

THE UNIVERSITY OF CALGARY

AN FTIR STUDY OF THE DIMERIZATION
AND POLYMERIZATION OF ETHENE ON PALLADIUM-LOADED
Y ZEOLITES

by

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ABSTRACT

The use of metal-loaded zeolites as bifunctional catalysts in the petrochemical industry has increased lately. Polymerization of ethene on Pd-loaded zeolites was studied in this work on acidic (HY) and non-acidic (NaY) zeolite supports using Fourier Transform Infrared Spectroscopy (FTIR). Fluorine was also successfully incorporated on these supports with a view to improving the acidic properties of the support.

Fourier Transform Infrared Spectroscopy (FTIR) of the catalyst surface, and of carbon monoxide and adsorbed pyridine on the surface were used to characterize the catalysts used in this study.

Infrared spectra of adsorbed carbon monoxide were used to identify the location of the loaded metal on the support and it was found that Pd was more accessible on the HY support than on the NaY support. It was also shown that the presence of the fluoride did not affect the location of the Pd on the support.

Infrared spectra of pyridine were used to identify the types and number of acid sites on the supports and the metal-loaded supports. NaY was observed to have no Bronsted or Lewis sites which shows that it is not cation deficient. HY has stronger Lewis sites than Bronsted sites. The loading of Pd on NaY was found to create Bronsted and Lewis sites and the treatment of the PdNaY sample in H_2 at 300°C created more Bronsted sites. Although Pd loaded on HY created more Bronsted sites, it was observed that dehydroxylation occurred to a large extent on this catalyst during calcination. Reduction of the PdHY sample was accompanied by a drastic reduction in Bronsted sites from dehydroxylation.

Ethene did not react on the NaY support whereas it polymerized to a very small extent on the HY support to give branched chain hydrocarbons. Ethene dimerized on PdNaY to give a mixture of the butenes (cis-2-, trans-2- and 1-butene) but polymerization was not observed. The rate of dimerization was not fast. It was

proposed that trans-2-butene is the first dimer formed in the reaction.

Ethene was found to form dimers and branched chain polymers on the PdHY sample. The rate of dimerization was very fast which confirms the easy accessibility of the Pd on the HY support compared to the NaY support. It was also identified that polymerization of ethene occurs on Lewis sites of the support while dimerization occurs on the Pd²⁺ cation.

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CHAPTER ONE

1. INTRODUCTION

1.1 OVERVIEW

The catalytic properties of naturally occurring zeolite minerals were discovered in the 1950's (1), and the interest in these compounds has increased since then. In fact, as the ability to synthesize zeolites with desirable properties has developed, both the interest and the number of applications have increased. Zeolites are used in about 90% of refineries for catalytic cracking and they are also used in hydroisomerization, selective reforming and as supports for metals in catalytic reactions. The thermal and structural stability and the very high surface area of zeolites makes them very useful as supports for metals in catalysis. Zeolites are also used as molecular sieves. The presence of apertures and cavities of different shapes and sizes in different kinds of zeolite allows the separation of molecules according to their size. This size restriction separates molecules, since big molecules will not be able to penetrate small cavities in the zeolite. An example of the use of this sieve property is found in the oil industry where the linear hydrocarbons are separated from the branched chain hydrocarbons.

It is also known that the loading of metal cations on zeolites gives them bifunctional activity. The presence of these metal cations on non-acidic zeolites creates Bronsted acid sites by cation hydrolysis (see section 4.1) and these metal cations have also been known to increase the Bronsted acid strength of acidic zeolites by polarizing the OH groups on them (1).

It has been known for quite a while that the efficiency of metal catalysts is

dramatically improved by increasing the metal dispersion. Metal catalyzed processes are becoming so important in petroleum industries that a lot of effort is spent on research on ways to develop highly dispersed metals (1).

Much work has been reported on acidic (H^+ -exchanged) zeolites and on metal-loaded non-acidic zeolites but much less work has been reported on metal-loaded acidic zeolites. In this thesis, an attempt will be made to use infrared spectroscopy to characterize such catalysts, in particular, Pd-loaded HY zeolites (see later), and to investigate the interaction between the metal and the support.

In this introductory chapter, a brief description of the structure and catalytic properties of zeolites will be given and the advantages of zeolites as support will be discussed; in addition, the topics to be presented in the different chapters of this thesis will be outlined.

1.2 ZEOLITES.

1.2(a) STRUCTURE

Zeolites are crystalline aluminosilicates with a framework structure consisting of cavities occupied by large ions and water molecules, all of which have enormous freedom of movement, permitting ion exchange and reversible dehydration. Zeolites have an extremely stable structure and catalytically active components can be introduced into their structure by ion exchange; all these properties have increased the use of zeolites in industrial applications.

The framework of zeolites consists of corner-linked tetrahedra with small atoms (denoted T atoms) which are at the centers of the tetrahedra with oxygen atoms at the corners of the tetrahedra. Natural zeolites mostly contain Al and/or Si in their T sites,

but synthetic zeolites can have Ga, Ge and P incorporated into their T sites. Charge-balancing metal ions can also be incorporated into the zeolite cavity; the ions could be monovalent or divalent or even trivalent, although the latter is unusual.

The ideal general formula for zeolites is usually given as $M_pD_q[Al_{p+2q}Si_rO_{2p+2q+2r}].sH_2O$ (1). The corner sharing of tetrahedra requires that the number of framework oxygen be twice that of the T atoms and charge balance requires that the sum of p (monovalent ions) and twice q (divalent ions) should equal the number of trivalent Al atoms in the framework.

M and D represent monovalent and divalent cations in the zeolite, respectively, while s indicates the number of H_2O molecules and r the number of silicon atoms in the zeolite. For a zeolite framework, linked tetrahedra are represented diagrammatically by lines joining the centers of adjacent tetrahedra, hence the zeolite framework can be represented by a three-dimensional network. The oxygen atoms lie near the center of each line. Fig.1.1 shows the building units (formed from the connected tetrahedra) that can be used to form different zeolites with varying pore sizes and shapes.

The exchangeable cations present in zeolites are usually located at well defined sites in the various cavities and channels within the structure, and the water molecules fill up the remaining space. Water can be expelled by heating and evacuation and it may be replaced by a number of small inorganic and organic molecules. The shape selectivity and molecular sieve property of a zeolite can be adjusted by the choice of the valency and size of the exchangeable cation. Also, the porosity of a zeolite can be enhanced by increasing the Si/Al ratio by a process called dealumination (2).

The presence of hydroxyl groups and tricoordinated aluminium atoms on the zeolite makes them acidic compounds. This acidic property makes them very important catalysts in industry, as mentioned earlier.

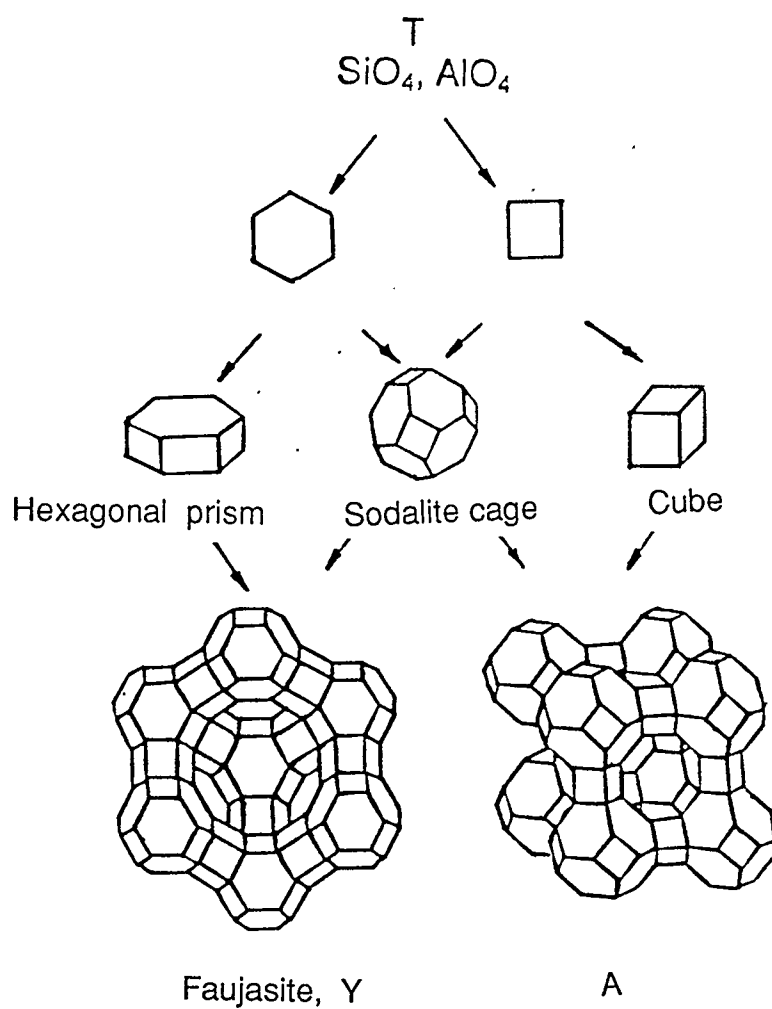


Fig. 1.1 Illustration of the assembly of building blocks to form faujasite-type zeolite and zeolite A.

1.2(b) FAUJASITE-TYPE ZEOLITES

Faujasite is a naturally occurring zeolite while zeolites X and Y are synthetic zeolites with similar aluminosilicate framework structures to that of faujasite. The zeolite Y is used more in industry catalytically than either X or faujasite. Zeolite X is less acidic and less thermally stable than zeolite Y. The unit cells are cubic with a cell dimension of about 25 Å and contain 192 Si and/or Al tetrahedra. The stable and rigid framework structure of faujasite-type zeolites has the largest void space of any zeolite known and this amounts to about 50% in volume of the dehydrated crystal (1). The capacity of the zeolite for adsorption is usually related to the free space or void volume available.

Zeolites X and Y are distinguished on the basis of chemical composition, structure and their related physical and chemical properties (3). Differences are found in cation composition and distribution, the Si/Al ratio and possible Si-Al ordering in tetrahedral sites. The Si/Al ratio is 1 to 1.5 for zeolite X and 1.5 to 3 for zeolite Y.

Zeolite X and Y (and faujasite) consist of linked cubooctahedra called β cages or sodalite units (fig. 1.1). They have a central cage of diameter 0.65 nm which is accessible through "six-rings", which are rings of alternating T and O atoms containing six Si or Al atoms; the rings have a diameter of 0.22 nm. The sodalite units are connected with bridging oxygen atoms along the six-rings. The sodalite units linked along two six-rings give rise to a cage called hexagonal prism (Fig. 1.1). The sodalite units and hexagonal prisms can be arranged to give a structure which encloses a supercage (α -cage) with an internal diameter of 1.25 nm which is accessible through four twelve-rings with an aperture of 0.75 nm (Fig. 1.2).

In zeolites X and Y, the extra-framework cations occupy sites S(I), S(I'), S(II) and S(II') sites. These are shown in fig 1.2. X-ray studies (1) have revealed two types of cationic sites; in the S(II) sites, on the internal zeolitic surface, divalent cations have only

threefold coordination with the oxygen ions; whereas in S(I) sites, between six-rings, they have sixfold coordination to the oxygen ions. It can be seen that cations with higher coordination numbers usually occupy S(I) sites and that adjacent S(I) and S(I') sites are not simultaneously occupied by cations, and also that S(II) sites which are situated on the walls of the supercages tend to be occupied.

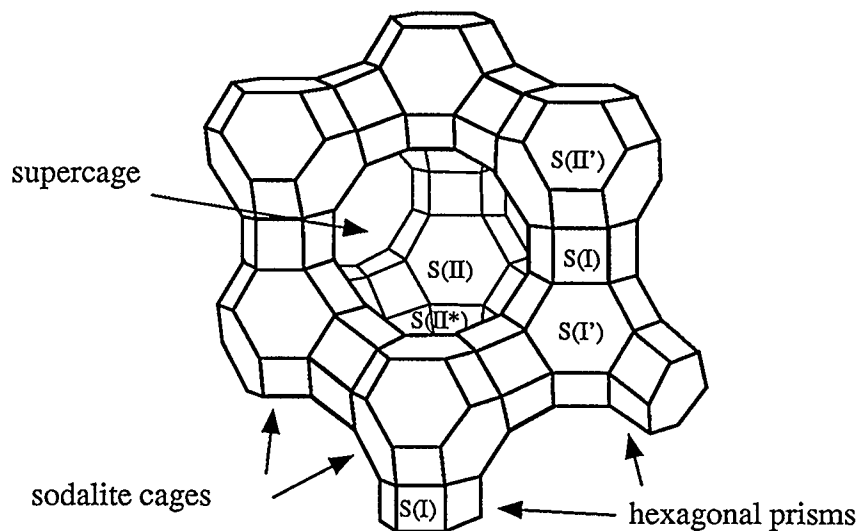


Fig. 1.2 Cationic sites of zeolite Y

Site S(I) is the center of the hexagonal prism while S(I') is a site displaced from S(I) into the sodalite cage. S(II) is the center of the six-ring window between the sodalite cage and the supercage, and S(II') and S(II*) correspond to displacement from site S(II) into the sodalite cage and into the supercage cage, respectively, along an axis perpendicular to the to the six-ring window.

1.3 CATALYTIC APPLICATIONS

Zeolites are very important catalytic materials for two reasons. Firstly, they have intrinsic catalytic activity because of their acidic nature. Secondly, they are very useful as supports and molecular sieves.

1.3(a) ACIDIC NATURE

Zeolites are very important catalysts because they can develop high acidity in their H^+ -exchanged forms. There are two kinds of acidity on a zeolite :

- 1) Lewis acid sites (electron acceptor)
- 2) Bronsted acid sites (proton donor)

Lewis acid sites result from coordinatively unsaturated trivalent aluminium atoms in the zeolite structure. Bronsted acid sites can be formed either from acidic protons in the zeolitic framework or from the hydrolysis of water coordinated to cations in the zeolite matrix.

Some acid-catalyzed reactions occurring on zeolites include isomerization of alkenes and cycloalkanes, olefin hydration, alcohol dehydration, alkylation reactions, ring transformation of heterocycles, polymerization and catalytic cracking. All the above mentioned acid catalyzed reactions occur through a carbonium ion intermediate. Zeolites also contain basic sites, but these are not catalytically important in industry (4).

Acidity of a zeolite is also enhanced by polarization of the framework caused by cations, which is proportional to the charge/radius ratio for the cation (5), and by any increase in the framework Si/Al ratio. For example, zeolite X has a lower Si/Al ratio than zeolite Y and it is known to have lower acidity, this might appear as a contradiction since acid sites are usually associated with the presence of aluminium atoms. However, if a zeolite has a lower Si/Al ratio, the density of the AlO_4^- groups will be higher, and this means that the charge-balancing cations will be able to effectively balance the

charges on the AlO_4^- groups. This means the cations will have less tendency to undergo cation hydrolysis during dehydration since the "naked" cation can still effectively balance the charges as the solvated cation. For a particular zeolite, polyvalent cation forms of this zeolite will be more acidic than the monovalent cation form since cation hydrolysis will be favoured on the former.

Interactions between zeolites and adsorbed species are enhanced because of the charged nature of the framework and the presence of cations which generate electrostatic fields. These fields are higher in zeolites having a high concentration of aluminium, which corresponds to a high cation content. The AlO_4^- units may not be adjacent to each other (Lowenstein's rule (6)). Also, they may not be equally close to the charge-balancing cation; e.g. a charge balancing trivalent cation might not be located at the same distance from the three AlO_4^- units and this consequent charge separation would result in a high field gradient.

Calculations indicate that the magnitude of the electrostatic field surrounding the divalent cation in S(II) sites is more than adequate to cause substantial electronic shifts of the bonding electrons in adsorbed molecules (7).

As the Si:Al ratio increases, cation density and electrostatic field strengths decrease and the affinity of the zeolite surface for non-polar sorbates increases (as compared to polar sorbates). Aluminium rich zeolites sorb water in preference to hydrocarbons; the converse is true for silica rich zeolites (2,8).

The monovalent-metal cationic forms of the type X and type Y zeolites tend to promote radical type reaction intermediates. Exchange of the monovalent for multivalent cations gives rise to carbonium-ion type activity which increases with increasing silica-alumina ratio and with the extent of multivalent cation exchange (9). Carbonium ion activity is also imparted to the zeolites by decationization.

1.3(b) ZEOLITES AS SUPPORTS

Apart from the acidic properties of zeolites, they can also be used as supports for metals. Metal catalysts are used in hydrogenation and dehydrogenation, isomerization, cyclization and similar reactions. It has long been recognised that the efficiency of a metal catalyst is improved by increasing the metal dispersion. Also, the pore size of the zeolite makes the metal-loaded zeolite a shape selective catalyst for the metal-catalysed reaction, depending on the location of the metal on the zeolite.

Highly dispersed metal particles on a suitable support have obvious practical advantages, e.g. ease of handling, suitability for use in fixed or fluidized bed flow reactors, and high thermal stability (10).

The most common method used to get highly dispersed metal particles is the dispersion of the active metal on a high surface area support like zeolites, silica and alumina. Catalytically active metals can be dispersed within the zeolite pores by ion-exchange with heavy-metal cations. Evidence indicates that metals introduced by this process, followed by reduction to the elemental form can be atomically dispersed. In this state they may show an unusually high activity and resistance to poisons in reactant streams. Traditional thinking regarding this type of catalyst was that the effect of the support was just to stabilize the metal as small metal particles, thereby producing a large increase in the ratio of surface metal atoms to bulk metal atoms, without changing the specificity of the catalyst (10). This mode of thinking has been changed since it could not explain much of the experimental data.

It became apparent that the rate and selectivity of several chemical reactions were controlled by the size of the metal particles formed on the support. The explanation given for this observation was that the properties of the surface metal atoms are changed when the metal particle size decreases, because the number of edge and/or corner atoms (which have a different coordination number from those in the bulk) are increasing.

Evidence supporting the importance of these structural effects of supports on catalysis exists. For example, the support can preferentially influence the growing of a particular crystallographic plane or it can have an electronic effect, i.e. the support can induce charge transfer (10).

The complete modification of the catalytic properties of metals by zeolites can be a result of any of these three possible processes:

i)The possibility of a strong interaction between the carrier and metal leading even to charge transfer between the carrier and metals.

ii)The possibility of geometric effects. It is known that varying particle size can influence the overall reaction observed (11).

iii)The possibility exists for stabilizing the metal in different oxidation states on the zeolite and this can decide which reaction will be favoured.

Recently, it was discovered that in special experimental conditions, supports like zeolites can completely modify the catalytic properties of the metals. This has made it obvious that no completely unifying theory can explain the metal support interaction since one or combinations of the above factors can affect the catalytic properties of the metals on the support.

From theoretical studies (12,13), it was concluded that the ionisation potential and electron affinity are higher for small particles than for bulk metals and they converge to the value of the work function for particles bigger than about 200 atoms. Based on these theoretical studies, it can be seen why zeolites can completely modify the catalytic properties of metals since it is possible to have on a zeolite surface, isolated single metal atoms and metal particle dispersion of varying sizes (14). Different particle sizes could be active for different reactions.

The temperature treatment of a metal-loaded zeolite with reducing or oxidizing agents can stabilize the metals in various oxidation states which can be active for

different reactions.

1.4 PURPOSE OF THIS THESIS

The purpose of the work carried out for this thesis has been to attempt to understand how the acidic and /or basic properties of a particular zeolite, used as a support for a metal catalyst, affect the interaction between the metal and support. The system chosen for study is palladium supported on a zeolite Y support.

The hydrogen-exchanged form of zeolite Y (HY) which is a highly acidic material has been studied extensively with various acid-catalyzed reactions; its large pore size, three-dimensional pore structure and very large void volume (see earlier) make it an extremely active catalyst for a wide range of reactions. The "rare-earth" exchanged form of this zeolite is used in industrial catalytic cracking.

Zeolite Y in its non-acidic form (NaY) is an effective support for transition metals which catalyze hydrogenation, dehydrogenation and isomerization among others. Pd-loaded NaY is a very effective catalyst for one of the simplest reactions, ethene dimerization to butenes, which has been studied quite extensively (15,16,17,18). Recent work done using ESR have identified Pd(I) as the active site for ethene dimerization (15,16) and a mechanism has been proposed. An induction period has also been observed for this reaction and various reasons have been put forward (15,16,19,20). Bai (15) using ESR has proposed that the induction period is a result of the formation of the active $\text{Pd}^+-(\text{C}_2\text{H}_4)_2$ from the Pd^{2+} while others (16,19,20) attribute it to the migration of the Pd cation from inaccessible sites to the accessible supercages where they form the active intermediate species with ethene.

There has been no report in the literature for the study of this reaction on Pd supported on acidic Y zeolite (HY). An attempt will be made to understand the interaction between the metal and the support and, in particular, how the acidity affects

the interaction. IR spectroscopy will be used to characterize the support, i.e. oxidation state of cation, catalyst acidity etc., after various catalyst pretreatments. Also, IR will be used to study the reaction of interest to see if it is possible to confirm the reaction mechanism and to identify the processes involved in the induction period.

The infrared spectra of carbon monoxide will be used to study the oxidation state and position of the metal in the zeolite after treatment at different temperatures in both oxidizing and reducing environments. Pyridine adsorption, also studied by infrared, will be used to measure the acidity of the support and to determine whether this is changed either by the addition of Pd or by the treatment with fluoride ions, which are known to affect the acidity of the zeolite. Finally, the reaction of ethene on these catalyst surfaces will be studied. Although this reaction has often been investigated in the past, recent ESR studies have suggested a mechanism for ethene dimerization over non-acidic Pd-loaded zeolites. In this work, an attempt will be made to use infrared studies to confirm this mechanism and also to see how changes in the surface acidity affect the ethene reactions.

1.5 ORGANISATION OF THESIS

A brief layout of the thesis will be presented below to give an idea of the studies done in this work.

CHAPTER TWO	EXPERIMENTAL METHODS
CHAPTER THREE	CO STUDY OF Pd OXIDATION STATES
CHAPTER FOUR	HYDROXYL GROUP STUDY OF SURFACE ACIDITY
CHAPTER FIVE	PYRIDINE STUDY OF SURFACE ACIDITY
CHAPTER SIX	ETHENE REACTION OVER Pd-LOADED Y ZEOLITES

Because chapters three to six deal with different procedures, an "introduction" section will be included in each chapter, rather than try to discuss all the introductory material in one chapter.

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CHAPTER TWO

2. EXPERIMENTAL METHOD

In this chapter, the method used in studying ethene dimerization and polymerization will be described and the various methods used in characterizing the metal-loaded zeolite catalysts will be discussed.

2.1 REAGENT AND ZEOLITE SOURCES

The ammonium form of zeolite Y, NH_4Y (LZY-62) and the sodium form, NaY (LZY-52) were obtained in powder form from Union Carbide Corp. Tetraamminepalladium(II) dichloride (reagent grade) was obtained from Aldrich Chemical Co. Ltd. Carbon monoxide and 1-butene were obtained from Matheson (Canada) and cis-2- and trans-2-butene were obtained from Aldrich Chemical Co. Ltd. Ethene was obtained from Linde (Union Carbide) and sodium fluoride, sodium hydroxide, hydrochloric acid (reagent grade) and pyridine were obtained from Fisher Scientific Company. Sodium tartrate and tris(hydroxymethyl)aminomethane (reagent grade) were obtained from BDH Chemicals.

2.2 CATALYST PREPARATION

2.2.1 ION-EXCHANGE AND CALCINATION

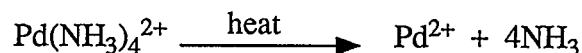
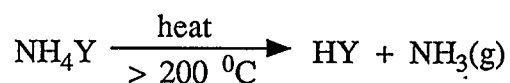
The Pd-loaded forms of NH_4Y and NaY zeolites were obtained in our laboratory by ion-exchange using palladium tetraammine chloride, $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$.

5 g of Y zeolite support was refluxed with 100 ml of ion-exchange solution at room temperature overnight. Salt solutions of 1×10^{-4} , 1×10^{-3} and 1×10^{-2} M concentration were used for the ion-exchange.

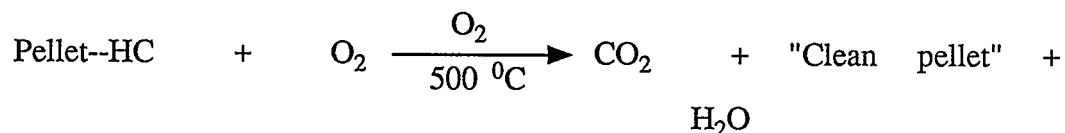
For example, the Pd-loaded NaY sample was prepared by refluxing 100 ml of 1×10^{-2} M of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ at 25°C on 5 g of NaY overnight. The ion-exchanged catalyst was then filtered and left to dry at room temperature or in the oven at 100°C . The prepared catalyst was then pressed into pellets using an applied load of 1000 to 2500 Kg on 20 to 25 mg of sample powder for about 5 - 30 mins. The pellets were 13 mm in diameter.

A basic "cleaning" treatment given to the pellets used in this work involves the removal of all organic adsorbates from the pellets. The sample pellet is put into the sample holder and then loaded into the IR cell (described below). The cell is evacuated to about 10^{-5} mmHg and the pellet was slowly heated from room temperature to 100°C at a rate of $2^\circ\text{C}/\text{min}$. using a temperature controller (1). This temperature was maintained for 30 - 60 mins. This gradual heating will prevent the collapse of the zeolitic framework caused by rapid desorption of H_2O .

The temperature is then raised at a rate of $3^\circ\text{C}/\text{min}$ to 500°C . This treatment will convert the NH_4^- form of the zeolite to the H- form of the zeolite with loss of NH_3 (2). The treatment will also strip the tetraammine palladium cation (loaded on the zeolite) of the ammonia ligand and leave the bare Pd^{2+} cation in the zeolite (see below).



Then about 350 mmHg of O_2 is admitted into the cell at 500°C and this is left overnight. This treatment should clean the surface of organic hydrocarbon adsorbates (HC) adsorbed on the pellet (see below).



The cell is then evacuated at 500°C for 30 mins until a pressure of 10^{-5} mmHg

is reached; then the sample is cooled to room temperature and it is ready for use in the catalytic reaction. A sample pretreated in this way is called a "fresh" sample. A "used" sample will be a sample that has been pretreated as above having been previously used in a catalytic study.

2.2.2 REDUCTION OF LOADED Pd CATION

The calcination done above will leave the loaded cations in their high oxidation states (Pd^{2+} , Pd^{3+}), and the subsequent reduction will leave the cations as Pd^+ and Pd^0 . After the calcination in O_2 and evacuation at 500°C for 30 mins, the sample is then cooled to the appropriate temperature to be used for reduction (300 or 500°C). About 350 mmHg of H_2 is then admitted into the cell and it is left at this temperature for 1 hour (or as required). The cell is then evacuated at this temperature for 30 mins. and subsequently cooled to room temperature.

2.2.3 ZEOLITE FLUORIDATION AND ANALYSIS

Fluoridation involves refluxing 5 g of the HY and NaY zeolite support at room temperature with 100 ml of a 0.1 M fluoride solution for 24 hours. For HY, the fluoride solution was prepared using NH_4F salt while for NaY zeolite, the solution was made from an NaF salt. The fluoridated sample is then filtered and dried at room temperature; the sample is then put in a glass container, heated in a furnace for 30 mins at 100°C and then at 450°C overnight. The fluoride sample treated above can then be used for ion-exchange to load Pd on the zeolite support.

Fluoride analysis to measure the amount of fluoride on the catalyst is done after the ion-exchange with Pd has been completed. This can be done by using a fluoride electrode (Orion fluoride electrode, model 96-09-00). The electrode is calibrated before use with different concentrations of NaF solution and a calibration curve is obtained.

About 0.1 g of the fluoridated sample is initially digested in 10 ml of 0.1M NaOH solution overnight, the solution is decanted and about 10 ml of ionic buffer Tisab IV, prepared according to the procedure in reference (3), is added to the solution. Tisab IV is also added to the standard solutions of NaF used in the calibration (10 mL NaF/10 mL Tisab IV).

Tisab IV is a solution that contains HCl, sodium tartrate and Tris(hydroxymethyl)aminomethane; this solution will prevent interference from other ions in the solution and it also maintains a constant pH. The electrode is dipped into the solution and the potential measured is then used to determine the concentration of the fluoride in the catalyst from the calibration curve. The solution is stirred during the measurement.

2.3 GLASS INFRARED CELL

The cell (shown in fig. 2.1) is designed such that the samples can be thermally treated and the gas phase and the pellet surface reaction of ethene polymerization can be monitored.

Half of the cell was made of quartz glass which is resistant to high temperatures and the other half of the cell is made of pyrex glass. Both halves are joined together during use by a clamp at the O-ring joint (grease free). BaF₂ windows are used and the cell has a glass connector which can be attached to a vacuum line. This allows the cell evacuation and admittance of gases into the cell.

For a typical catalytic reaction, two pellet wafers (20-25 mg) are put into the sample holders which are then mounted on a stainless steel rod such that the pellet can slide to the quartz section for temperature treatment using a furnace or to the pyrex section with the BaF₂ windows for infrared studies.

Some pellets (about 50 mg) are also put into a glass "boat" which is left at the

quartz section of the cell. These additional pellets increases the gas phase product and hence increased infrared absorption.

The diffusion of gases to the catalyst surface in this cell could be a problem, but because there are such large differences in rate of reaction between the HY and the NaY samples, the effect of diffusion on catalytic rate will be minimal and so the cell can be used for our catalytic study.

The glass cell can also be used for studying ethene reactions at high temperatures by sliding the sample holder between the quartz half of the cell (for heating at the appropriate temperature) and the Pyrex glass half (for spectral measurement). The need to slide the pellet back and forth between the heating section and the infrared section of the glass cell prevents *in-situ* study of the high-temperature ethene polymerization.

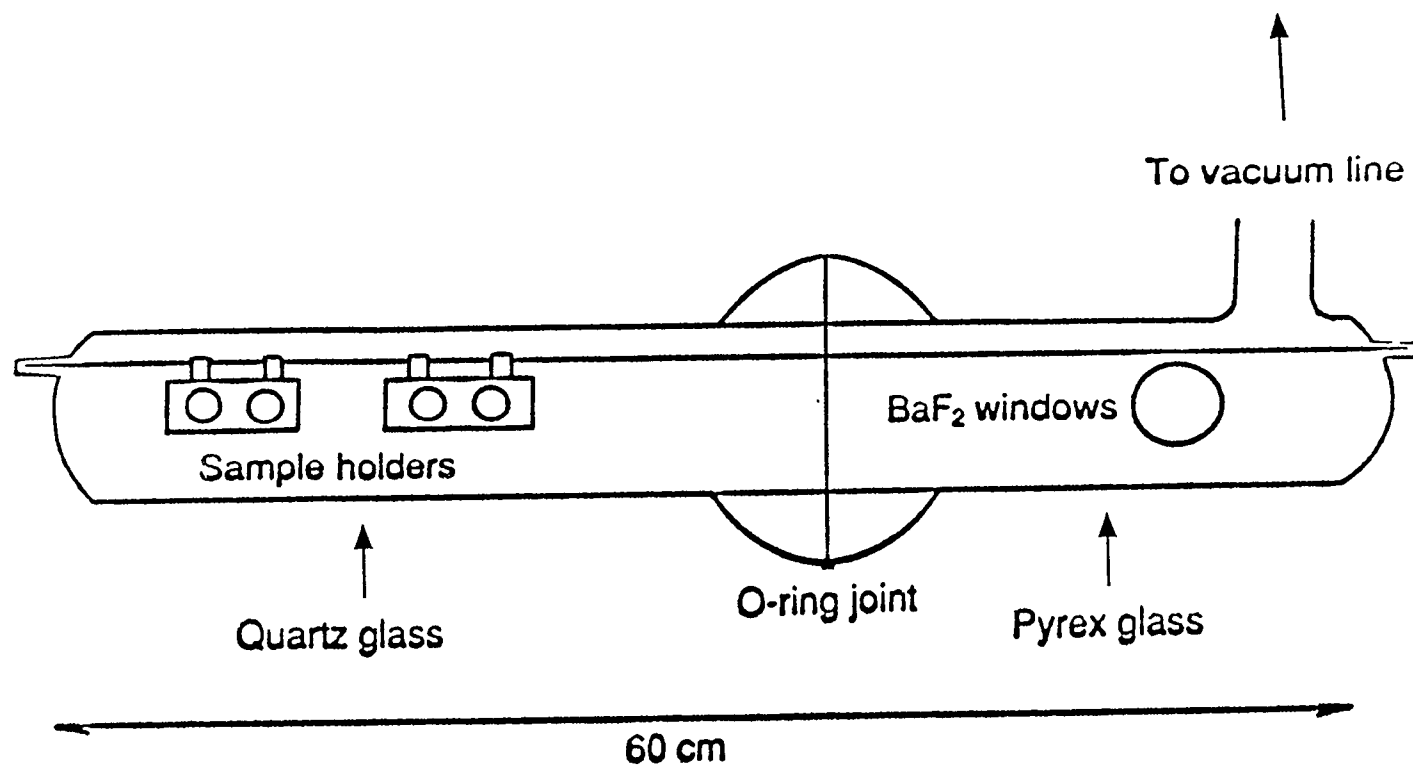


Fig. 2.1 Diagram of the glass IR cell.

