formation of a nickel isocyanate surface species[52]. This species was also formed if the carbon monoxide was preadsorbed.

Isocyanates are known to be quite stable. This fact was verified when the intensity of the 2201 cm^{-1} band did not change during prolonged degassing at room temperature, or at 60°C, by the addition of oxygen, or after reaction with hydrogen. However, isocyanate compounds are known to be sensitive to hydrolysis and the sharp reduction in the intensity of the 2201 cm^{-1} band after reaction with water, therefore, provides additional evidence for a nickel isocyanate surface species.

The formation of a nickel isocyanate surface species has not been previously reported. Blyholder and Allen[2] did carry out an experiment in which CO and NO were coadsorbed onto a Ni/hydrocarbon oil sample, as discussed in chapter 4. A band was generated at 2180 cm^{-1} during this reaction. This band was attributed to NO^{+} adsorbed on Ni. However, in light of the evidence presented in the present work, this band (2180 cm^{-1}) was undoubtedly due to an isocyanate species. In a study of the adsorption

of NO,on nickel Batychko et al[28] added CO,at 20°C, to nitric oxide which was adsorbed on nickel. They observed the formation of two 'new' bands at 2190 cm^{-1} and 2050 cm^{-1}. The latter band was easily removed by degassing the sample at 50°C whereas the former band disappeared only when the sample was evacuated at temperatures between 350-400°C. These authors[28] attributed the 2190 cm^{-1} band to a special form of adsorbed NO which was stimulated by the presence of CO. Again, based on the present study, the 2190 cm^{-1} band observed by Batychko et al[28] is more likely to be due to a nickel isocyanate species.

Blyholder and Sheets[4] attempted to produce an isocyanate species on several metals, suspended in hydrocarbon oil (see Chapter 4). In their study[4], these authors reacted carbon monoxide separately with ammonia and hydrazine over a nickel surface but observed no absorption bands attributable to a nickel isocyanate species. Interestingly, they did discover isocyanate formation on vanadium and iron at room temperature.

Mechanisms of Isocyanate and CO_2 Formation

In the present study, the mass spectrometric results showed that the product gas phase contained only carbon dioxide. Further when adsorbed ^{14}NO was reacted with $C^{18}O(g)$ or vice versa, only one band was observed, which was attributed to $Ni\text{-}NC^{18}O$.

Therefore, it appears that NO and CO react over Ni to produce a surface isocyanate species and $CO_2(g)$ as the major products. Based on the known dissociation of NO on Ni, at 20°C, (as discussed in Chapter 4) it would appear that the CO reacts with adsorbed N and O. However, the mechanism is unclear since the relative proportions of each species

(NiNCO, NiNO, NiCO & CO_2) are not known. It is suspected that very little isocyanate is formed, on the basis of comparison with an infrared study[52] of isocyanate adsorption on silica (50 and 100 mg. discs). In the latter study[52] it was concluded that a surface Si-NCO species was responsible for absorption bands at 2313 and 1470 cm^{-1}. The 2313 cm^{-1} band was totally absorbing. Therefore in the present study, the intensity of the 2201 cm^{-1} band is extremely weak by comparison. Our understanding of the overall mechanism is further complicated by the mass spectrometric data from the $^{14}NO/C^{18}O$ experiments which showed that the product carbon dioxide contained a mixture of $C^{16}O_2$, $C^{16}O^{18}O$ & $C^{18}O_2$, a result which was independent of the order in which the reactants were adsorbed. This probably indicates that either gaseous CO_2 readsorbs dissociatively on the oxygen covered Ni surface such that exchange takes place or that simple exchange of $C^{18}O(g)$ with $Ni^{16}O$ takes place prior to oxidation to CO_2. Both processes have been reported in the literature[53-56] and this aspect of the present work has not been further investigated.

Conclusions

Infrared spectral data have indicated that NO chemisorbs on silica-supported nickel to form linear, neutral Ni-NO. There is strong evidence that NO_2 dissociatively chemisorbs on Ni, forming linear, neutral NO and adsorbed O. When CO is added to chemisorbed NO on Ni a surface nickel isocyanate species is generated and mass spectrometric data show that the product gas phase contains mainly $CO_2(g)$. It is known that NO can dissociate on Ni, and, it has been presumed that CO reacts with adsorbed N and O forming Ni-NCO and $CO_2(g)$ although very little NiNCO is believed to have been formed.

CHAPTER 6

THE CHEMISORPTION OF THE OXIDES OF NITROGEN ON PLATINUM

Results: Nitric Oxide

An intense, complex infrared spectrum was observed when nitric oxide chemisorbed on silica supported platinum, at room temperature. As shown in Figure 9, strong bands appeared at 1785 and 1612 cm^{-1}, both of which had half-widths of approximately 50 cm^{-1}. As well, the ratio of their intensities did not remain constant throughout the 'in situ' addition of successive doses of nitric oxide. A shoulder appeared at 1690 cm^{-1} after several additions of nitric oxide and, at high coverage, an additional shoulder appeared at 1710 cm^{-1}, as shown in Figure 9, curve 9.

The intensities of all the bands were not diminished after evacuation at temperatures below 175^{o}C but if the platinum sample was heated, briefly, at 175-200^{o}C under vacuum, the bands disappeared.

If nitric oxide N-15 was used in place of NO N-14 the bands shifted to lower wavenumbers by approximately 40 cm^{-1}, as illustrated in Figure 10. Although not shown, the band at 1710 cm^{-1}, produced at high coverage, has been observed to undergo a similar isotopic shift. Therefore, all the observed bands must contain N.

Treatment with Hydrogen

5 torr of NO was added to a Pt/SiO_2 sample for 30 minutes (Figure 11-1), followed by degassing for 1.5 h at 20^{o}C. Then, successive small doses of hydrogen were added to the adsorbed nitric oxide and the

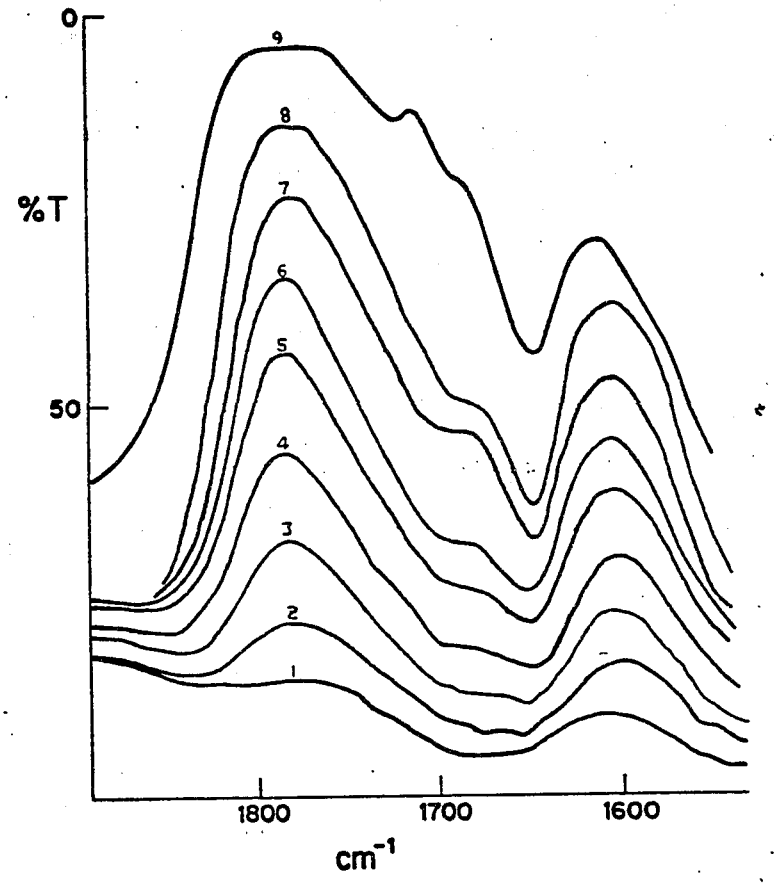
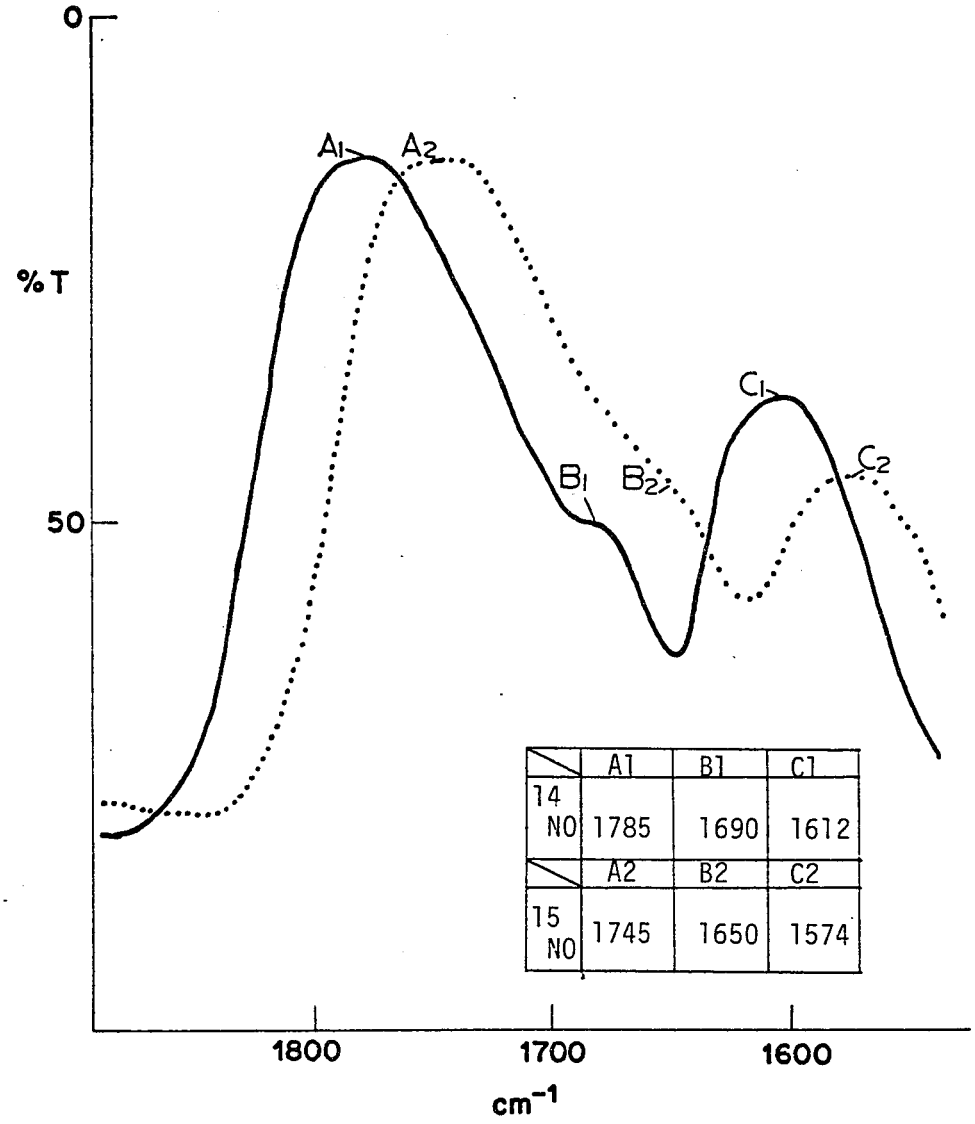


FIGURE 9

'IN SITU' ADSORPTION OF NO ON Pt/SiO_2

1. Background infrared spectrum of a compensated Pt/SiO_2 sample.
2. After adding 0.011 torr of NO to (1) in 4 additions, at 20°C. (All subsequent additions at 20°C).
3. After adding 0.009 torr of NO to (2) in 3 additions,
4. After adding 0.015 torr of NO to (3) in 3 additions,
5. After adding 0.019 torr of NO to (4) in 2 additions
6. After adding 0.026 torr of NO to (5) in 2 additions.
7. After adding 0.150 torr of NO to (6) in 5 additions.
8. After adding 0.230 torr of NO to (7) in 3 additions, followed by degassing for 12 hr. at 20°C.
9. After adding 5 torr of NO to (8) for 30 min., followed by degassing for 1.5 h. at 20°C.

The % T scale refers to curve (1).



	A1	B1	C1
^{14}NO	1785	1690	1612
	A2	B2	C2
^{15}NO	1745	1650	1574

FIGURE 10

COMPARISON OF THE INFRARED ADSORPTION SPECTRUM OF CHEMISORBED ^{14}NO WITH THAT OF CHEMISORBED ^{15}NO on Pt/SiO_2

———— Infrared spectrum of chemisorbed ^{14}NO on a compensated Pt/SiO_2 sample.

---------- Infrared spectrum of chemisorbed ^{15}NO on a compensated Pt/SiO_2 sample.

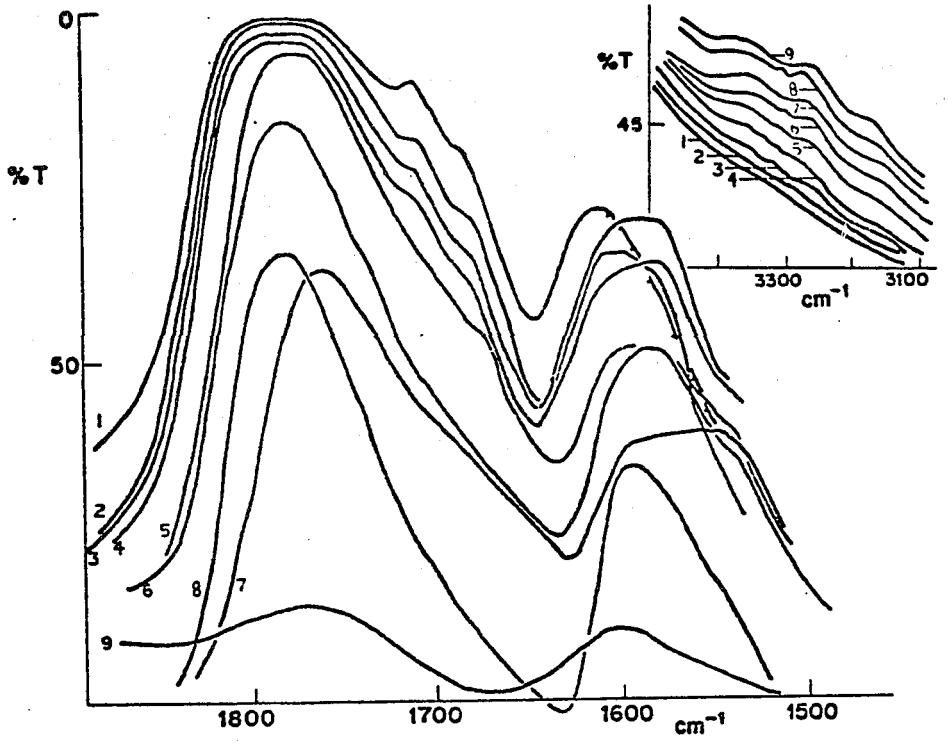


FIGURE 11

THE REACTION OF ADSORBED NO WITH $H_2(g)$ on Pt/SiO_2 .