2.4 CHARACTERIZATION OF CATALYST

Apart from using these catalysts for ethene reactions, it was also important to try and characterize the surface of these catalysts. The valency and location of the loaded palladium cation after various pretreatment conditions can be identified by using CO as discussed in Chapter Three; the effect of various pretreatment conditions on the Bronsted and Lewis acid sites will be identified by using pyridine adsorption on the catalyst surface as discussed in Chapter Five.

2.4.1 USE OF CARBON MONOXIDE

After the initial cleaning treatment with O₂ on the catalysts in the glass cell (and subsequent reduction in hydrogen if reduced catalysts are being studied), the catalyst is evacuated until a pressure of 10⁻⁵ mmHg is attained; then about 20 - 40 mmHg of CO is admitted into the cell at room temperature. About four different catalysts can be studied at the same time. The infrared spectra of the catalysts (with the CO gas still present in the cell) is then taken, the gas is then evacuated from the cell and the infrared spectra of the pellet surface (with adsorbed CO) is then taken at room temperature. Evacuation of the pellet surface is done at progressively higher temperatures (50, 100, 150 and 200°C) and infrared spectra are taken when the catalysts cool to room temperature after each high-temperature desorption. The spectral region in the range 2350 - 1660 cm⁻¹ is usually studied.

2.4.2 USE OF PYRIDINE

After the various pretreatment procedures done on the zeolite supports such as calcination, ion-exchange, fluoridation and reduction, pyridine is used to determine the effect of all these on the Bronsted and Lewis acid sites.

Characteristic bands appear in the infrared spectra after pyridine adsorption on

the pellets, depending on the type of site pyridine is adsorbed on; more will be said about this in Chapter Five.

After the pretreatment of the catalyst in the glass cell, pyridine vapour is adsorbed on the catalyst surface at 100°C for 30 seconds, then the cell is evacuated at this temperature for 1 hour to prevent spectral interference from the large amount of physisorbed pyridine. The sample is then cooled to room temperature and the spectrum of the catalyst surface is taken; up to four catalyst pellets can be put in the cell at the same time. The desorption for 1 hour is then repeated at successively higher temperatures (100, 200, 300, 400 and 500°C) and the surface spectra are taken after each desorption.

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CHAPTER THREE

3. CARBON MONOXIDE STUDY

3.1 INTRODUCTION

CO is usually used to study the surfaces of catalysts loaded with metals (1). It has a diameter of 3.5 Å and the IR absorption bands associated with the CO bond-stretching vibrational modes are very strong since CO has a very large extinction coefficient.

In the figure below, the bonding involved in the chemisorption of CO to metals is shown :

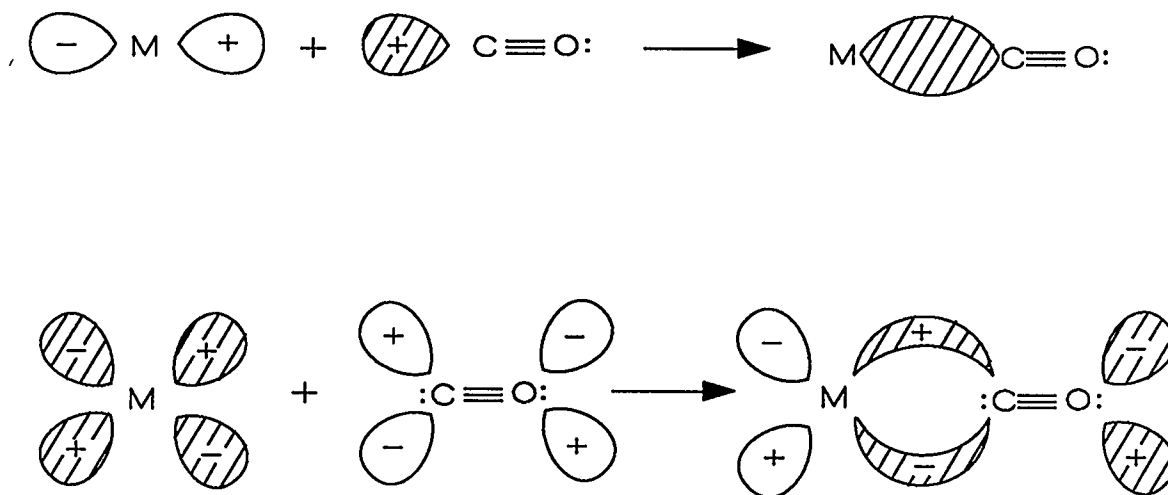


Fig. 3.1 Bonding of carbon monoxide to metals

a) The 3σ molecular orbital containing the lone pair of electrons overlaps an empty metal orbital to give a σ bond.

b) Back-donation of electrons from a filled metal $d\pi$ -orbital into a vacant CO π^*

antibonding orbital gives a metal-carbon π bond.

The back-donation decreases the force constant of the CO bond since the donated electron enters an antibonding orbital of the CO, resulting in a lowering of the CO stretching frequency in comparison to that of the CO(g) band at 2143 cm^{-1} . So the higher the back-donation, the lower the observed frequency for CO stretch (2). Hence the frequency of $\text{Pd}^{2+}\text{---CO}$ is greater than the frequency of $\text{Pd}^+\text{---CO}$ due to differences in back-donation.

Eischens et al. (3a) in their study have grouped the adsorption modes of CO into two types :

- i) Linearly (terminal) adsorbed CO (L_1)
- ii) Bridged CO (B_2) - which adsorbs on two equivalent metals.



Fig. 3.2 Bonding species of carbon monoxide

In B_2 , the M---C bonds were formed by the contribution of electrons from both the adsorbent and adsorbate. In L_1 , both bonding electrons of the M---C bond come from the CO.

Eischens and Pliskin (3b) attributed any CO band between the region $2100 - 1950\text{ cm}^{-1}$ to linear CO and the range $1900 - 1800\text{ cm}^{-1}$ to bridged CO.

Blyholder (4) gave a different explanation from that of Eischens et al. (3a) for the CO bands observed. This has helped to account for previously unexplained results.

While not doubting the presence of bridging carbon monoxide, he has proposed the possibility of a linear CO with a frequency below 2000 cm^{-1} . He explained that a range of linear CO frequencies could occur due to the different extents of backbonding possible by the d - electrons of the metal into the antibonding orbitals of the CO molecule.

Blyholder postulated that an edge or corner atom gives more backbonding to CO. This would result in a stronger metal-carbon bond and a weaker carbon-oxygen bond to give a CO vibrational frequency lower than 2000 cm^{-1} . Since the fraction of edge or corner atoms depends on the degree of crystallinity, the frequency observed for linear CO is dependent on the degree of crystallinity.

Sheppard and Nguyen (5) have recently given a detailed assignment summarizing the positions of the CO bands :

$2200 - 2130\text{ cm}^{-1}$

Bands here are due to linearly adsorbed CO on incompletely reduced salts or oxidized metal cations, e.g Fe^{2+} , Pd^{2+} .

$2130 - 2000\text{ cm}^{-1}$

Bands here are due to linearly adsorbed CO molecules on low valence states of metal cations. The possibility of a large number of different one-atom sites has made this range difficult to assign.

$2000 - 1800\text{ cm}^{-1}$

Bands here are due to CO species bridging two metal atoms (B_2 sites).

The separate absorption bands observed in this latter region (each of which increases in frequency with increasing coverage) are assigned to CO adsorbed on B_2 sites formed on different crystal planes. Frequencies decrease in the order $(111) > (100)$

> (110). The coordination numbers on the (111), (100) and (110) planes are 9, 8 and 7 and these are usually denoted as C_9 , C_8 and C_7 sites, with the implication that the lower the value of the coordination number, the greater is the number of unsaturated valencies at the site. This implies a greater availability of electrons for bond formation to adsorbed species.

This trend in frequency observed on these crystal planes is consistent with Blyholder's idea, since the number of neighbouring atoms decreases in the order shown on these crystal planes.

The lower frequency bands appear first, and they are assigned to CO bonded to pairs of metal atoms coordinated to the lowest numbers of neighbouring metal atoms.

1880 - 1650 cm^{-1}

Bands in this region are due to highly bridged species; it is the low-frequency bands in this region which appear first and this corresponds to the most strongly held CO species. Bands here are usually assigned to multi-center adsorption sites with decreasing frequency as shown : $B_3(111)$ plane > $B_4(100)$ plane > $B_5(110)$ plane. This sequence agrees with theoretical predictions given by Doyen and Ertl (6) and Blyholder (7) of the strength of binding at different types of metal sites, although it is not necessarily definitive.

Eischens et al. (8) have observed on Pd supported on silica that as the concentration of CO increased, the frequency of the broad band below 2000 cm^{-1} increased and subsidiary maxima appeared. At higher coverages, bands appeared due to linearly bonded CO at 2060 cm^{-1} .

Below 2000 cm^{-1} , the first band (1830 cm^{-1}) was assigned to adsorption by the most active site, which was completely filled before adsorption occurred on the second

most active site (1890 cm^{-1}). When this site was completely filled, CO then adsorbed on the weakest site (1920 cm^{-1}).

Assuming mobility of adsorbed CO, the above observation confirms the heterogeneity of the catalyst surface. The more active sites would chemisorb CO first, with higher heats of adsorption, to give bridged CO and the less active sites were later filled with lower heats of adsorption. It is easily deduced (1) (see CO interpretation by Blyholder above) that metal atoms at corners or edges will give more energetic sites than metal atoms on planar sites since they will provide the greatest back-bonding (π - character) to the metal - carbon bond. Therefore, adsorption should occur on these sites first to give chemisorbed CO bands.

If adsorption were localized, the adsorption sites would be filled in random order and this will result in a uniform growth of bands at these three frequencies 1830 , 1890 and 1920 cm^{-1} .

The linear species (2060 cm^{-1}) appears at higher coverages when all the B_2 sites have been filled. Desorption experiments showed that the high-frequency band species are less strongly held than the low frequency ones. This can be explained by the strength of the M--C bond as seen from the differences in the extent of back-bonding (from metal to CO) between a linear species and a bridged species.

It is also observed on single crystal planes that the frequency of adsorbed CO increases with increasing surface coverage, but this is contrary to our expectation of a fixed infrared frequency with increasing surface coverage (9,10).

These observations have been explained by interactions between adjacent adsorbed molecules at higher coverages. These observations are likely to have at least two origins, although the overall effect might be a combination of both.

i) Electron density:- The adsorption of a molecule on one site can affect the electron density and hence the chemisorption bond at an adjacent site (10). This can be

explained by a change in the force constant of the M--C bond with increasing coverage. This effect is an example of a phenomenon termed "induced heterogeneity" by Boudart (11) to account for changes in the work functions of metals resulting from the adsorption of molecules on their surfaces. Blyholder (4) explained the continuous shift to higher frequencies with higher coverages as due to the fact that, as the number of adsorbed molecules increased, the competition is higher for metal d-electrons in order to form π -bonds with the adsorbate. Consequently, the strength of the metal-adsorbate bond will decrease (force constant decreases) and the CO stretching frequency will increase.

This explanation is supported by work done by Eischens and Pliskin on Pd (3b) and Primet et al. on Pt (12). Coadsorption of gas molecules with electron-donating property leads to increased π -character of the M--C bond and a lowering of the CO stretch, while electron withdrawing molecules give opposite frequency displacements.

ii) Lateral "across space" electrical or steric interactions:- These interactions occur between neighbouring adsorbed molecules (5,10) causing shifts to higher wavenumbers with increasing surface coverage. This is usually referred to as vibrational dipole-dipole coupling (13). This wavenumber shift may be caused by the coupling of the carbon-oxygen stretching vibrations of adjacent CO molecules at high coverages or the shifts could be from direct repulsive forces from neighbouring adsorbed molecules which will cause weakened chemisorption and hence lower back-bonding to give the large wavenumber changes observed with coverage (10).

The observed frequency changes with increasing surface coverage vary, depending on whether adjacent adsorbed molecules repel each other, attract each other or have no effect on each other so that adsorption is random.

Assuming mobility of adsorbed molecules, the first two cases above will respectively lead to maximization and minimization of distances between the adsorbed molecules.

Considering a model of an infinitely extensive single-crystal plane, the "repulsive model" will give a very narrow adsorption band (corresponding in position to the frequency of the coupled in-plane vibrations of all the adsorbed molecules) and this will change gradually in position with increasing coverage.

The "attraction model" will cause a very rapid change of frequency with coverage from the frequency of an "isolated" molecule towards the extreme value corresponding to full coverage with nearest-neighbour adsorbed molecules. Under this condition, if the spectral sensitivity is low, it is difficult to locate experimentally the absorption frequency of an isolated molecule; under this condition, it will appear as if the observed frequency hardly changes with coverage.

In the case of random adsorption, different "clusters" of adjacent adsorbed molecules will occur each with a separate contribution at a different frequency such that, at intermediate coverages, a broad adsorption region will be observed overall, possibly with sub-structure.

For all the above three cases, as surface coverage approaches its maximum value, the spectrum approaches the same limiting extreme of a sharp absorption at the highest (or lowest) frequency.

With finely divided metals, the same type of spectral behaviour will be observed although several limiting absorption bands may occur at high coverages due to different types of crystal faces. For each type of face, there will be somewhat different extreme frequencies depending on the sizes of the crystal faces.

The interpretation of the observed CO bands used in this thesis will be based on the band assignment by Sheppard and Nguyen since it is more recent and detailed than that given by Eischens et al. (3a).

Figueras et al. (14) have also used the adsorption of CO to show the effects of the Lewis acid sites of supports on the loaded metal. The frequencies of the CO bands

above 2000 cm^{-1} should increase as the Lewis acid sites of a support increase in strength and/ or number since the Lewis acid site will withdraw electrons from the metal on the support and reduce backbonding between the metal and the support. Y zeolites have very strong Lewis acid sites.

From a detailed consideration of the above properties of chemisorbed CO, it will be possible to gain an insight into the structure of the catalyst, that is, the oxidation state and position of the metal after each pretreatment and this will allow us to understand the catalytic reactivity of the catalyst better.

From previous study by Homeyer and Sachtler (15a,15b) it was shown that after calcination of a Pd-loaded zeolite in oxygen above 250°C , the bare Pd^{2+} cation is stabilized in sodalite cages, since multivalent metal ions stripped of their ligands migrate from the supercages to smaller cages. The smaller sodalite cages and the hexagonal prisms have higher negative charge densities than supercages and this is the cause of the potential difference between them. This charge density will depend on the Al/Si ratio of the zeolite. This means metal ions migrate during calcination to locations which provide greater electrostatic stabilization and higher coordination to lattice oxygen ions with the extent of migration and location depending on the size-to-charge ratio of the cation.

Gallezot and Imelik (16) have also found that calcination in oxygen increases dispersion of the metal cation. Michalik et al. (17) also pointed out that if the concentration of the Pd cation is low, it will be preferably stabilized in the hexagonal prism at sites S(I) after calcinations.

3.2 RESULTS

CO will be used to identify the location and valency of the Pd cation after the various pretreatment conditions. Also, the effect of fluoridation on the location and valency of Pd will be investigated. Figs. 3.3 to 3.6 show the infrared spectra of CO adsorbed on some of the catalyst samples. The other spectra obtained are not included in order to keep the thesis from becoming too large. The assignment of peaks found on the zeolite samples after CO adsorption is given in tables 3.1 and 3.2.

Table 3.1: Infrared studies of CO on oxidized catalysts : observed wavenumbers

Supports		Pd on HY ^a			Pd on NaY ^a	Assignment
NaY	HY	0.019%	0.171%	1.62%	1.58%	
				2208		CO on Pd ³⁺
				2185		CO on Pd ²⁺ near Lewis
		2137	2136		2138	antisym. } two CO on
		2115	2115		2115	sym. } Pd ²⁺
				2095	2092	CO on Pd ²⁺ or Pd ⁰ , S(II)
		2014				CO on Pd ⁰
					1984	} CO bridging two Pd ²⁺
		1956	1959			
					1930	
				1889		
1638	1638	1638	1637	1637	1638	Bidentate carbonate

^a Mass percent palladium is given

Table 3.2: Infrared studies of CO adsorbed on
reduced catalysts: observed wavenumbers

<u>Support</u>	<u>Pd on HY</u>				<u>Pd on NaY</u>		<u>Assignment</u>
	<u>.019% Pd</u>		<u>1.62% Pd</u>		<u>1.58% Pd</u>		
300°C and 500°C	300°C	500°C	300°C	500°C	300°C	500°C	
		2132		2132			Physisorbed CO
					2082	2086	CO on Pd ⁺
		2078	2078	2078			CO on Pd ⁰
2072	2072	2072	2072	2072	2072	2072	Physisorbed CO
2033	2029	2029	2029	2029	2033	2033	Physisorbed CO
1998	1998	1998	1998	1998	1998	1998	Physisorbed CO
					1951	1948	CO bridging two Pd ²⁺
			1924				CO bridging two Pd ²⁺
		1897		1897			CO bridging two Pd ⁰
1638	1637	1638	1637	1638	1637	1637	Bidentate CO

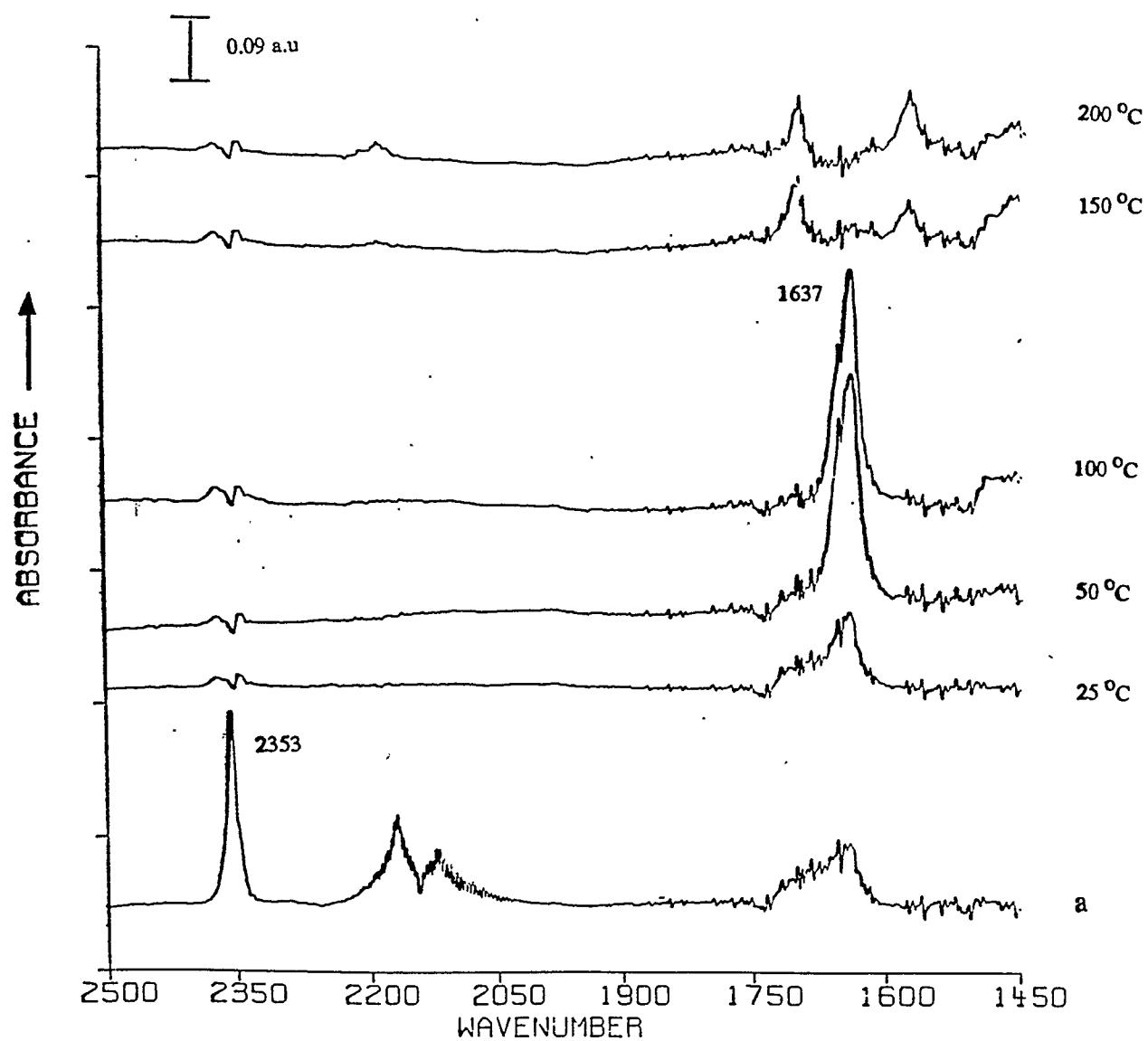


Fig. 3.3. Spectra of carbon monoxide adsorbed on a sample of calcined NaY after evacuation at different temperatures. a= spectra taken in the presence of gas phase carbon monoxide.

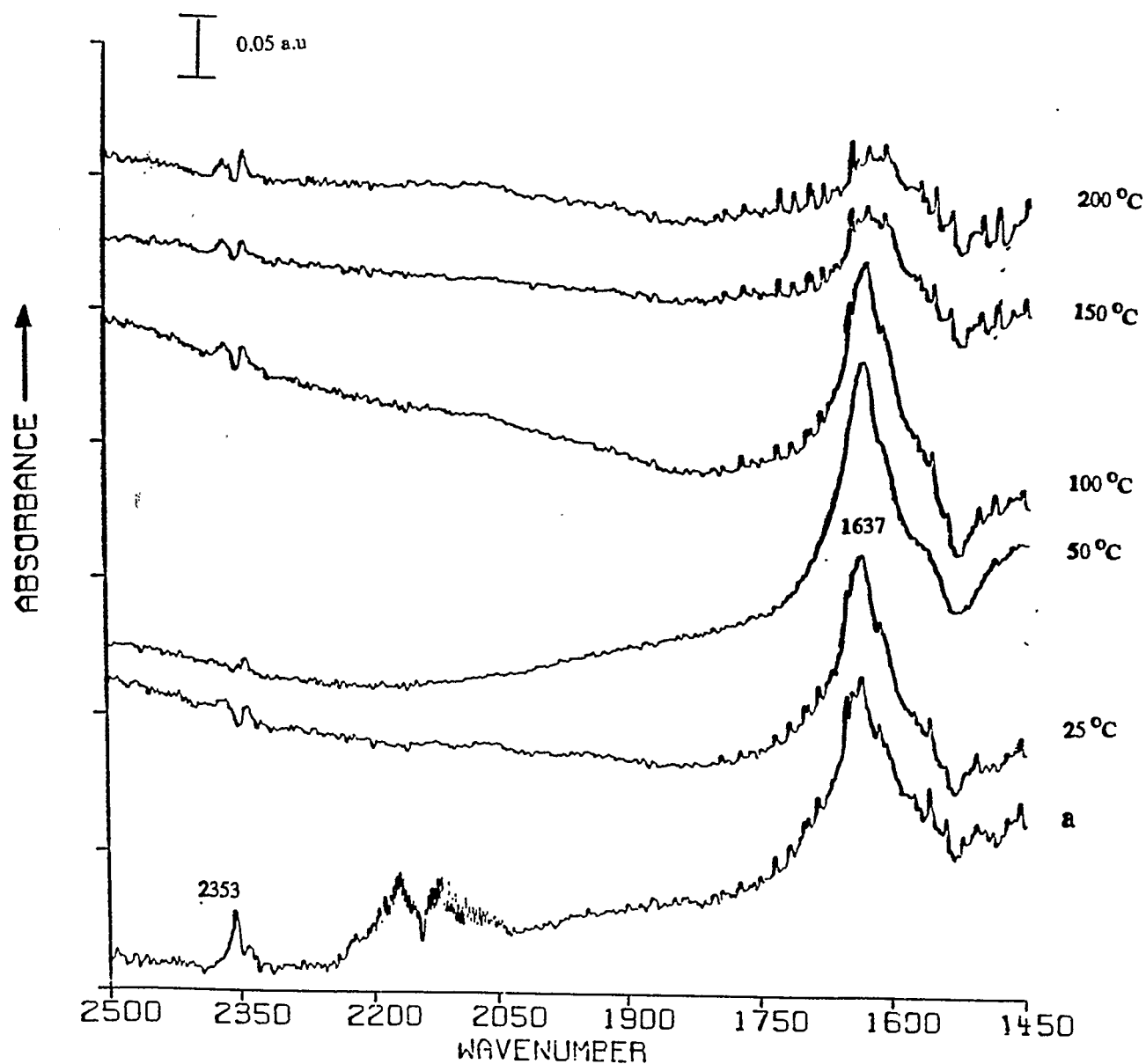


Fig. 3.4. Spectra of carbon monoxide adsorbed on a sample of calcined HY after evacuation at different temperatures. a= spectra taken in the presence of gas phase carbon monoxide.

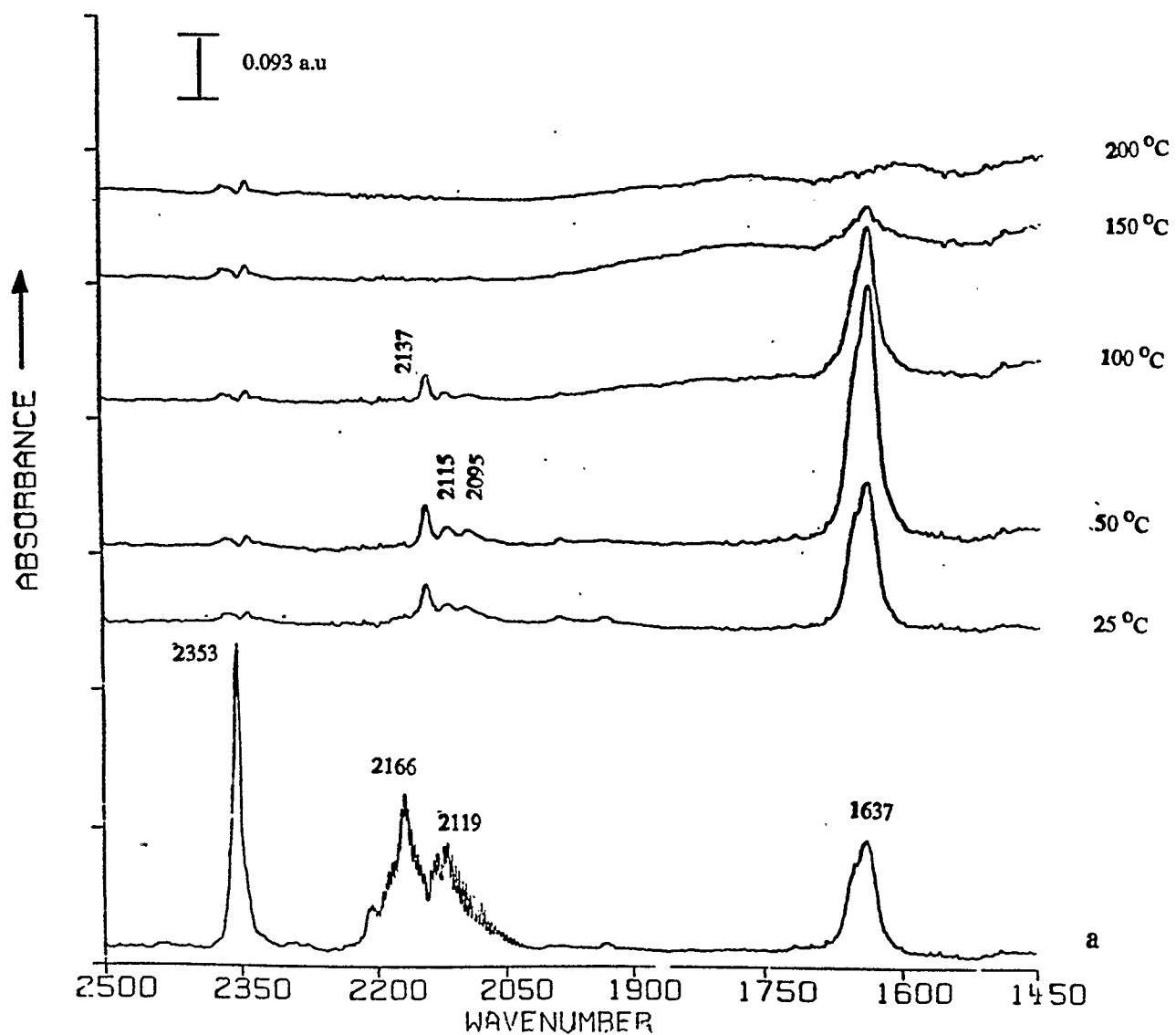


Fig. 3.5. Spectra of carbon monoxide adsorbed on a sample of calcined 1.58wt. %PdNaY after evacuation at different temperatures. a= spectra taken in the presence of gas phase carbon monoxide.