1. Infrared spectrum of adsorbed nitric oxide (at high coverage) on a compensated Pt/SiO_2 at 20°C.
2. After adding 0.18 torr of H_2 to (1) in 2 additions followed by degassing for 17 h. at 20°C.
3. After addint 0.18 torr H_2 to (2) in 2 additions at 20°C.
4. After evacuation of (3) for 5 min., followed by the addition of 0.09 torr of H_2 at 20°C.
5. After adding 0.27 torr of H_2 to (4) in 3 additions at 20°C.
6. After evacuation of (5) for 5 min. followed by the addition of 0.18 torr of H_2 at 20°C.
7. After evacuation of (6) for 5 min., followed by the addition of 0.18 torr of H_2 at 20°C.
8. After evacuation of (7) for 18 h at 20°C.
9. Reference: Infrared spectrum of adsorbed NH_3 on a freshly reduced (H_2) Pt/SiO_2.

The % T scale refers to curve (4).

spectra which were observed are shown in Figure 11.

The shoulders at 1710 and 1690 cm^{-1} disappeared after several additions of hydrogen and the 1785 cm^{-1} band decreased slightly in intensity. Hydrogen had a more complex effect on the 1612 cm^{-1} band. Initial small doses of H_2 caused the 1612 cm^{-1} band to shift to lower wavenumber and a new band appeared to form on the low wavenumber side of this band, such that both bands combined to form a broad band centred at about 1590 cm^{-1} which showed asymmetry to the low wavenumber side. Upon the further addition of equal small doses of H_2, the broad band intensified and became symmetrical but on further additions this band decreased slightly in intensity and showed asymmetry to the high wavenumber side. At this point, absorption bands also appeared at 3370, 3270, and 3156 cm^{-1} which can be assigned to Pt: NH_3 accompanied by an additional band at 3303 cm^{-1}. Subsequent additions of H_2 caused the 1785 cm band to further decrease in intensity whereas the shifted 1612 cm^{-1} band disappeared such that only the new lower wavenumber band remained at about 1590 cm^{-1}. Then, on the next addition of H_2 both the 1785 cm^{-1} and 1590 cm^{-1} bands broadened and shifted to lower wavenumber and, at this point, the bands in the 3100-3400 cm^{-1} region intensified. Upon evacuation for 18 h at 20°C the latter bands remained unchanged and the strong bands in the 1500-1800 cm^{-1} region shifted to high wavenumber again, that is, to 1785 and 1595 cm^{-1}, and both bands became narrower. In an independent experiment, NH_3 was added to adsorbed NO on Pt/SiO_2 and bands appeared at 3370, 3270, and 3156 cm^{-1} and the bands at 1785 and 1612 cm^{-1} shifted considerably to lower wavenumber. But upon evacuation the latter bands returned to their original positions and the bands in the 3100-3400 cm^{-1} remained unchanged.

Treatment with Oxygen

When successive, small doses of oxygen were added to nitric oxide, which was adsorbed at high coverage on at Pt/SiO_2 sample, the spectra that are shown in Figure 12 were observed. All the adsorbed nitric oxide bands shifted, slightly, to higher wavenumber after each addition of oxygen. After several additions of oxygen, the intensities of the band at 1785 cm^{-1} and of the shoulder at 1690 cm^{-1} decreased whereas the shoulder at 1710 cm^{-1} intensified. Simultaneously, a new, broad band appeared at 1530 cm^{-1} and the intensity of the band at 1612 cm^{-1} increased slightly. Upon addition of a large dose of oxygen (28 torr), the new band at 1530 cm^{-1} intensified considerably while the other bands correspondingly decreased in intensity.

If nitric oxide was adsorbed onto a platinum sample at low coverage only the major bands at 1785 and 1612 cm^{-1} were observed. If successive small doses of oxygen were then added to the adsorbed nitric oxide, a sharp absorption band appeared and intensified at 1718 cm^{-1}, the band at 1785 cm^{-1} decreased in intensity and the intensity of the 1612 cm^{-1} band did not appear to change.

Nitrogen Dioxide

The addition of small successive doses of nitrogen dioxide to a platinum sample produced the infrared spectra shown in Figure 13. Initially, the spectra resembled that of nitric oxide, chemisorbed at low coverage, that is, with two broad bands centred at 1785 and 1610 cm^{-1}. With the addition of a larger dose of nitrogen dioxide, the resulting spectra strongly resembled the spectrum produced when oxygen was added

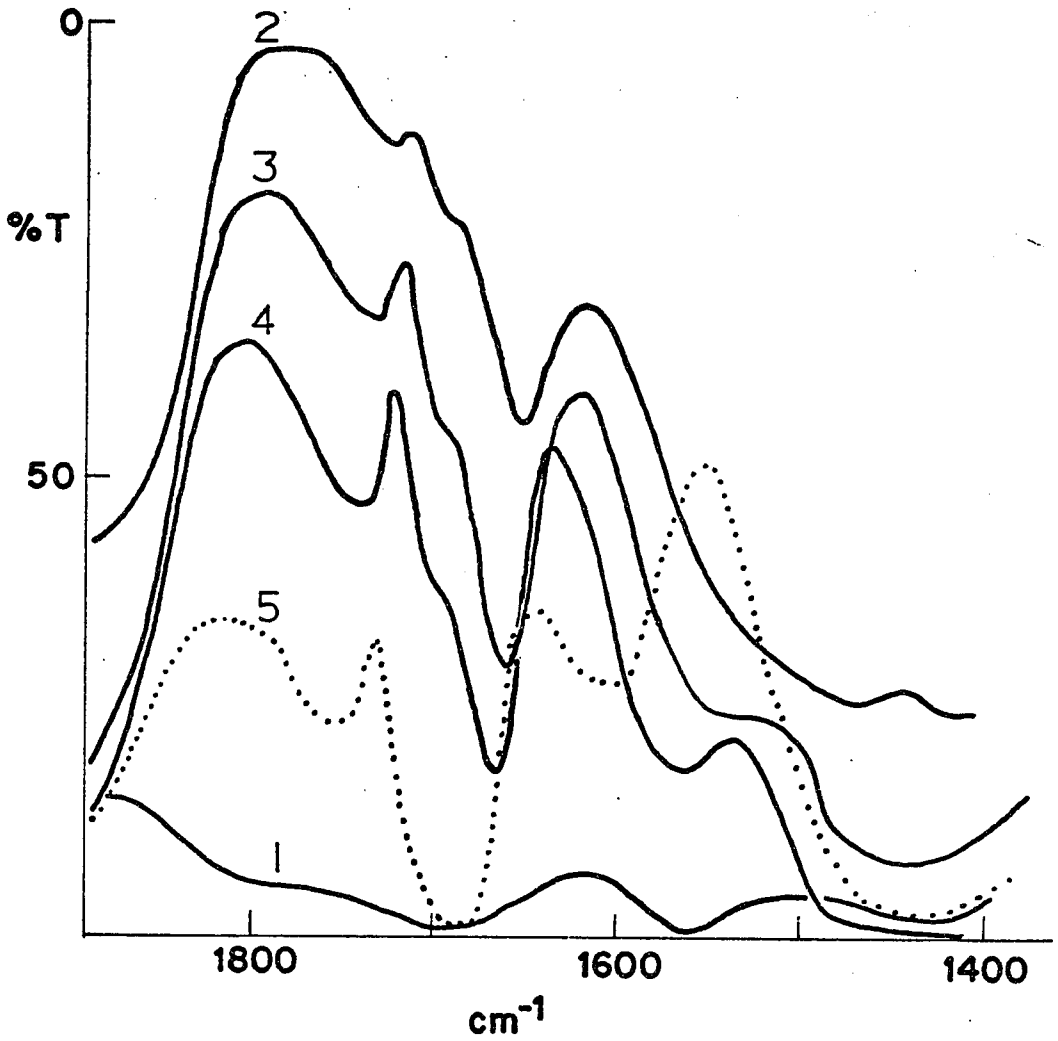


FIGURE 12

THE REACTION OF ADSORBED NO WITH O_2(g) on Pt/SiO_2

1. Background infrared absorption spectrum of a compensated Pt/SiO_2 sample.
2. After adding 5 torr of NO to (1) for 25 min., followed by degassing for 20 min. at 20°C.
3. After adding 0.30 torr of O_2 tp (2) in 4 additions, followed by degassing for 10 min. at 20°C.
4. After adding 0.50 torr of O_2 to (3) in 3 additions, followed by degassing for 10 min., at 20°C.
5. After adding 22.2 torr of O_2 to (4) in 7 additions, followed by degassing for 10 min., at 20°C.

The % T scale refers to curve (1)

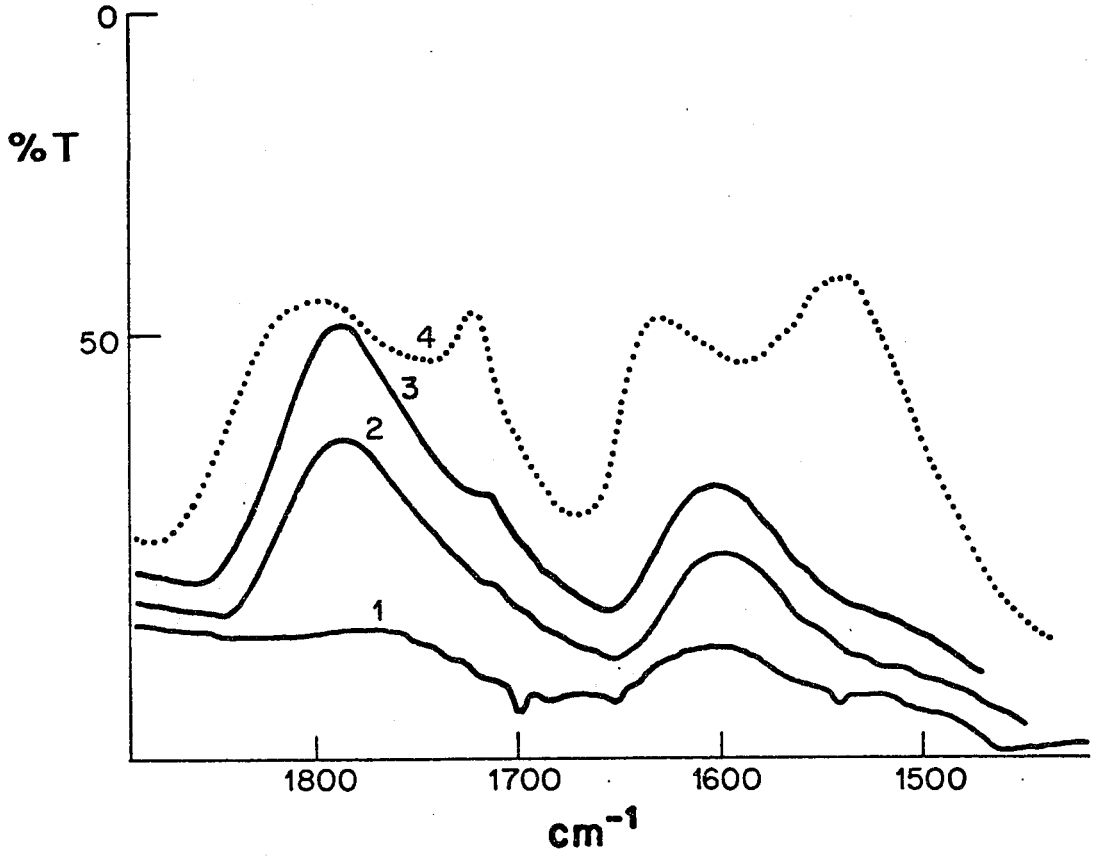


FIGURE 13

THE ADSORPTION OF NO_2 on Pt/SiO_2

1. Background infrared absorption spectrum of a compensated Pt/SiO_2 sample.
2. After adding 0.05 torr of NO_2 to (1) in 4 additions, at 20°C.
3. After adding 0.05 torr of NO_2 to (2) at 20°C.
4. After adding 0.45 torr of NO_2 to (3) in 3 additions, followed by degassing for 17 h., at 20°C.

The % T scale refers to curve (3).

to adsorbed NO. This similarity is illustrated in Figure 14.

Nitric Oxide + Carbon Monoxide

Nitric oxide was adsorbed, at low coverage, on a platinum sample, producing a spectrum attributable to chemisorbed nitric oxide. When 4 torr of carbon monoxide was added to this sample an intense, sharp band was observed at 2065 cm^{-1} and a broad band was observed between 1800-1930 cm^{-1}, due to adsorbed CO whereas the NO absorption bands disappeared. Simultaneously, a weak band appeared at about 2285 cm^{-1}. The carbon monoxide was left in the sample cell, at room temperature, and after two hours, the new band was centred at 2290 cm^{-1} and had intensified, as shown in Figure 14. After 20 hours, the carbon monoxide was evacuated and the new band was accurately calibrated and was found to be centred at 2301 cm^{-1}, while the ν(CO) band remained at 2065 cm^{-1}. The final spectrum is shown in Figure 15.

If nitric oxide N-15 was chemisorbed, at low coverage, on the platinum surface, in place of NO N-14 and then was reacted with carbon monoxide, a new band appeared at 2285 cm^{-1} (calibrated). Similarly, if carbon monoxide C-13 or carbon monoxide O-18 was added to nitric oxide N-14, chemisorbed on the platinum sample, identical bands appeared at 2254 or 2280 cm^{-1}.

If a larger dose of carbon monoxide (50 torr) was added to the nitric oxide, chemisorbed at low coverage, the band at 2301 cm^{-1} was more intense and several sharp bands appeared in the spectral range 2000-2100 cm^{-1}. These bands were presumably due to adsorbed CO and adsorbed cyanides[9,49], which are possible products. Because of the

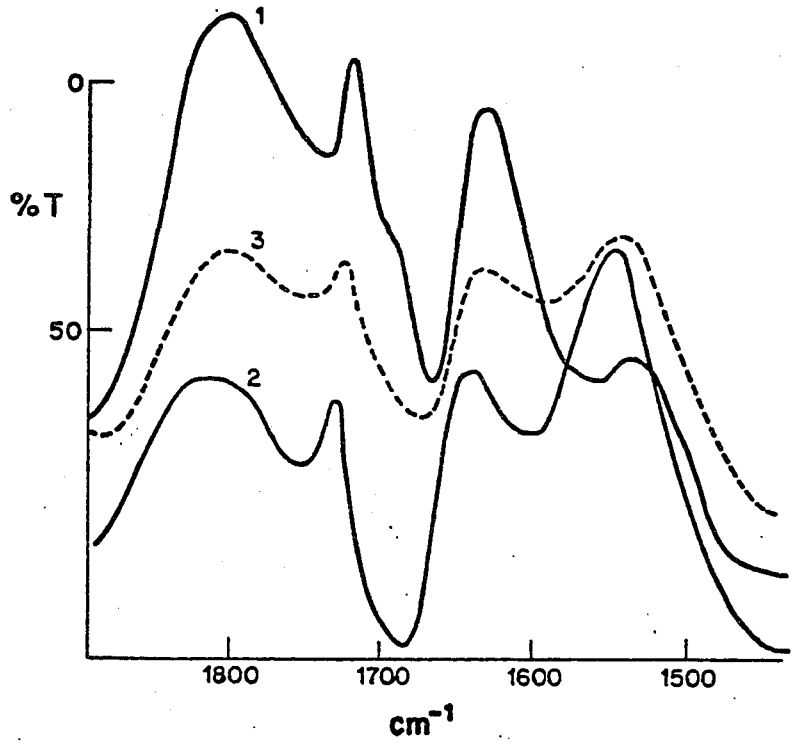


FIGURE 14.

COMPARISON OF ADSORBED NO_2 WITH THE REACTION BETWEEN ADSORBED NO and O_2 (g), on Pt/SiO_2.