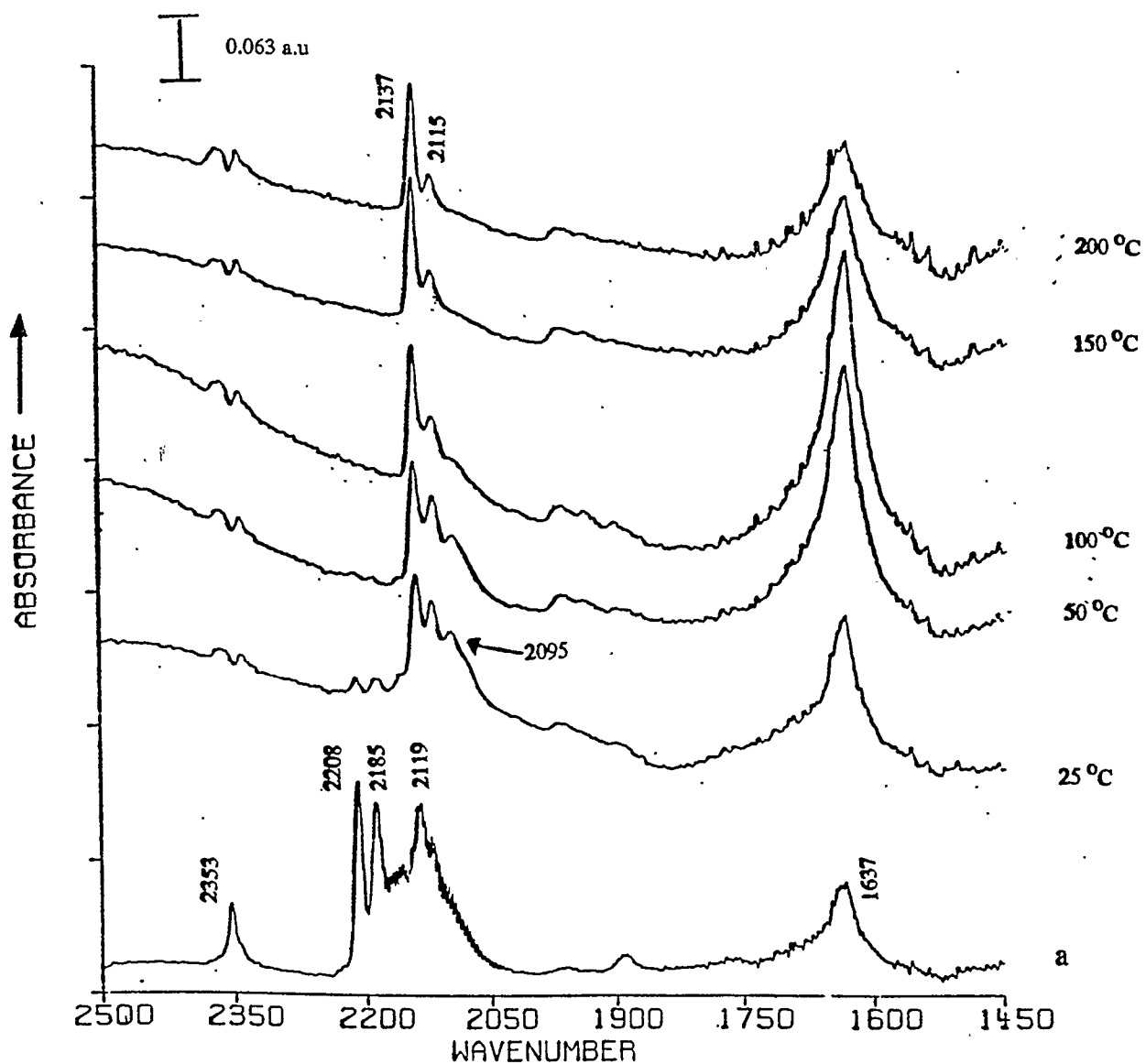


Fig. 3.6. Spectra of carbon monoxide adsorbed on a sample of calcined 1.62wt. %PdHY after evacuation at different temperatures. a= spectra taken in the presence of gas phase carbon monoxide.

3.3 DISCUSSION

3.3.1 CARBON MONOXIDE STUDY ON OXIDIZED CATALYST

3.3.1(a) Pd ON HY ZEOLITE SUPPORT

When CO was adsorbed on a low concentration PdHY sample (0.0193wt. %) calcined in O₂ at 500°C, there was no band due to CO bonded to Pd³⁺ or Pd²⁺ observed (Table 3.1). This shows that with this low loading of metal on this catalyst the Pd cation is stabilized in the hexagonal prism S(I) of the zeolite after the calcination treatment of the catalyst (17), where it is inaccessible to CO.

The only peak observed was that at 1638 cm⁻¹ which is due to a bidentate carbonate species (1) shown in fig. 3.7. This peak disappears after desorption at temperatures above 100°C indicating that the carbonate is weakly bound to the surface.

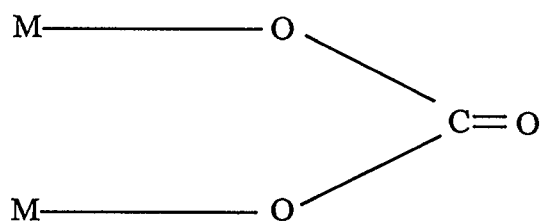


Fig. 3.7 Bidentate carbonate species

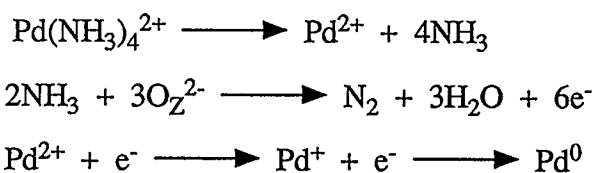
The fact that this peak is also observed on HY zeolite (without Pd) shows that the carbonate is probably bonded to Al in the zeolite framework rather than to a charge-balancing metal. This carbonate species is probably formed by the interaction of CO with lattice oxygens on the structural aluminium.

On adsorption of CO to 0.171wt. %PdHY, peaks were observed at 2137, 2115, 2014, 1956 and 1637 cm⁻¹. This is in contrast to the 0.019wt. %PdHY sample which

showed no peak for Pd--CO. This shows that even at these slightly higher Pd loadings, Pd has spilled over into accessible sodalite cages or supercages on the HY zeolite. At this stage, it is not possible to identify which of these cages contain Pd since CO can enter both of them; but in chapter four, we will use pyridine to identify the position of Pd since pyridine cannot enter sodalite cages because of its size.

The 2137 and 2113 cm^{-1} peaks have been assigned to two CO molecules linearly bonded to Pd^{2+} (18a). These peaks are due to the symmetric and antisymmetric stretching vibrations of two CO molecules bonded to the same Pd(II) cation. According to X-ray studies (16), this Pd cation is trigonally coordinated in sodalite cages to give a trigonal bipyramidal structure with the CO groups occupying the axial and equatorial positions (18b).

The 2014 cm^{-1} band is due to linear $\text{Pd}^0\text{---CO}$. The Pd(0) can be formed during the calcination in O_2 if the deamination (removal of the ligand) is done too rapidly (18a) as shown below.



O_Z is zeolitic lattice oxygen.

The subsequent calcination in O_2 might not completely remove the Pd^0 . The very low intensity of this band after oxidation supports this view.

It is generally accepted that the peak at 1956 cm^{-1} is due to bridged CO on two Pd^{2+} cations (5).

The bands associated with the "linear" peaks disappear after CO evacuation at 50°C; the fact that they disappear at low temperature is a result of the weakness of the

M---C bond due to the weak backbonding between the oxidized metal (Pd^{2+} , Pd^{3+}) and CO as explained earlier (see section 3.1).

When CO was adsorbed on 1.62wt. %PdHY (fig. 3.6), peaks were found at 2208, 2185, 2136, 2115, 2095, 1959, 1963, 1936, 1889 and 1636 cm^{-1} in the infrared spectrum.

The 2208 cm^{-1} band is for linear Pd^{3+} ---CO. The increased frequency is due to lower backbonding from the metal. The low intensity results because only a small amount of Pd^{3+} is formed with this calcination process. It should be pointed out that this Pd^{3+} species was not formed on the catalyst with lower Pd loading (0.171wt. %Pd). This might mean more of the Pd^{2+} are now in accessible cages where they can be easily oxidized to Pd^{3+} .

The 2185 cm^{-1} band is probably due to CO linearly bonded to Pd^{2+} close to a Lewis acid site (14). The presence of the Lewis site will have a tendency to increase the frequency of the CO stretch (from 2137 cm^{-1}) due to lowered backbonding from the metal.

Peaks below 2000 cm^{-1} (see Table 3.1) are due to bridged CO groups in different metal sites with varying extent of backbonding. These bridged species are very few in number (low intensity) which confirms that calcination in oxygen promotes dispersion of oxidized Pd. It should also be mentioned that as the Pd content of the catalyst increases, the peaks due to linearly adsorbed CO increase in intensity. This is because, although the Pd content is increasing, the O_2 treatment favours dispersion and hence an increased number of linear peaks is observed.

The 2095 cm^{-1} band is probably due to CO bonded to PdO or Pd^{2+} in S(II) sites of the sodalite cages in the zeolite. This is because a Pd^{2+} in S(II) sites of the sodalite cages has fewer lattice oxygen ions to interact with than PdO or Pd^{2+} in S(I') sites of the sodalite cages; this decreased interaction with lattice oxygen causes an increase in

backbonding between Pd and CO which will cause the frequency of the CO stretch to decrease from 2137 cm^{-1} (CO in S(I') sites of sodalite cages) to 2095 cm^{-1} (CO in S(II) sites of sodalite cages). The intensity of this 2095 cm^{-1} peak is too high to be assigned to a linear $\text{Pd}^{+}\text{---CO}$ species based on the oxidation treatment used on the catalyst.

3.3.1(b) Pd ON NaY ZEOLITE SUPPORT

On adsorption of CO on 1.58wt. %PdNaY calcined in oxygen at 500°C (fig. 3.5), there were a few differences from the spectra of the (1.62wt. %)PdHY sample as seen in Table 3.1. There was no peak at 2208 cm^{-1} from $\text{Pd}^{3+}\text{---CO}$. The absence of the 2208 cm^{-1} peak must mean either that oxidation of Pd^{2+} to Pd^{3+} is more favoured on PdHY than PdNaY or that there is more accessible Pd^{2+} to oxidize on PdHY (as explained earlier) than on PdNaY. It was also observed that the intensity of the 2095 cm^{-1} peak was very small in comparison to that of PdHY, and this must mean that Pd on NaY is not stabilized in S(II) sites of sodalite cages or as PdO to the same extent as seen on PdHY. Also, the intensity of the 2136 and 2115 cm^{-1} bands due to $\text{Pd}^{2+}\text{---}(\text{CO})_2$ is lower in comparison to that on PdHY, which suggests that much of the Pd^{2+} is stabilized in hexagonal prisms rather than sodalite cages as seen on PdHY.

The explanation for these differences cannot be related to the quantity of Pd present, because the amounts of Pd present in the two catalysts are nearly equal (1.58wt. % PdNaY, 1.62wt. %PdHY). Instead it would appear that in NaY zeolites, Pd has greater tendency to occupy the hexagonal prism and hence it is less readily available to bond to CO. A possible explanation for this tendency to occupy hexagonal prisms could be the lower mobility of Pd in NaY as compared to that in HY due to the decrease in available space in the zeolitic cages when Na^{+} instead of H^{+} is used as a charge-balance cation, since the former cation is bigger. Alternatively, the increased mobility of H^{+} at higher temperatures (19) might account for this difference. The mobile H^{+} could more

readily move away from the mouth of these cages so that Pd can easily migrate into more accessible zeolite cages.

It was observed that only a few bridged species exist on the 1.58wt. % PdNaY after calcination in O_2 which was what we observed on PdHY; this confirms that calcination in O_2 increases the dispersion of the Pd cation.

3.3.2 CARBON MONOXIDE STUDY ON REDUCED CATALYST SAMPLES

3.3.2(a) Pd ON HY ZEOLITE SUPPORT

The reduction of 0.0193wt. %PdHY at $T_R=300^\circ\text{C}$ does not give bands due to linear or bridged species, but reduction at $T_R=500^\circ\text{C}$ shows peaks at 2132 cm^{-1} due to a physisorbed species of CO on Pd^+ and at 2078 cm^{-1} due to linear $\text{Pd}^0\text{---CO}$. The frequency of the latter species changes to 2066 cm^{-1} as the surface coverage of CO decreases. A weakly adsorbed bridged species at 1897 cm^{-1} due to CO on two Pd^0 atoms was also observed; this band is lost after evacuation at 50°C . It is worth remembering that the calcined form of this 0.0193wt. %PdHY did not show any peak due to linear or bridged species. This shows that calcination in O_2 causes migration of Pd into inaccessible parts of the zeolite during dispersion, while reduction in H_2 favours migration to the surface and accessible cages of the zeolite; that is, agglomeration of Pd is favoured by reduction. The observation of bridged species after reduction on this catalyst and our inability to observe bridged CO species on the oxidized form of this sample (0.0193wt. %PdHY) confirms that reduction promotes agglomeration. There is also a possibility that our inability to observe bands from CO bonded to linear or bridged species after $T_R=300^\circ\text{C}$ is due to the fact that the Pd^{2+} cation was indeed reduced in the hexagonal prism but that it remains in these cages rather than migrating as expected after

reduction. It has been observed by Bai (19b) using ^{23}Na -nmr that on reduction of PdNaY zeolite, the reduced Pd migrates to accessible sites while the Na cation migrates to inaccessible sites. This observation rules out the possibility highlighted above, and suggests simply that at 300°C , reduction of Pd^{2+} located in hexagonal prisms is not effective.

The total lack of reduction of Pd^{2+} on the low concentration PdHY(0.0193wt. %) at $T_R=300^\circ\text{C}$ agrees well with Homeyer and Sachtler (15a,15b) which says that the ease of reduction of metal in a zeolite depends on location; supercages > sodalite cages > hexagonal prism. Since we have shown that at low Pd content, Pd cations will occupy hexagonal prisms, a higher T_R then has to be applied to reduce Pd^{2+} . Since CO cannot enter hexagonal prisms, the observation of peaks due to linear and bridged species after $T_R=500^\circ\text{C}$ shows that the higher reduction temperature caused the reduced Pd species to migrate to more accessible sites. It is known (15a) that the direction of migration of cations during reduction is the reverse of that during oxidation. Presumably, this is due to the charge on the Pd after each pretreatment and the availability of more lattice oxygen ions in the hexagonal prism than in the sodalite cages.

The Pd^{3+} and Pd^{2+} formed during calcination will prefer the highly negatively charged hexagonal prisms, while the Pd^+ and Pd^0 formed during reduction will remain more easily in the supercages and sodalite cages.

After reduction of all catalysts at either $T_R=300^\circ\text{C}$ or $T_R=500^\circ\text{C}$ as required, peaks are found at 2072, 2023 and 1998 cm^{-1} which are assigned to physisorbed CO on the zeolite support, since they are also found on NaY and HY zeolites without any loaded Pd, even after fluoridation of the zeolite support. These peaks pump off easily.

These peaks are not found on oxidized NaY or HY catalyst, with or without Pd, nor on the fluoridated samples. This shows that reduction creates sites on the zeolite support which physisorb CO.

It is also observed that after doing reduction at $T_R=300^\circ\text{C}$, these peaks will pump off at room temperature on NaY and HY zeolites with or without loaded Pd. However, after reduction at 500°C , while these peaks still pump off very readily at room temperature on NaY and Pd/NaY catalysts, on HY and Pd/HY (after $T_R=500^\circ\text{C}$), these peaks are only removed after evacuation at 50°C .

In summary, it is seen that reduction creates sites which physisorb CO on the supports (NaY and HY) although stronger sites are created on HY than NaY as seen from the situation after reduction at 500°C . It is also observed that the presence of the fluoride on the support does not affect the strength of these sites. The fact that these sites are present on reduced NaY supports shows that these sites are not Bronsted or Lewis acid sites, since it was shown in section 5.3.1 (pyridine study) that this support does not have any of these acid sites after the reduction treatment. The exact nature of these sites cannot be identified; however, since they only weakly physisorb CO, it is probable that they will not play any role in the catalytic reaction to be studied.

The reduction of 1.62wt. %PdHY sample at $T_R=300^\circ\text{C}$ definitely shows that reduction causes aggregation of Pd^0 as shown by the low intensity of the "linear" peak at 2078 cm^{-1} due to $\text{Pd}^0\text{---CO}$, compared to the higher intensity of the "bridge" CO bands below 2000 cm^{-1} . The intensity maximum of this bridged CO band moves from 1924 to 1889 cm^{-1} as CO is desorbed at higher temperature. Movement to lower wavenumber has been attributed to the effect of dipole-dipole interactions between adsorbed CO molecules (3). The decrease in frequency of the bridged CO band with a decrease in surface coverage could also be an indication of surface heterogeneity, possibly from different crystal faces (20).

Reduction at $T_R=500^\circ\text{C}$ shows a band at 2132 cm^{-1} assigned to a form of physisorbed CO on Pd^+ ; this CO is weakly adsorbed and pumps off at 50°C . Linear $\text{Pd}^0\text{---CO}$ (2078 cm^{-1}) is also observed. This peak changes from 2078 cm^{-1} to 2066 cm^{-1}

as desorption of CO is carried out.

Unlike samples treated at $T_R=300^\circ\text{C}$ which showed a strong band from bridged CO (which pumps off at 150°C), only a weak bridge species is observed at 1897 cm^{-1} (after reduction at $T_R=500^\circ\text{C}$) which is lost after desorption was done at 50°C . So, although reduction at 500°C is expected to increase the agglomeration of Pd (and increase the amount of bridged CO species), suprisingly, reduction at 300°C gave more bridged species.

The reason for the difference in the amount and strength of the bridge species of $T_R=300^\circ\text{C}$ and that of $T_R=500^\circ\text{C}$ must be that $T_R=500^\circ\text{C}$ favours formation of well defined crystallites, while $T_R=300^\circ\text{C}$ creates more edges and corner sites as explained by Blyholder (4). Metals at edges and corner sites (which have fewer coordinating neighbouring metal atoms) give higher backbonding to CO and hence linear species attached to these sites could have absorptions in the region normally assigned to "bridged" CO. Yang and Garland (21) showed for rhodium on alumina, that as the crystallite size increased, the proportion of CO strongly bonded to edges and corner sites was decreased. Consequently, the intensities of the bands below 2000 cm^{-1} decreased during sintering. This means that in the study carried out here, $T_R=500^\circ\text{C}$ increases agglomeration over $T_R=300^\circ\text{C}$ to give more well defined crystallites (22).

3.3.2(b) Pd ON NaY ZEOLITE SUPPORT

With PdNaY at $T_R=500^\circ\text{C}$ only a weak peak at 2086 cm^{-1} due to linear $\text{Pd}^+ \text{---CO}$ is observed, there was no peak at 2078 cm^{-1} due to $\text{Pd}^0 \text{---CO}$. This shows that reduction of Pd on NaY is more difficult than on HY due probably to the inaccessibility of Pd on the NaY support. The results of reduction of PdNaY samples agreed with what has been observed on PdHY, that is, $T_R=300^\circ\text{C}$ favours the bridge species over the

linear species while the $T_R=500^\circ\text{C}$ favours linear species over bridge species. From the discussion above (section 3.3.2(a)) on the differences between the intensities of the IR bands of the bridged species formed during reduction at 300 and 500°C , it is obvious that this catalyst also undergoes reorganization to expose well organized crystallites as observed on the PdHY samples.

3.3.3 CARBON MONOXIDE STUDY ON FLUORIDATED ZEOLITE SAMPLES

3.3.3(a) Pd ON FLUORIDATED NaY SUPPORT

For Pd on NaY samples, fluoridation does not seem to affect the location or valency of Pd after calcination in O_2 . The same peaks on PdNaY were found on PdNaFY and they still had the same relative intensity ratios. The only difference was that the bands on PdNaFY have a lower intensity. The intensities of the peaks on PdNaFY were about 50% lower than that on PdNaY. The lower intensity of linear and bridged CO on PdNaFY as compared to PdNaY is probably due to the leaching identified in section 5.3.3(a). Various workers have identified the leaching of aluminium atoms from the zeolite lattice as fluoroaluminates (which are soluble in aqueous solutions) when zeolites are fluoridated (23).

Reduction gave the same spectra for PdFNaY and Pd/NaY, and the intensity ratio between the IR bands of the linear and bridged species was the same on both catalysts.

It is also noticeable that the fluoridation does not affect the frequency of the CO stretch. This means that the fluoride does not affect the electron density around the Pd cation on PdNaY substantially.

3.3.3(b) Pd ON FLUORIDATED HY SUPPORT

For (1.58wt. %)PdFHY and (1.62wt. %)PdHY, calcination in O₂ gave the same sets of peaks, but intensities were different and not in the same ratios. Peaks were found on these catalysts at 2208, 2185, 2136, 2119, 2095, 1963, 1936 and 1891 cm⁻¹. On Pd/FHY, the 2136 and 2119 cm⁻¹ bands (due to asymmetric and symmetric stretch of two CO molecules bonded to one Pd²⁺) were not in the same ratio found on Pd/HY. On Pd/HY, the ratio was 3:1 even after desorption at 150°C but, on Pd/FHY, the ratio was 3:1 after evacuation at room temperature and later changed to 1:1 after desorption at 50°C; it changed to 2:1 after desorption at 150°C. The reason for this variation in ratio is not understood.

For PdFHY, the 2095 cm⁻¹ band was weaker than that produced by PdHY and this might mean that there are less PdO or Pd²⁺ in S(II) sites of sodalite cages on PdFHY than PdHY. There were also fewer bridged species on PdFHY than on PdHY. What this means is that either the presence of the fluoride favours the location of Pd in S(I') sites of the sodalite cages or that the presence of the fluoride increases dispersion during the oxidation of the catalyst as seen by the small amount of bridged species. Remember that the presence of fluoride on Pd/NaY samples did not affect the location or valency of Pd.

For reduced samples, T_R=300°C, there was no difference in the spectra or intensity of the peaks between PdHFY and PdHY.

3.4 CONCLUSION

The CO study has shown that migration of metal on HY zeolite is more favoured than on NaY. It has also shown that at concentrations of 0.0193wt. %PdHY, Pd is located in hexagonal prisms but at higher concentrations on PdHY used (≥ 0.171wt.

%), the sodalite cages or supercages are occupied. It is not possible to tell which of these cages are occupied in this study since CO can enter both cages.

On the 1.62wt. %PdHY sample, calcination in O₂ gave some Pd³⁺ cations; this is not formed at lower loadings of PdHY nor on the 1.58wt. %PdNaY sample, and this indicates the improved accessibility of Pd²⁺ at highest loadings of PdHY since they are easily oxidized. Infrared evidence suggests that on the two heavily loaded samples (1.58wt. %PdNaY and 1.62wt. %PdHY), the location of the Pd is somewhat different. On PdNaY, Pd occupies the hexagonal prisms to a higher extent and on PdHY at this loading it also spreads more into the sodalite cages.

Fluoride treatment does not affect the location or valency of Pd on NaY, but it appears that there are minor differences in the location of Pd on PdHY and PdFHY samples.

Peaks due to physisorbed CO were observed at 2072, 2023 and 1998 cm⁻¹ after reduction although the exact nature of the sites was not identified. These sites are assumed not to be catalytically active (for the ethene reaction to be studied) since they could only weakly physisorb CO.

It was observed that reduction at 300°C is not sufficient to cause migration of Pd²⁺ out of hexagonal prisms of the 0.019wt. %PdHY sample; but at 500°C, reduction will do it. Generally, it was observed that mild reduction promotes formation of metal aggregates with more atoms at corners and edges, while drastic reduction favors formation of well defined crystallite aggregates. Also, higher temperatures are required to reduce cations in inaccessible sites.

It is also seen that calcination in O₂ causes metal dispersion and stabilization in smaller cages of the zeolite.

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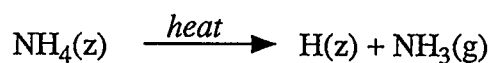
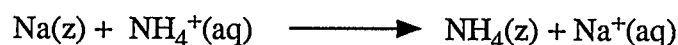
CHAPTER FOUR

4. ZEOLITE HYDROXYL GROUPS

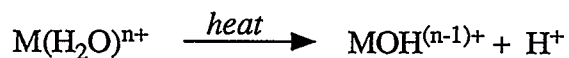
4.1 INTRODUCTION

The structural hydroxyl groups (Bronsted acid sites) of zeolites can be formed in three different ways (1):

i) From calcination of ammonium-exchanged zeolite

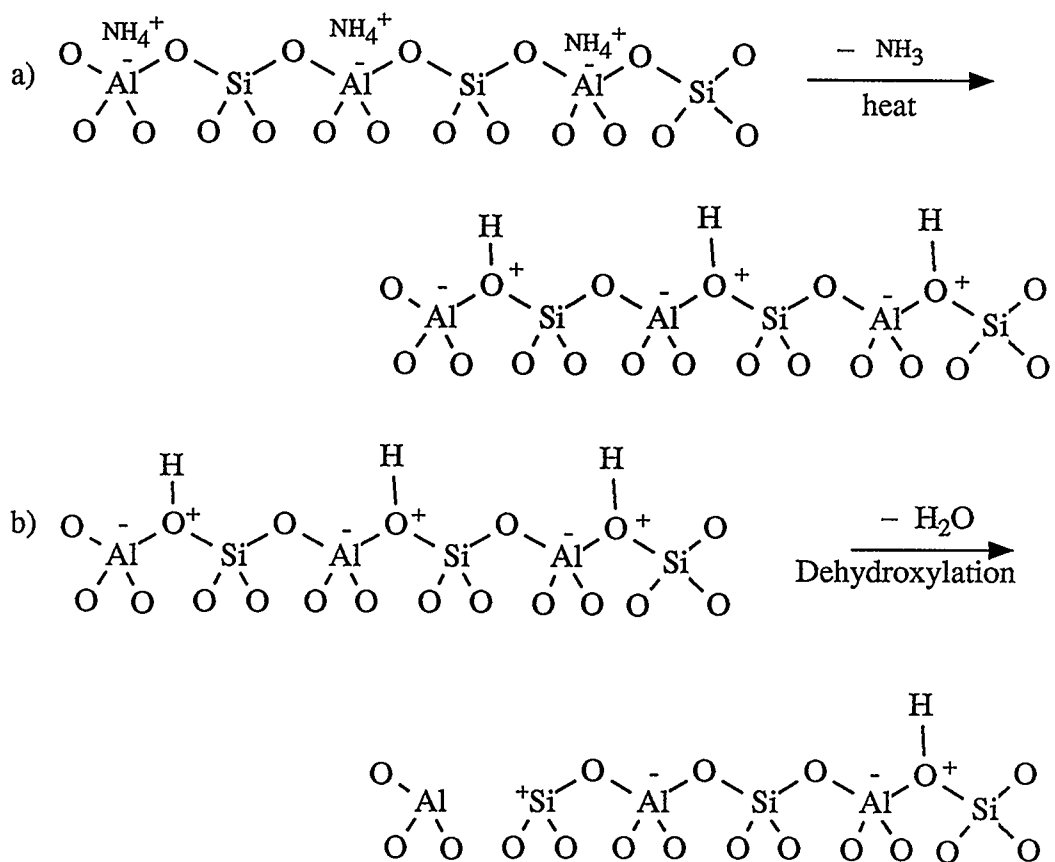


ii) From water coordinated to cations in zeolite



iii) Direct exchange of Na^+ ions by H^+ using dilute acids.

Decationized zeolite (HY) is the product of thermal decomposition of ammonium-exchanged zeolite. After dehydration and removal of NH_4^+ as NH_3 , further thermal treatment will result in loss of hydrogen and framework oxygen as water by dehydroxylation, resulting in an oxygen-deficient site between a tricoordinated Si and Al. So the thermal treatment of the ammonium-exchanged zeolite done at 500°C will leave an unspecified amount of the decationized and dehydroxylated forms of the zeolite (see reaction mechanism below).



For hydrogen X and Y (decationized) zeolites, three infrared bands assigned to zeolite OH groups are observed (1,2) in the spectrum of these zeolites and another arises if the protons are replaced with polyvalent cations:

$$\underline{3740 \text{ cm}^{-1}}$$

This band is assigned to OH groups on the zeolite surface terminating the crystal structure at positions where bonding would normally occur with adjacent tetrahedral aluminium or silica ions within the zeolite. In most cases, this hydroxyl group is inert to adsorbates and it is regarded as a very weak Bronsted acid site (3). This band may also contain some contribution from Si-OH groups in regions of the zeolite with low aluminium content (4).

$$\underline{3650 \text{ cm}^{-1}}$$

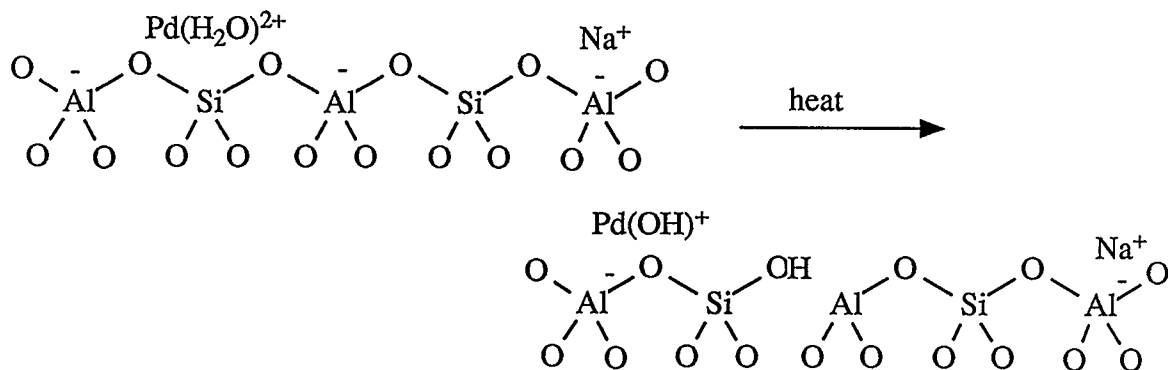
This band is due to an hydroxyl group in the accessible supercages of the zeolites (2). This is known because it readily interacts with most adsorbents. This band is attributed to protons bonded to framework oxygen atoms in the supercages (5). These OH groups are regarded as highly acidic and account for most of the Bronsted acidity of the zeolite.

3550 cm⁻¹

This band is due to an hydroxyl group in the less accessible sodalite cages or hexagonal prisms. This group does not readily interact with moderately large molecules adsorbed on the zeolite (6). This band is attributed to protons bonded to the framework oxygen atoms in the hexagonal prisms (5). This band has been shown sometimes to interact with big molecules like pyridine which can not enter the hexagonal prisms and the explanation for this contradiction is rationalized as being due to proton mobility (7), which shows that strong bases can induce proton movement without temperature increases.

3570 - 3605 cm⁻¹

The OH band in this range is due to an MOH⁺ species formed during cation hydrolysis (see reaction mechanism in scheme 1 below). This band is found to be non-acidic to pyridine. The frequency of this band varies with the cation M; the smaller the cation, the stronger the electric field it generates and hence the higher the frequency. This OH group is very sensitive to the level of hydration and it disappears on mild dehydroxylation, probably to give M-O or M⁺-O-M⁺ groups (8).

SCHEME 1

The 3645 and 3550 cm^{-1} OH bands have their maximum intensity after sample evacuation at 300°C, but the intensity starts to decrease after treatment at higher temperature due to dehydroxylation. The 3740 cm^{-1} band is not changed till 550°C, thereafter, it starts to increase as the 3645 and 3550 cm^{-1} peaks start to decrease due to loss of crystal structure of the zeolite. The temperature required for dehydroxylation increases with increasing Si/Al ratio (9).

The monovalent or alkali cation-containing zeolites with no cation deficiency, should have no structural hydroxyl groups (1,10). The only hydroxyl group observed on alkali zeolite should be hydroxyl groups (3740 cm^{-1}) necessary to terminate the crystal lattice. Habgood (11) has shown that alkali zeolites will contain structural hydroxyl groups if they contain cation deficiencies, multivalent cation impurities and slight amounts of siliceous impurities.

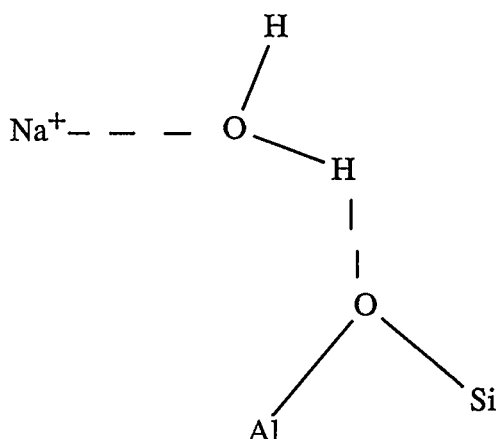
Divalent cation-containing zeolites contain (at high levels of loadings), the three bands found on decationized Y zeolites, HY (3740, 3645, 3550 cm^{-1}) although to a smaller concentration (1); but the OH group concentration is greater than that found on alkali metal-loaded zeolites with cation deficiency. The concentration of OH groups on these divalent cation loaded zeolites also varies with the type of cation present on the

zeolite. These structural OH groups are formed during dehydration. The electrostatic field of the cation will induce the dissociation of the coordinated water molecules to produce MOH^+ and H^+ species. The H^+ will then react with lattice oxygen at a second exchange site to produce the structural hydroxyl groups at 3645 and 3550cm^{-1} (1,10) (see scheme 1 above).