1. Infrared spectrum obtained by adding 0.80 torr of O_2(g) to chemisorbed NO (at high coverage) on a compensated Pt/SiO_2 sample at 20°C.
2. After adding 22.2 torr of O_2 to (1) in 7 additions, followed by degassing for 10 min. at 20°C.
3. Infrared spectrum obtained by adding 0.55 torr of NO_2 to a compensated Pt/SiO_2 sample followed by degassing for 17 h. at 20°C.

The % T scale refers to curve (2).

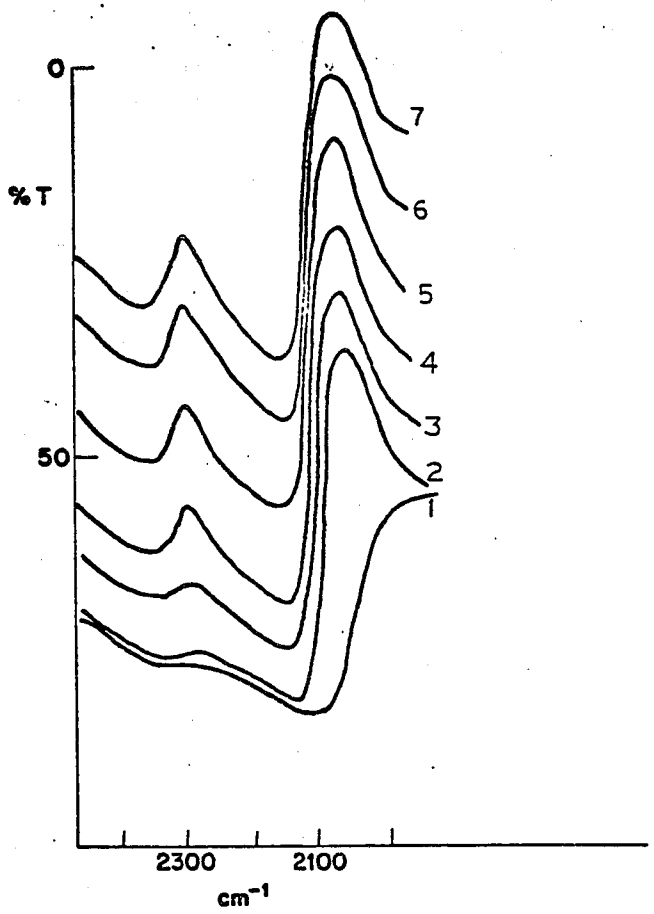


FIGURE 15

THE REACTION OF ADSORBED NO WITH CO(g) ON Pt/SiO_2

1. Infrared spectrum obtained after adding 0.80 torr of NO to a Pt/SiO_2 sample, followed by degassing for 10 min. at 20°C.
2. After adding 4.1 torr of CO to (1) for 5 min. at 20°C.
3. As for (2), but for 20 min.
4. As for (2), but for 1 h.
5. As for (2), but for 2 h.
6. As for (2), but for 20 h.
7. As for (6), but degassed for 30 min. at 20°C.

The % T scale refers to curve (4).

difficulty with band resolution in this spectral region, as discussed for NO + CO over Ni/SiO_2 in Chapter 5, bands observed in this study between 2000-2100 cm^{-1} were not investigated further.

The band at 2301 cm^{-1} was not observed if nitric oxide was adsorbed on platinum at high coverage and then reacted with the CO(g). Likewise, when carbon monoxide was adsorbed on platinum and then reacted with NO(g) no infrared absorption bands appeared in the 2400-2200 cm^{-1} region and the carbon monoxide and nitric oxide were observed to coadsorb.

10 torr of water was added to a platinum sample containing the species responsible for the band at 2301 cm^{-1}. The 2301 cm^{-1} band immediately (5 min.) diminished in intensity and over a longer period of time it disappeared, whereas the band due to chemisorbed carbon monoxide remained, but was observed to broaden.

The band at 2301 cm^{-1} (with nitric oxide N-14) was not influenced by the addition of 20 torr of hydrogen but its intensity slightly decreased upon addition of 5 torr of oxygen. The ν (CO) band shifted to lower wavenumber in the presence of hydrogen but disappeared when oxygen was added.

Discussion: Nitric Oxide

The relative intensities of the bands at 1785 cm^{-1} and 1612 cm^{-1} changed as successive doses of NO were adsorbed on Pt. Further these bands altered differently when O_2 or H_2 was added. We can conclude that these bands can be assigned to different adsorbed species and from the band positions (by comparison with those of known compounds as discussed in Chapter 3) it might be possible to assign the 1785 cm^{-1} band to linear, neutral PtNO and the 1612 cm^{-1} band to bent PtNO. These bands will be

discussed further below.

The most notable effect that the addition of oxygen had was to cause the 1785 cm^{-1} band to decrease in intensity relative to the slight intensification of the band at 1612 cm^{-1}. Further all the bands due to adsorbed NO shifted, slightly, to higher wavenumbers. The decrease in the 1785 cm^{-1} band intensity, when O_2 was added, was accompanied by the growth of a new band at 1530 cm^{-1} and by an intensification of the 1710 cm^{-1} band (or by its first appearance when NO was adsorbed at low coverage). Coordinated, monodentate nitrate complexes, M - ONO_2, characteristically show strong infrared absorption bands between 1480-1530 cm^{-1}, due to the asymmetric stretching vibration of NO_2[58] and therefore the 1530 cm^{-1} band is assigned to $PtONO_2$. When oxygen is added, this new species is presumably formed at the expense of some of the linear NO. The shift of all the observed bands to higher wavenumber upon the addition of oxygen is undoubtedly related to the strong electron withdrawing property of oxygen. The number of electrons available for π-donation from the Pt surface (i.e. Pt d-orbitals) to the adsorbed NO species would be reduced upon the addition of oxygen, and, consequently, back-donation from NO π-antibonding orbitals to the Pt surface would occur, with an accompanying increase in bonding character and, hence, the frequency of the ν(N-O) vibrations would increase. The results obtained by Primet et al[25] for the influence of metal particle size on the chemisorption of NO on Pt/Al_2O_3 support our conclusion. These authors concluded that the smaller the particle size, the smaller the number of electrons for back-donation, and the higher the ν(N-O) frequency.

The decrease in the intensities of the 1785 cm^{-1} and 1612 cm^{-1} bands and the disappearance of the shoulders at 1710 cm^{-1} and 1690 cm^{-1} upon the addition of hydrogen is presumably related to the reduction of PtNO since adsorbed NH_3 was generated. The unusual changes in intensity and position of the 1612 cm^{-1} band after each addition of hydrogen are undoubtedly due to the presence of the adsorbed NH_3. Coordinated NH_3 has a weak antisymmetric deformation mode[51] at 1600 cm^{-1} but, unfortunately, we cannot ascertain how the 1612 cm^{-1} band would be influenced by this vibrational mode, especially since NO, NH_3, and H_2 are all present on the Pt surface at the same time. Finally the addition of small quantities of NH_3 to NO, which is adsorbed on Pt, caused both the 1785 and the 1612 cm^{-1} bands to shift considerably to lower wavenumbers and also to broaden. This provides further evidence that NH_3 is very much involved with the highly unusual changes in intensity and position of the 1612 cm^{-1} band and to a somewhat lesser extent with the position of the 1785 cm^{-1} band, when H_2 is added to adsorbed NO on Pt.

Ghorbel and Primet[37] observed a strong band at 1780 cm^{-1} and several weaker bands at 1600, 1320, and 1220 cm^{-1} when they added 20 torr of NO to a Pt/Al_2O_3 sample at 25°C. The band at 1780 cm^{-1} was attributed to nitric oxide adsorbed on a reduced platinum surface. They concluded that the adsorbed NO was acting as a three electron donor with respect to the metal, with some back donation of charge from the metal to the π-antibonding orbitals of the NO species. The 1780 cm^{-1} band corresponds closely to that observed, in the present study, at 1785 cm^{-1}. As discussed in Chapter 5, Ghorbel and Primet[37] attributed the weaker bands at 1600,

1320, and 1220 cm^{-1} to nitrate ions coordinated to aluminum ions, which formed as a result of the interaction between NO_2 groups and the alumina support. Consequently, infrared absorption bands between 1200 and 1600 cm^{-1}, due to adsorbed NO on Pt may not have been observed. Therefore, direct comparison between Ghorbel and Primet's[37] study and the present work, particularly with respect to the 1350-1600 cm^{-1} spectral region, is not useful.

Brown and Gonzalez[38] recently studied the reaction between NO and CO over Pt/SiO_2. They observed a single broad band centred at 1760 cm^{-1} when 5 torr of NO was added to a 6% Pt/SiO_2 sample at 25°C which they assigned to NO adsorbed on Pt. This band undoubtedly corresponds to the 1785 cm^{-1} band in the present study. Unfortunately, these authors[38] did not investigate the nature of the adsorption of the NO on their Pt/SiO_2 sample in detail, so that further comparison between their work[38] and the present study is not worthwhile.

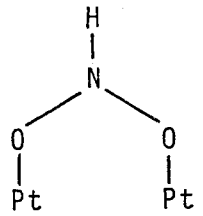
Shoulders at 1710 cm^{-1} and 1690 cm^{-1}

The intensity of the shoulder at 1710 cm^{-1} increased upon the addition of oxygen but decreased and eventually disappeared when hydrogen was added. Further this band could be generated by adding successive doses of oxygen to nitric oxide adsorbed at low coverage. The bands at 1710 and 1690 cm^{-1}, which were observed at high coverage, are assigned to complexes between NO and PtO produced by the partial dissociation of NO on the Pt surface. These bands (at 1710 and 1690 cm^{-1}) were noted to be much more intense when NO was added to a Pt sample, pretreated with oxygen or when nitrogen dioxide was added to a bare Pt surface. Further

evidence for the formation of nitrogen-oxygen surface complexes was demonstrated by the appearance of the strong band at 1530 cm^{-1} when oxygen was added to NO, which was adsorbed on Pt. The 1530 cm^{-1} band was assigned earlier to a coordinated, monodentate nitrate complex.

Hydrogen

When hydrogen was added to nitric oxide chemisorbed on Pt/SiO_2, absorption bands appeared at 3370, 3270, and 3156 cm^{-1}, which were attributed to ammonia adsorbed on platinum. These bands have been documented by Cody[9,51]. An additional weak band was observed at 3303 cm^{-1}. A band at this position was assigned by Morrow and Cody[51] to a Pt_2O_2NH species,



on the basis of evidence from a study of the oxidation of ammonia over Pt/SiO_2. Morrow and Cody[51] also found that this band was accompanied by a very weak band at about 1425 cm^{-1}. It is not unreasonable that the same partially reduced species has been formed under the present circumstances and in view of the extreme weakness of the 3303 cm^{-1} band, failure to detect the accompanying 1425 cm^{-1} band was not unexpected.

Nitrogen Dioxide

The spectrum of adsorbed NO_2 at low coverage was virtually identical to that of adsorbed NO at low coverage except that a weak band at 1710 cm^{-1} was also present (Figure 13). At higher coverage, a

strong, additional band appeared at 1530 cm^{-1} and the 1710 cm^{-1} band was quite intense. In both cases (high and low coverage) the resulting spectrum was very similar to that which was observed when oxygen was added to pre-adsorbed NO (Figure 14). This evidence strongly indicates that NO_2 initially dissociates to NO and O on the Pt surface.

Ghorbel and Primet[37] recently observed that nitrogen dioxide dissociated on alumina supported platinum, as evidenced by the appearance of a band at 1850 cm^{-1}. But, as discussed in Chapter 4, their spectra were complicated by the interaction of nitrogen dioxide with the alumina support. To this author's knowledge no other studies of the adsorption of NO_2 on Pt have been reported in the literature.

Nitric Oxide + Carbon Monoxide

When carbon monoxide was added to nitric oxide adsorbed on Pt/SiO_2, the well known band due to PtCO[47] was observed at 2065 cm^{-1}. At the same time, the bands due to chemisorbed nitric oxide disappeared and a new band developed at 2301 cm^{-1}. This new band shifted to lower wavenumber by 16 cm^{-1} with ^{15}NO, 47 cm^{-1} with ^{13}CO, and 21 cm^{-1} with $C^{18}O$ indicating that the species responsible for this band (2301 cm^{-1}) contained N,C, and O. The magnitude of these shifts is consistent with the formation of a platinum isocyanate surface species[52].

As discussed in Chapter 5 (Ni), isocyanates are known to be quite stable. This was verified in the present study by observing that the 2301 cm^{-1} band intensity did not change following prolonged degassing at 20°C nor after reaction with hydrogen and the band intensity only slightly decreased after reaction with oxygen. However, the immediate

disappearance of the 2301 cm^{-1} band upon the addition of water is reminiscent of the known sensitivity of isocyanate compounds to hydrolysis.

Several studies[37-42] have been reported in the literature, dealing with the reaction between NO and CO over Pt and these were summarized in Chapter 4. These works[37-42] were unanimous in establishing that a platinum surface isocyanate species was not formed if a mixture of NO and CO, containing excess NO, was adsorbed on the Pt sample, or, if a large dose of NO was adsorbed on the Pt surface, prior to reaction with the CO(g). This observation was confirmed by the present study (under the latter conditions). However, in the present work, it was also shown that no surface isocyanate species was formed if the CO was preadsorbed.

Of the studies mentioned above[37-42], only Undland[39-41] and Tanaka et al[42] investigated the NO/CO reaction over Pt/Al_2O_3 by varying the relative proportions of the reactants. Undland[39-41] found that if a mixture of NO and CO, containing an excess of CO, was added to a Pt sample at 300°C, then an isocyanate species was formed, as evidenced by the appearance of a strong absorption band at 2267 cm^{-1}. Further, he observed that if the NO concentration in the NO/CO mixture was raised, the band at 2267 cm^{-1} decreased in intensity. Tanaka et al[42] confirmed Undland's[39-41] work when they[42] observed the formation of a band at about 2250 cm^{-1} after a mixture of NO and CO was added to a Pt/Al_2O_3 sample under the same conditions employed by Undland[39-41]. However, it should be stressed that these workers[39-42] did not observe the formation of a surface isocyanate species below 300°C, nor did they study the NO/CO reaction over Pt by preadsorbing either reactant, as was done in the present study.

Undland[39-41] generally used a 5% NO, 10% CO, and 85% N_2 mixture

in his experiments and, as mentioned above, intense isocyanate bands were only observed if the reaction temperature was at least 300°C. His spectra do not show that there is appreciable formation of PtCO, unlike the spectra in the present study. In view of this, it is not unreasonable that the frequency of the PtNCO mode could be quite different when the isocyanate species is coadsorbed on a surface which is covered with a high concentration of an electron withdrawing species such as CO, than when it is on a bare surface. Such effects are now well established [61, 62 and Chapter 7 of this thesis].

This might account for the puzzling fact that the band which has been assigned to PtNCO absorbs at 2301 cm^{-1} whereas that reported by Undland[39-41] was at 2267 cm^{-1}. Further, the isotopic shifts were slightly different in the present work [47 cm^{-1} for ^{13}C, Undland 62 cm^{-1}, 16 cm^{-1} for ^{15}N, Undland 12 cm^{-1}] but in view of the fact that the 2301 cm^{-1} band (in the present study) shifted considerably to higher wavenumber with increasing surface coverage, the measured shifts may have a high degree of uncertainty. Further, the 2301 cm^{-1} band is quite broad and is much less intense than that reported by Undland[39-41]. In view of what was said in Chapter 5, regarding the intensity of the NiNCO band, it would have to be concluded that a very small fraction of adsorbed NO on Pt is converted to PtNCO.