By correlating with other data, Angel and Schaffer (9) found that the frequencies of the 3645 and 3550cm^{-1} bands decreased with increasing electron affinity of the cation.

A sharp band at $3685\text{--}3695\text{cm}^{-1}$ found on metal loaded zeolites is assigned to adsorbed molecular water on the cation in the zeolite (10). This assignment is supported by the presence of the water bending band at 1640cm^{-1} . This band is not observed on monovalent cation zeolites (except sodium zeolite) so it must represent the interaction of the water and a cation rather than with the zeolite lattice.

This sharp band is said to be from the free hydrogen atom of the bonded water in the structure below:



Tsitsishivilli (12) reported on the spectra of potassium L zeolite as a function of evacuation at different temperatures from $40\text{--}500^\circ\text{C}$ and he has shown that the bands observed near $1602, 1630$ and $1650\text{--}1660\text{cm}^{-1}$ (water bending vibration) are an indication of different locations for adsorbed water.

Ward (13) has shown that on initial exchange of NaY zeolite with NH_4^+ , only the 3645 cm^{-1} band is formed and increases in intensity until about 55-60% of the Na is exchanged; beyond this point, the 3550 cm^{-1} band then appears and grows quickly. Sherry (14) has also shown that the last 16 Na cations in a NaY zeolite are more difficult to exchange than the initial 32 cations since it is highly probable that the former cations are located in hexagonal prisms while the latter are located in supercages. Additional studies using Cs exchange of NH_4Y zeolite have shown the location of the 3550 cm^{-1} OH group. Since the Cs ion is large, it should only influence the 3645 cm^{-1} OH group in the supercages and leave the 3550 cm^{-1} group in the hexagonal prism untouched; and this was observed.

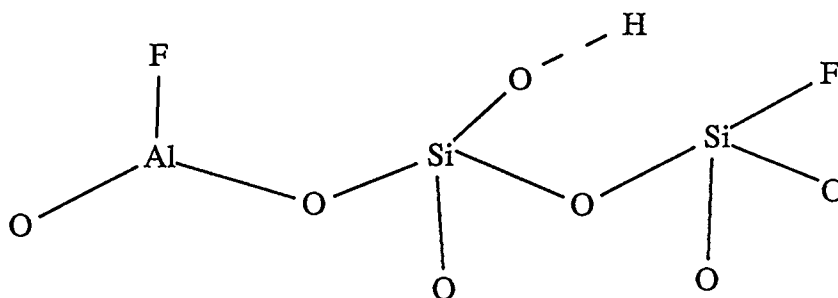
More studies by Ward (15) using increasing exchange levels of Mg and Ca on NH_4Y show that after calcination at 450°C , the intensity of the 3550 cm^{-1} band of NH_4Y decreased linearly with increasing divalent exchange up to about 50% exchange level and the band then subsequently decreased more slowly to zero. Also, the 3645 cm^{-1} band initially remained essentially constant to about 55% exchange and then decreased rapidly. This result shows that the Mg and Ca cations preferentially occupy the hexagonal prism and after 50% exchange spill over into the supercages. This observation is similar to that for Ni where the 3550 cm^{-1} peak decreases up to about 60% exchange and the 3645 cm^{-1} band is unaffected until about 65% exchange is achieved.

From a study of PdNH_4Y zeolite (1) with different levels of loading of cations, it was suggested that the Pd cations introduced as tetraamino complexes exchange randomly into the NH_4Y zeolite.

From the above discussion, it is obvious that the effect of ion-exchange of a NaY or NH_4Y zeolite by a cation as seen from the observation or perturbation (respectively) of the OH groups will help to identify the position of the exchanged cation in the zeolite structure.

4.2 FLUORIDATION

Fluoridation is another way of modifying the reactivity of zeolites. Fluoride incorporated into the zeolitic framework replaces surface O or OH (see structure below); since fluorine is very electronegative, it will polarize the zeolite lattice and increase the acidity of the zeolite by affecting the Bronsted and Lewis acid sites (16) as shown in the sketch below.



The electronegative fluorine withdraws electrons from any neighbouring OH bonds and weakens the OH bond such that the proton becomes a good "leaving group" in acid-catalyzed reactions; also, the Lewis site becomes a stronger electron acceptor due to the electron withdrawing effect of the fluoride.

Incorporation of fluoride into a catalyst can be brought about by vapour phase fluoridation or impregnation with a solution of a fluoride compound like NaF, NH_4F and NH_4SiF_6 . The fluorided sample is then dried at higher temperature.

A comprehensive review on the fluoridation of catalyst is given by Ghosh and Kydd (16).

4.3 RESULTS

This chapter examines the effect of various pretreatment conditions on the hydroxyl groups of all catalysts and supports used in the catalytic studies, and the effect of the loaded cations on the number of hydroxyl groups.

The infrared spectra of these catalysts in the region between $3750 - 3530 \text{ cm}^{-1}$ will be used for the analysis. Figs. 4.1 - 4.6 show, the infrared spectra of the surface of zeolite samples used in this study.

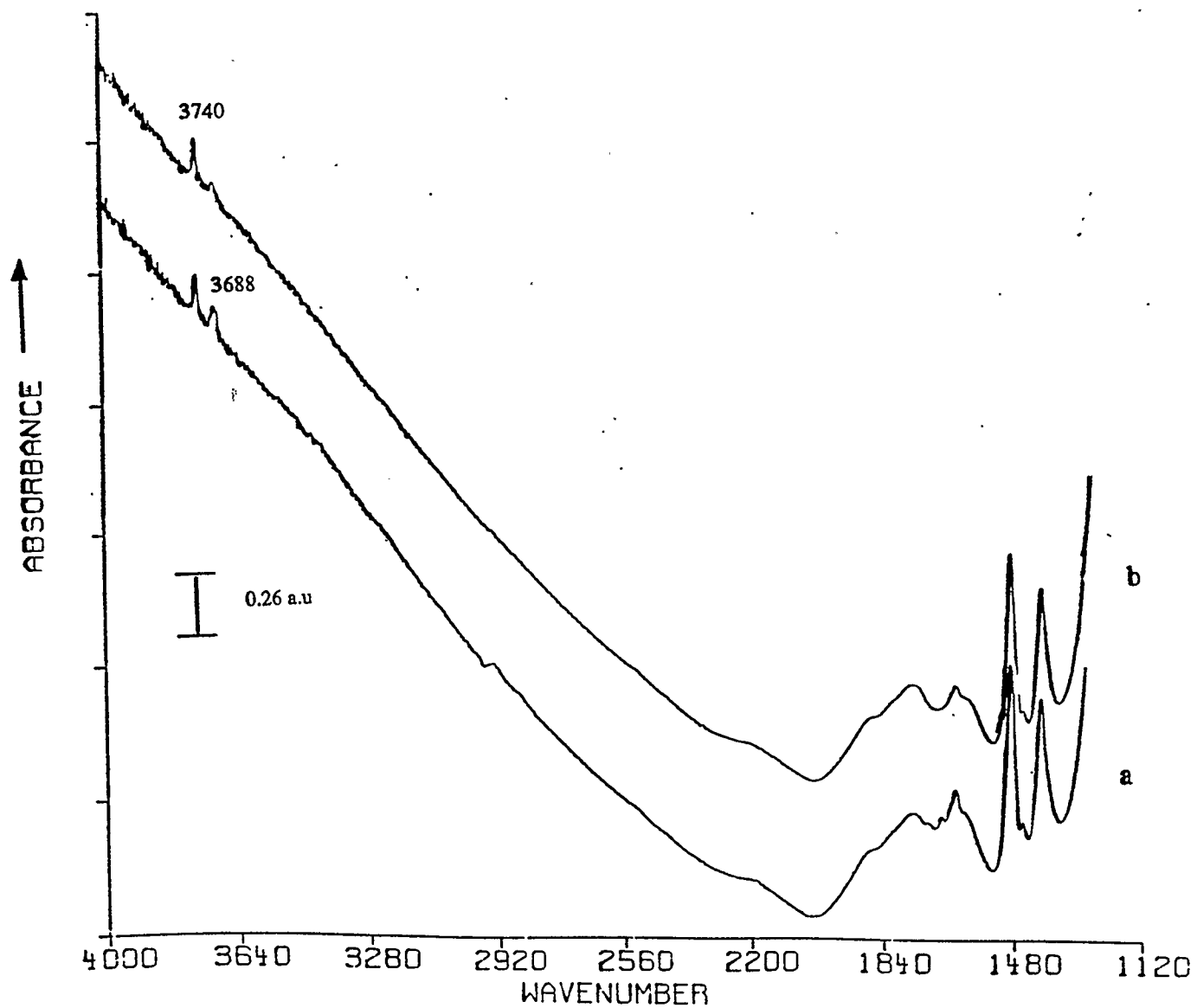


Fig. 4.1 IR spectra of NaY zeolite surfaces
a= sample calcined in O₂ at 500 °C overnight.
b= sample calcined in O₂ at 500 °C overnight and in H₂ at 300 °C for 1 hour.

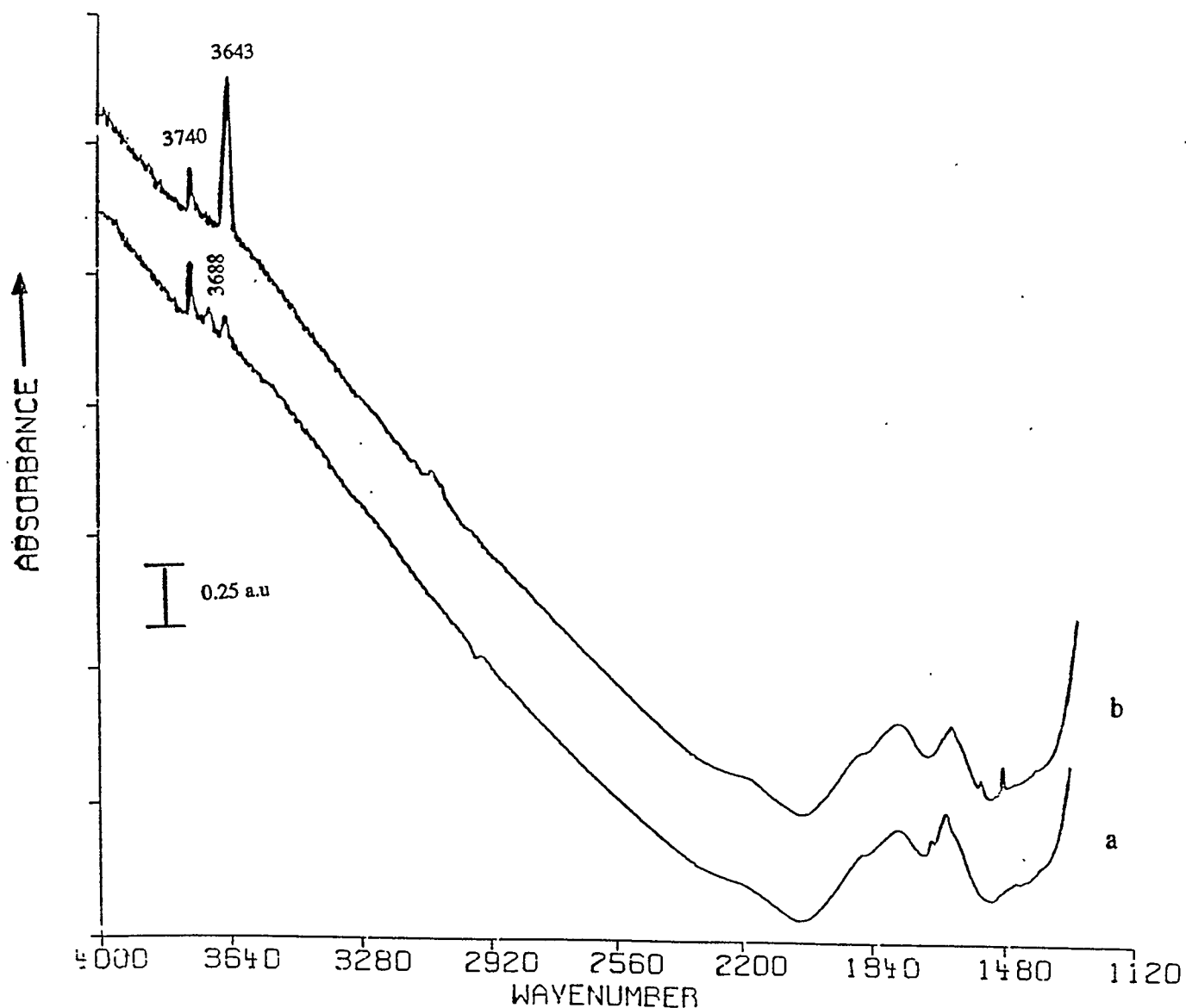


Fig. 4.2 IR spectra of 1.58wt. %PdNaY zeolite surfaces

a= sample calcined in O₂ at 500 °C overnight.

b= sample calcined in O₂ at 500 °C overnight and in H₂ at 300 °C for 1 hour.

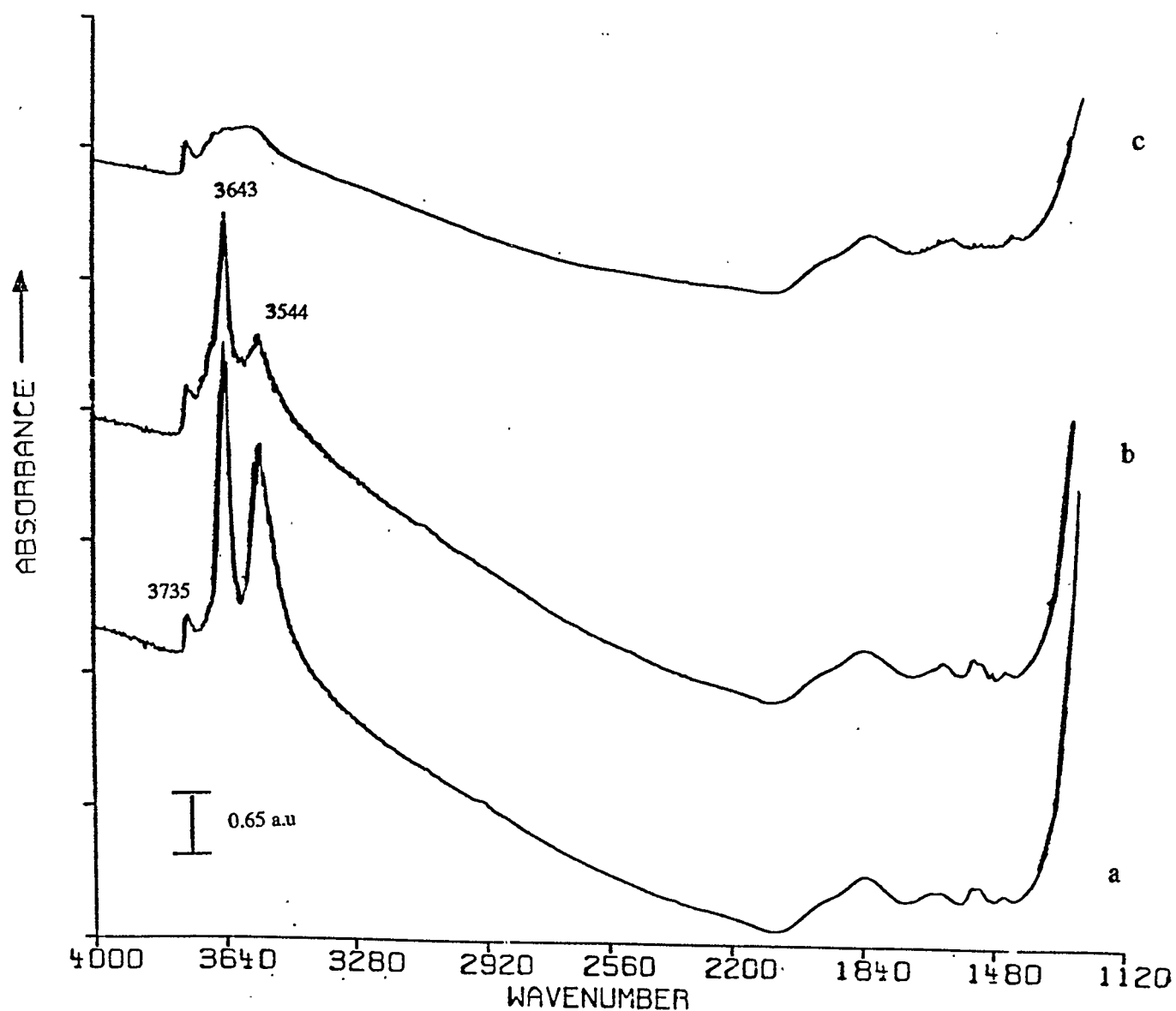


Fig 4.3 IR spectra of HY and fluoridated HY zeolite surfaces
a= HY calcined in O₂ at 500 °C overnight.
b= HY calcined in O₂ at 500 °C overnight and in H₂ at 300 °C for 1 hour.
c= calcined sample of fluoridated HY.

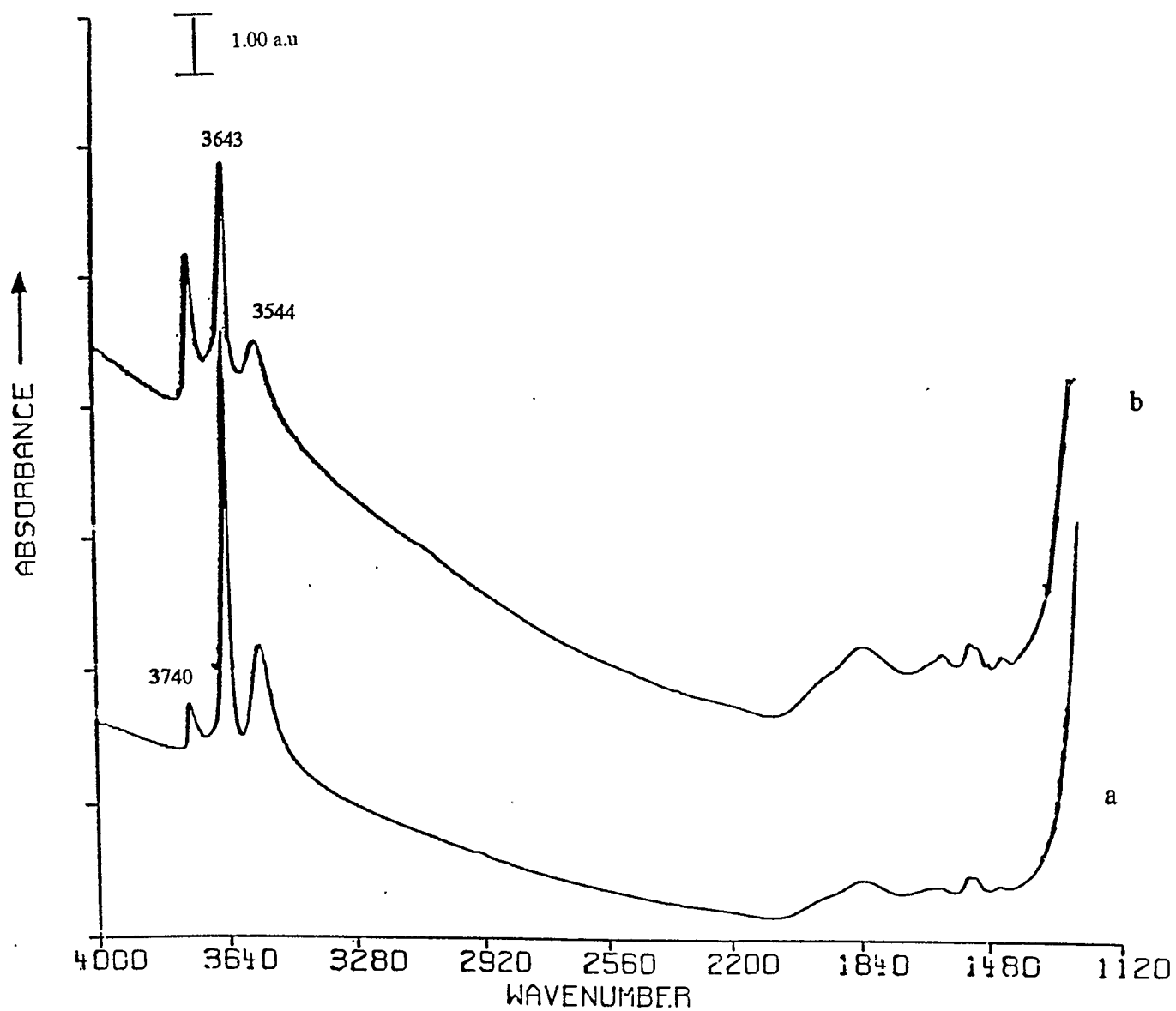


Fig. 4.4 IR spectra of 0.0193wt. %PdHY zeolite surfaces
a= sample calcined in O₂ at 500 °C overnight.
b= sample calcined in O₂ at 500 °C overnight and in H₂ at 300 °C for 1 hour.

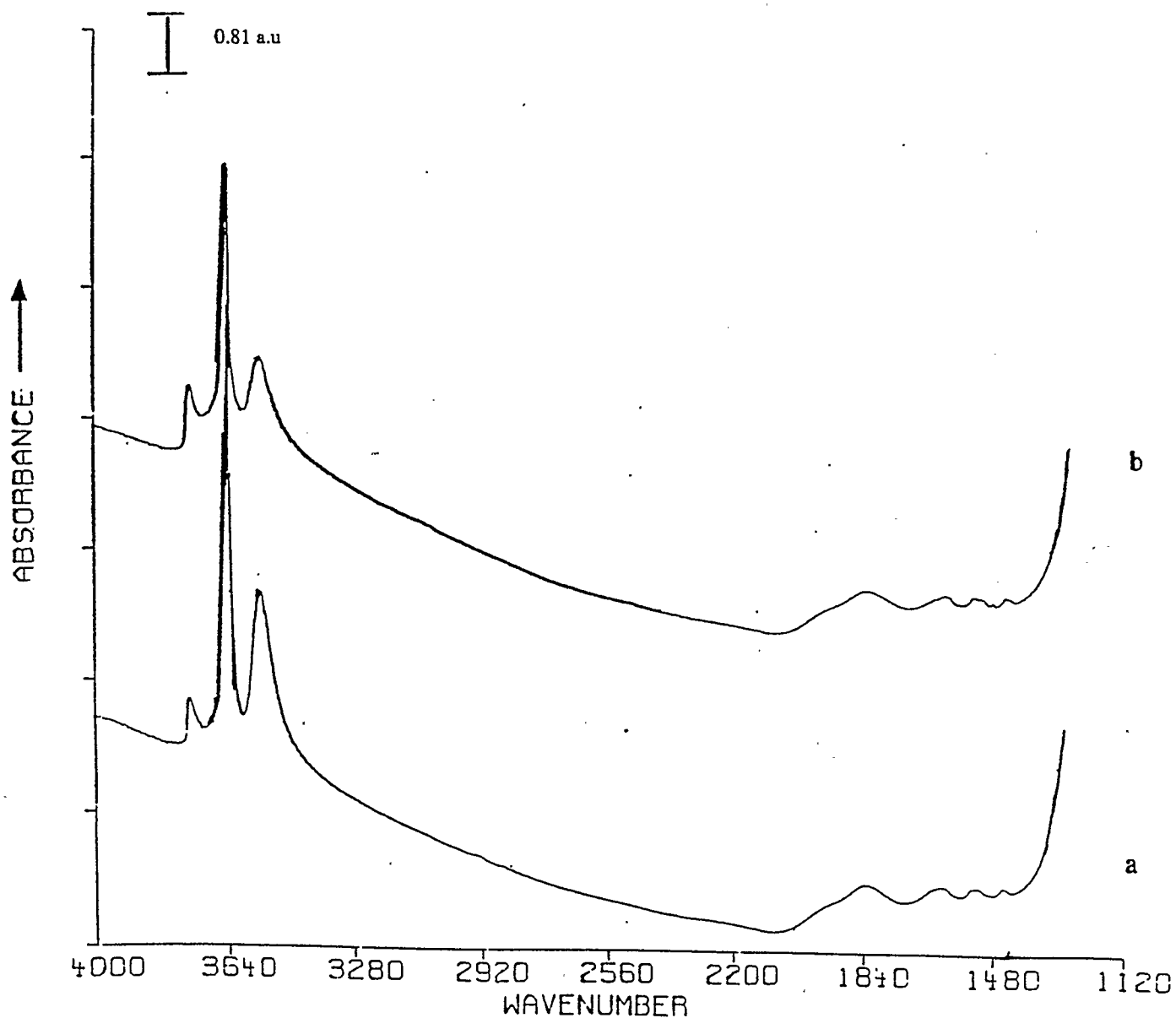


Fig. 4.5 IR spectra of 0.171wt. %PdHY zeolite surfaces
a= sample calcined in O₂ at 500 °C overnight.
b= sample calcined in O₂ at 500 °C overnight and in H₂ at 300 °C for 1 hour.

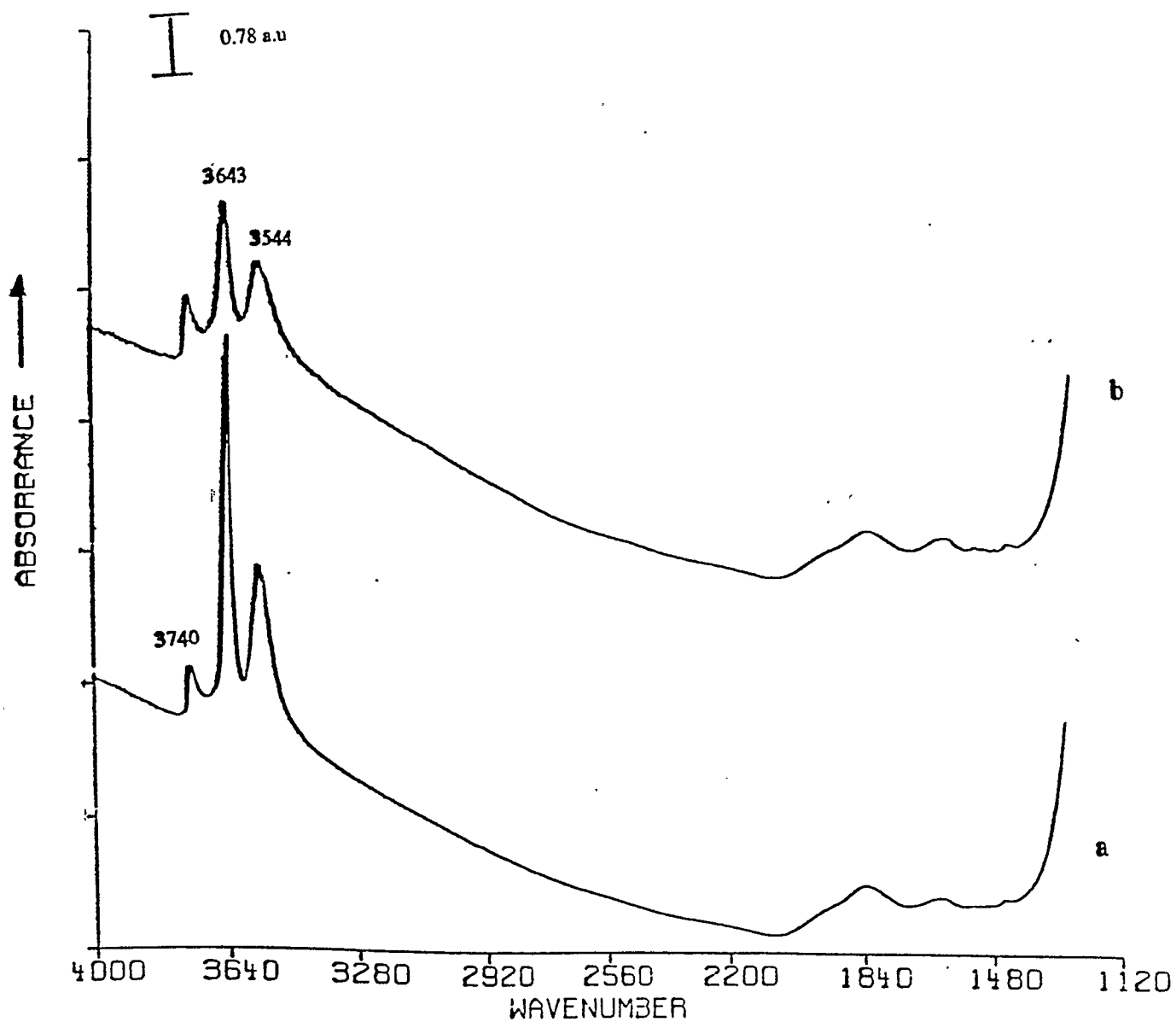


Fig. 4.6 IR spectra of 1.62wt. %PdHY zeolite surfaces
a= sample calcined in O₂ at 500 °C overnight.
b= sample calcined in O₂ at 500 °C overnight and in H₂ at 300 °C for 1 hour.

4.4 DISCUSSION

4.4.1 NaY ZEOLITE

From the spectrum (fig. 4.1), the O₂ treated NaY sample has only terminal hydroxyl groups. There was no band due to structural OH groups. This shows that our NaY sample is not cation deficient (1,10). The peak at 3688 cm⁻¹ is due to adsorbed water on the Na cations. This is confirmed by observation of the peak due to water bending mode at 1638 cm⁻¹. The peaks at 1886, 1759, 1621, 1490 and 1400 cm⁻¹ are probably due to overtones of the zeolite lattice vibrations. Neither mild reduction of NaY with H₂ at T_R=300°C nor drastic reduction at T_R=500°C changed the spectrum.

4.4.2 PdNaY ZEOLITE

The O₂-treated 1.58wt. %PdNaY sample showed peaks due to terminal OH groups at 3740 cm⁻¹ (fig. 4.2). There were also peaks at 3688 cm⁻¹ due to adsorbed water and the water bending band at 1643 cm⁻¹. This water might be bonded to Na or Pd, but since at this level of cation concentration one might expect that most of the Pd is located in the hexagonal prisms (17,18,19), the water can be assumed bonded to the Na ions.

These water peaks were present on all reduced and oxidized samples. The oxidation treatment also gave a peak at 3643 cm⁻¹ due to structural OH groups in supercages. There was no peak at 3544 cm⁻¹ due to OH group in the hexagonal prisms of the zeolite. This 3643 cm⁻¹ OH band is formed by cation hydrolysis during dehydration (1,9). Since the Pd is proposed as being stabilized mostly in hexagonal prism (in the CO study), it means that the proton produced during cation hydrolysis is formed in a hexagonal prism but migrates to supercages where it will attack a framework oxygen. The preference of H⁺ for the supercages could be due to repulsions between the

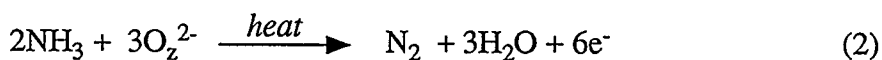
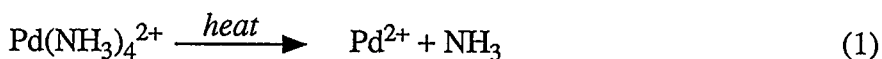
cations in the crowded hexagonal prism.

The above proposal does not explain the formation of water found adsorbed on the catalyst, but since adsorbed water was also found on NaY, it might not be related to the presence of Pd.