Conclusions

Infrared spectral data have indicated that NO chemisorbs on silica-supported platinum forming two major surface species which have been assigned to linear, neutral PtNO and bent PtNO. In addition the

data have indicated that, at high coverage, nitrogen-oxygen complexes are formed due to the interaction between NO and PtO, the latter being produced by the partial dissociation of NO on Pt to adsorbed N and adsorbed O.

When H_2 is added to chemisorbed NO on Pt, adsorbed NH_3 is formed, accompanied by an additional adsorbed species which has been tentatively assigned to Pt_2O_2NH.

The infrared data have indicated that NO_2 dissociatively chemisorbs on Pt, forming adsorbed NO and adsorbed O.

When CO is added to chemisorbed NO on Pt, a new surface species is produced which has been identified as PtNCO, although only a very small fraction of adsorbed NO is converted to this.

CHAPTER 7

PYRIDINE

General

Numerous investigations have been carried out in order to characterize the active sites on catalyst surfaces. These studies have involved the adsorption of molecules such as ammonia and pyridine onto the surface of solids with subsequent analysis of the bonding of these 'probe' molecules to the surface. A number of techniques have been employed to analyze the adsorbed species. These have included low energy electron diffraction,electron spectroscopy for chemical analysis (ESCA), ultraviolet spectroscopy, and infrared spectroscopy.

Of these techniques, infrared spectroscopy is of particular interest because this method can yield information regarding the bonding of a probe molecule to the surface. For example, pyridine is both a Lewis base (electron donor) and a Brønsted base (proton acceptor). By observing the infrared spectrum of adsorbed pyridine in the 1700 to 1350 cm^{-1} spectral region, where the in-plane ring deformation modes and the C-H deformation modes absorb, it is possible to distinguish among pyridine molecules hydrogen bonded to surface hydroxyl groups, those coordinately bonded to Lewis acid sites and those that form pyridinium ions, PyH^{+}, with Brønsted acid sites.

Several infrared spectroscopic studies, using pyridine as a probe molecule, have been reported for a variety of surfaces.
In an infrared investigation of the adsorption of pyridine on oil-covered nickel films, Sheets and Hansen[61], found that the nickel must be pretreated with oxygen or carbon monoxide in order for chemisorption to occur. Under these conditions they concluded that pyridine coordinately adsorbed on the

nickel. Primet et al[62] studied the adsorption of pyridine on alumina-supported Pt which had been pretreated with carbon monoxide. Although absorption bands, attributable to pyridine chemisorbed on platinum could be distinguished, facile characterization of all the peaks was hindered by pyridine chemisorbed on the alumina support.

Kageyama et al[63] used ultraviolet spectroscopy to study the adsorption of pyridine on acidic solids and Kishi and Ikeda[64] conducted a similar study for nickel. Gland and Somorjai[65,66] have employed low energy electron diffraction for the study of pyridine adsorption on platinum single crystals. Several workers have studied the hydrogen-deuterium exchange reaction of pyridine over both nickel and pyridine[67-70]. In these investigations, the consensus of opinion has been that, on nickel, pyridine coordinately bonds to the surface via the nitrogen lone pair of electrons and the molecule lies perpendicular to the surface, whereas on platinum a variety of structures have been postulated. These will be discussed further below.

The present investigation is concerned with an infrared spectroscopic study of the adsorption of pyridine on silica-supported platinum and nickel and on oxygen or carbon monoxide covered platinum and nickel. Initial work on platinum was conducted by Cody[9] in this laboratory. However in the light of new evidence and improved I.R. spectra (resulting from silica compensation) this further study has enabled a more representative model to be postulated for the mode of adsorption of pyridine on Pt. The salient features of the previous work by Cody[9] will be discussed further below whenever applicable.

Results: Platinum

A 200 mg silica disc was prepared and pretreated in hydrogen at 400°C in the same manner that the hydrogen-reduced, silica-supported platinum disc was prepared. Excess hydrogen was removed by evacuation at 400°C for 2 hours, followed by cooling to R.T. for 2 hours. When 8 torr of pyridine was added to the sample, only the well documented[59,65] infrared bands at 1596, 1486 and 1444 cm^{-1} due to hydrogen-bonded pyridine were observed. (Fig. 16). These bands disappeared following evacuation for 24 hrs. at 20°C or after 1 hr at 50°C. When 10 torr of pyridine was added to a silica-supported platinum sample, additional strong bands were observed at 1567, 1536, 1431 and 1410 cm^{-1} (Figure 17) which were not removed with the hydrogen-bonded pyridine by evacuation at 130-150°C. Three weak ν(CH) bands also appeared at 3072, 3040, and 3018 cm^{-1}. Figure 18-2 shows the equivalent spectrum of pyridine-d_5 adsorbed on a deuterated Pt/SiO_2 sample with two bands at 1526 and 1500 cm^{-1}.

The new bands, evidently, are due to a strongly bound species and will hereafter be referred to as chemisorbed pyridine. The intensities of these bands did not alter following prolonged evacuation at temperatures up to 150°C but at higher temperatures the relative intensities of all the bands decreased uniformly, disappearing after evacuation at 300°C. Identical spectra of chemisorbed pyridine were observed if pyridine was added to a hydrogen covered platinum sample or to a hydrogen-free sample. When a small dose of pyridine was added to a Pt/SiO_2 sample and left in contact with the sample the initial spectrum showed that both hydrogen bonded and chemisorbed pyridine were immediately observed. However, after one hour the bands attributed to hydrogen-bonded pyridine disappeared and those assigned to chemisorbed pyridine intensified. Finally, the bands due to

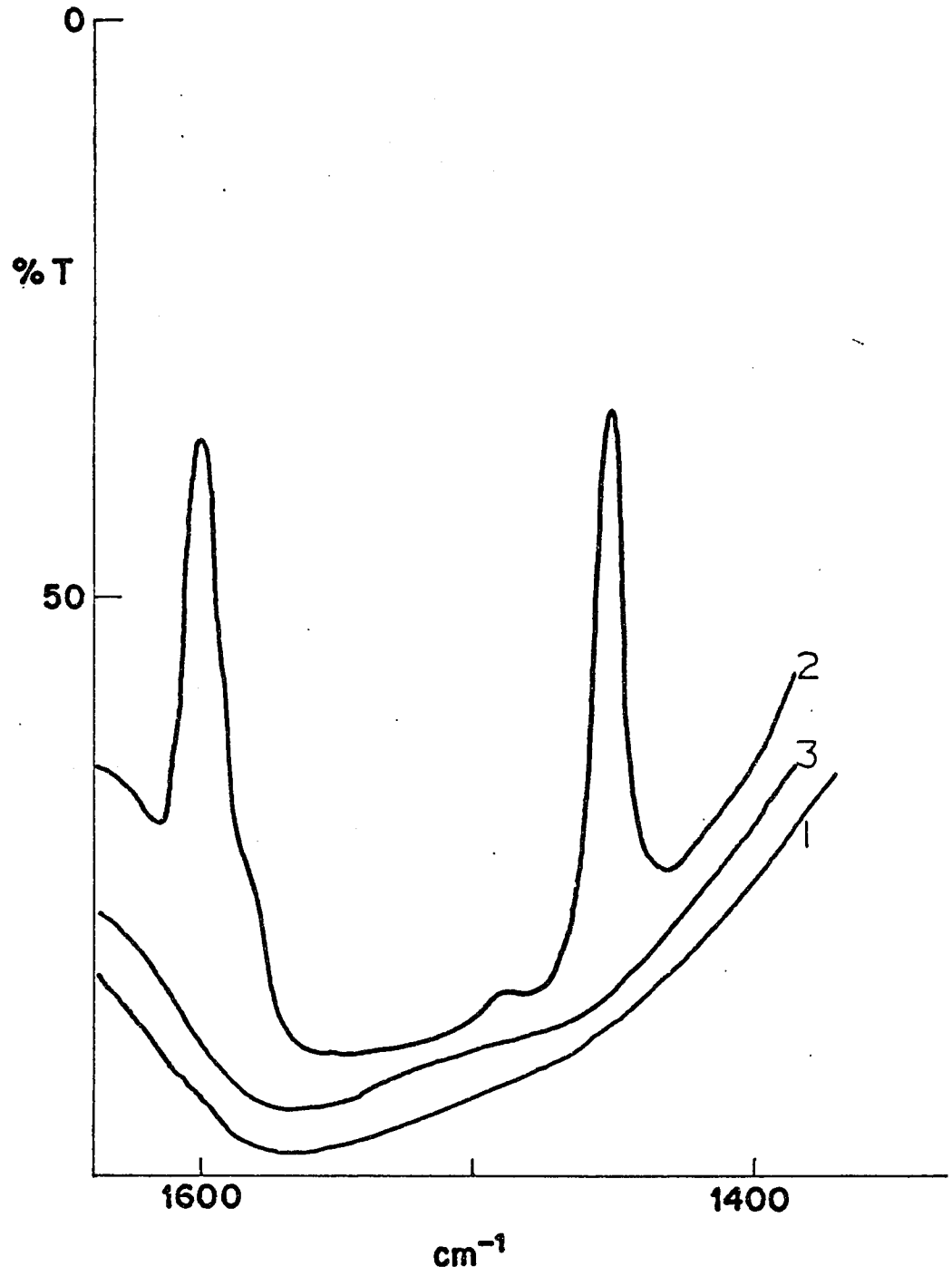


FIGURE 16

PYRIDINE ON SiO_2

1. Background infrared spectrum of a compensated SiO_2 sample.
2. After adding 8.0 torr of pyridine to (1), followed by degassing for 2 h. at 20°C.
3. After evacuating (2) for 1 h. at 50°C.

The % T scale refers to curve (2).

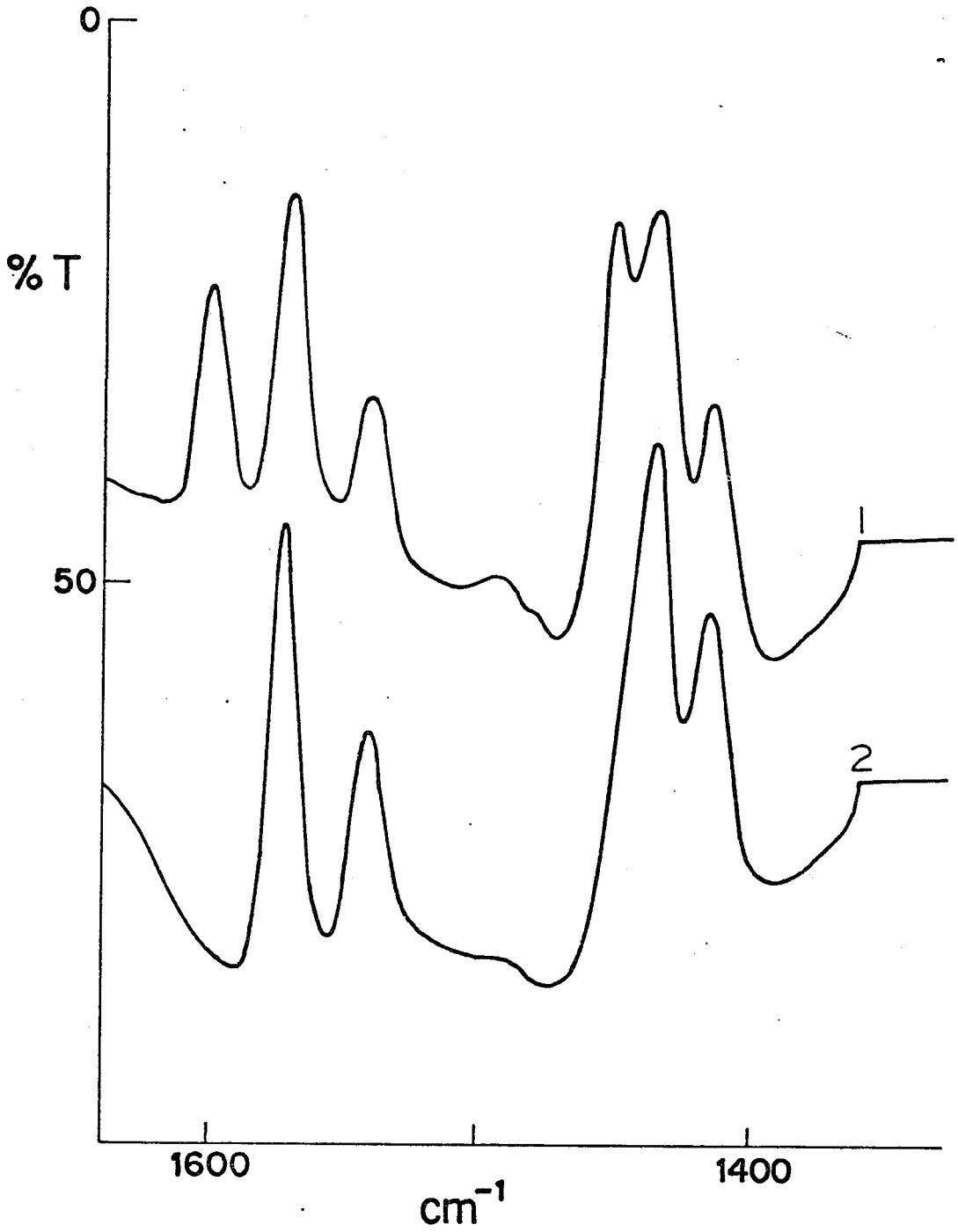


FIGURE 17

PYRIDINE ON Pt/SiO_2

1. Infrared spectrum of adsorbed pyridine on a Pt/SiO_2 sample after degassing for 20 min. at 20°C.
2. After evacuation of (1) for 1.5 h. at 150°C.

The % T scale refers to curve (2)

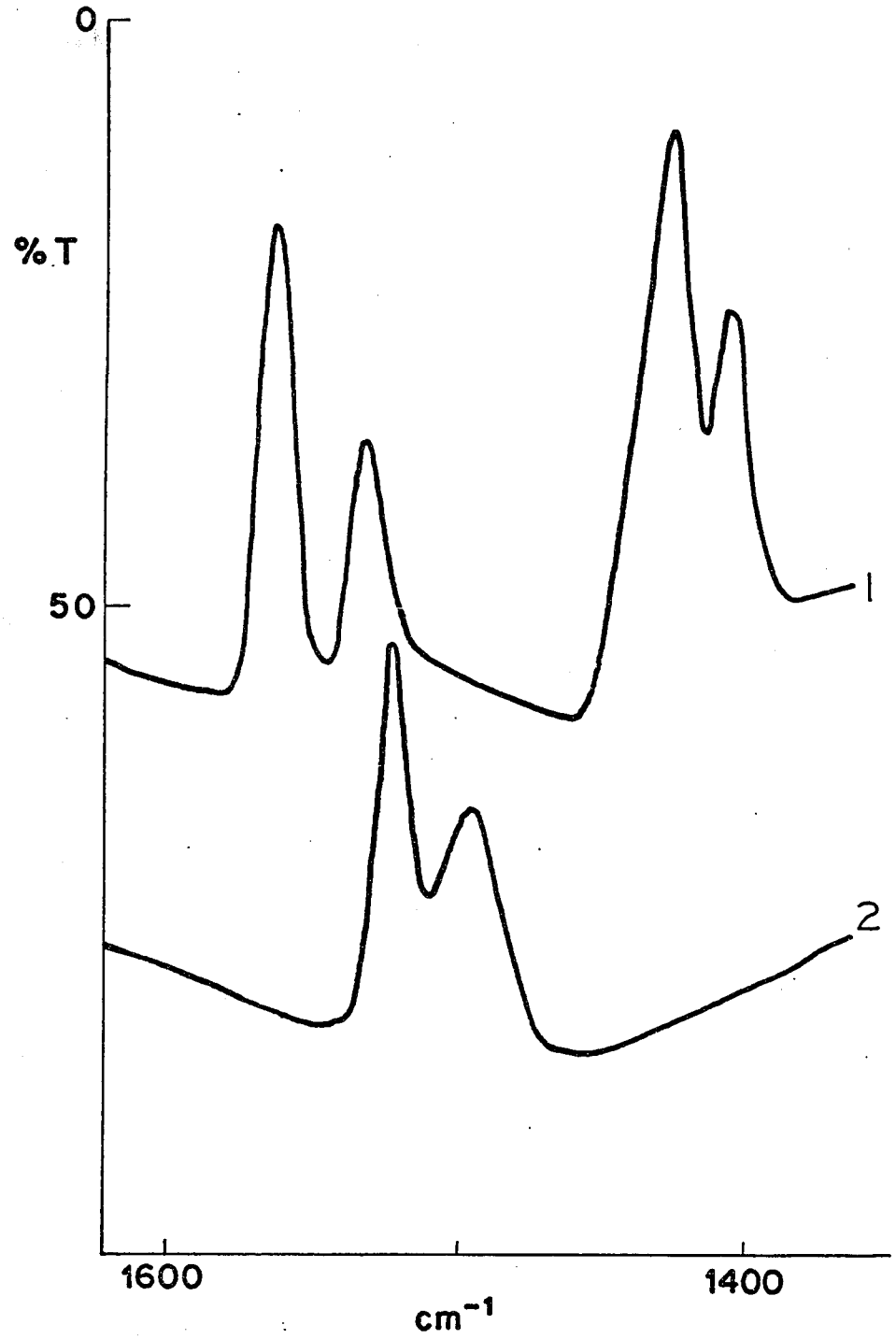


FIGURE 18

PYRIDINE VS PYRIDINE d_5 ON Pt/SiO_2

1. Infrared spectrum of adsorbed pyridine on a Pt/SiO_2 sample after degassing for 1.5 h at 150°C.
2. As for (1) with pyridine-d_5

The % T scale refers to curve (2)

chemisorbed pyridine were studied in the temperature range of -70°C to + 150°C by Cody[9]. He found that the ratio of the intensities of these bands did not change, suggesting that a single chemisorbed species is present.

Nickel

A spectrum showing the bands at 1597, 1487, and 1445 cm^{-1} due to hydrogen-bonded pyridine on a compensated 200 mg silica sample is shown in Figure 19-1. The spectrum observed following a similar adsorption sequence on a Ni/SiO_2 sample (45 minute evacuation) is shown in Figure 19-2. Under these conditions some hydrogen bonded pyridine is undoubtedly still present, but the weakest band is now centred at 1482 cm^{-1} and it is relatively more intense than the corresponding band due to hydrogen bonded pyridine. Following evacuation under conditions which would ensure the removal of the latter (Figure 19-3, 19-4) three bands remain at 1605, 1482, and 1447 cm^{-1}. Subsequent evacuation of the nickel sample at higher temperatures resulted in the bands decreasing uniformly in intensity and the bands disappeared after several hours degassing at 200°C. Weak bands were also evident in this spectrum between 3100-3000 cm^{-1}, and, as well, they disappeared under evacuation at 200°C.

Sheets and Hansen[61] studied pyridine adsorption on oil-covered nickel films but they did not observe any bands due to adsorbed pyridine. However, if the nickel was pre-exposed to oxygen or carbon monoxide, adsorption was observed. To confirm this, similar experiments were performed in this laboratory. A nickel/silica sample was pretreated with 200 torr of oxygen for 30 minutes at room temperature and another nickel sample was pre-exposed

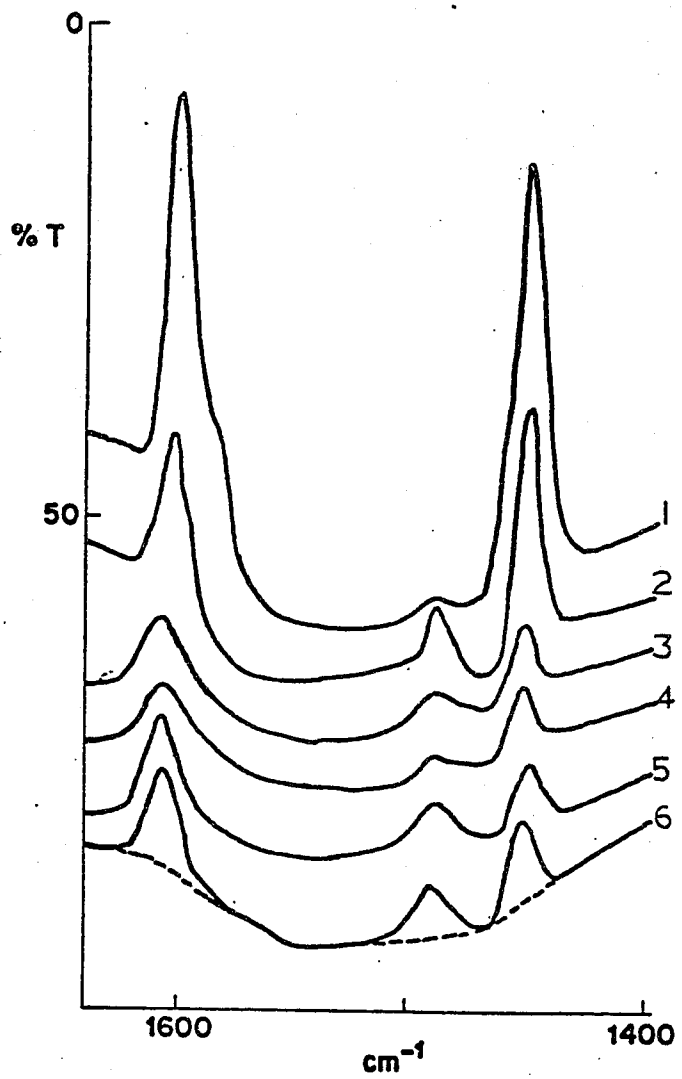


FIGURE 19

PYRIDINE ON Ni/SiO_2

1. Infrared spectrum of pyridine adsorbed on a compensated SiO_2 sample after degassing for 1.5 h. at 20°C.
2. Infrared spectrum of pyridine adsorbed on a compensated Ni/SiO_2 sample after degassing for 45 min. at 20°C.
3. After degassing (2) for 18 h. at 20°C.
4. After degassing (3) for 2 h at 100°C.
5. Pyridine adsorbed on oxygen-treated Ni/SiO_2 sample after evacuation for 14 h. at 20°C, then for 1 h at 70°C.
6. Pyridine adsorbed on CO-treated Ni/SiO_2 after degassing for 18 h. at 20°C (dashed line indicates background spectrum).

The % T scale refers to curve (6).

to 0.45 torr of carbon monoxide for 5 minutes at room temperature. The spectra shown in Figure 19-5 (O_2 pretreatment) and Figure 19-6 (carbon monoxide pretreatment) were obtained when pyridine was adsorbed followed by evacuation to remove the hydrogen bonded pyridine. As noted by Sheets and Hansen[61], the band due to NiCO shifted to lower wavenumber by approximately 70 cm^{-1} upon adsorption of the pyridine. The reaction between pyridine adsorbed on a Ni/SiO_2 disc and 400 torr of hydrogen at room temperature produced no spectral changes.

Discussion

The spectral features observed when pyridine reacted with platinum were attributed to a single chemisorbed species. A very different spectrum was observed with nickel or with CO or oxygen pretreated nickel and for convenience this system will be discussed first.

Nickel

Sheets and Hansen[61] observed two bands at 1605 and 1450 cm^{-1} when pyridine was adsorbed on nickel films which were suspended in hydrocarbon oil and pretreated with either oxygen or carbon monoxide. The 1450 cm^{-1} band appeared only as a low wavenumber shoulder of a hydrocarbon oil band at 1475 cm^{-1}. Any additional features in this region were obscured by this hydrocarbon band. Further, they observed four bands below 1350 cm^{-1} and attributed all of them to coordinated pyridine. The infrared spectral region below 1350 cm^{-1} is inaccessible in the present study because the silica support is totally absorbing below this wavenumber. Sheets and Hansen[61] assigned these bands to coordinated

pyridine on the basis of a) an observed low wavenumber shift of the NiCO band upon the adsorption of the pyridine which indicated electron donation to the surface and because, b) all the observed bands had wavenumbers similar to those in $NiPy_4(NCS)_2$ which contains coordinated pyridine. This assignment was supported by their parallel study[61] of the ultraviolet spectrum of pyridine adsorbed on silica supported nickel.

In the present study, the strongly adsorbed species observed on the nickel surface, also is attributed to coordinated pyridine. A similar low wavenumber shift of the NiCO band is observed and an additional band is observed at 1482 cm^{-1}. All compounds known to contain coordinated pyridine have major infrared bands between 1650 and 1350 cm^{-1}, at 1605 cm^{-1} (strong), 1485 cm^{-1} (medium), and 1445 cm^{-1} (strong). Also, a single strong band appears for pyridine-d_5 near 1560 cm^{-1}. (73-75). An identical spectrum was obtained in this laboratory, as shown in Figure 19. Pyridine which is hydrogen bonded to the silica support exhibits a spectrum with bands at 1597, 1487, and 1445 cm^{-1}. However, the band at 1487 cm^{-1} has been shown, by an experiment in which pyridine is adsorbed on silica alone, to have zero intensity when the band intensities are the same as those encountered with the silica supported nickel sample. Moreover, when pyridine is hydrogen bonded to a silica surface, a strong very broad band is observed near 3000 cm^{-1} due to pyridine hydrogen bonded to SiOH groups. This band disappeared under prolonged evacuation and therefore it can be assumed that the hydrogen bonded pyridine has been removed. Hence, because this broad band was not observed after evacuation of the pyridine adsorbed on the nickel sample, it can be concluded that the bands which remain in the spectrum are attributable to coordinated pyridine and that the band at

1482 cm^{-1} is especially indicative of pyridine coordinated to the nickel surface.

Sheets and Hansen[61] did not observe any bands that could be assigned to pyridine coordinated on a bare nickel film. This conflicts with the observation in the present study that a weak spectrum similar to that of coordinated pyridine was produced if pyridine adsorbed on bare nickel. Kishi and Ikeda[64] studied the adsorption of pyridine on evapourated nickel using ultraviolet spectroscopy and they concluded that pyridine did form a weakly coordinated species. Nevertheless, it is concluded that the interpretation put forth by Sheets and Hansen[61] for the adsorption of pyridine on a nickel surface pretreated with a strong electron withdrawing species (O_2, CO) is correct since experiments in the present study confirm their observations.

Calf et al[67] studied the hydrogen-deuterium exchange reaction over nickel powder in the liquid phase at 130°C. They found that the exchange occurred almost exclusively at the "2" and "6" positions in the pyridine ring but that exchange was severely deactivated with 2-methyl pyridine and completely deactivated with 2,6 dimethyl pyridine [68]. The authors interpreted these observations as demonstrating that the pyridine molecule was adsorbed on the surface via the nitrogen atom with the ring perpendicular to the surface. They argued that this mode of adsorption would make the "2" and "6" positions most susceptible to the H/D exchange reaction, a process which would be sterically hindered for the ortho substituted pyridines. Moyes and Wells[69] arrived at a similar conclusion after they observed that exchange occurred at the "2" and "6" positions

almost exclusively when deuterium gas reacted at 42°C with pyridine adsorbed on a nickel film. Both groups found that a greater degree of exchange occurred with Pt and suggested that a different type of adsorbed species was present on this metal. Those results will be discussed below.

Platinum

The four I.R. bands which were attributed to chemisorbed pyridine are at positions which are quite different from those to be expected for a simple coordinately bound molecule[59,71,72] or for a pyridinium ion[59,65]. Indeed Cody[9] has shown that pyridinium chloride could be generated from chemisorbed pyridine if gaseous HCl was added to the latter. Cody[9] also showed that αα'- dipyridyl was not formed as contended by Primet et al[62] but like Primet et al[62] he observed a low wavenumber shift of the band due to preadsorbed CO when pyridine was chemisorbed which implied that charge was donated to the metal either from the π electrons of the ring or from the nitrogen atom.

When H_2 was added to chemisorbed pyridine at 20°C, Cody[9] found that all bands immediately disappeared and were replaced by a pair of strong bands in the ν (CH) region at 2950 and 2865 cm^{-1} and two broad weak bands at 1457 and 1520 cm^{-1}. Little spectral change resulted following a brief evacuation of the H_2 at 20°C although a trace of piperidine was identified in a mass spectrometric analysis of the desorption products which could be trapped in liquid nitrogen. However, following 20 hours evacuation of the H_2 the new bands gradually diminished in intensity and those due to chemisorbed pyridine reappeared although they were less intense than those observed before H_2 was added. This process could be

accomplished with one hour's evacuation at 75°C. An identical "new" spectrum was observed if piperidine alone was adsorbed on to a Pt/SiO_2 sample and if this was evacuated at 75°C for 1 hour the spectrum also reverted to that of chemisorbed pyridine. Such reversible hydrogenation-dehydrogenation cycles have been noted[73,74] previously for unsaturated hydrocarbons adsorbed on transition metals and it is assumed that the new bands can be attributed to chemisorbed piperidine. If H_2 was added at 150°C all infrared bands due to chemisorbed pyridine immediately disappeared and large quantities of n-pentane and ammonia were identified in a mass spectrometric analysis.

In an attempt to further characterize the nature of chemisorbed pyridine the H/D exchange reaction was studied in the present investigation. When pyridine-d_5 was added to a hydrogen-covered Pt sample (see Chapter 2, Experimental) the surface silanol groups instantaneously exchanged to become surface SiOD groups and after several hours a very complex spectrum was observed in the 1600-1400 cm^{-1} region indicating that mixed isotope species were present. However, after reaction with a hydrogen-free sample, only a very slight degree of SiOH exchange occurred and there was no indication of the formation of mixed isotopic species, that is a spectrum like that in Figure 18-2 was observed. This SiOH exchange phenomenon is commonly encountered when hydrocarbons interact with silica-supported Pt[73,74] and it is an indication that CH bond rupture occurred whereby the liberated surface deuterium subsequently exchanged with SiOH. Since SiOH exchange still took place on the essentially hydrogen-free surface, this probably indicates that dissociative chemisorption had occurred.

The above results, taken in conjunction with the observations noted earlier from Cody's[9] work and particularly the data pertaining to the hydrogenation-dehydrogenation sequence, strongly suggest that the observed bands can be assigned to a monomeric cyclic C_5N species. Having ruled out a simple nitrogen coordinated species, the structures shown in Figure 20 might be possible.

Structure A is proposed to lie "edge-on" with respect to the surface, i.e. perpendicular to the surface, whereas B.C and D are assumed to be involved in π bonding via the ring system and lie flat. Structures A and C have a conventional Pt-C σ bond at the "2" position. The reasons for postulating bonding at this position are two-fold. Firstly, it is known that pyridine is a poison for platinum surfaces[75,76] yet 2,6 dimethyl pyridine is much less so[68,76] which implies that the "2" position on pyridine has some special significance in connection with the mode of bonding. Secondly, exchange studies[68,69] have also indicated that the "2" position is very susceptible to exchange, a point which will be discussed further below.