Naccache et al. (20) have proposed a mechanism for the process that occurs when a PdNaY zeolite is heated in vacuo and then in an O₂ atmosphere (scheme 2):

SCHEME 2

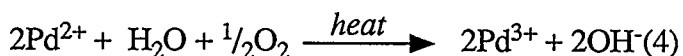
Heating in vacuo:



(O_z = Framework oxygen)



Heating in O₂ in the presence of the H₂O molecules formed in equation (2) above gives Pd³⁺:



Although this scheme explains the formation of Pd³⁺ and H₂O, it does not explain the formation of the OH groups responsible for the 3643 cm⁻¹ band. These OH groups are usually formed from cation hydrolysis during the removal of H₂O by dehydration. As the catalyst is being dehydrated, the naked Pd²⁺ will not effectively balance the charge on the AlO₄⁻ units and so it will undergo hydrolysis to give H⁺ and OH⁻ groups:

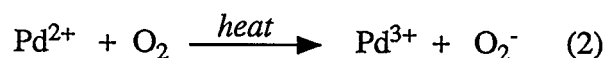
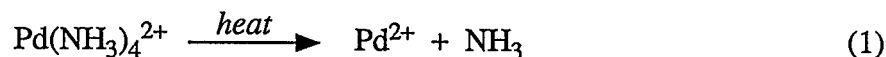


The H⁺ will attack zeolitic oxygen atoms to form the hydroxyl groups.

Naccache et al. identified the formation of Pd⁺ (proposed in scheme 2) but Michalik et al. (21) using PdCaX zeolite could not identify Pd⁺ and they have proposed

an alternative scheme shown below:

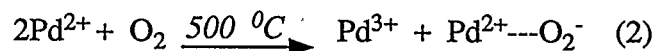
SCHEME 3



The O_2^- radical ion was not stabilized in the zeolite lattice but was supposed to have filled an oxygen framework vacancy.

Ghosh and Kevan (17) have in turn proposed another scheme for the oxidation of the catalyst:

SCHEME 4



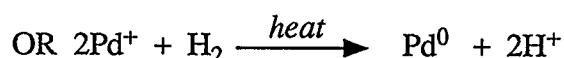
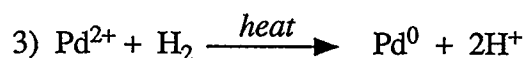
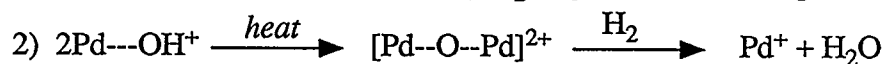
They have proposed that the $\text{Pd}^{2+}\text{---O}_2^-$ and O_2^- species are stable and have been observed (18) by ESR.

The latter two schemes do not explain the formation of water observed on the pellets in our study after calcination; we will assume the water was from from the "wet" O_2 gas used in the calcination. None of the workers who observed peaks due to water took extra precautions to dry the O_2 gas used in the calcination.

Mild reduction of PdNaY at $T_R=300^\circ\text{C}$ did not affect the 3740 cm^{-1} peak and this shows that this treatment did not destroy the zeolitic structure. But the 3643 cm^{-1} peak increases drastically in intensity. Peaks were still observed at 3688 and 1643 cm^{-1} due to adsorbed water. Various other workers have also observed the simultaneous increase in the 3643 cm^{-1} OH group and the formation of water during reduction of PdNaY (20,22).

Various schemes were proposed for the reduction of PdNaY to explain the formation of water and or the OH groups :

1) Removal of framework oxygen by H_2 to give water and trigonal aluminium.



The first two schemes do not explain the formation of OH groups, so the reduction of PdNaY must occur by a combination of the above schemes (22).

Note that no OH group was formed on the NaY support after H_2 treatment suggesting the active role of the Pd cation. The possibility that the adsorbed water also came from the "wet" gas cannot be ruled out.

The presence of an OH peak at 3643 cm^{-1} rather than at 3544 cm^{-1} (since Pd was identified as not occupying the supercages in our CO study) is due to proton migration to the supercages from the hexagonal prism and sodalite cages as explained earlier.

Drastic reduction at $T_R=500^\circ\text{C}$ seemed to have slightly decreased the intensity of the 3643 cm^{-1} peak probably from removal of OH groups by dehydroxylation.

On a fluorided PdNaY sample, there was no difference from the observation on PdNaY samples. The fluoride did not affect the peak at 3740 cm^{-1} which shows that the fluoridation of a NaY zeolite does not replace the terminal OH group with fluoride and the structure was not destroyed.

It should be mentioned that peaks found at 1490 and 1402 cm^{-1} on NaY disappear when Pd is loaded on the zeolite.

4.4.3 HY ZEOLITE

As reported in literature (1,2), there are three OH peaks for a decationized zeolite at 3735 cm^{-1} (terminal OH), 3643 and 3540 cm^{-1} after calcination (fig. 4.3). The intensity of the 3643 and 3540 cm^{-1} peaks are nearly equal as expected on this catalyst (1).

There are no peaks due to adsorbed water on HY and PdHY zeolites studied in this laboratory. The peaks at 1424 , 1828 and 1616 cm^{-1} are due to overtones of the framework lattice. The peak at 1532 cm^{-1} which might be due to lattice vibration is removed when HY is loaded with metal cation.

Mild reduction of HY in H_2 at $T_R=300^\circ\text{C}$ reduces the intensity of the structural OH groups (fig. 4.3). This is in contrast to PdNaY where reduction increases formation of OH groups. The reason for this reduction in intensity is due to increased dehydroxylation which occurs as we reduce the catalyst (see section 5.3.4). From a comparison of intensity ratios of the 3643 cm^{-1} and 3540 cm^{-1} for the oxidized and reduced samples of HY, it appears like the OH group at 3540 cm^{-1} is affected by H_2 reduction more than the 3643 cm^{-1} OH group.

Drastic reduction, $T_R=500^\circ\text{C}$, decreases both OH groups. This observed effect of reduction was also observed on PdHY at all exchange levels.

Fluoridation of HY does not affect the terminal OH group (3740 cm^{-1} band) (fig. 4.3). This was also observed on NaY zeolite and this means that the fluoride does not replace terminal OH groups or destroy the lattice structure.

On the HY zeolite, most of the structural OH groups were replaced during the fluoridation treatment (fig. 4.3). The fluoride does not seem to have any preference in replacing the OH groups in the supercages or hexagonal prisms.

4.4.4 PdHY ZEOLITE

The three types of OH groups are observed as expected on all the samples of PdHY (1.62, 0.171 and 0.0193wt. %Pd) as shown in figs. 4.4 - 4.6. But it is surprising to find the 3643 cm^{-1} band on the 0.0193wt. %Pd sample stronger than that on HY. This is in contrast to what is observed in the literature (1).

The intensity ratio of the 3643 cm^{-1} and 3544 cm^{-1} $\{I_{3643}/I_{3544}\}$ peaks on 0.0193wt. %Pd (fig. 4.4) after calcination is bigger than that of HY (fig. 4.3) and this means that at low exchange levels of Pd, Pd prefers the hexagonal prism as seen from the replacement of the 3540 cm^{-1} OH group of HY (1). At higher exchange levels, it spills over into the sodalite cages.

The 3544 cm^{-1} peak of higher loadings of Pd is of nearly equal intensity with that on HY, and this shows that higher loadings of Pd on HY show no preference for hexagonal prism (15).

From analysis of the intensity ratio of the 3643 cm^{-1} and 3544 cm^{-1} peaks $\{I_{3643}/I_{3544}\}$ for increasing loadings of Pd on HY (figs. 4.5 - 4.6), we find a decrease in this ratio; which shows that Pd loaded on HY spills over into sodalite cages and/or supercages (15) at higher loadings. This was the same conclusion reached with the CO study done in this laboratory on these samples.

On mild reduction, $T_R=300^\circ\text{C}$, the 3740 cm^{-1} peak on the 0.0193wt.% PdHY sample increases over that on HY, while the same peaks on zeolites with higher loadings of Pd are not affected by the reduction.

The reduction greatly diminished the 3643 cm^{-1} and the 3544 cm^{-1} peaks which was what we observed on HY. This is in contrast to the observation on PdNaY.

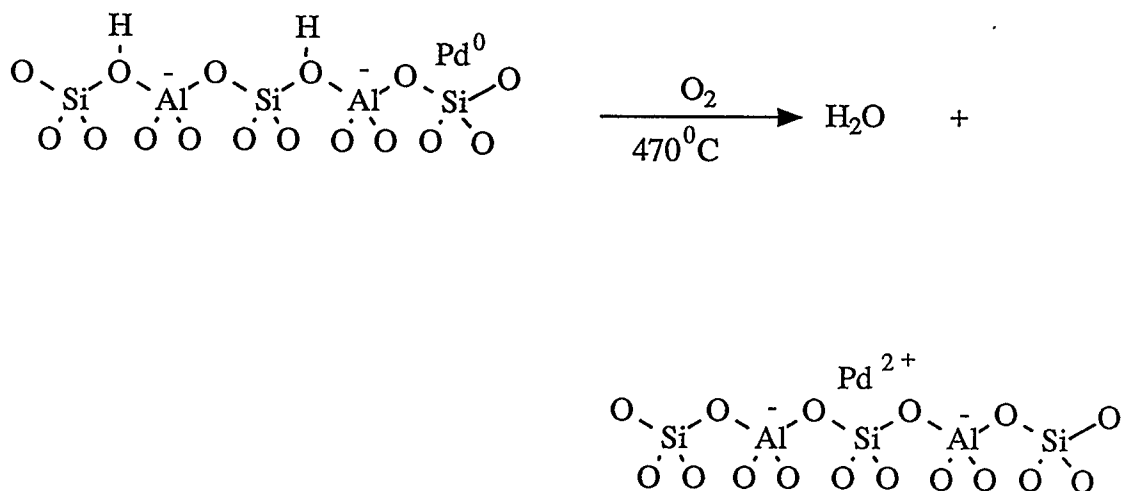
By comparing the intensity ratio $\{I_{3643}/I_{3544}\}$ of oxidized and reduced samples for each PdHY zeolite (figs. 4.4 - 4.6), it was apparent that with increasing loading of Pd on HY, the intensity ratio of reduced samples increasingly decreased in comparison to

the oxidized samples, that is, the 3643 cm^{-1} OH group is preferentially lost. Also, it was noted that on HY zeolites, although reduction decreased both 3643 cm^{-1} and 3544 cm^{-1} peaks, the 3544 cm^{-1} peak is lost preferentially. This is in contrast to the observation on Pd-loaded HY where the 3643 cm^{-1} is preferentially lost.

The obvious absence of water peaks on HY and PdHY samples in comparison to PdNaY, shows that the peak due to adsorbed water observed on PdNaY is due to water bonded to sodium cation rather than Pd.

Drastic reduction, $T_R=500^\circ\text{C}$, removes nearly all the structural OH groups while the 3740 cm^{-1} peak does not appear to be affected. This observation has already been explained as due to additional dehydroxylation occurring on the catalyst during reduction.

The reoxidation of a reduced 0.171wt. %PdHY showed a reduction of the structural OH groups. The 3740 cm^{-1} peak due to terminal OH was not affected. A mechanism for this observation was given by Bergeret et al. (23) (see below):



The presence of the water molecule is confirmed by peaks at 3688 and 1643 cm^{-1} .

The fluorided PdHY zeolite had reduced amount of structural OH groups in comparison to unfluorided PdHY samples as expected. But otherwise, the fluoride did not seem to affect the location of Pd on HY.

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CHAPTER FIVE

5. PYRIDINE SURFACE STUDY

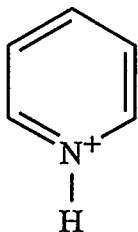
5.1 INTRODUCTION

Acid-catalyzed reactions which occur through a carbonium ion mechanism are very important in the petroleum industry. This has made catalysts with acid sites very important industrially. Zeolites are very acidic catalysts and they are used industrially in many acid-catalyzed reactions like polymerization, isomerization etc. The type and strength of the acid sites on zeolites can be studied by adsorbing basic molecules like ammonia ($pK_b=5$), piperidine ($pK_b=2.8$) and pyridine ($pK_b=9$).

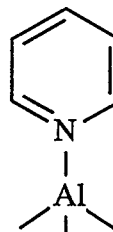
These basic molecules will interact with Bronsted acid sites, Lewis acid sites and cations ion-exchanged into the zeolite. NH_3 , which is a strong base, can interact with even the weakest acid sites, while pyridine (py.) will interact with only the strongest acid sites.

Adsorption of pyridine on Bronsted acid sites (Bpy) gives rise to an infrared band at 1545 cm^{-1} due to the pyridinium ion (structure I, shown below) (1). This band is due to a ring vibration of the pyridinium cation.

Lewis acid sites are coordinatively unsaturated sites, such as tri-coordinated aluminium atoms. Pyridine adsorbed on such sites (structure II, below) gives an infrared band at close to 1450 cm^{-1} (1).



I



II

Exchangeable cations on the zeolite also act as Lewis sites (pseudo-Lewis sites) and adsorbed pyridine on these sites absorbs at $1440\text{--}1449\text{ cm}^{-1}$. These sites are called pseudo-Lewis sites since they bind with pyridine through coordinate bonds like a true Lewis site, yet they are not in the zeolite framework structure. The strength of the interaction of pyridine with pseudo-Lewis sites differs from that on true Lewis sites; the M--py (M = Metal cation) infrared band is lost after evacuation at 200°C , while the pyridine bonded to true Lewis sites is still observed after evacuation till 400°C . The observation of a band due to cation--py interaction will confirm that the cation is stabilized in the supercages, since pyridine cannot enter the sodalite cages and hexagonal prisms.

The absorption frequency of M--py varies with cation type, increasing with a decrease in radius of the cation. This frequency changes with the cation electronegativity, and the electrostatic field of the zeolite (1). Pyridine combines more strongly with zeolites with smaller cations. The absorption band of pyridine bonded to true Lewis sites remains constant at or above 1450 cm^{-1} .

Hydrogen-bonded pyridine (Hpy) and physisorbed pyridine are identified from their absorption bands (see table 5.1) and their ease of removal with increasing temperature. They are removed after evacuation at 200°C .

Redistribution of pyridine has also been shown to occur during desorption (2); it migrates from weaker sites (e.g. Na^+) to stronger sites (e.g. Lewis sites).

Pure NaY and other group 1A cation-exchanged zeolites without any cation deficiency should show no Bronsted or Lewis acid sites. Pyridine adsorption on such zeolites should only show a band between the cation and pyridine (3).

The band assignments for the different species of adsorbed pyridine are given in table 5.1.

Table 5.1 Assignment of pyridine absorption bands (from ref. 5 pg. 226)

PY	LPY	BPY	HPY
1580	1620	1638	1614
1572	1577	1620	1593
1482	1490	1490	1490
1439	1450	1545	1445

PY - physically adsorbed pyridine

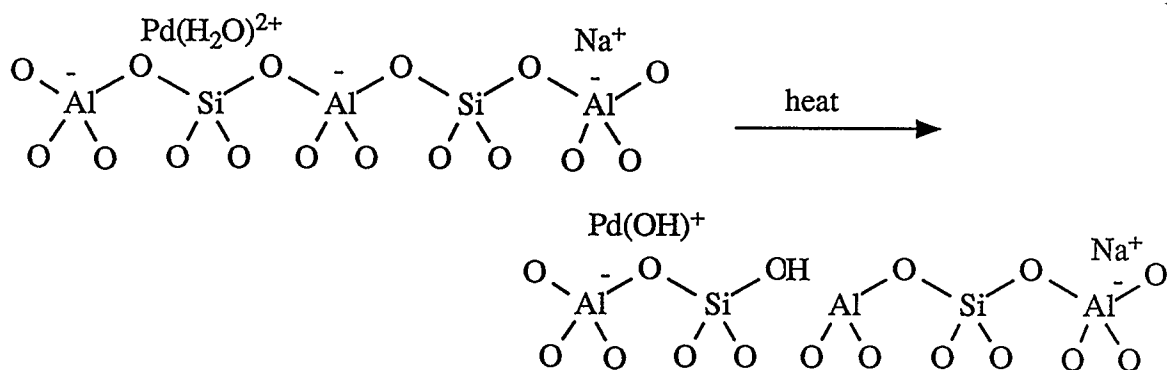
LPY - pyridine adsorbed on Lewis acid sites

BPY - pyridine adsorbed on Bronsted acid sites

HPY - pyridine adsorbed by hydrogen bonding

Ward (4) in a study using pyridine on transition-metal exchanged NaY has observed that these zeolites exhibited Bronsted and Lewis acidity. The protonic activity results from cation hydrolysis as shown in the reaction mechanism in scheme 1.

SCHEME 1



Different conclusions have been reached regarding the presence of Lewis sites on cation-exchanged zeolites. Ward (4) and Rabo in his review (5a) have reported the absence of Lewis acid sites on transition-metal-ion loaded NaY after calcination, although bands due to pyridine-cation interaction were observed. Other workers using Group IIA-exchanged zeolites have shown that Lewis sites are formed on the surface depending on the calcination conditions (5b).

It has also been mentioned that the $\text{Pd}(\text{OH})^+$ formed shows an absorption band at 3580 cm^{-1} due to the hydroxyl group. These OH groups have been found to be non-acidic to pyridine and above 400°C , they form MO or $\text{M}^+-\text{O}-\text{M}^+$ species on the zeolite (5c).

On decationized zeolites (HY), pretreatment done at $T < 300^\circ\text{C}$ has shown the presence of Bronsted acid sites only, with no Lewis sites, but after pretreatment at $T > 400^\circ\text{C}$, the zeolite will have both Bronsted and Lewis acid sites since dehydration and dehydroxylation are occurring at this temperature (5). As dehydroxylation increases, the number of Bronsted acid sites decreases and the number of Lewis sites increases. As OH groups are removed from the surface, coordinatively unsaturated sites are created.

Eberly (6) using pyridine on decationized zeolites (HY) has shown that the Lewis sites are stronger than the Bronsted sites, and he has also shown that only the OH

groups in the supercages giving the 3650 cm^{-1} band interact with pyridine while the OH groups in the sodalite cages giving the 3550 cm^{-1} band do not interact with pyridine. Some workers have observed that the OH groups in the sodalite cages do interact with pyridine at high vapour pressure (7a).

On transition metal cation loaded HY zeolites, it was also found that the 3650 cm^{-1} OH group interacts with pyridine while the 3550 cm^{-1} OH group does not. It is also expected that the reduction of the metal cation loaded on the zeolites should eliminate bands due to pyridine-cation interaction.

From Beer's law, we can derive an equation that will allow us to estimate the ratio of the number of Lewis acid sites to Bronsted acid sites. Ward (7b) has estimated the ratio of the absorption coefficients of the Lewis sites to the Bronsted sites, as shown below:

$$\frac{[\text{Lewis sites}]}{[\text{Bronsted sites}]} = \frac{I_L \epsilon_L}{I_B \epsilon_B}$$

ϵ_L = Absorption coefficient of the 1450 cm^{-1} band

ϵ_B = Absorption coefficient of the 1545 cm^{-1} band

$$\frac{\epsilon_L}{\epsilon_B} = 1.1 \pm 0.2$$

I_L = Intensity of the 1450 cm^{-1} band

I_B = Intensity of the 1545 cm^{-1} band

Also, by using the initial values of I_B and I_L , it will be possible to compare the number of Bronsted and Lewis sites on the various catalysts. A plot of intensity against desorption temperature will also make it possible to estimate the strength of the Bronsted and Lewis sites on these catalysts.

5.2 RESULTS

Pyridine was used to study the effect of :

- 1) cation exchange
- 2) calcination in oxygen
- 3) reduction in hydrogen
- 4) fluoridation

on the acidic properties of NaY and HY zeolites.

All samples showed characteristic peaks due to physisorbed pyridine, and hydrogen-bonded pyridine was observed on some catalyst samples. The infrared spectra between 1700 and 1400 cm^{-1} obtained for pyridine adsorbed on calcined samples of NaY, HY, 1.58wt. %PdNaY and 1.62wt. %PdHY are shown in figs. 5.1-5.4 respectively. The other spectra obtained have not been included, to keep this thesis from becoming too large, but many of the results are included in the desorption curves described in the next section.

5.2.1 TEMPERATURE DESORPTION CURVES

Each of these curves is the plot of the infrared intensity of characteristic bands versus the temperature of desorption of adsorbed pyridine on the catalysts after the application of various pretreatment conditions. Figs. 5.5-5.15 show the pyridine desorption curves after various treatments as described in the figure captions. The intensity of adsorbed pyridine after desorption at 100°C is not a very reliable indication of Bronsted or Lewis acidity because of the presence of physisorbed pyridine, and so less emphasis will be put on these values in interpreting the results.

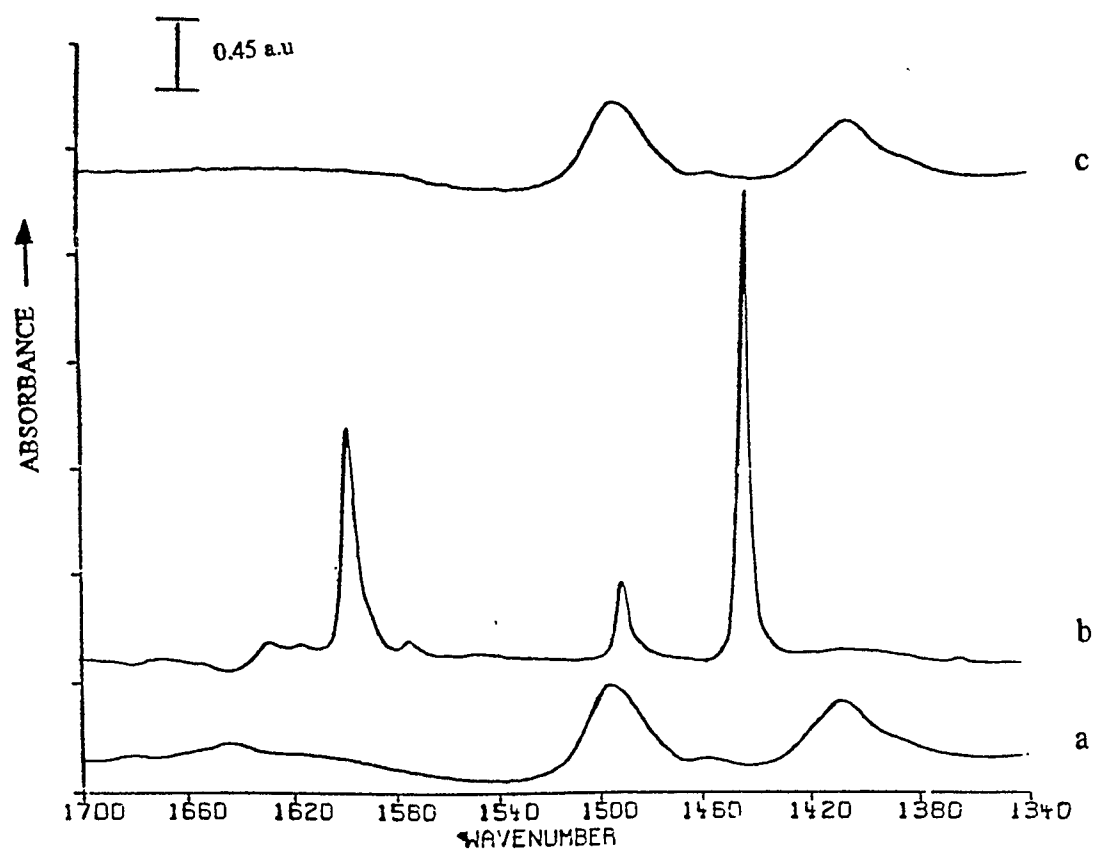


Fig. 5.1. Spectra of pyridine adsorbed on a calcined NaY, sample after desorption at different temperatures. a= clean pellet before adsorption of pyridine b= surface species after desorption at 200 °C c= pellet surface after desorption at 300 °C.

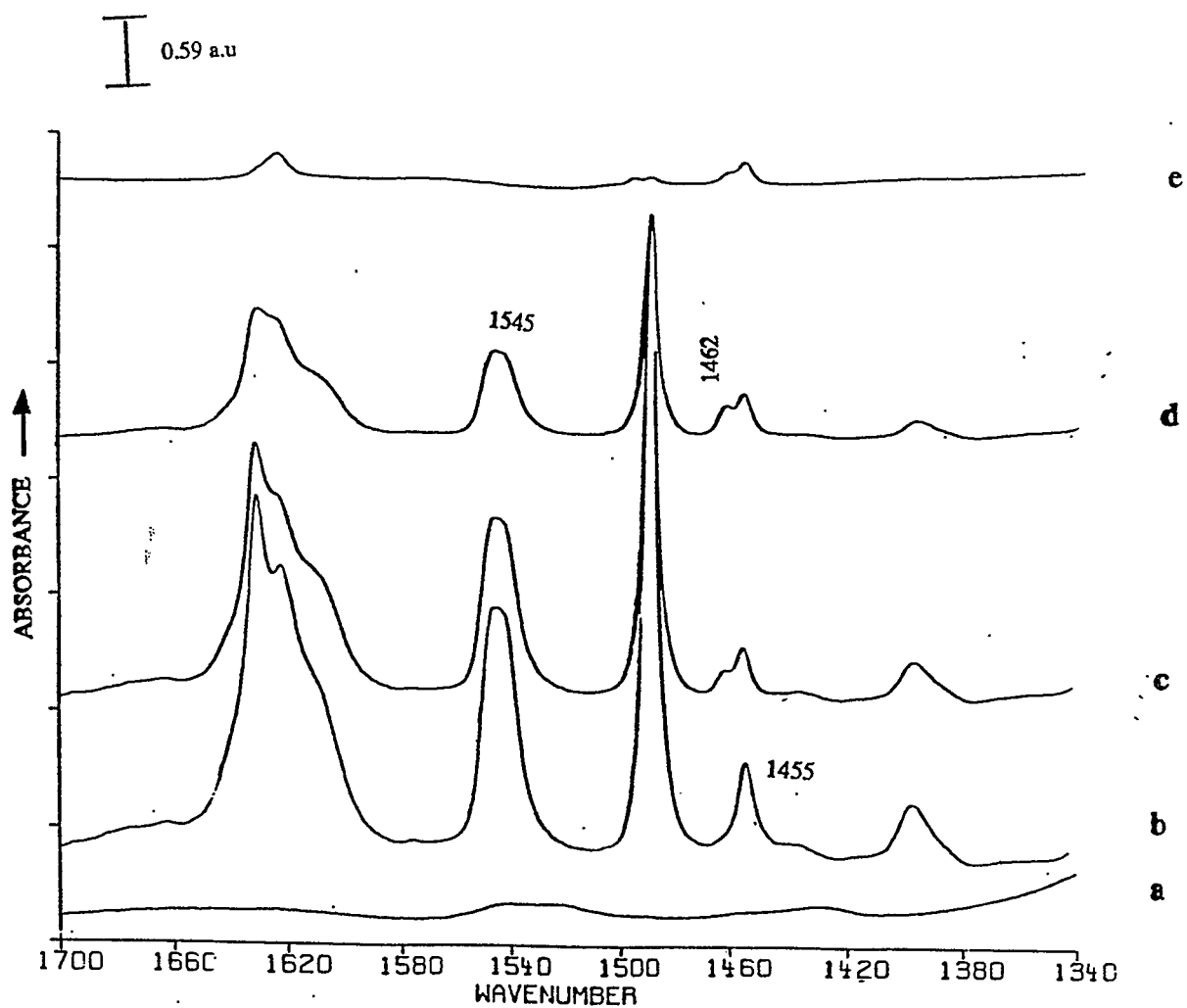


Fig. 5.2. Spectra of pyridine adsorbed on a calcined HY sample after desorption at different temperatures. a= clean pellet before adsorption of pyridine b= 200 °C evacuation c= 300 °C d= 400 °C e= 500 °C.

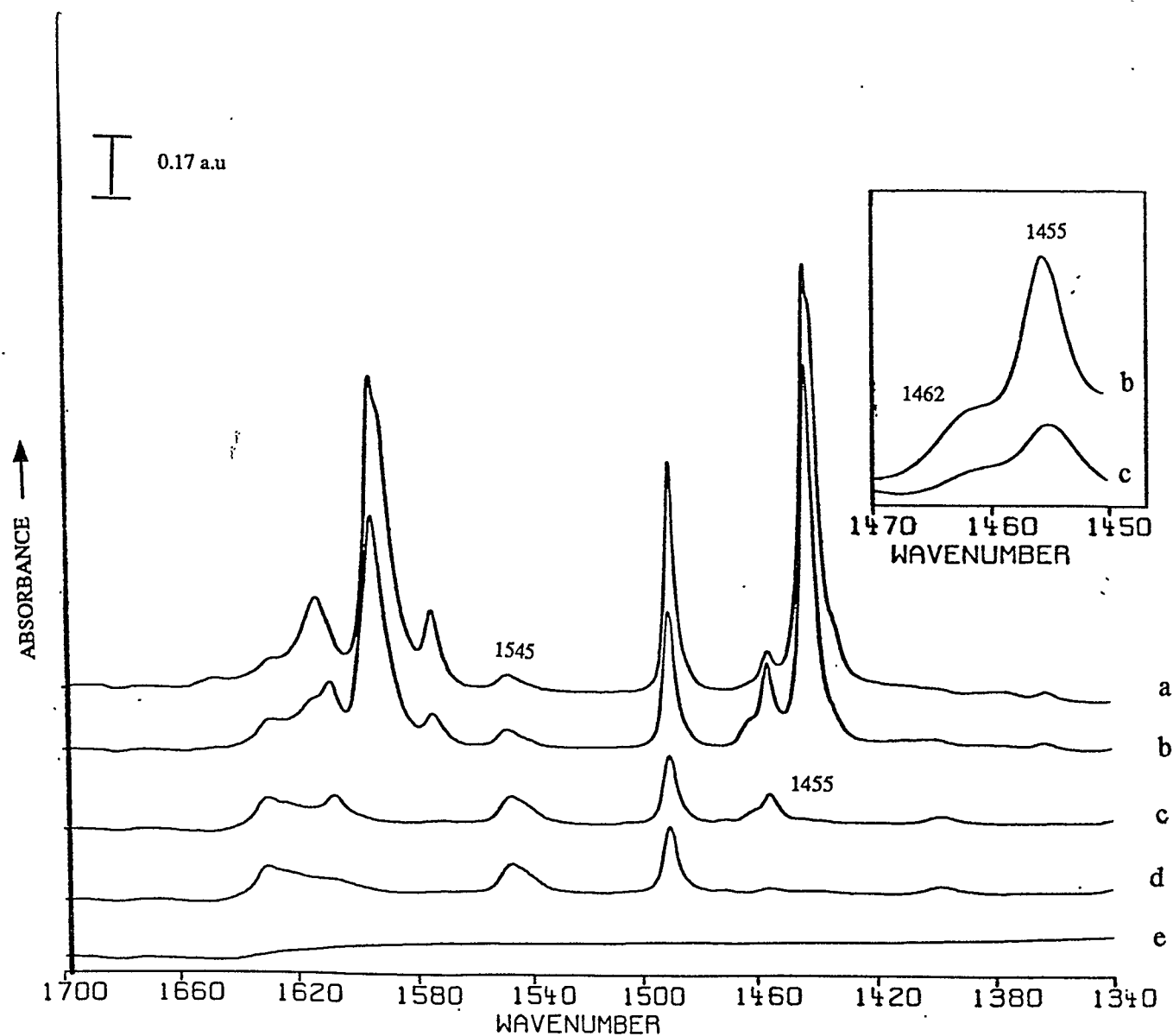


Fig. 5.3 Spectra of pyridine adsorbed on a calcined 1.58wt. %PdNaY after desorption at different temperatures.

a= surface species after desorption at 100 °C b= 200 °C c= 300 °C d= 400 °C e= 500 °C.