Each of the structures above provide charge to the metal surface either by donation from the nitrogen atom or from the ring, and each of these could account for the observed low wavenumber shift of the PtCO band. Such a shift is known to occur when benzene is π bonded to Pt which contains preadsorbed CO[62] . On the basis of the spectroscopic and chemical evidence so far discussed, it is not possible to definitively choose between these. However, structures C and D would appear unreasonable on steric grounds since the conventional bond with the surface (the Pt-C sigma bond in C or the Pt-N coordinate bond in D) would have to be at an appreciable angle with respect to the plane of the molecule. Of structures

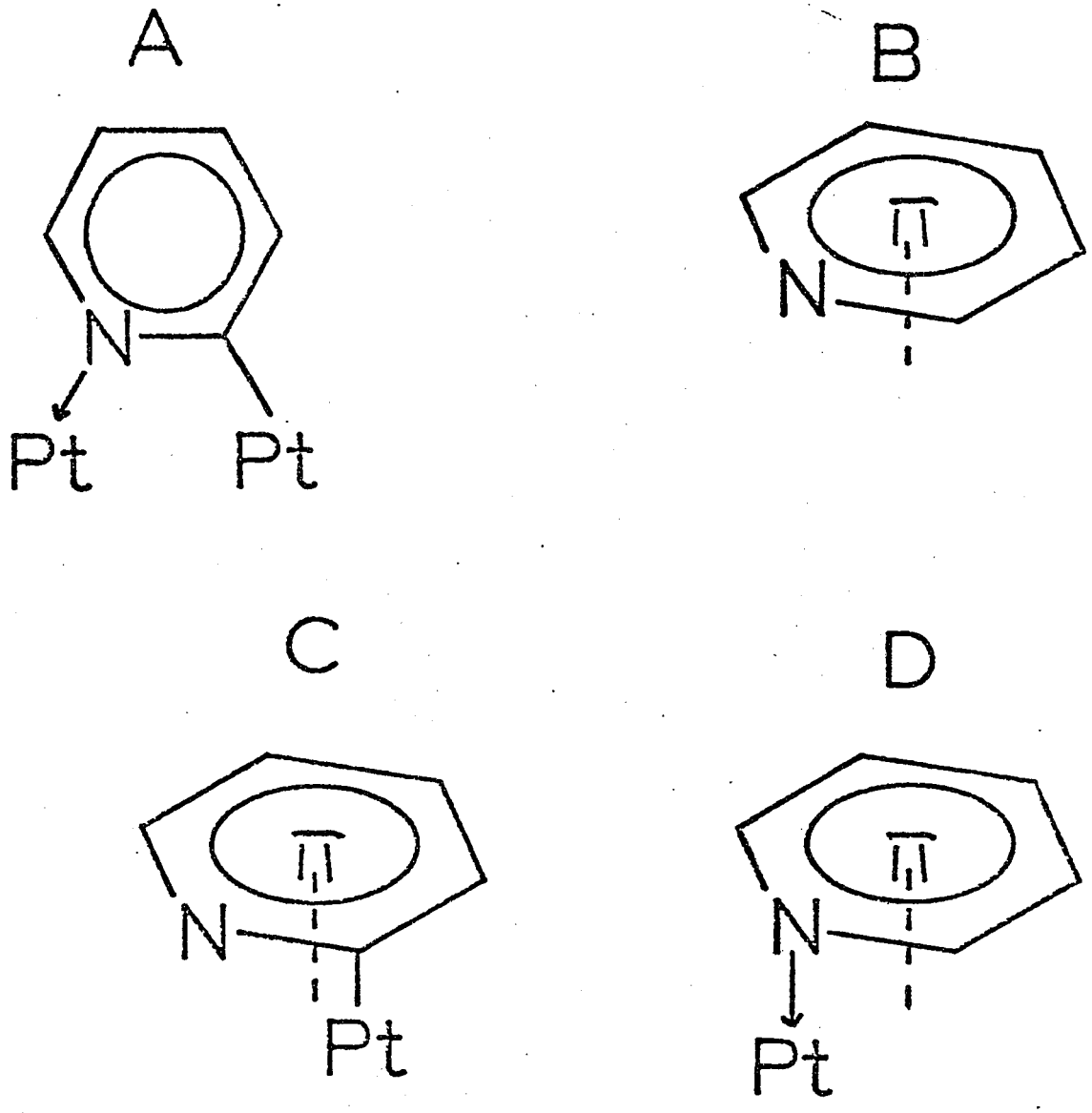


FIGURE 20

POSSIBLE STRUCTURES FOR ADSORBED PYRIDINE ON Pt/SiO_2

A and B, there are arguments which favour structure A.

The two high wavenumber bands of liquid pyridine (1580 and 1572 cm^{-1}) are due to in plane ring deformation modes whereas the two low wavenumber bands (1482 and 1439 cm^{-1}) are due to in plane CH deformation modes. The latter shift noticeably to lower wavenumber[78] when a heavy atom is substituted at the "2" position in the ring. It is conceivable that attachment of a surface Pt atom at this position might cause an even greater downward shift. It is difficult to predict what shifts, if any, might result if pyridine was π bonded as in B. However, no π bonded sandwich type compounds of pyridine exist.

There is evidence from the H/D exchange study that a small degree of dissociative chemisorption occurs. Moyes and Wells[69] studied the H/D exchange between gaseous D_2 and gaseous pyridine over Pt powder at 100°C and found that exchange mainly occurred in the 2 and 6 positions with a lesser degree of exchange at other positions, and postulated that species A above, played a dominant role in this process. (They also suggested that structure A was responsible for the 2,6 exchange for pyridine on nickel but could not convincingly rule out the possibility that a simple "addition-abstraction" mechanism solely involving coordinated pyridine on Ni was operative. This work has clearly shown that the structure of adsorbed pyridine on nickel is quite different from that on platinum). Calf et al.[67] likewise found that slight exchange occurred at positions other than 2 and 6 for pyridine on Pt but suggested that the molecule was involved in both nitrogen coordination and ring π bonding to Pt such that the ring was tilted with respect to the surface, thereby facilitating exchange at other positions. This model cannot be conclusively

ruled out except that the degree of tilt might be expected to alter with temperature such that fairly obvious spectral changes would have been observed as the temperature was varied from ~70 to ~150°C.

Gland and Somorjai[65,66] have recently carried out a low energy electron diffraction study of the adsorption of benzene and pyridine on Pt (111) and Pt (100) single crystal surfaces. They concluded that the LEED pattern and from the work function change on adsorption that benzene at low coverage laid flat on the surface and was π bonded via the ring system, whereas with pyridine, the ring lay perpendicular to the surface and charge was donated via the nitrogen atom. Their data could not conclusively rule out our structure A and indeed, they suggested that this was the structure if the adsorbed pyridine was heated to 250°C. There was no evidence that pyridine lay flat on the surface.

Although one has to be cautious in comparing the results from a LEED study on single crystal faces with the results obtained in an infrared study, nonetheless, it is felt that the LEED study strongly argues against our structure B. The only major point of difference in interpretation is that in the present study it can be firmly concluded that a simple nitrogen coordinated pyridine is not formed. It may be that the near saturation surface coverages employed in this work favor processes which cause CH bond rupture (note for example that adsorbed benzene changes from a predominantly π bonded structure to a σ bonded structure with increasing coverage[65,66]). Alternatively, the supported Pt catalyst undoubtedly has a relatively high step and kink density so that CH dissociation would be expected to be more favorable than on Pt (111) or Pt (100) surfaces[79].

In conclusion it is felt that the evidence argues strongly in favor of a model in which pyridine attaches itself to the platinum atom by forming a σ bond at the "2" position and a coordinate bond with the nitrogen lone pair electrons. Unsaturation is preserved and the molecule is presumed to lie perpendicular with respect to the surface.

CONCLUDING REMARKS

Pyridine and other nitrogen bases are notorious poisons for metal catalyzed hydrogenation reactions[76,77]. The present work has shown that a chemisorbed species of high thermal stability is readily formed on Pt. Freifelder[76] has shown that the "poison" is probably piperidine rather than pyridine itself. This was confirmed by Cody[9] since he observed that chemisorbed pyridine was readily hydrogenated to adsorbed piperidine. It is not known how the latter is attached to the surface but it is known that if piperidine itself is added to bare Pt the infrared spectrum is the same as is observed after adding H_2 to chemisorbed pyridine. In either case, prolonged evacuation at 20°C resulted in very little desorption and that if higher temperatures were employed, the adsorbed species dehydrogenated to give chemisorbed pyridine. This suggests that the H/D exchange results of Moyes and Wells[69] might bear little relationship to the present work in that the active exchange sites probably occupy a small fraction of the "poisoned" surfaces.

Interaction Between Adsorbed Pyridine and Oxygen on Platinum

Results

Because preadsorbed oxygen or carbon monoxide promoted the coordination of pyridine on nickel, it was considered worthwhile to investigate whether a similar phenomenon could occur on Pt in spite of the fact that pyridine chemisorbs very differently on bare Pt than on Ni. Only the normal chemisorbed pyridine formed on a CO pretreated Pt but with a pre-oxidized Pt sample a very complex spectrum was observed. A similar but less complex spectrum was observed if oxygen was added to chemisorbed pyridine and this will be discussed first.

The spectrum observed when 10 torr of oxygen was added to chemisorbed pyridine is shown in Figure 21. The initial bands all decreased in intensity but those at 1567 and 1410 cm^{-1} decreased to a greater extent than did those at 1536 and 1431 cm^{-1}, and all peak positions shifted to higher wavenumber by about 5 cm^{-1}.

At the same time, new bands grew at 1608 and 1462 cm^{-1}. The above spectral changes continued at a slow rate if the O_2 was left in the cell for several hours, but when the O_2 was evacuated the new bands slowly decreased in intensity, eventually disappearing and the spectrum of chemisorbed pyridine reverted to normal (the high wavenumber shift remained) but the overall intensity was about halved. The corresponding spectral changes for pyridine-d_5 are shown in Figure 22. The original bands again shifted slightly to high wavenumber but the intensity of the 1526 cm^{-1} band decreased more than that of the 1500 cm^{-1} band, and new bands appeared at 1567 (sharp) and 1418 cm^{-1} (broad). With $^{18}O_2$ only the 1418 cm^{-1} band shifted to 1395 cm^{-1}. Finally, apart from complex

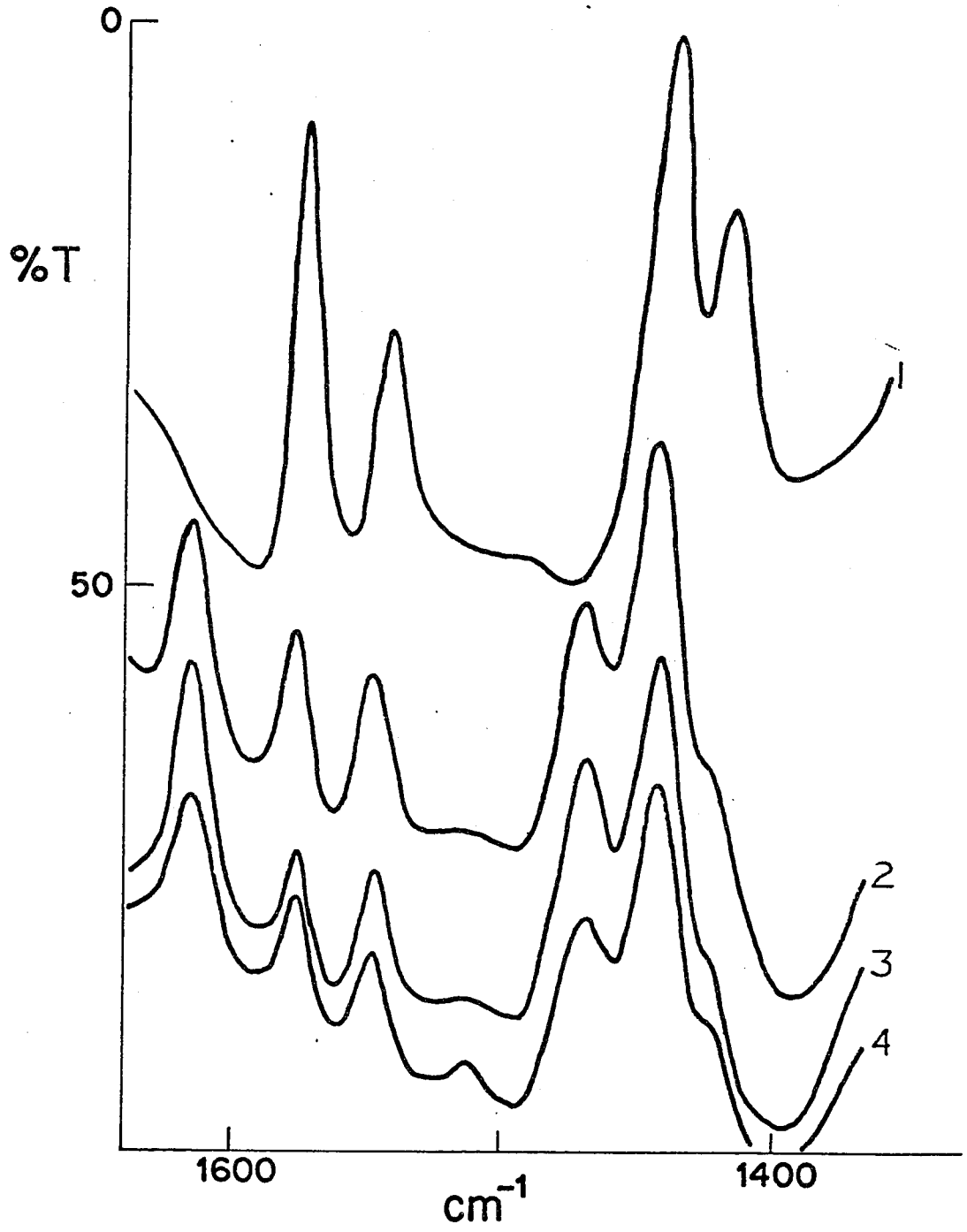


FIGURE 21

ADDITION OF O_2 TO CHEMISORBED PYRIDINE ON Pt.

1. Infrared spectrum of adsorbed pyridine on a Pt/SiO_2 sample after degassing for 1.5 h at 150°C.
2. After adding 10 torr of O_2 to (1) at 20°C (immediate scan)
3. As for (2) but for 17.5 h at 20°C.
4. After evacuation of (3) for 30 min. at 20°C.

The % T scale refers to curve 2.