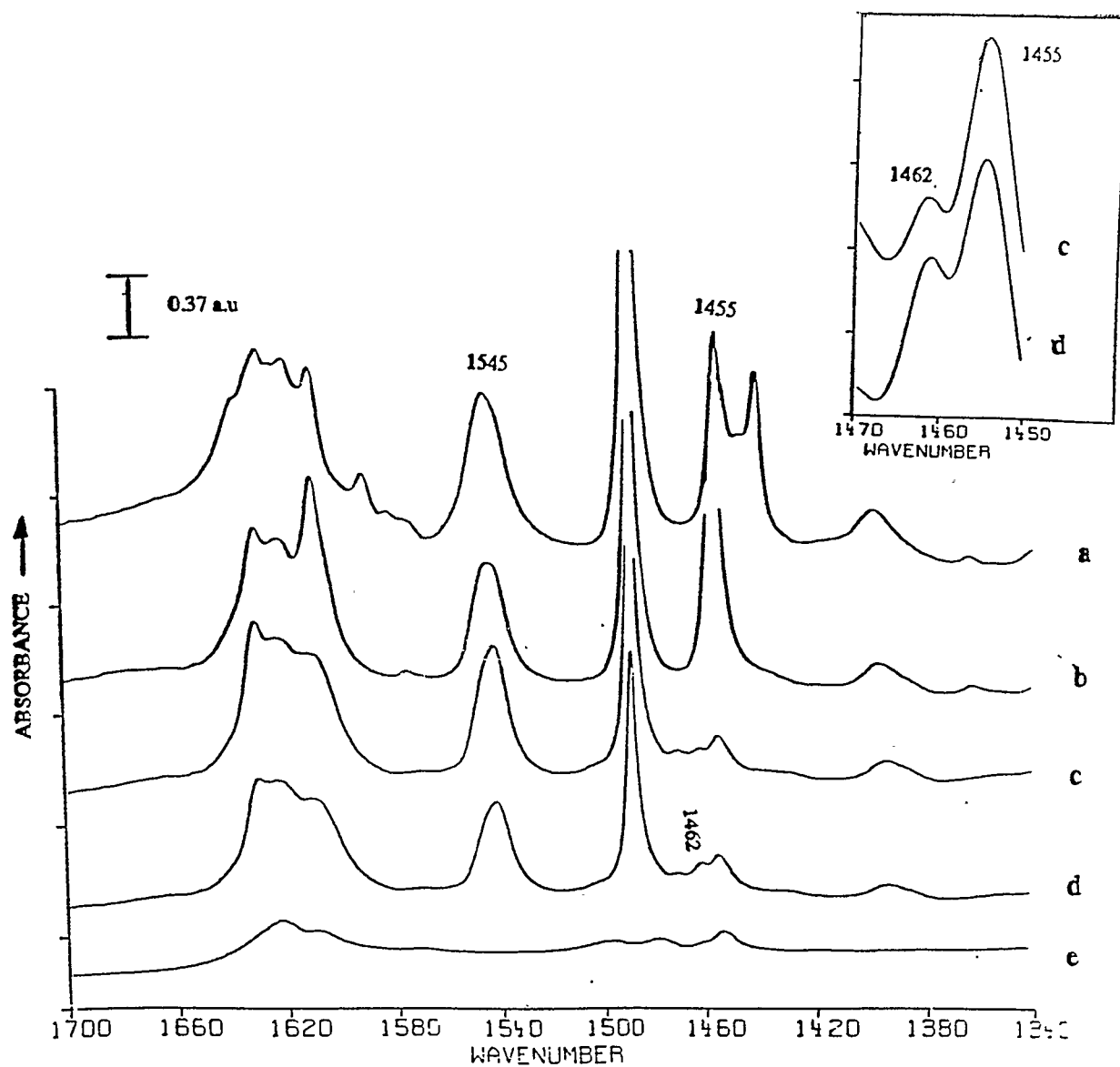


Fig. 5.4 Spectra of pyridine adsorbed on a calcined 1.62wt. %PdHY sample after desorption at different temperatures.

a= surface species after desorption at 100 °C b= 200 °C c= 300 °C d= 400 °C e= 500 °C.

Fig. 5.5 Pyridine adsorbed on "special" Lewis sites of various oxidized catalysts (1462 cm^{-1} peak).

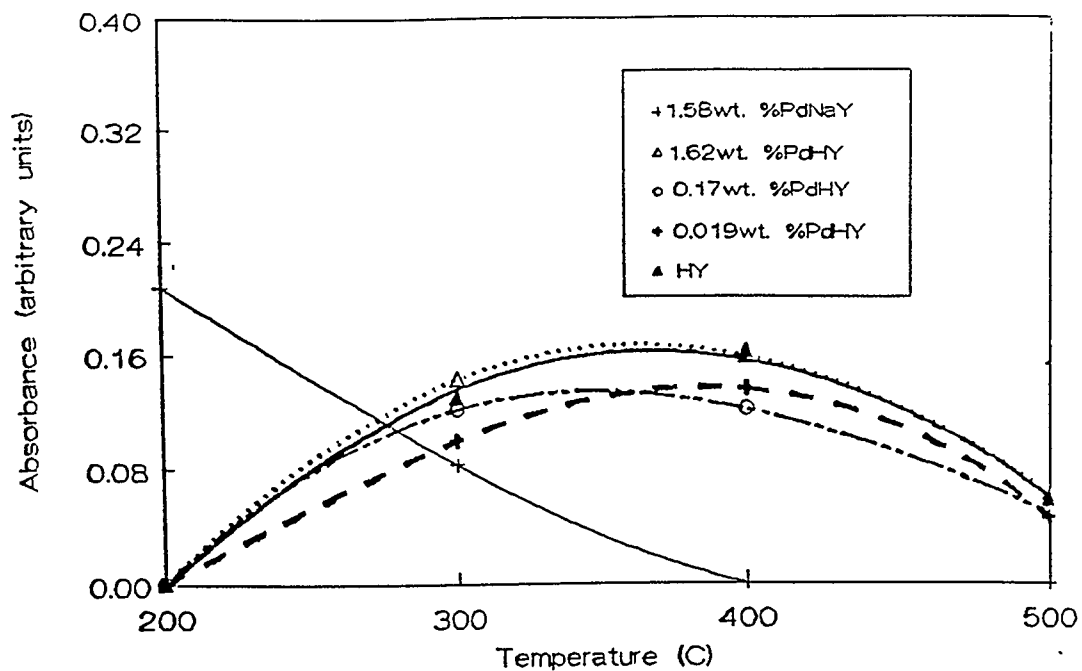


Fig. 5.6 Pyridine adsorbed on Bronsted and Lewis sites of oxidized and reduced samples of 1.58wt. %PdNaY

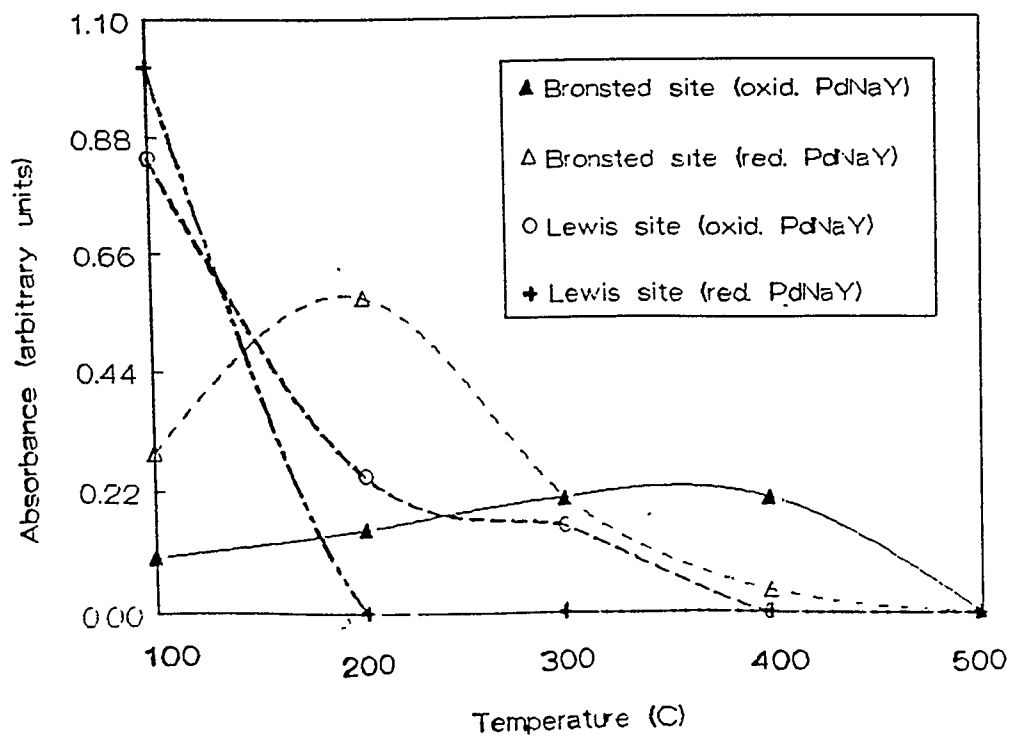


Fig. 5.7 Pyridine adsorbed on Bronsted and Lewis sites of oxidized and reduced samples of 1.58wt. %PdNaY and 1.50wt. %PdFNaY.

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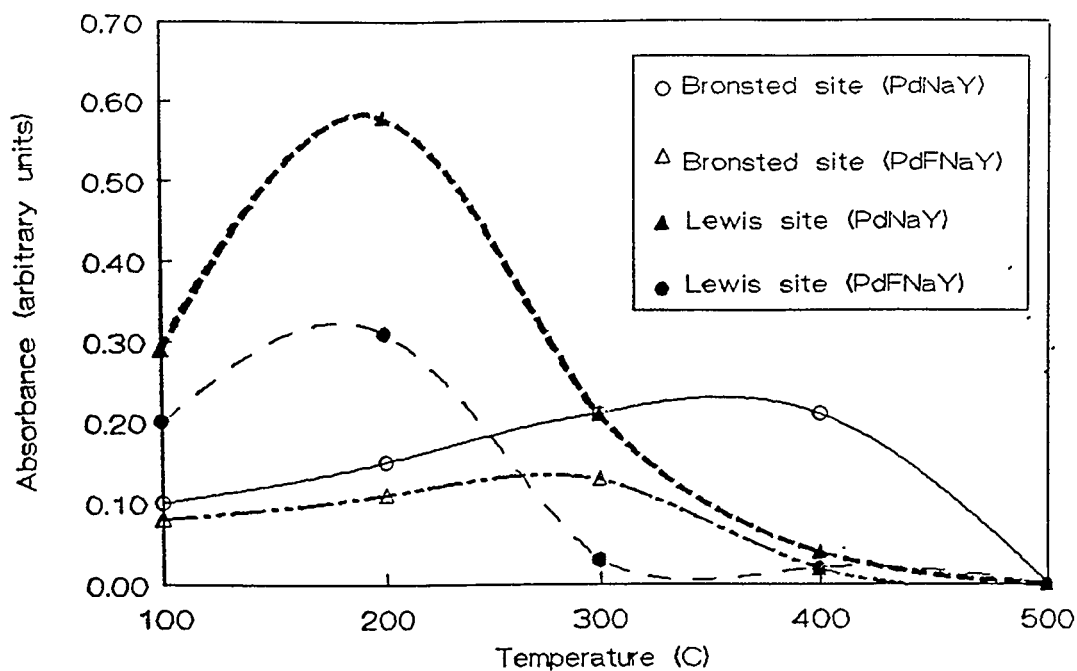


Fig. 5.8 Pyridine adsorbed on Bronsted and Lewis sites of calcined and reduced samples of HY.

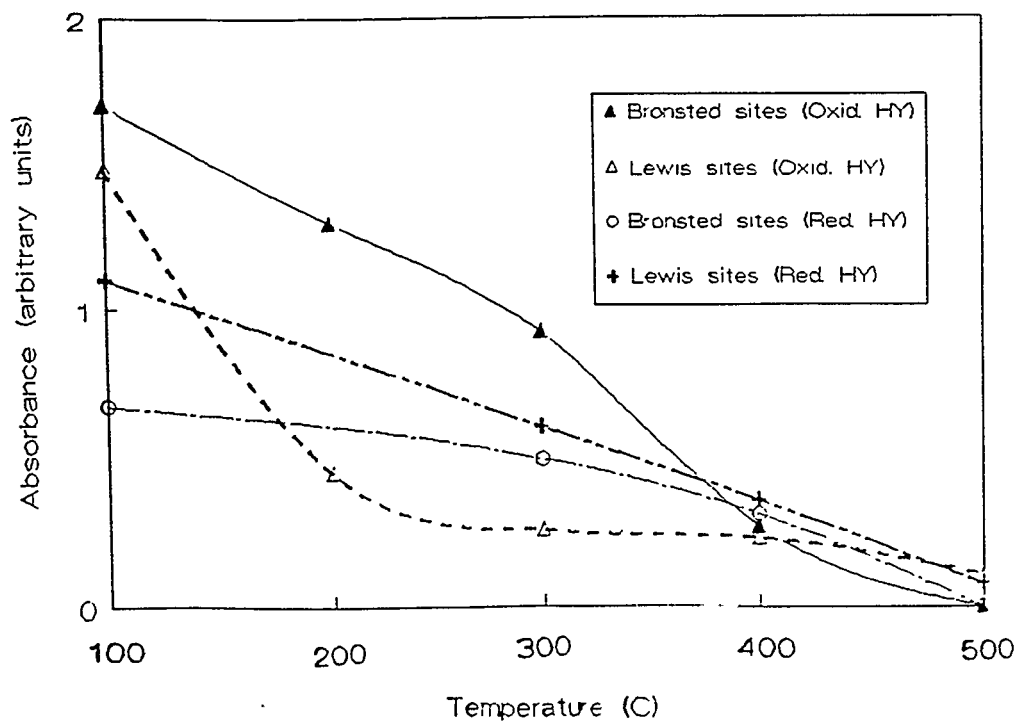


Fig. 5.9 Pyridine adsorbed on Bronsted and Lewis sites of oxidized samples of HY and FHY catalysts.

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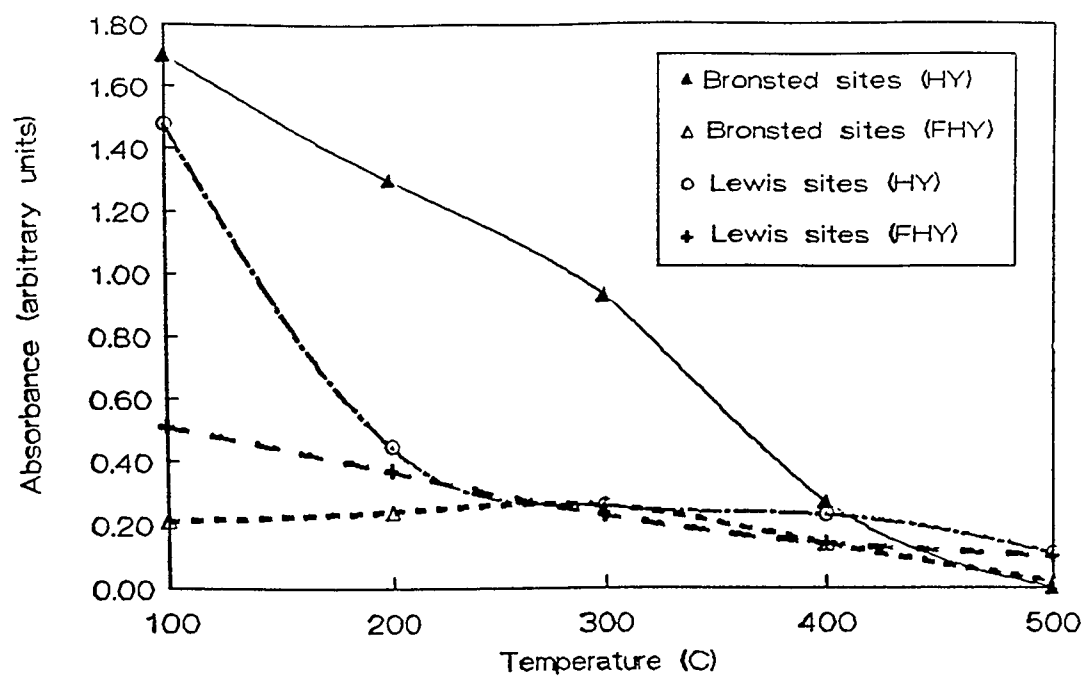


Fig. 5.10 Pyridine adsorbed on Bronsted and Lewis sites of oxidized and reduced samples of FHY.

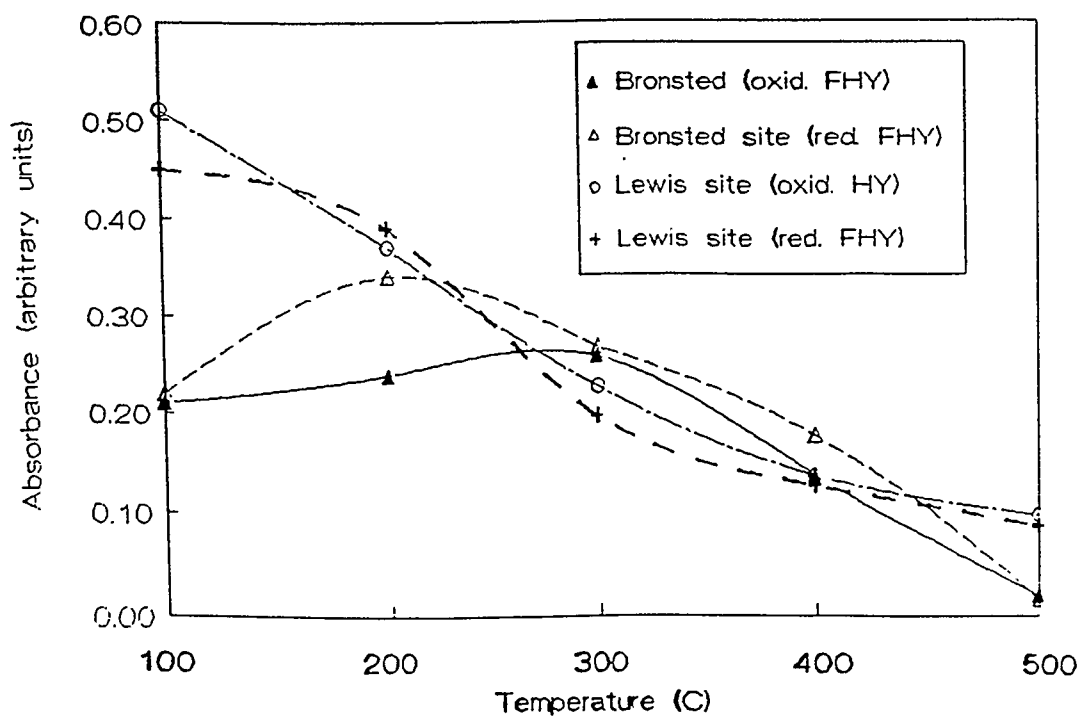


Fig. 5.11 Pyridine adsorbed on Bronsted sites of various oxidized samples of PdHY catalysts.

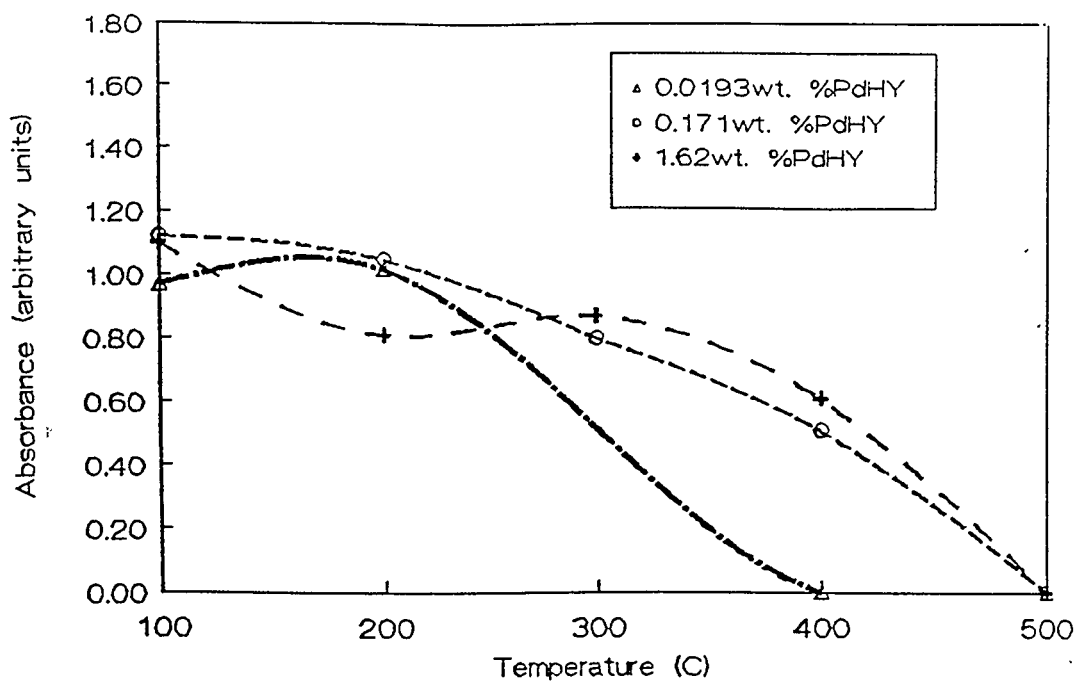


Fig. 5.12 Pyridine adsorbed on Lewis sites of various oxidized samples of PdHY.

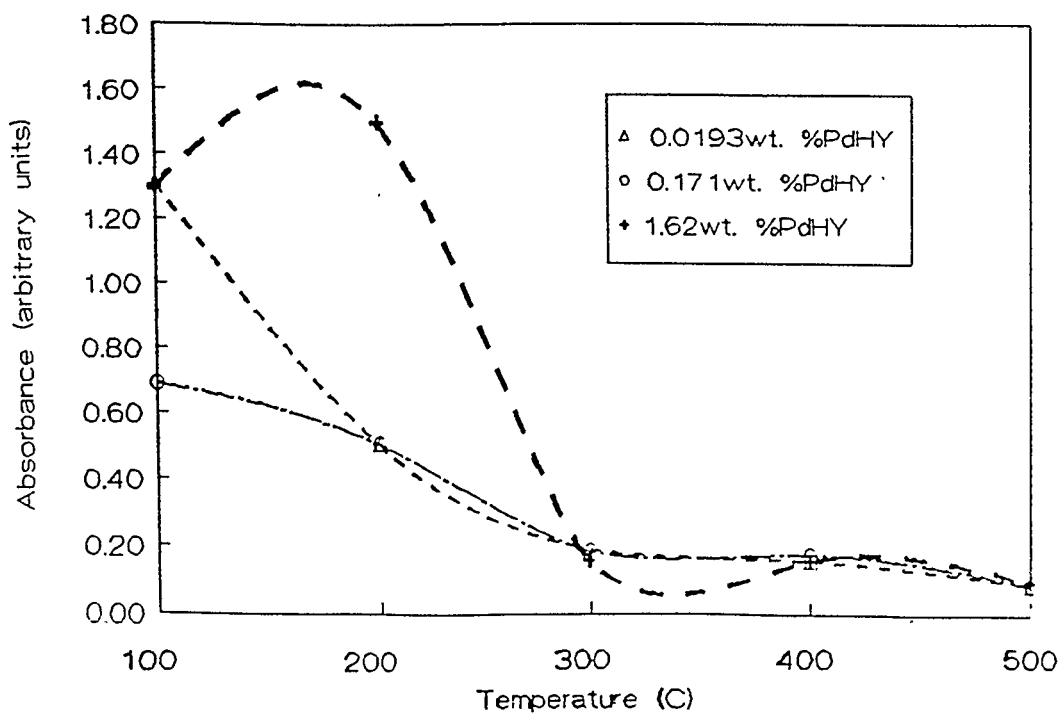


Fig. 5.13 Pyridine adsorbed on Bronsted and Lewis sites of oxidized and reduced samples of 0.019wt. %PdHY.

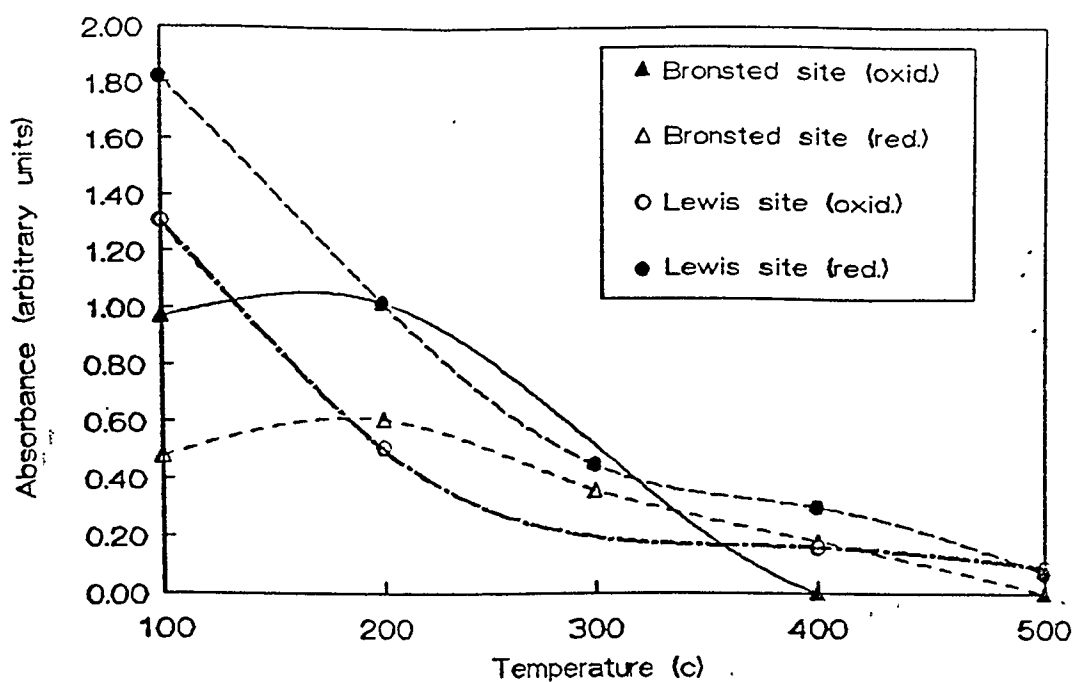


Fig. 5.14 Pyridine adsorbed on Bronsted and Lewis sites of oxidized and reduced samples of 0.17wt. %PdHY.

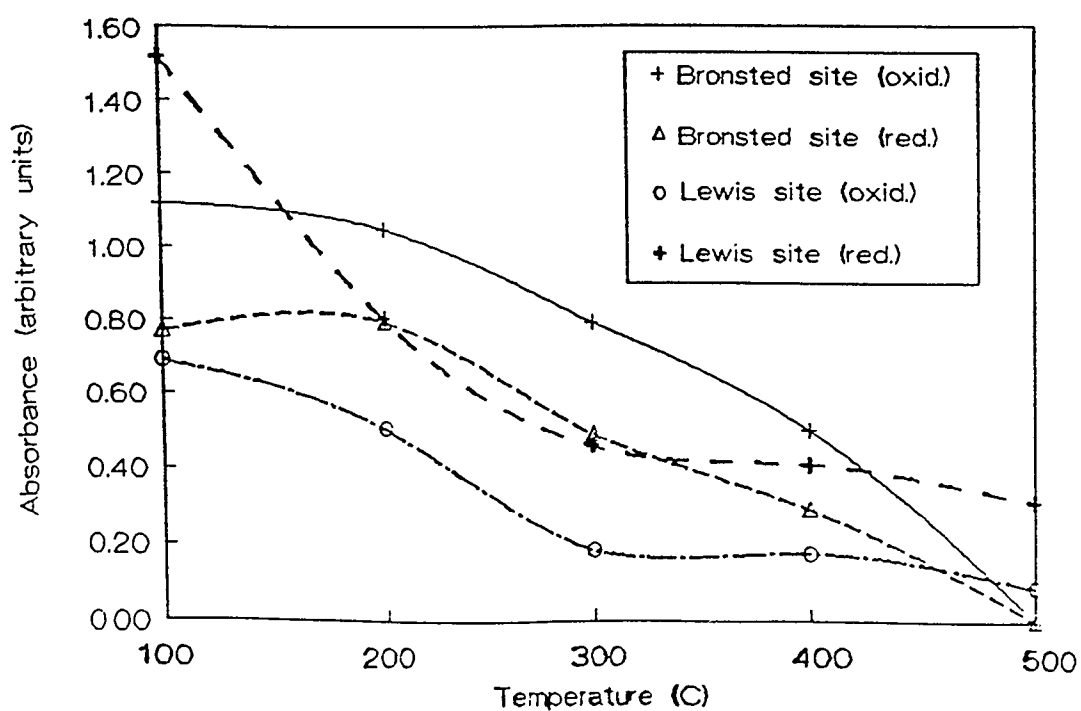
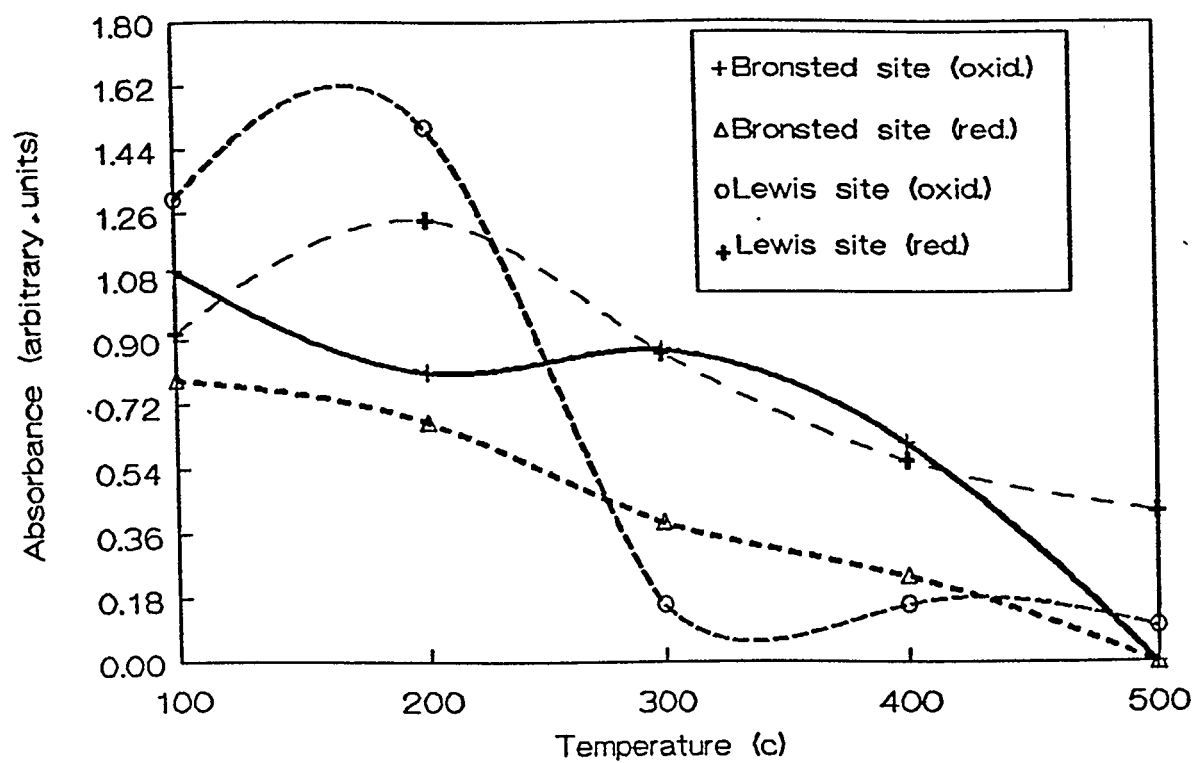


Fig. 5.15 Pyridine adsorbed on Bronsted and Lewis sites of oxidized and reduced samples of 1.62wt. %PdHY.