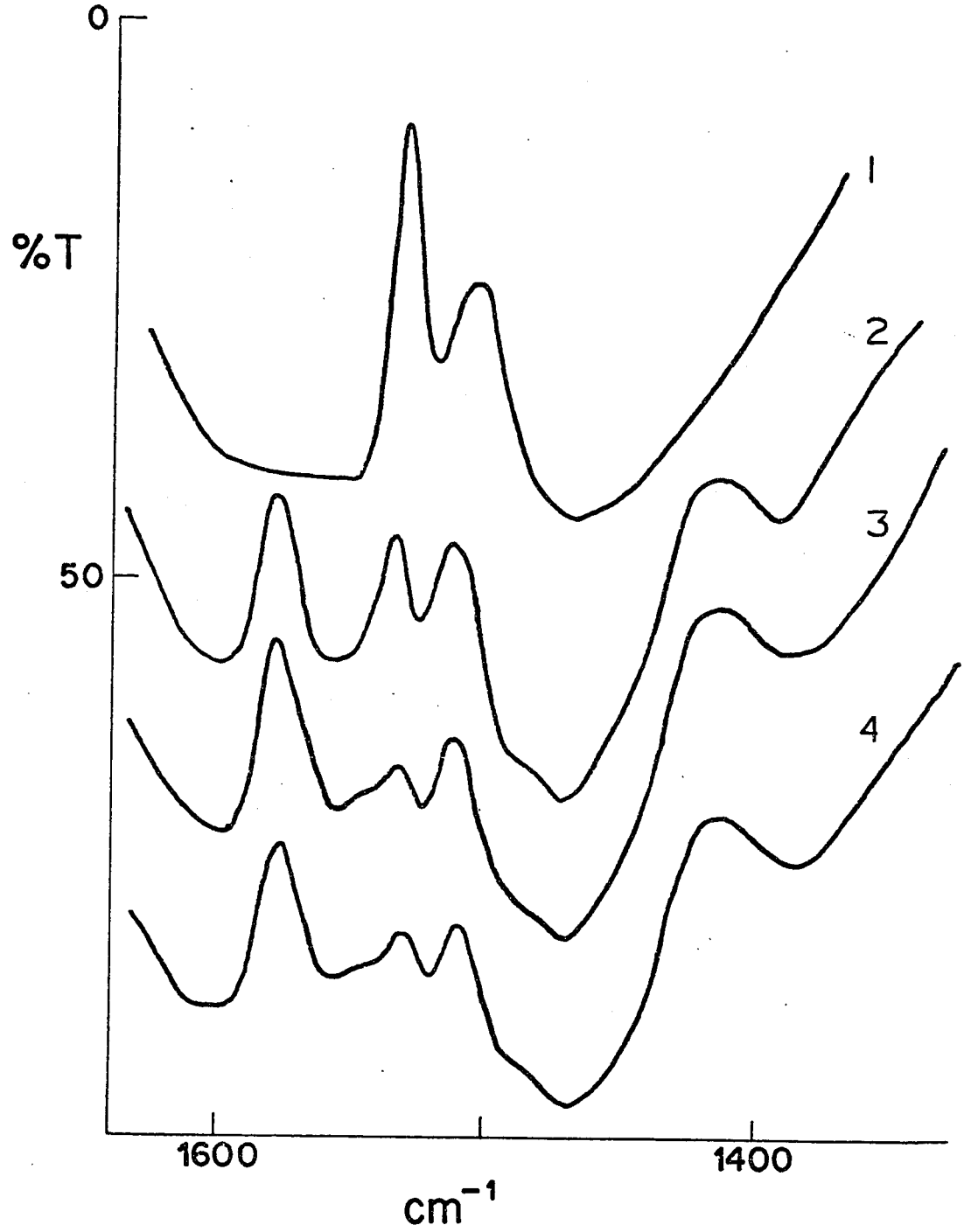


FIGURE 22

ADDITION OF O_2 TO CHEMISORBED PYRIDINE-d_5 on Pt

1. Infrared spectrum of adsorbed Pyridine-d_5 on a deuterated Pt/SiO_2 sample after degassing for 1 h at 125°C.
2. After adding 20 torr of O_2 to (1) at 20°C (immediate scan).
3. As for (2) but for 21 h at 20°C.

The % T scale refers to curve 3.

changes in the spectral region associated with the olefinic CH stretching modes after oxygen was added, no other new spectral features were generated, and particular attention was paid to the regions where CN, CO, or NCO absorb.

The experiments described above suggest that a single new species is produced when oxygen is added to chemisorbed pyridine. This will be termed species I (for reasons that will become apparent later when the spectrum of pyridine on oxidized Pt is discussed) and its presumed infrared absorption bands are listed in Table 5. All attempts to trap this species in a liquid nitrogen trap and obtain its mass spectrum failed. The experiments involving oxidized Pt will now be described.

Various types of oxidized Pt/SiO_2 surfaces were prepared either by adding oxygen to a reduced sample at 20^oC (a condition that generated type I PtOH surface species[80]), or by adding oxygen at 200^oC or at 400^oC, followed by cooling in oxygen to 20^oC. In all cases, a spectrum of the type shown in Figure 23 was obtained, after the adsorption of 10 torr of pyridine and a brief evacuation. The spectrum was very similar to that of hydrogen bonded pyridine except that the band at 1481 cm^{-1} was relatively more intense and was shifted to lower wavenumber by 6 cm^{-1}, and there was a weak band at 1540 cm^{-1}. Following prolonged evacuation at 20^oC or at 55^oC (conditions which are known to remove hydrogen-bonded pyridine), the spectrum gradually changed as shown in Figure 23-2 and 23-3. The peak position of the 1597 cm^{-1} band gradually shifted to about 1605 cm^{-1}, a band developed near 1570 cm^{-1}, and a relatively complex profile emerged at low wavenumber with four maxima at 1481, 1462, 1450, and 1434 cm^{-1}. The bands at 1481 and 1450 cm^{-1} appeared to grow or diminish in intensity at a uniform

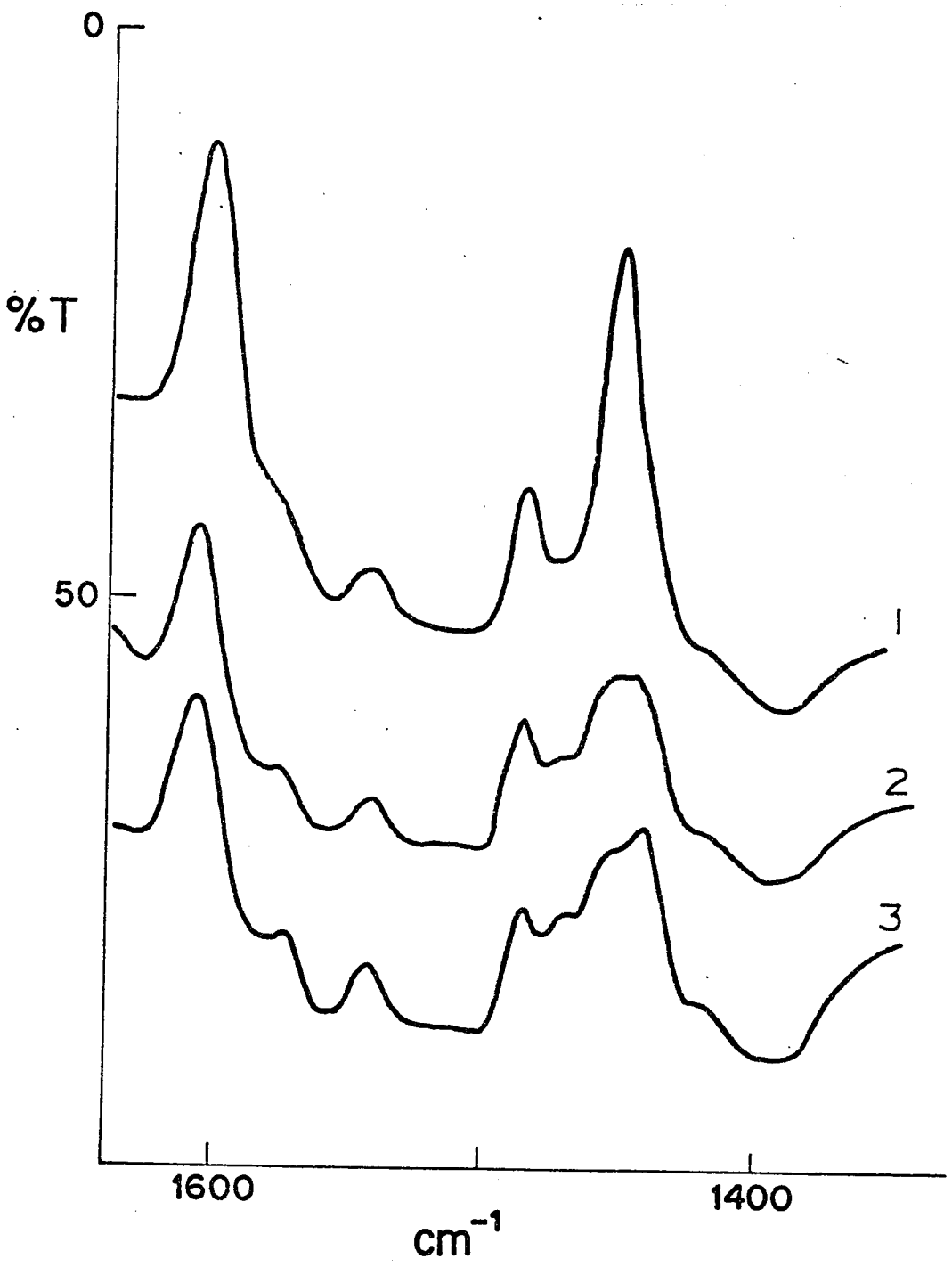


FIGURE 23

PYRIDINE ON OXIDIZED Pt/SiO_2

1. Infrared spectrum obtained after adding 10 torr of pyridine to an oxidized Pt/SiO_2 sample, followed by evacuation for 30 min. at 20°C.
2. After evacuation of (1) for 18 h at 20°C.
3. After evacuation of (2) for 1 h at 55°C.

The % T scale refers to curve 3

rate as did the 1462 and 1434 cm^{-1} pair, whereas little change occurred near 1600 cm^{-1}. Upon degassing at 100°C, all bands disappeared except for a weak set of bands attributable to chemisorbed pyridine on bare Pt, and a spectrum of PtCO were observed.

The corresponding spectra for pyridine-d_5 on oxidized Pt are shown in Figure 24. The intense band at 1547 cm^{-1} due to hydrogen bonded pyridine-d_5 diminished after evacuation for 16 or 27 hours, the peak position shifted to 1558 cm^{-1} and a shoulder developed on the high wavenumber side. After evacuation at 90°C, the 1558 cm^{-1} component had disappeared leaving a band at 1567 cm^{-1}. Throughout this sequence of change a broad band at 1418 cm^{-1} remained. There were also weak features at 1531 and 1504 cm^{-1} which are characteristic of chemisorbed pyridine-d_5 on bare Pt. The spectrum in Figure 24-4 closely resembles that shown in Figure 22-4 after oxygen had been added to chemisorbed pyridine-d_5, except that the relative intensity of the bands due to chemisorbed pyridine-d_5 on the bare Pt are weaker.

Discussion

From a consideration of the above, it appears that three species are formed when pyridine is adsorbed on oxygen covered Pt. Weak bands due to chemisorbed pyridine on Pt and of species I are evident, and a new set of bands at 1605, 1481, and 1450 cm^{-1} due to a new species which will be termed species II (Table 5).

Species II was only generated when pyridine was adsorbed on oxidized Pt and the band positions and relative intensities (as far as can be seen from the badly overlapped spectra) are virtually identical to those which were assigned to coordinated pyridine on nickel. It is

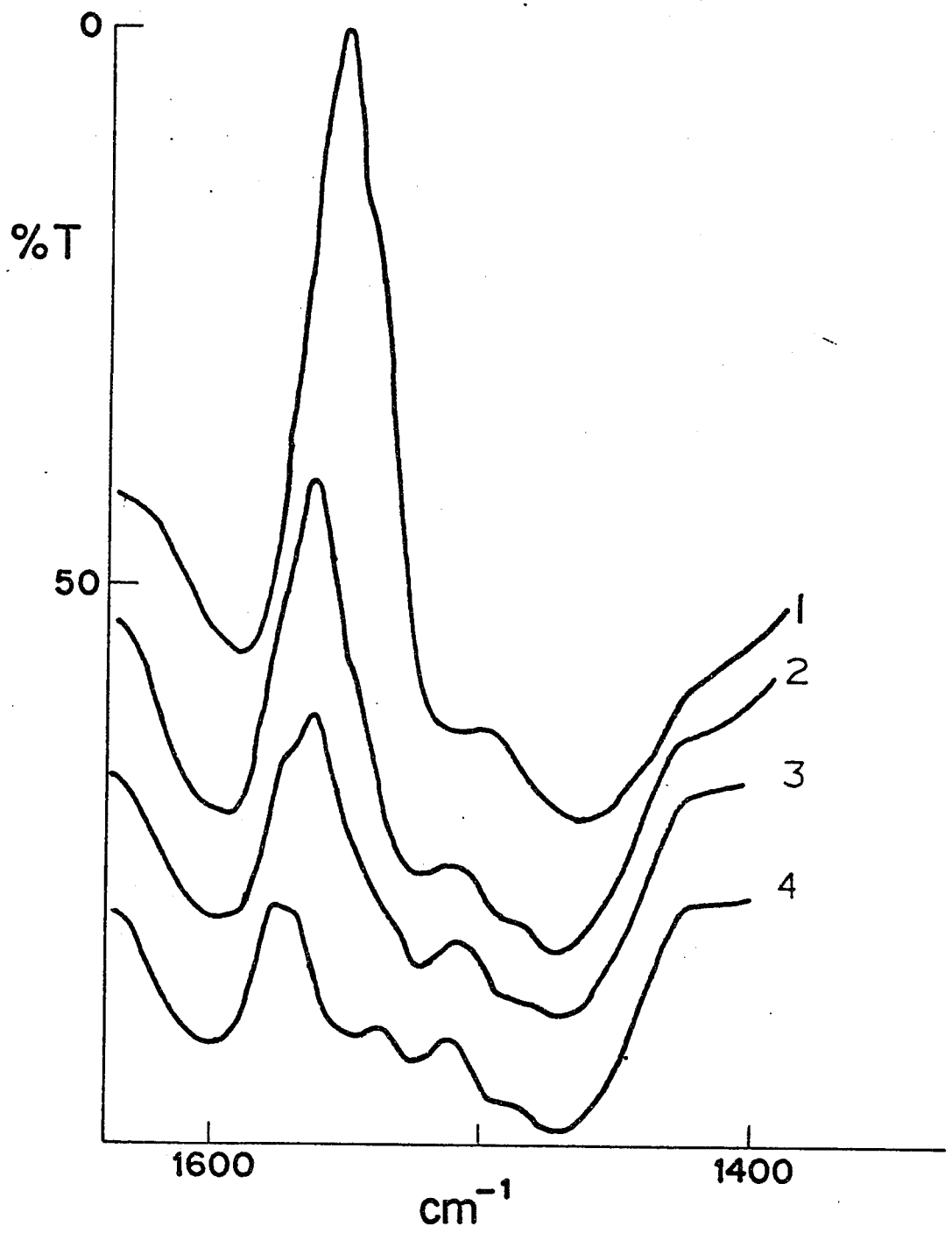


FIGURE 24

PYRIDINE-d_5 ON OXIDIZED Pt/SiO_2

1. Infrared spectrum obtained after adding 10 torr of pyridine-d_5 to an oxidized Pt/SiO_2 sample, followed by evacuation for 1 h at 20°C.
2. After evacuation of (1) for 16 h at 20°C.
3. After evacuation of (2) for 11 h at 20°C.
4. After evacuation of (3) for 2 h at 90°C.

The % T scale refers to curve 3

TABLE 5

Infrared Absorption Bands due to Pyridine-h_5 and Pyridine-d_5 on Pt + O_2 and on PtO.

	Pyridine-h_5 Infrared absorption band (cm^{-1})	Pyridine-d_5 Infrared absorption band (cm^{-1})
Species I	1608	
	~1540[1]	1567
	1462	~1500[1]
	~1435[1]	1418[2]
Species II	~1605	
	1481	1567
	1450	

1. So assigned because of overlap with a band due to chemisorbed Pyridine which only slightly decreased in intensity relative to other bands when O_2 was added.
2. Only this band shifted (1395 cm^{-1}) when $^{18}O_2$ was used.

not unreasonable that oxygen could promote the coordination of pyridine on Pt as it did on Ni so species II will be so assigned. As to why dissociation to give chemisorbed pyridine is inhibited, there is evidence[81] that the major C-H cleaving sites on Pt catalysts (step sites) can be deactivated when oxygen is present so that it is reasonable to assume that dissociative chemisorption of the type postulated for chemisorbed pyridine on bare Pt will be less favourable on an oxygen treated catalyst.