5.3 DISCUSSION

5.3.1 NaY ZEOLITE

Pyridine adsorption on calcined NaY (fig. 5.1) shows, as expected, that there are no peaks due to pyridine adsorbed on Bronsted or Lewis acid sites. This shows that our NaY sample is not cation deficient. The only peak observed on this zeolite was at 1441 cm^{-1} due to $\text{Na}^+\text{-py}$ (pseudo-Lewis sites).

Reduction of the NaY zeolite did not show any changes in the spectra. The peak at 1441 cm^{-1} was still observed after reduction.

5.3.2(a) Pd-EXCHANGE OF NaY ZEOLITE

The peak at 1545 cm^{-1} observed on the sample loaded with 1.58wt. %Pd (fig. 5.3) is due to the pyridinium ion and confirms that the presence of the Pd^{2+} created the Bronsted acid sites, presumably through cation hydrolysis. These Bronsted acid sites are generally accepted to involve a hydrogen in close proximity to both an aluminium and a silicon atom in the zeolitic framework. The structure of this type of site is depicted in either of the two resonance forms shown below:



Depictions of a Bronsted site

The spectra in the region assigned to Lewis-adsorbed pyridine ($1450\text{-}1465\text{ cm}^{-1}$)

are interesting because two bands are seen in this region during desorption. A band at 1455 cm^{-1} appears after desorption at 100°C and persists till 400°C . This band is attributed to pyridine bonded to trigonally coordinated aluminium. Another band at 1462 cm^{-1} appears at 200°C and it decreases in intensity until it disappears at 400°C (fig. 5.3). The appearance of a second peak in this region has been noted on occasion by other workers, but only for hydrogen-exchanged forms of some zeolites (8). It has never been reported on Na-exchanged zeolites before. This peak was also observed on HY-based catalysts studied in this work; on these catalysts, the 1462 cm^{-1} peak appears after desorption at 300°C and it stays till 500°C desorption. It is not clear whether the peak at 1462 cm^{-1} arises from the same type of sites on PdNaY and the HY samples, since there are some differences in their behaviour (fig.5.5). The discussion of the origin of this peak will be postponed to section 5.3.4(a).

The reason for the inability of some other workers (4,5a) to observe Lewis sites after pyridine adsorption on calcined metal/NaY is not clear yet; it might be due to the fact that they used a lower pretreatment temperature. Another possible explanation might be the mistaken assignment (by these workers) of pyridine bands in this spectral region to metal-cation interaction with pyridine, rather than pyridine interaction with Lewis sites.

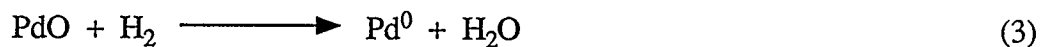
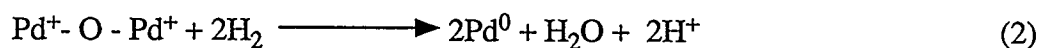
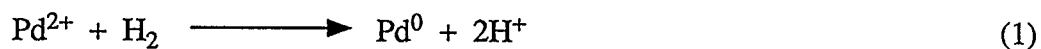
The peak at 1441 cm^{-1} is due to $\text{Na}^{+}\text{--py}$ interaction; the high intensity of this peak and the absence of any other peak in this spectral region shows that it is due to $\text{Na}^{+}\text{--py}$ rather than $\text{Pd}^{2+}\text{--py}$. The fact that this peak is not seen on HY samples supports the assignment of the band to $\text{Na}^{+}\text{--py}$ species. Our inability to observe a band due to $\text{Pd}^{2+}\text{--py}$ is consistent with the earlier proposal (Chapter Three) that Pd^{2+} is not in accessible supercages on this 1.58wt. %PdNaY sample. The Pd^{2+} must be in sodalite or hexagonal prisms. From studies using CO, it is most likely in both hexagonal prisms and sodalite cages at this level of loading on NaY (1.58wt. %Pd).

From the change of intensity of the pyridinium ion band (I_{BPY}) and the Lewis adsorbed pyridine (I_{LPY}) at different desorption temperatures (fig. 5.6), it is obvious that the Bronsted sites are stronger than the Lewis sites on oxidized PdNaY. This contrasts to the situation on HY and PdHY samples where Lewis sites are stronger than Bronsted sites as discussed later in section 5.3.4. The reason for this might be an interaction between the Bronsted sites and the palladium cation species on the zeolite. The palladium cation might be withdrawing electrons from the OH bond, making the proton a better "leaving" group and hence a stronger acid site than it should normally be. This suggestion is supported by the fact that the Bronsted sites become weaker after reduction when Pd^{2+} has been removed to give Pd^0 which will not affect the OH bond (fig. 5.6). The differences in the relative strength of Lewis and Bronsted sites on PdHY and PdNaY could be due to various reasons. Since there are fewer OH groups on PdNaY, it would be expected that the polarizing effect of the loaded Pd will be more apparent while only a small fraction of the large number of OH groups on PdHY are affected. Also, since the Pd on NaY created the OH groups by cation hydrolysis, it will be in close proximity to them and so affect them more than observed on PdHY.

The calcination in O_2 of Pd^{2+} exchanged NaY also seemed to create twice as many Lewis sites as Bronsted sites, as seen by using the formula by Ward (7b) given earlier, although the strength of these Lewis sites was lower than that of the Bronsted sites created. The lower strength of Lewis sites in comparison to Bronsted sites is explained by the increased strength of the Bronsted site due to the palladium cation. There will possibly be a more direct influence of Pd^{2+} on Bronsted sites than on Lewis sites. The lower number of Bronsted sites can be explained by the fact that dehydroxylation occurred on the Pd/NaY zeolite during calcination to give more Lewis sites.

5.3.2(b) REDUCTION OF PdNaY

After reduction of this 1.58wt. %PdNaY, Bronsted acidity was still observed when pyridine was adsorbed on the pellet (fig. 5.6). Comparison of I_{BPY} before and after reduction particularly at low temperature showed that reduction increased the number of Bronsted acid sites. The increase in the number of Bronsted acid sites after reduction was also identified earlier in chapter four and the following mechanism showing the various possibilities was proposed :



Either reaction (1) or (2) must occur to some degree since protonic sites are observed on PdNaY. Although reduction increased the number of Bronsted sites, it decreased the strength of these sites when compared to the oxidized sample (fig. 5.6). Reduction also seemed to have removed the strong Lewis sites on the PdNaY sample and the remaining Lewis sites were very weak. The reason for the decrease in strength of Bronsted sites after reduction has been explained (section 5.3.2) by the removal of the polarizing effect of Pd^{2+} on the OH bond of the catalyst.

The reason for the removal of the strong Lewis sites during reduction could be due to proton formation by cation reduction (proposed earlier) which converts Lewis sites to Bronsted sites.

There was still the peak at 1441 cm^{-1} due to Na^+-py after reduction. There was no peak at 1462 cm^{-1} for reduced Pd/NaY, as mentioned earlier.

In summary, it seems that the removal of the polarizing effects of Pd^{2+} can

explain the decrease in strength of the Bronsted acid sites while strong Lewis sites are removed during reduction to form Bronsted sites. There was also no peak at 1462 cm^{-1} in the spectra of the reduced sample as observed for the oxidized sample.

5.3.3(a) FLUORIDATION OF PdNaY

The adsorption of pyridine on calcined fluorided PdNaY (PdFNaY) with 1.50wt. %Pd²⁺ and 0.012wt. %F⁻ showed bands due to Bronsted acid sites (1547 cm^{-1}) and two true Lewis sites (1462 and 1455 cm^{-1}). The Na⁺--py interaction at 1441 cm^{-1} was also observed. A Pd²⁺--py species was not observed, which confirms that Pd²⁺ is not stabilized in supercages, as mentioned earlier in chapter three.

From fig. 5.7, it can be seen that the shapes of the desorption curves for PdNaY and PdFNaY are very similar, except that the treatment with the fluoride seems to have removed the stronger Bronsted and Lewis sites. One possible explanation for this is that the fluoride may attack the lattice of NaY and this could have leached out some of the lattice aluminium atoms by formation of fluoroaluminates which are soluble (9) in aqueous solutions.

On PdFNaY, the Bronsted sites are stronger than the Lewis sites and this means that the loaded Pd cation is polarizing the OH groups; this was also observed on PdNaY.

5.3.3(b) REDUCTION OF PdFNaY

Reduction of the PdFNaY sample increased the number of Bronsted acid sites and their strength was reduced just as was seen on PdNaY (see above). Reduction also seems either to have completely removed the Lewis sites, or to have weakened them such that they cannot adsorb pyridine. It should be remembered that reduction also removed strong Lewis sites on PdNaY to give Bronsted sites, and the same process may be occurring on PdFNaY.

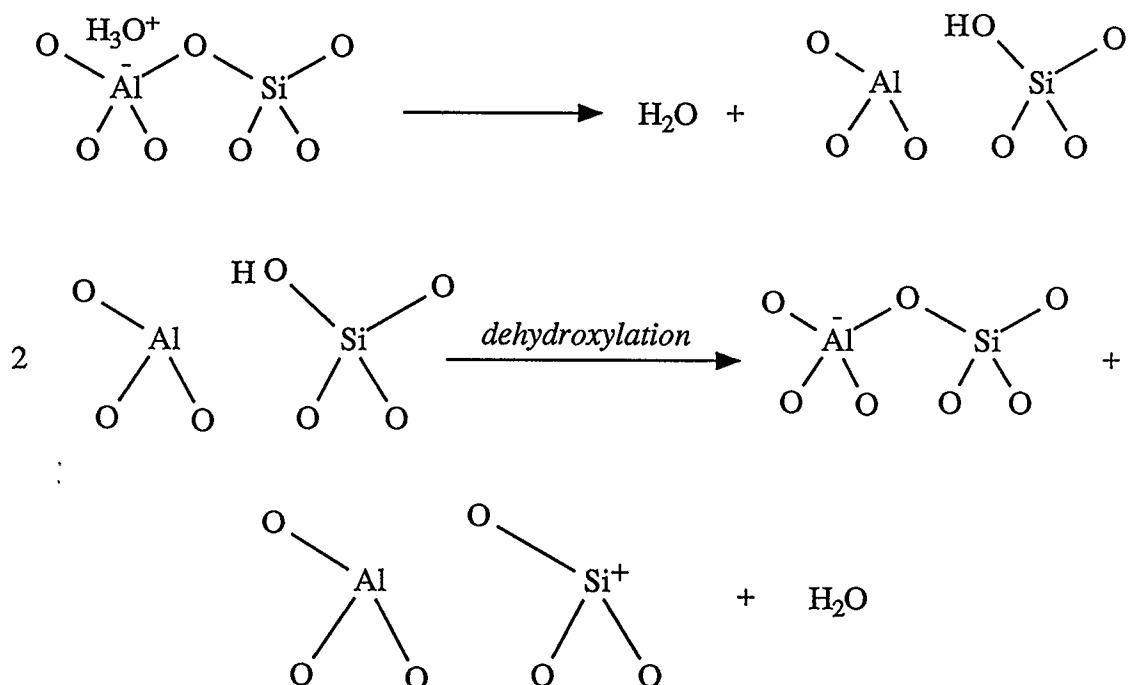
5.3.4 HY ZEOLITE

5.3.4(a) SPECIAL LEWIS ACID SITE (1462 cm^{-1})

Pyridine adsorption on calcined HY (fig. 5.2) gave characteristic peaks at 1545, 1455 and 1462 cm^{-1} . This zeolite shows the presence of Bronsted sites as expected (1545 cm^{-1}). It also shows the presence of two true Lewis sites (1455 and 1462 cm^{-1}). Bronsted sites were weaker than Lewis sites on calcined HY (fig.5.8).

The unusual 1462 cm^{-1} band has been observed on H^+ exchanged zeolite by various workers and various reasons have been advanced for the formation of the species responsible for this band. As mentioned earlier, this band at 1462 cm^{-1} was found on PdNaY and fluorided PdNaY only after calcination, but disappeared after reduction. On PdHY and fluorided PdHY of varying metal loading, it was present both before and after reduction. It is also found on oxidized and reduced samples of HY and fluorided HY.

Cannings (8a) observed a band in the infrared at 1462 cm^{-1} on H-mordenite after pyridine desorption at 300°C . He attributed it to pyridine coordinately bonded to an SiO_3^+ species formed during the zeolite pretreatment during which dehydroxylation occurs (10) (scheme 2).

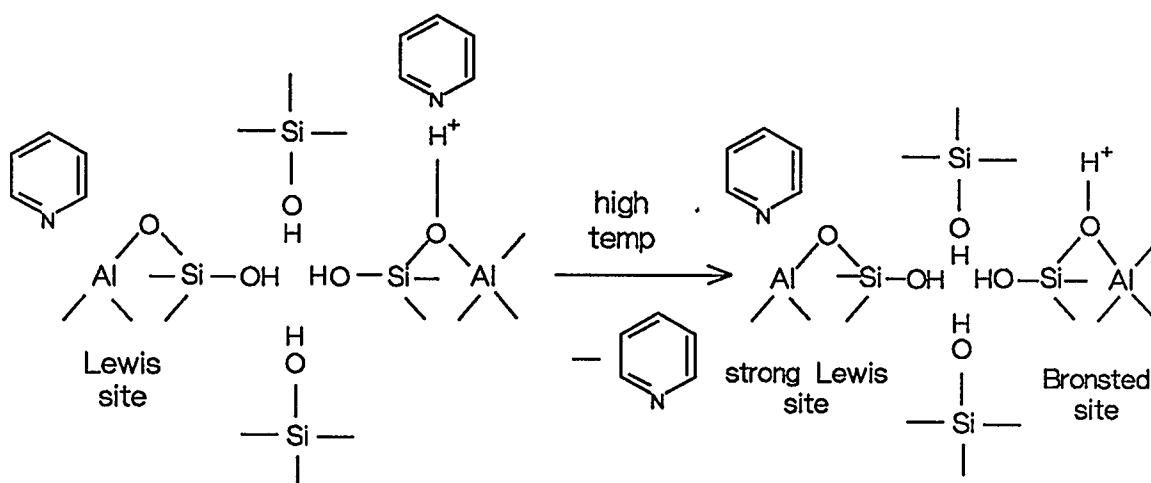
SCHEME 2

In the above scheme, it is suggested that the SiO_3^+ group is formed on the zeolite during dehydroxylation. One would therefore expect the 1462 cm^{-1} band to appear when the sample was dehydroxylated at high temperature with subsequent adsorption of pyridine at 100°C , but this was not the case. This 1462 cm^{-1} band did not appear until pyridine desorption at elevated temperatures; 300°C on HY samples and 200°C on NaY samples. This means that Cannings' scheme does not fully explain the formation of the 1462 cm^{-1} band.

Ghosh and Curthoys (11) using H-mordenite showed that the lack of accessibility of this strong Lewis site to pyridine was not responsible for the observation of the 1462 cm^{-1} band only at higher temperatures. They explained the formation of this

Lewis bound pyridine as due to the fact that when a pyridine molecule adsorbed on a Bronsted site is desorbed, the Lewis acid site becomes stronger due to polarization by a hydroxy nest (12) or an electrophilic Al atom (13) (scheme 3).

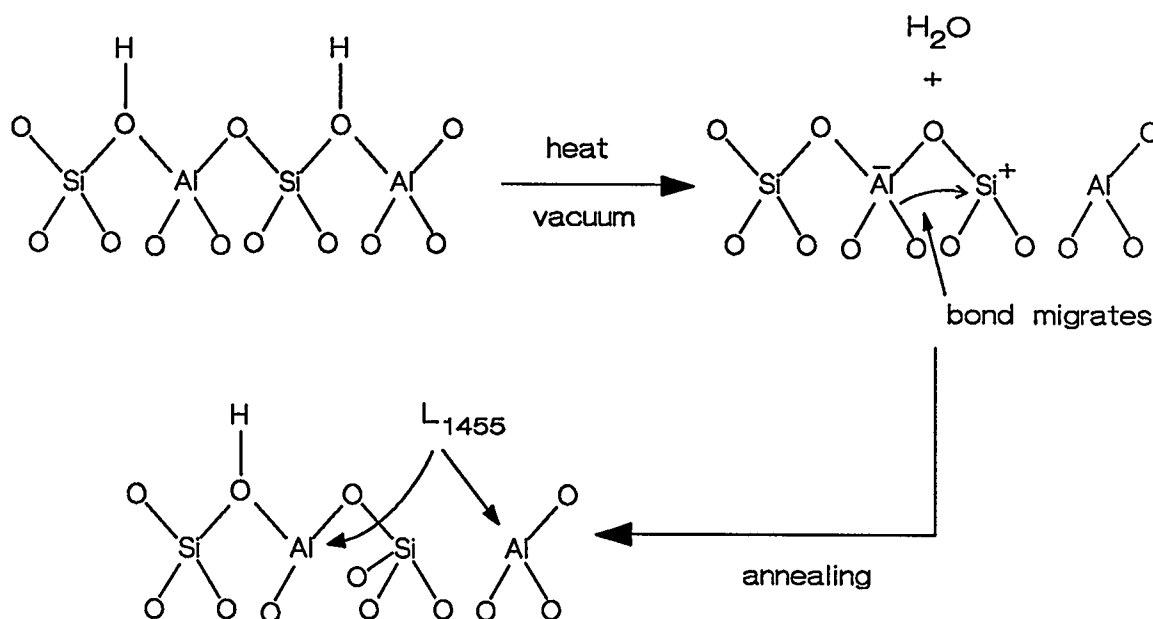
SCHEME 3



Ghosh also proposed an alternative possibility, i.e. that a Lewis site adjacent to a hydroxy nest can polarise (through the lattice) the electron cloud between the Lewis aluminium and the bonded nitrogen of the pyridine, thereby making the Py.--Al bond stronger.

The proposal by Ghosh does not seem to satisfy the observations in our work. We observed that this 1462 cm^{-1} band was not present on a reduced PdNaY catalyst which had more hydroxyl groups than a calcined form of this catalyst. From Ghosh's proposal, since there are more hydroxyls, one would expect more hydroxyl nests, and therefore a more intense 1462 cm^{-1} band.

After considering these results, it has been possible to propose another scheme to explain the formation of the species giving the 1462 cm^{-1} band on pyridine desorption on these zeolite samples (scheme 4).

SCHEME 4

The above scheme shows the removal of Brønsted sites to give Lewis sites by dehydroxylation. The coordinatively unsaturated silicon group (SiO_3^+) formed during the dehydroxylation is subsequently removed by annealing. This involves a bond migration from a tetragonally bonded aluminium to give another Lewis site. This explains why only the 1455 cm^{-1} band is seen when pyridine is first adsorbed after dehydroxylation. Then as the temperature is raised, and evacuation carried out with pyridine present, additional dehydroxylation will occur. Pyridine is known to make dehydroxylation easier (14). When SiO_3^+ groups are created in the presence of pyridine, it could immediately bond to the SiO_3^+ group (giving the 1462 cm^{-1} band) and eliminate the bond migration step. While it is not possible to prove that this proposed scheme is correct, it does explain all the observed characteristics of the unusual 1462 cm^{-1} band better than the previous proposals do.

5.3.4(b) HYDROGEN TREATMENT OF HY ZEOLITE

H₂ treatment of HY gave the same characteristic peaks as seen on the calcined sample. Bronsted sites are still weaker than Lewis sites on this catalyst.

Reduction was also found to decrease the number of OH groups on the HY sample; the more weakly acidic groups in particular were affected as seen in fig. 5.8. A decrease in the number of Bronsted sites after reduction was also observed on PdHY (as explained below). This confirms that the presence of Pd has nothing to do with the loss of the Bronsted acid sites observed after H₂ treatment of PdHY as already mentioned in chapter four, since this situation was observed on HY zeolite. The above observation contrasts with that on PdNaY, where reduction increased the number of OH groups and decreased their strength (from pyridine results in fig.5.6).

The observed decrease in Bronsted acid sites on HY can be explained by the higher level of dehydroxylation that occurs when the catalyst is being reduced. As explained in our experimental procedure, a calcined sample which had been used for pyridine study was reused for reduction. The used sample was treated in oxygen at 500°C overnight and then subsequently treated in hydrogen at 300°C for one hour. It is proposed that the decrease in Bronsted acid sites occurs during the treatment in oxygen and subsequent evacuation where additional dehydroxylation occurs.

On PdNaY samples, it was identified that reduction increased the number of Bronsted acid sites (fig.5.6); the reason for this difference compared to the HY sample appears to be because of the differences in concentration of OH groups on HY and PdNaY. The former has an extremely high concentration of OH groups in comparison to the latter, and this means that dehydroxylation on the former will be easier, as OH groups will more often be adjacent to each other. The reaction that will be favoured on

PdNaY during H_2 treatment will be the reduction of palladium cations to give protons as proposed in equations 1 to 3 (see section 5.3.2(b)).

Reduction also increased the number of Lewis sites on HY, but the strength of these sites created was found to be low (fig.5.8) (the reduced sample lost pyridine faster than the calcined sample). The increase in the number of Lewis sites agrees well with our proposal that more dehydroxylation occurs during reduction.

The overall strength of the Lewis sites on HY was unchanged after H_2 treatment, although it can be seen that the Lewis sites created during reduction lost pyridine faster than those sites on the calcined sample.

5.3.5(a) FLUORIDATED HY (FHY)

The adsorption of pyridine on calcined FHY showed the presence of Bronsted sites (1543 cm^{-1}), two true Lewis sites (1455 and 1462 cm^{-1}) and another peak at 1445 cm^{-1} . The presence of this peak at 1445 cm^{-1} on FHY is interesting, since this peak was not found on HY. Since we have no metal cation on this zeolite (FHY) it cannot be due to a Pd^{2+} --py interaction. This peak was also found on reduced and oxidized Pd/FHY and only on oxidized PdHY samples.

Since this peak is lost after evacuation at 200°C , it must be from a weakly bonded pyridine species. Cannings (8a) and Lefrancois and Malbois (8b) using hydrogen mordenite have assigned a peak at this position to a hydrogen bonded species on H-mordenite; we would then assume, based on this assignment, that this peak is due to a weak hydrogen bonded species.

Fluoridation of HY zeolite drastically reduced the number and strength of Bronsted sites (fig.5.9), probably as a result of the leaching proposed earlier in section 5.3.3. At the same time, the fluoride treatment increased slightly the number of weak

Lewis acid sites.

5.3.5(b) HYDROGEN TREATMENT OF FHY

On H_2 treatment of FHY (fig.5.10), the number and strength of the Bronsted sites is unchanged. The fact that the number of OH groups does not decrease after H_2 treatment on FHY as it did on HY shows that dehydroxylation does not occur to any appreciable extent on FHY presumably because of the low concentration of OH groups on this sample (see section 5.3.5(a)). The fact that the number of Lewis sites does not change during reduction (fig. 5.10) is consistent with this explanation. The strength of these Lewis sites is also unchanged by reduction.

In summary, fluoride treatment on HY reduces the number of Bronsted sites by leaching. Hydrogen treatment of FHY did not remove OH groups since dehydroxylation was not favoured.

5.3.6(a) Pd-LOADED HY (PdHY)

Pyridine adsorption on calcined PdHY samples with different loadings of Pd confirmed the presence of Bronsted sites (1545 cm^{-1}), two true Lewis sites (1455 and 1462 cm^{-1}) and the "special" hydrogen bonded species (1445 cm^{-1}).

There was no peak to identify Pd^{2+} --py species, which shows that Pd^{2+} is not located in supercages at the highest loading of Pd (1.62wt. %Pd).

For the calcined PdHY samples, the strength of the Bronsted sites seems to increase with increasing loading of Pd (fig. 5.11); this suggests that Pd interacts with the Bronsted acid sites as proposed on PdNaY samples. Pd seems to polarize the neighbouring OH bonds and makes them stronger, and it is this group of polarized OH

bonds that are observed as the strong sites on these PdHY samples.

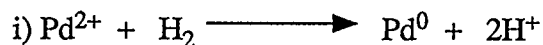
The behaviour of pyridine adsorbed on Lewis sites was very similar for the three different PdHY samples, except that the weak Lewis acid sites for the most heavily loaded sample were greatly increased in number (fig. 5.12).

5.3.6(b) REDUCTION OF PdHY SAMPLES

Reduction of the PdHY sample gave two true Lewis sites (1455 and 1462 cm⁻¹) as previously discussed (section 5.3.4(a)).

Comparing the calcined and reduced samples for the different loadings of PdHY, it was observed that :

1) Reduction seems to decrease the number of Bronsted acid sites at all loadings of Pd (figs. 5.13-5.15). This was in contrast to PdNaY samples where reduction increased the number of OH groups. The reason for this probably is because of the differences in the initial concentration of OH groups on PdNaY and PdHY. There are two possible processes that can occur on Pd/zeolite during reduction, and the favourable process depends on the initial concentration of OH groups on the Pd/zeolite before reduction:



ii) Dehydroxylation during the reduction treatment as explained in section 5.3.4(b).

The first process appears to be favoured on PdNaY, and the proton formed will then attack the lattice oxygen atom to form the Bronsted sites. The second process will be less likely to occur on PdNaY because of the low concentration of OH before reduction. On PdHY samples, both processes will occur since there is a much higher

concentration of OH groups than on PdNaY, and this will cause the reduction in the number of Bronsted sites observed.

On the samples with higher loadings of Pd (0.171% and 1.62wt. %Pd) (figs.5.14 - 5.15), reduction, as expected, seemed to decrease the acid strength of the OH groups, since the Pd^0 formed after reduction will not polarize the OH bond; an overall decrease in strength of Bronsted acid sites was observed after reduction. The amount of Pd on the 0.0193wt. %Pd sample (fig.5.13) was too low to have any significant effect.

It should be mentioned that the plot of intensity of the pyridinium ion band versus temperature for all PdHY samples after reduction was similar in shape as seen in figs. 5.13-5.15; and this might point to the fact that the same kind of OH groups are left on these catalysts after reduction.

2) On the Pd-loaded HY zeolites, reduction generally caused an increase in the number of Lewis sites present on the zeolite (figs. 5.13-5.15), and for the two samples with the higher loadings, the strength of these sites also increased. This increase in strength is unexpected, since reduction of the Pd^{2+} would eliminate any polarizing effect it would have. Probably the explanation is that the dehydroxylation proposed earlier (during evacuation after H_2 treatment, see section 5.3.4(b)) has created some strong Lewis sites.

In summary, it is obvious that on loading Pd on the HY zeolite the Pd^{2+} cation polarized neighbouring OH bonds, especially at higher loadings, and this makes the Bronsted acid sites stronger.

Reduction of PdHY catalyst seemed to have reduced the number and strength of OH groups, and for Lewis sites, reduction generally increases the number of strong Lewis acid sites by dehydroxylation.

5.3.7 FLUORIDATED PdHY (PdFHY)

Pyridine adsorption on calcined PdFHY samples showed peaks due to Bronsted acid sites (1541 cm^{-1}), two Lewis sites (1455 and 1462 cm^{-1}) and the "special" hydrogen-bonded pyridine (1445 cm^{-1}) mentioned earlier. There was no peak due to Pd^{2+} --py species, which shows that Pd^{2+} is not stabilized in supercages at this level of loading (1.48wt. % Pd).

Fluoride treatment decreased the number of Bronsted sites, presumably because of the leaching mentioned earlier, and did not increase significantly the strength of those sites remaining. As mentioned earlier (section 5.3.6(a)), Pd^{2+} usually increases the strength of Bronsted acid sites, and this effect is also observed on the Pd-loaded FHY samples.

5.3.8 SUMMARY

In summary, it has been observed that cation exchange into the zeolite supports (NaY and HY) created Bronsted and Lewis sites on NaY (by hydrolysis) and increased the strength of the Bronsted sites present on HY while the number of Lewis sites on this support was increased. It was also observed that the loaded cation is not present in the supercages at the highest level of loading used on our catalyst.

Hydrogen treatment of PdNaY zeolite created more Bronsted acid sites although their strength was decreased; also, the strength of the Lewis sites was decreased. The decrease in strength of Bronsted sites after reduction of PdNaY is attributed to the removal of the polarizing effect of the palladium cation.

Fluoridation of PdNaY seemed to have removed strong Bronsted and Lewis sites by leaching, while fluoridation of HY reduced the number and strength of Bronsted sites. Weak Lewis sites were created by the fluoride treatment but the overall strength

of the Lewis sites was unaffected.

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CHAPTER SIX

6. ETHENE STUDY

6.1 INTRODUCTION

The reaction of ethene on Pd-loaded zeolite catalysts is an interesting process to study for various reasons :

Ethene is known to undergo two types of reaction - dimerization to give butenes and polymerization - depending on the type of active site available on the catalyst. So this reaction can be used to study the interaction between the acid sites of the surface and to determine if these interactions will affect either the rate or product of reactions. It is also observed that no study of ethene reaction on PdHY catalyst has been reported in the literature.

Recent ESR studies of ethene reaction on non-acidic catalysts have suggested a mechanism for the dimerization process and an attempt will be made to confirm this. Also, an induction period for this reaction has been observed by various workers and it is thought that it involves either migration and/or change in oxidation state of the active metal species; an attempt will be made in this study to see if the induction period can be observed with infrared. It will also be investigated to see if any species can be identified on the catalyst surface during this period since it is observed, in other reactions like methanol conversion to gasoline on HZSM-5 (1), that active carbonaceous species are formed on the catalyst surface during the induction period.

It is also apparent that despite much study of the polymerization process, controversy still exists over the role of Bronsted and Lewis acid sites in this reaction; there is no agreement on which of these sites is the active site or whether a synergism exists between them. Infrared spectra will be used to investigate this.

Another advantage of using ethene is that it is the simplest alkene and so the products can be easily identified in infrared studies; this is an important point since different alkanes and alkenes often have similar spectra, especially the adsorbed species; so if products are simpler, that will help in identification.

6.2 BRIEF SUMMARY OF PREVIOUS WORK

6.2.1 ETHENE DIMERIZATION

The dimerization of ethene to butenes can occur on non-acidic metal-loaded catalysts (2a) and has been observed to occur remarkably easily on Pd-loaded catalysts (2b). It will be very interesting to know which of the dimers form first during ethene dimerization reaction on Pd loaded zeolites. Yashima et al. (2a) have shown that the first product of C_2H_4 over NiY, RuY and RhY is 1-butene which isomerizes to produce an equilibrium composition of n-butenes. This has been confirmed by Ghosh and Kevan (3) and by Michalik (4). The rate of isomerization of 1-butene on Pd-CaX zeolite was found to be much faster than that of ethene dimerization (4). Ghosh and Kevan (3) in a recent study using various metal-loaded zeolites have identified Pd as the active site for 1-butene isomerization, although this contradicts the earlier work by Michalik (4) which proposed Bronsted acid sites as the active site for 1-butene isomerization. Since 1-butene is mostly used for polymerization in industry it is obvious that the identification of the active site of 1-butene isomerization will allow the use of catalysts that will promote polymerization over isomerization of 1-butene.

It is known that the activity of PdY for C_2H_4 dimerization is very dependent on the oxidation state of Pd; but the exact nature of the active valence state of Pd on PdY is not yet clear and is full of controversy. Also, the mechanism for formation of the

different valence states of Pd observed on the zeolite after different pretreatment procedures is still highly controversial. While IR spectroscopy will not be useful for clarifying these points, a brief discussion is necessary for understanding the reaction.