The identity of species I is unclear. The fact that the 1418 cm^{-1} band undergoes a 23 cm^{-1} shift when $^{18}O_2$ is used strongly suggests that a N=O containing species is generated (the frequency is too low to be assigned to any known carboxylate type species) and indeed, this shift is almost identical to that encountered in NO_2^- or NO_3^- ions, both of which are known to have a strong infrared band near 1418 cm^{-1}. One must also consider bridging nitrosyl groups here since the 1418 cm^{-1} band is in the spectral region attributed to these species, from 1300 to 1550 cm^{-1}. Some platinum-nitrosyl complexes that contain bridging nitrosyl groups are known[20,21] and these are described in Chapter 3. In view of the known reactivity of pyridine at the "2" position (see earlier discussion) cleavage of the ring and splitting out of the nitrogen is not unreasonable. Further, although oxygen can inhibit C-H cleavage, it does not inhibit C-C cleavage, and therefore, presumably it does not inhibit C-N cleavage. There are two difficulties with this assignment. Firstly, it is strange that no bands were generated anywhere near 1418 cm^{-1} in the study of the adsorption of NO

or NO_2 on Pt. Admittedly, the surface is quite different when it is covered with a pre-adsorbed layer of pyridine. Although compounds containing $Pt(NO_2)_2L_2$ (L = neutral ligand) have a strong ν (N=O) band near 1418 cm^{-1} [82,83], it would not seem reasonable to postulate the formation of ionic species under the present experimental conditions. Further, there is not sufficient experimental evidence available to permit us to make a strong case in favour of bridged NO structures. Nonetheless, the facts strongly indicate that a surface N=O containing species has been formed. With pyridine-h_5 the ν (N=O) band is undoubtedly hidden under the complex envelope of bands between 1405-1481 cm^{-1}. [Species I is almost certainly not a pyridine N-oxide derivative; the ν(N-O) mode[84] is always in the range 1200-1100 cm^{-1}].

The second difficulty concerns the assignment of the remaining bands of species I. If nitrogen has been cleaved, and bearing in mind that PtCO is not formed, then a C_5 fragment remains. (A mass spectrometric analysis of possible volatile desorption products revealed nothing - not even CO_2). The only conclusion is that some sort of cyclic C_5 unsaturated species remains, perhaps bonded to two or more surface Pt atoms. Such cyclic species are expected to have several ring deformation and in-plane CH stretching modes which would absorb in this spectral region. Beyond this, species I has not been identified.

Conclusions

Infrared spectral data have indicated that pyridine dissociatively chemisorbs on silica-supported platinum forming a Pt-C σ bond at the "2" position and a coordinate bond with the nitrogen atom such that the molecule lies perpendicular to the surface. In the presence of HCl this

is reversibly transformed into pyridinium chloride and with H_2 it is instantaneously hydrogenated to adsorbed piperidine. The latter does not appreciably desorb upon evacuation but dehydrogenates to reform chemisorbed pyridine. The same phenomenon occurs when piperidine is adsorbed on Pt/SiO_2 and confirms earlier speculation that adsorbed piperidine is mainly responsible for the poisoning of Pt during hydrogenation. On silica-supported nickel a different strongly adsorbed species is formed which has been identified as a simple nitrogen-coordinated pyridine which also lies perpendicular to the surface. As proposed by others, the coordination of pyridine on nickel can be promoted if the nickel had been pretreated with O_2 or CO.

When O_2 is added to chemisorbed pyridine on Pt two new adsorbed species are formed which have been tentatively identified as a (N=O) containing species of the type $PtNO_x$ ($x = 2,3$) or Pt_2NO, and a cyclic C_5 derivative of unknown structure. These species are also formed when pyridine is added to preoxidized Pt, but in addition, coordinated pyridine is formed.

"SUGGESTION FOR FURTHER RESEARCH"

The reaction between NO and CO on Ni/SiO_2 was studied in Chapter 5. The formation of a surface isocyanate species and $CO_2(g)$ during this reaction was believed to involve the dissociation of NO into adsorbed N and adsorbed O. The latter decomposition reaction has been observed to occur, at room temperature on Ni, by several authors[26,27,2].

A similar study is proposed for the reaction between nitrous oxide and carbon monoxide over Ni.

The adsorption of N_2O on Ni has not been studied but several studies[85-87] of the decomposition of N_2O on NiO have been reported. This reaction is believed to involve the following steps;

$$N_2O \text{ gas} \rightleftharpoons N_2O \text{ ads}$$

$$N_2O \text{ ads} \rightleftharpoons N_2(\text{gas}) + O \text{ ads}$$

The rate-determining step is assumed to be the desorption of the O_2(gas).

Winter[88] has studied the decomposition of NO over 40 metallic oxides and has proposed the following steps;

$$2NO(\text{gas}) \rightleftharpoons 2NO \text{ ads}$$

$$2 \text{ NO ads} \rightleftharpoons N_2(\text{gas}) + 2 \text{ O ads}$$

$$2 \text{ O ads} \rightleftharpoons O_2 \text{ gas}$$

The rate-determining step is assumed to be the dissociation of the adsorbed NO into adsorbed N and adsorbed O, with either or both atomic species remaining adsorbed until recombination to N_2 or O_2 occurs.

The decomposition of NO and of N_2O over NiO show a general similarity. Further, if N_2O decomposed on pure Ni by a mechanism similar

to that of NO on Ni, then the reaction between the decomposed N_2O and CO could be studied with infrared spectroscopy and the gas phase products could be monitored with a mass spectrometer. Such a study could help refine our understanding of the mechanism involved in the reaction of NO and CO on Ni.

BIBLIOGRAPHY

1. Blyholder, G., J. Chem. Phys. 36, 2036 (1962).

2. Blyholder, G. and Allen, Marvin C., J. Phys. Chem. 69, 3998 (1965).

3. Blyholder, G. and Allen, Marvin C., J. Phys. Chem. 70, 352(1966).

4. Sheets, R.W. and Blyholder G., J. Phys. Chem., 79, 1572(1975).

5. Flynn, Peter C. and Wanke, Sieghard E., J. Catal. 34, 390(1974).

6. Baddour, Raymond F., Modell, Michael, and Goldsmith, Robert L., J. Phys. Chem. 74, 1787 (1970).

7. Somorjai, G.A., Catalysis Reviews 7, 87 (1972).

8. Morrow, B.A., and Cody, I.A., J. Phys. Chem. 80, 1995 (1976).

9. Cody, I.A. PhD Thesis, University of Ottawa, Ottawa, Canada (1976).

10. Shelef, M. and Kummer, J.J., Chemical Engineering Symposium Series, No. 115, 67, (1971).

11. Klimisch, Richard L.,and Larson, John G., "The Catalytic Chemistry of Nitrogen Oxides" Plenum Press, New York-London, 1975.

12. Mason, Joan, J. Chem. Educ. 52, 7 (1975).

13. Lipscomb, W.N., Wang F.E., May, W.R., Lippert E.L., Acta Cryst. 14, 1101 (1961).

14. Guillory, W.A., and Hunter C.F., J. Chem. Phys. 50, 3516, (1969).

15. Hodgson, D.J. and Ibers, J.A., Inorg. Chem., 7, 2345, (1968).

16. Pratt C.S., Coyle, B.A., and Ibers, J.A., J. Chem. Soc., A, 2146 (1971).

17. Adams, Robert W., Chatt, Joseph, Hooper, Norman E., and Leigh, G. Jeffrey, J. Chem. Soc., Dalton, 1974 p. 1075.

18. Finn, Patricia and Jolly, William L., Inorg. Chem.II, 893 (1972).

19. Pierpont, Cortlandt G., Van Derveer, Donald G., Durland, William, and Eisenberg, Richard, J. Am. Chem. Soc., 92, 4760 (1970).

20. Epstein, Joel M., White, Allan H., Wild, S. Bruce, and Willis, Anthony C., J.C.S. Dalton 1974, p.436.

21. deMeester, P., Skapski, A.C., and Heffer, J.P., J.C.S. Chem. Comm., 1972, 1039.

22. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds", 2nd Edition, John Wiley and Sons Inc., New York, N.Y. 1970.

23. Hightower, J.W. and Van Leirsburg, D.A. "The Catalytic Chemistry of Nitrogen Oxides" p. 63, Plenum Press, New York-London 1975, Editors, Klimisch, Richard L., and Larson John G.

24. Voorhoeve, R.J.H. "The Catalytic Chemistry of Nitrogen Oxides" p.92, Plenum Press, New York-London 1975 Editors, Klimisch, Richard L., and Larson, John G.

25. Primet, M. Basset, J.M., Garbowski, E., Mathieu, M.V., J. Am. Chem. Soc., 97, 3655, (1975).

26. Conrad, J., Ertl G., Kuppers, J., and Latta, E.E.,Surf. Sci., 50, 296 (1975).

27. Batra, I.P. and Brundle, C.R., Surf. Sci., 57, 12 (1976).

28. Batychko, S.V., Rusov, M.T., and Roev, L. Doklady Akad. Nauk. S.S.S.R., 191, 328, (1970).

29. Lambert, R.M. and Comrie, C.M., Surf. Sci., 46, 61 (1974).

30. Shelef, M. and Otto, K., J. Catal. 29, 138 (1973).

31. Nijyama, Hiroo and Echigoya, Etsuro, J. Catal. 38, 238 (1975).

32. Blyholder, G., J. Phys. Chem. 68, 2772 (1964).

33. Yates, J.T., J. Phys. Chem. 68, 2777 (1964).

34. Terenin, A. and Roev, L., Spectrochim. Acta 11, 946, (1959).

35. Dunken. H. and Hobert, H., Z. Chem. 3, 398 (1963).

36. Arai, Hiromichi and Tominaga, Hiroo, J. Catal. 43, 131 (1976).

37. Ghorbel, Abdelhamid and Primet, Michel, J. Chim. Phys. 73, 89 (1976).

38. Brown, Mary F. and Gonzalez, Richard D., J. Catal. 44, 487 (1976).

39. Undland, Mark, L., Science 179, 567 (1973).

40. Undland, Mark L., J. Catal. 31, 459 (1973).

41. Undland, Mark L., J. Phys. Chem. 77, 1952 (1973).

42. Niiyama, Hiroo, Tanaka, Motoo, Iida, Hiroshi, and Echigoya, Etsuro, Bull. Chem. Soc. Japan 49, 2047 (1976).

43. London, J.W. and Bell, A.T., J. Catal. 31, 96 (1973).

44. Morrow, B.A. and Lee, Lydia SM unpublished results

45. Parkyns, N.D., Proceedings of Vth Int. Cong. Catalysis, Palm-Beach, 1972, North Holland Ed. Vol I p. 255.

46. Griffiths, D.W.L., Hallam, H.E., and Thomas, W.J., Trans. Faraday Soc. 64, 3361 (1968).

47. Eischens, R.P., Francis, S.A., and Pliskin, W.A., J. Phys.Chem. 60, 194 (1956).

48. Blyholder, G. Proceedings of the Third International Congress on Catalysis, North-Holland, Amsterdam, 1965, p. 657.

49. Müller-Litz, Von W. and Hobert, H., Z. Phys.Chem., 236, 84 (1967).

50. Pliskin, W.A., and Eischens, R.P., Z. Phys. Chem. (Frankfurt) N.F.24, 11 (1960).

51. Morrow, B.A., and Cody, I.A., J. Catal. 45, 151 (1976).

52. Morrow, B.A., and Cody, I.A., J.C.S. Faraday I, 71, 1021 (1975).

53. Eischens, R.P., and Pliskin, W.A., "Advances in Catalysis" Vol. IX, p. 662, Academic Press Inc., New York (1957).

54. Neff, L.D. and Sturdivant, A.E., Chem. Comm. 918 (1976).

55. Yates, J.T. J. Phys. Chem., 68, 1245 (1964).

56. Shobaky, G. El., Gravelle, P.C., and Teichner, S.J., J. Catal. 14, 4-22 (1969).

57. Blyholder, G. and Sheets, R.W., J. Catal. 27, 301 (1972).

58. Gatehouse, Bryan M., Livingstone, Stanley E., and Nyholm, Ronald S., Coordination Chemistry Reviews 8, 75 (1958).

59. Parry, E.P., J. Catal. 2, 371 (1963).

60. Basila, M.R., Kantner, T.R., and Rhee, K.H., J. Phys. Chem., 68, 3197 (1964).

61. Sheets, R.W., and Hansen, R.S., J. Phys. Chem. 76, 972(1972).

62. Primet, M., Basset, J.M., Mathieu, M.V., and Prettre, M. J.Catal. 29 213 (273).

63. Kageyama, Yoshiteru, Yotsuyanagis, Takao, and Aomura, Kazuo, J.Catal. 36, 1 (1975).

64. Kishi, K., and Ikeda, S., J. Phys.Chem. 73, 2559 (1969).

65. Gland, J.L., and Somorjai, G.A., Surf. Sci. 38, 157 (1973).

66. Gland, J.L., and Somorjai, G.A., Adv. Coll. Interface Sci. 5, 203 (1976).

67. Calf, G.E., Garnett, J.L., and Pickles, V.A., Aust. J. Chem. 21, 961 (1968).

68. Calf, G.E., and Garnett, J.L., Aust. J. Chem., 21, 1221 (1968).

69. Moyes, R.B., and Wells, P.B., J. Catal. 21, 86 (1971).

70. Macdonald, C.G., and Shannon, J.S. Tetrahedron Lett., 3351 (1964).

71. Gill, N.S., Nutall, R.H., Scaife, D.E., and Sharp, D.W.A., J. Inorg. Nucl. Chem. 18, 19 (1961).

72. Durig, J.R., Mitchell, B.R., Sink, D.W., Willis, J.N., and Wilson, A.S., Spetrochim. Acta 23A, 1121 (1967).

73. Avery, N.R., J. Catal. 19, 15 (1970).

74. Morrow, B.A., and Sheppard, N., Proc. Roy. Soc. London Ser. A 311, 391, 415 (1969).

75. Badger, G.M., and Sasse, H.F., Adv. Heterocyclic Chem. 2, 179 (1963).

76. Freifelder, M., Adv. Catal. 14, 203 (1963).

77. Bond, G.C., "Catalysis by Metals," p. 297, Academic Press, New York (1962).

78. Green, J.H.S., Kynaston, W., and Paisley, M.H., Spectrochim. Acta 19, 549 (1963).

79. Somorjai, G.A., and Blakeley, D.W., Nature (London) 258, 580 (1975).

80. Morrow, B.A. and Ramamurphy, P., Can.J. Chem. 49, 3409 (1971).

81. Somorjai, G.A. (Private Communication).

82. Cenini, S., Ugo, R., LaMonica, G., and Robinson, S.D. Inorg. Chim. Acta. 6, 182 (1972).

83. Ross, S.D., "Inorganic Infrared and Raman Spectra" McGraw-Hill Book Company (U.K.) Limited 1972.

84. Colthup, N.B., Daly, L.H., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York and London 1964.

85. Winter, E.R.S. J. Catal. 15, 144 (1969).

86. Winter, E.R.S., J. Catal. 19, 32 (1970).

87. Gay, Ian D., J. Catal. 17, 245 (1970).

88. Winter, E.R.S., J. Catal. 22, 158 (1971).