Palladium can exist as Pd(0), Pd(I), Pd(II) and even Pd(III) when supported on substrates. Lapidus (5) used X-ray Photoelectron spectroscopy (XPS) and GC on a Pd-CaNaY catalyst to show that Pd⁰ is inactive for C₂H₄ dimerization and the active site should be Pd²⁺ or Pd⁺. Michalik (4) using ESR and GC has proposed that Pd²⁺ is the active species for formation of C₂H₄ dimers on Pd/CaX zeolite catalysts; he showed that a reduced PdX (containing Pd⁺) showed a three-fold decrease in activity.

Bai (6), using XPS and ESR, has however suggested that Pd⁺ is indeed the active species for C₂H₄ dimerization on PdNaY. Ghosh and Kevan (7) used ESR and GC to show that Pd³⁺ on PdNaX is not catalytically active for this reaction.

Michalik (4) said that the oxidation with oxygen at 773K of the CaX zeolite exchanged with Pd(NH₃)₄²⁺ resulted in the formation of Pd³⁺ and Pd²⁺ cations, with Pd²⁺ as the major product; this was supported by Naccache et al. (8).

Naccache et al. (9) also identified the formation of Pd⁺ when the CaX zeolite loaded with Pd(NH₃)₄²⁺ is heated in vacuo. These different oxidation states of Pd can be formed during calcination in O₂ or by mechanisms proposed by various workers, some of which involve cation oxidation, disproportionation, etc. While the existence of the various oxidation states is not in doubt, the mechanism by which they are formed is still a matter of controversy.

Various workers have identified an induction period during the dimerization of C₂H₄ on Pd loaded zeolites (3-7) and many reasons have been proposed for this observation. Some workers have proposed that the induction period is due to the time needed for the Pd cation to migrate from inaccessible sites into accessible sites while others have proposed that it is due to the time taken to form the active species between

Pd^+ and C_2H_4 . The induction period was also found to decrease with increasing Pd content on the zeolite due probably to an increase in the number of active Pd sites (3).

The effect of the temperature of evacuation on the induction period was studied by Bai (6); they observed that on lowering the evacuation temperature, the induction period becomes shorter. On PdY samples, they found that the induction period disappeared at 373 K, and higher evacuation temperatures caused a longer induction period. Using X-ray photoelectron spectroscopy (XPS), they observed that Pd^{2+} was being converted to Pd^+ and Pd^0 at progressively higher evacuation temperatures. They also showed by XPS and ^{23}Na -nmr that the surface concentration of Pd is almost unchanged when evacuation was done at 373 K, but the surface concentration decreased gradually with increasing evacuation temperature which shows that the Pd cations migrate into inaccessible sites during evacuation and hence the induction period increases during subsequent C_2H_4 dimerization.

Yashima et al. (2a) studied the effect of evacuation temperature on the activity for C_2H_4 dimerization of RhY and NiY. They found that the activity increased until an evacuation temperature of 673 K on RhY and subsequently dropped; and on NiY, the activity increased until an evacuation temperature of 773 K. The crystal structure of RhY was partially destroyed at 773 K while NiY held its crystallinity to 973 K. They interpreted these results as meaning that Rh(0) and Ni(0) are the active sites. The above study on RhY and NiY indicate that the increase in induction period of ethene dimerization observed on PdY with increase in the evacuation temperature might be due to increased formation of Pd(0) which has been shown to be inactive for ethene dimerization.

Bai (6) and Ghosh and Kevan (3) using ESR have identified the formation of $\text{Pd}^+-\text{C}_2\text{H}_4$ and $\text{Pd}^+-(\text{C}_2\text{H}_4)_2$ species prior to butene formation although both workers (6,7) have observed that the preformation of a Pd^+ cation on the PdY catalyst does not

remove the induction period. The above result might rule out the possibility that the induction period is due to the time it takes to form a $\text{Pd}^{+}\text{--C}_2\text{H}_4$ species.

The effect of the valence state of Pd cation and its location and migration in the zeolite on the induction period are still open questions.

Bai (6) used ^{23}Na nuclear magnetic resonance (nmr) to indicate the migration of cations among zeolite cages during the calcination and evacuation of PdY zeolites and their activation with C_2H_4 ; the ^{23}Na nmr provides information on the location of Na^{+} ions in S(I) sites in dehydrated type zeolites (10).

The intensity of the ^{23}Na nmr spectra of PdY after evacuation at different temperature decreased with increasing evacuation temperature. This shows that the evacuation of Pd-NaY at high temperature is accompanied by migration of Na^{+} ions out of S(I) sites in hexagonal prism, i.e it was displaced by other cations like Pd^{2+} , Pd^{+} , H^{+} .

Bai (6) have also observed that the preadsorption of C_2H_4 reduces the induction period. Using ^{23}Na -nmr, they observed that on preadsorbing C_2H_4 , the Na^{+} moved from S(II) sites to S(I) sites which means Pd^{2+} or Pd^{+} is migrating from S(I) or S(I') sites to S(II) sites. This shows that C_2H_4 adsorption causes the migration of Pd to more accessible sites in the zeolite. They postulated that the induction period is due to the migration of Pd^{+} to accessible sites where it forms the $\text{Pd}^{+}\text{--C}_2\text{H}_4$ complex. This is supported by the observation of C_2H_4 dimerization on Pd/NaY and Pd/CaY zeolites pretreated identically. In the former, Pd is stabilized in S(I) or S(I') sites, while in the latter, Pd is stabilized in more accessible S(II) or S(II') sites. Dimerization has a longer induction period on the Pd/NaY catalyst.

It has been observed that the presence of other cations like Ca^{2+} , Mg^{2+} , Na^{+} and K^{+} influences the position and activity of Pd in PdX zeolites. It is found that the presence of divalent cations promotes formation of C_2H_4 dimers over PdX at low concentrations {2 Pd^{2+} per unit cell} at low temperatures. Under these same conditions,

PdX zeolites with monovalent cocations are completely inactive for C_2H_4 dimerization. It should be mentioned that, above a certain critical concentration of the monovalent ions, the activity for C_2H_4 dimerization is comparable to divalent metal loaded zeolite.

The reason for this observation is that divalent cations have a high affinity for S(I') sites in the zeolite and it is anticipated that Pd^{2+} cations will be forced to occupy more accessible sites like S(II') or S(II) in the zeolite. The C_2H_4 molecule is too bulky to enter the β -cages, so the formation of a $Pd^+-C_2H_4$ complex needs a migration of Pd^{2+} into supercages.

Che et al. (11) have also shown by X-ray, ESR and IR that the adsorption of nitrogen oxide (NO) on PdY samples at 298K leads to migration of one half of the Pd^{2+} ions from the S(I') site in sodalite cages to supercages.

The migration of the Pd cation under the influence of C_2H_4 and the evacuation temperature has been illustrated by various workers and this might lend support to the proposal that the induction period is due to the migration of the active Pd cation to accessible sites rather than to the formation of the active $Pd^+-C_2H_4$ species.

The induction period has been found to also depend on the reaction temperature (3-7). The lower the temperature, the longer the induction period. This is explained as due to faster migration of Pd species towards sites accessible to C_2H_4 . Bai (6) found that the activity of the catalyst increased with increasing reaction temperature to 473 K and subsequently decreased at higher reaction temperature (6). Catalyst deactivation is also faster at higher reaction temperature. The increase in deactivation rate at higher reaction temperature is attributed to increased reduction of Pd^+ to Pd^0 , zeolite pore blocking or coke deposition on the zeolite. The fact that evacuation or calcination in O_2 could not completely return the catalyst activity makes the former a more likely possibility (3,7).

6.2.2 ETHENE POLYMERIZATION

There is a lot of controversy regarding the active site for alkene polymerization. Various workers have proposed Bronsted acid sites while others have proposed Lewis acid sites and some workers have proposed a kind of synergism between these two kinds of sites. The polymerization of alkenes has usually been proposed to proceed through a carbonium ion mechanism (12) although the manner in which the carbonium ions are formed is not fully understood; van den Berg using HZSM-5 has proposed that ethene polymerization occurs on Bronsted sites (13) while Turkevich et al. (14) have proposed Lewis sites as the active site for ethene polymerization.

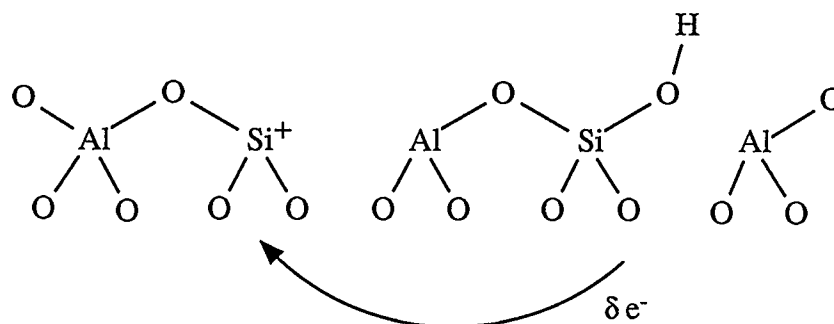
Liengme and Hall (15) studied the adsorption of ethene and propene on HNaY zeolite pretreated at 480°C. The zeolite contained about 55% of residual sodium. Ethene interacted with the 3650 cm^{-1} OH group and a new band at 3300 cm^{-1} was detected. This band is assigned to hydrogen bonded C_2H_4 species. Ethene did not interact with the 3550 cm^{-1} OH groups at low pressures and it is not very clear if C_2H_4 did interact with them at higher pressures. It was also found that no exchange occurred between C_2D_4 and the zeolite below 150°C and no polymerization was detected at or below 240°C. The C_2H_4 was observed to have adsorbed on the Na cation present in the supercages. It was also found that a dehydroxylated form of this catalyst (with more Lewis sites) irreversibly adsorbed ethene and polymerization products were detected. The above shows that a dehydroxylated HNaY zeolite irreversibly adsorbed and polymerized C_2H_4 , while a dehydrated form will only weakly and reversibly adsorb C_2H_4 .

These authors have concluded that there must be other equal or more effective ways of forming the carbonium ions required for the acid catalyzed polymerization than just through Bronsted acid sites.

This view is supported by various other workers; Turkevich et al. (14) have

proposed the Lewis sites as the site for ethene polymerization; Pickert et al. (16) have observed that maximum alkylation activity is achieved when all Bronsted acid sites are removed by dehydroxylation. Kubelkova et al. (17) have also observed that a certain ratio of Lewis centers to OH groups was necessary in order to achieve the maximum ethene oligomerization rate on a given type of zeolite.

Synergism between these acid sites was investigated by Lunsford (18). He observed that the maximum activity for catalytic cracking (which is normally attributed to the presence of Bronsted acid sites) was found on a catalyst calcined at a temperature where the Bronsted acid sites had diminished considerably and he has proposed that the active sites are formed by partial dehydroxylation of the zeolite to produce a small amount of what Utterhoeven et al. (19) called "defect sites". These sites are made up of SiO_3^+ and AlO_4^- cation-anion pairs in the zeolite lattice. The zeolite also retained some Bronsted OH groups after the partial dehydroxylation and Lunsford proposed that the positively charged SiO_3^+ group acts inductively through the lattice on a Bronsted OH group to produce a partial negative charge across the lattice as shown in the structure below :



This electrostatic interaction between the Lewis acid site and the SiOH group reduces the OH group's electron density and makes the proton more acidic. Although the above theory requires the presence of some Bronsted acid sites, Lewis acid sites are

also important.

Fajula and Gault (20) studying the cracking of $[2-^{13}\text{C}]$ methylpropene has proposed that strong Lewis sites are formed from interaction between Bronsted and Lewis acid sites.

There has been a lot of disagreement on the exact nature of these "super" Lewis acid sites (21-23) formed during dehydroxylation which increase the acidity of Bronsted acid sites by synergism. While the true nature of the "super" Lewis acid sites might differ from the representation given above, the idea of synergism between Bronsted and Lewis sites is valid based on experimental results (18,24,25).

When propene was adsorbed on the hydroxylated HNaY zeolite (15), irreversible adsorption and polymerization was observed contrary to the case of ethene adsorption. The propene also interacted with the 3650 cm^{-1} OH group and a new band due to hydrogen-bonded propene grew at 3200 cm^{-1} . This H-bonding shift of the 3650 cm^{-1} OH band is about 100 cm^{-1} greater than the case with ethene and this shows a greater interaction of propene with the OH group than ethene. A peak at 3560 cm^{-1} grew up after several days which indicates an interaction of the saturated polymer formed and the OH group. This shows that higher alkenes can polymerize on acid catalysts since they can form stable carbonium ions.

Yashima et al. (2a) observed that dimerization of propene and 1-butene on NiY and RhY was initially greater than ethene but, after a few minutes, they observed that the rate of dimerization was much slower than that of C_2H_4 . This observation was in contrast to that observed on a solid catalyst like HY. On HY, C_2H_4 remained unconverted till 200°C , and at a higher reaction temperature, various lower hydrocarbons were formed by polymerization followed by cracking. These results have made these workers believe that polymerization on NiY and RhY does not proceed through a carbonium-ion mechanism.

6.3 RESULTS

On adsorption of C_2H_4 on the various catalysts, peaks due to dimers, saturated and unsaturated polymers were observed growing on the catalysts as the reaction progressed. These peaks are assigned on table 6.1.

A plot of the intensity of the 1386 cm^{-1} peak (CH_3 deformation) against time will be used to measure the rate and extent of the overall reaction on the catalysts; the reason for using this peak is because all the products formed during the reaction contribute to the intensity of this peak, while the 1366 cm^{-1} peak will be used to measure the rate and extent of production of branched products on the catalysts. Only branched chain products show this vibration.

Fig. 6.1 - 6.4 show the spectra of ethene reaction on samples of hydroxylated HY, 1.62wt. %PdHY, 1.58wt. %PdNaY and an highly dehydroxylated HY. For the sake of brevity, many spectra are not included but they are summarized in the form of graphs as a plot of intensity against time.

Table 6.1 Observed IR bands from products formed during ethene reaction

<u>wavenumbers(cm^{-1})</u>	<u>Assignments</u>
1298	C-H bend of trans-2-butene
1381 - 1387	symmetrical C-H bending vibration of methyl groups
1367	symmetric C-H bend of branched chain groups
1407	olefinic bending vibration of cis- 2-butene
1440 - 1443	C-H bend of $=\text{CH}_2$ groups
1456	C-H bend of methylene
1464	asymmetric bending vibration of methyl groups
1628	C=C stretch of 1-butene
1645	C=C stretch of cis- and trans-2-butene
2870	symmetric C-H stretch of methyl and methylene groups
2932	asymmetric C-H stretch of methylene groups
2962	asymmetric C-H stretch of methyl groups

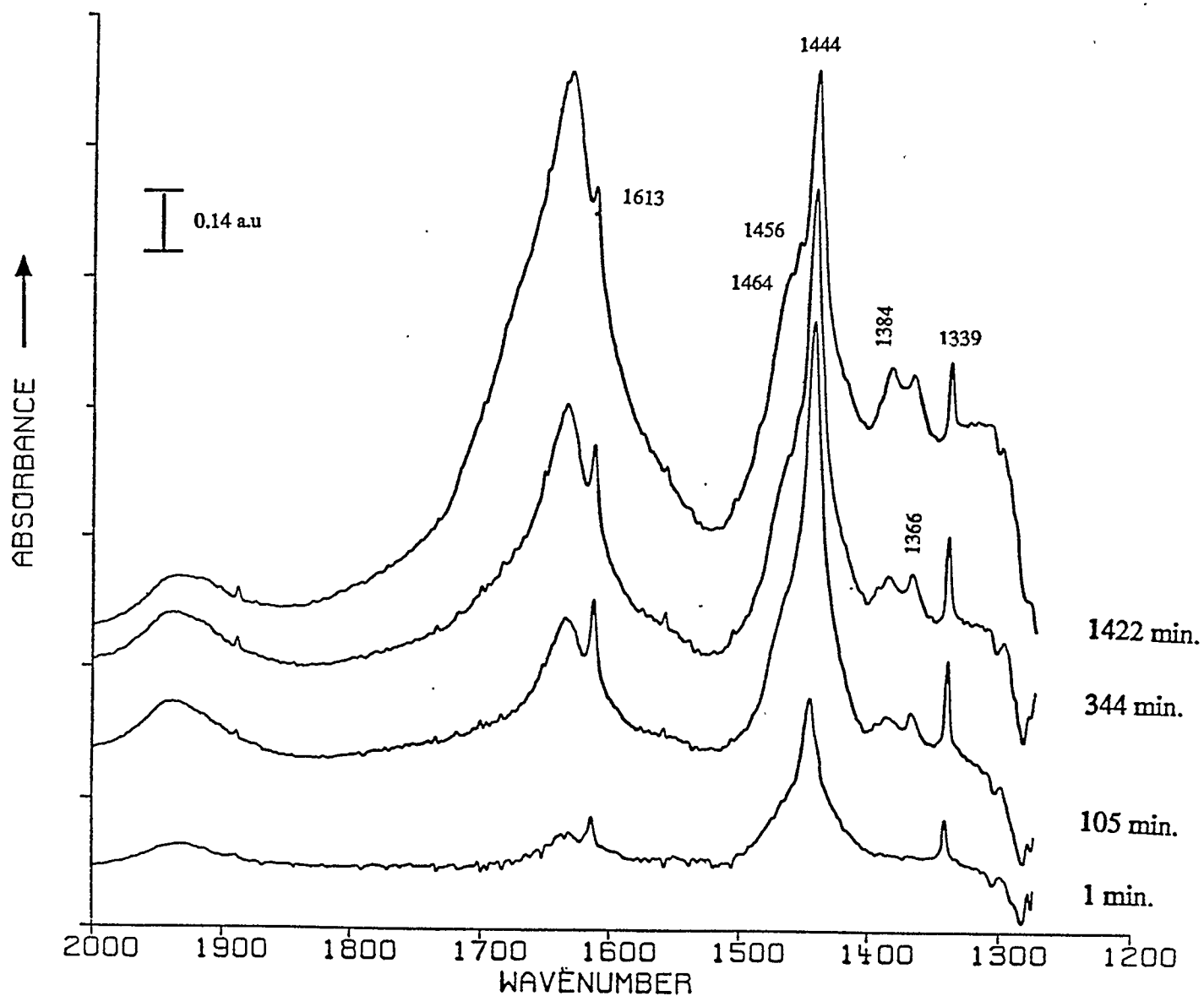


Fig. 6.1. Spectra showing the reaction of ethene on calcined HY at 25 °C. Spectra taken at different stages of the reaction.

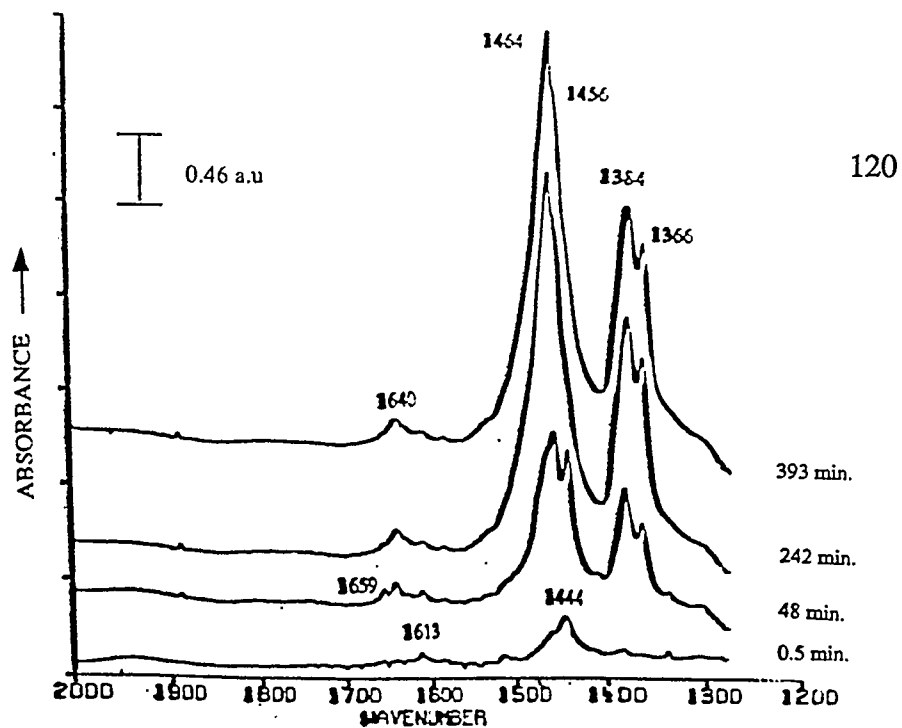


Fig. 6.2. Spectra showing the reaction of ethene on calcined 1.62wt. %PdHY at 25 °C. Spectra taken at different stages of the reaction.

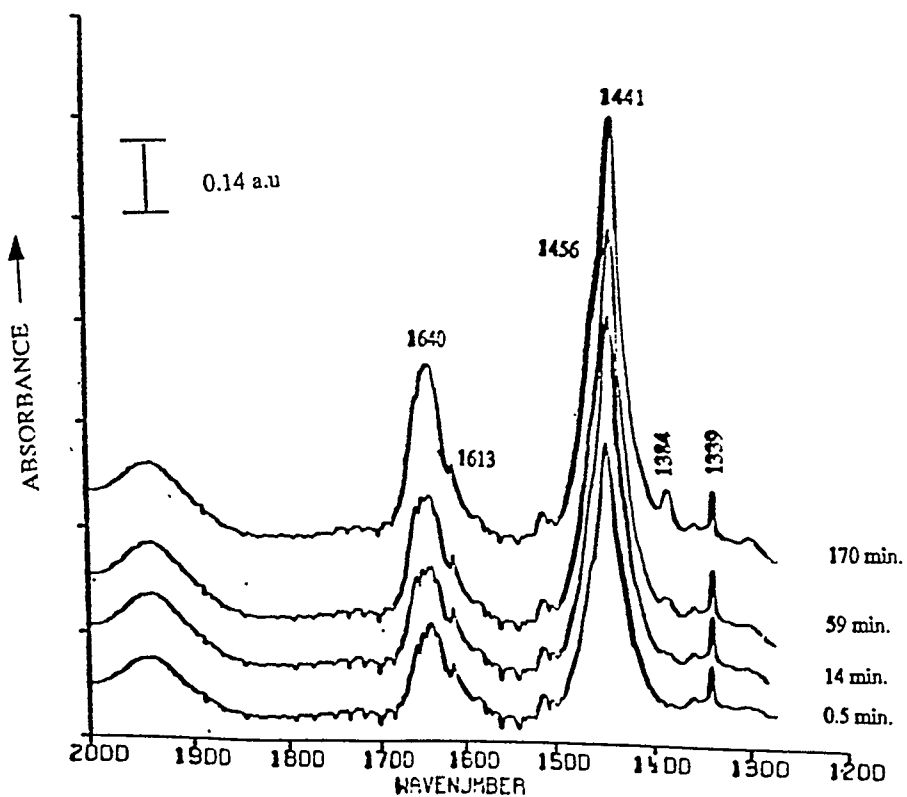


Fig. 6.3. Spectra showing the reaction of ethene on calcined 1.58wt. %PdNaY at 25 °C. Spectra taken at different stages of the reaction

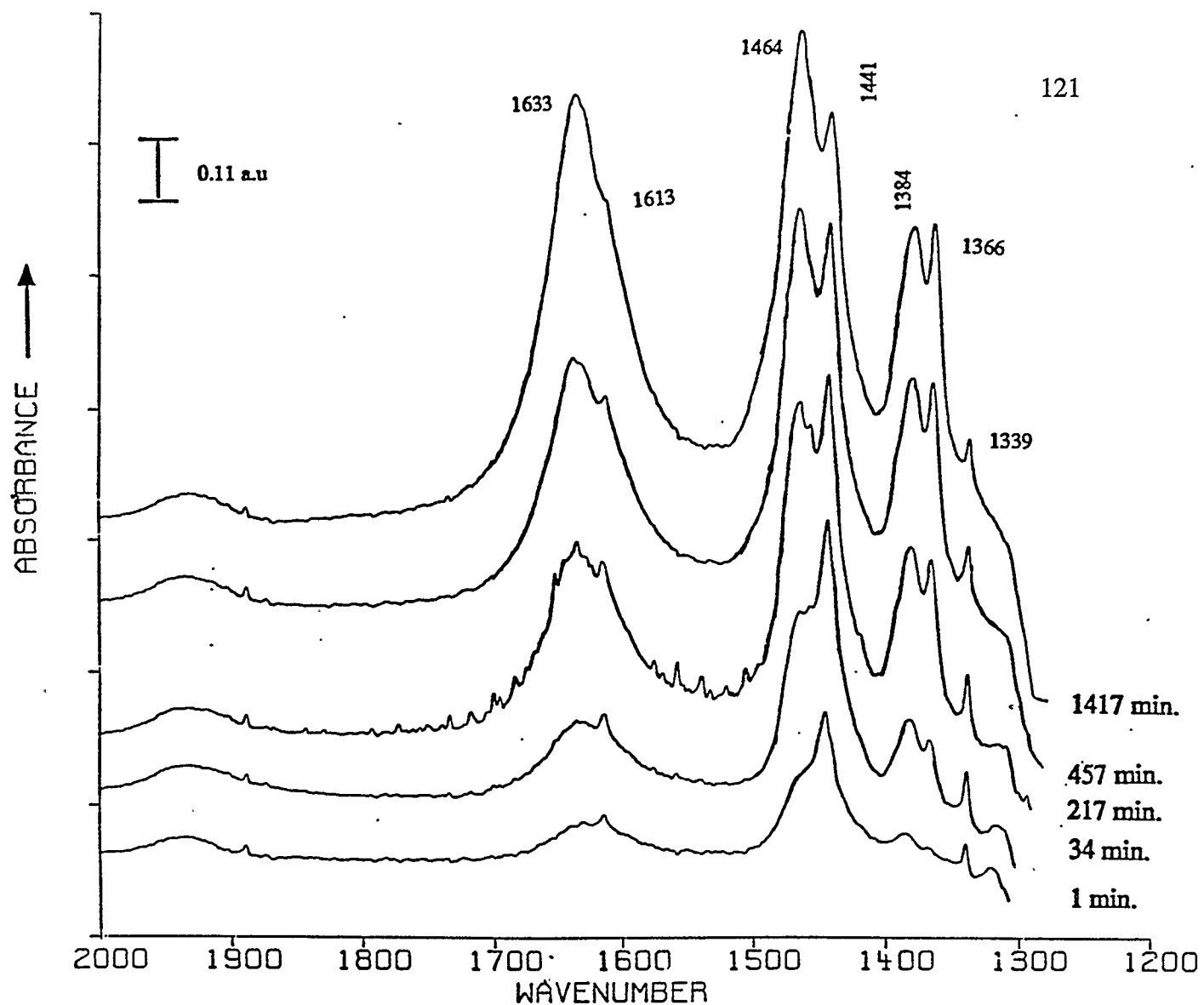


Fig. 6.4. Spectra showing the reaction of ethene on a highly dehydroxylated HY sample at 25 °C. Spectra taken at different stages of the reaction.

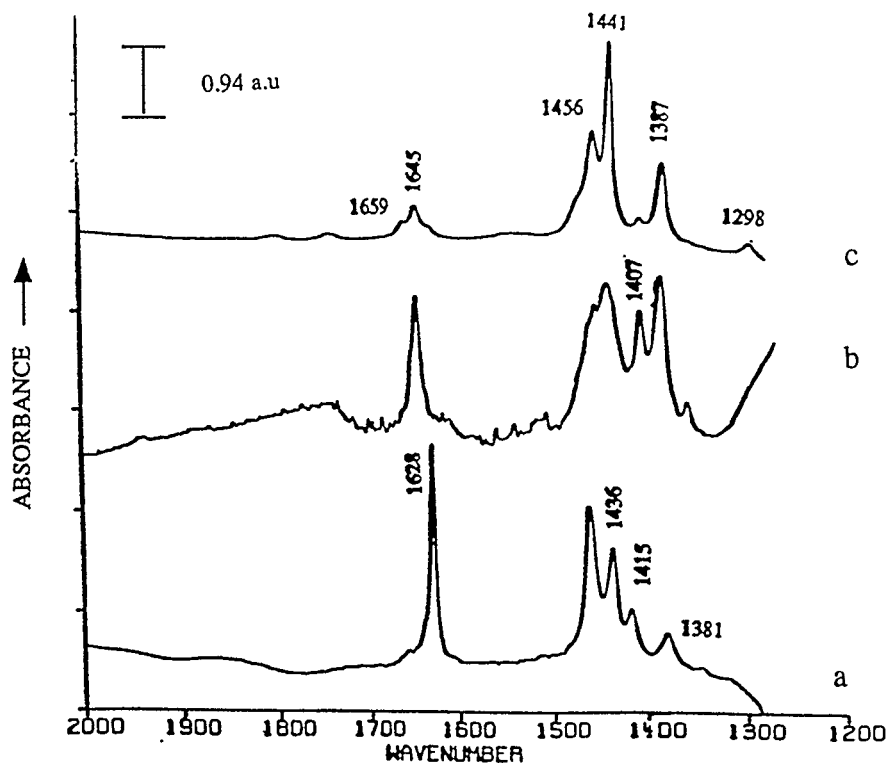


Fig. 6.5. Spectra showing the adsorbed species of butene isomers on 1.58wt. %PdNaY. a= 1-butene b= cis-2-butene c= trans-2-butene.

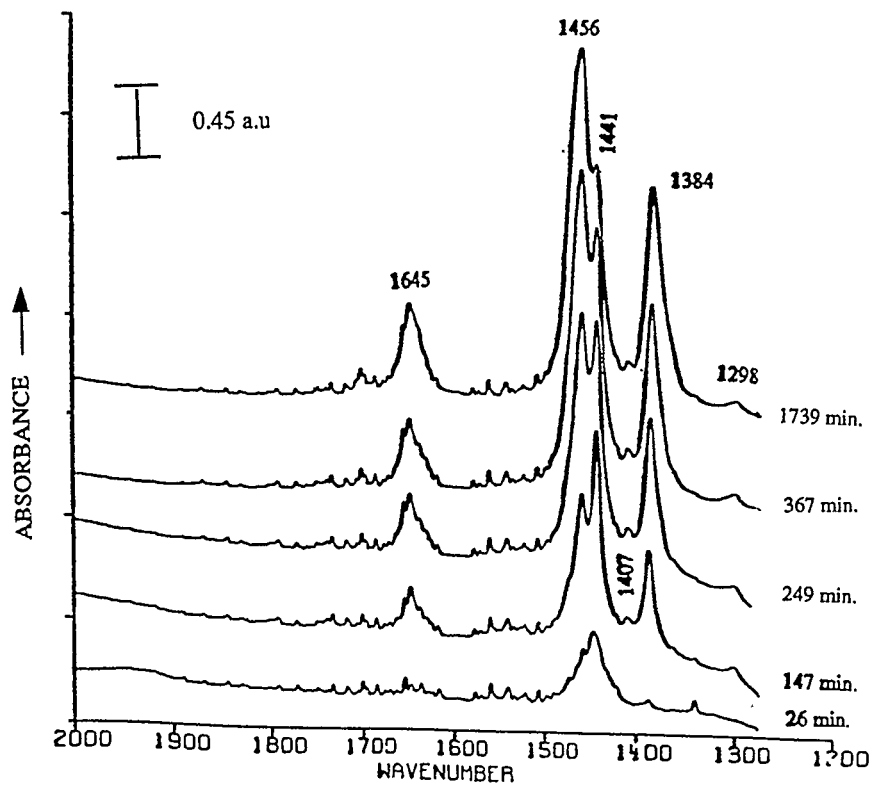


Fig. 6.6. Spectra showing the reaction of ethene on calcined 1.58wt. %PdNaY at 75 °C. Spectra taken at different stages of the reaction.

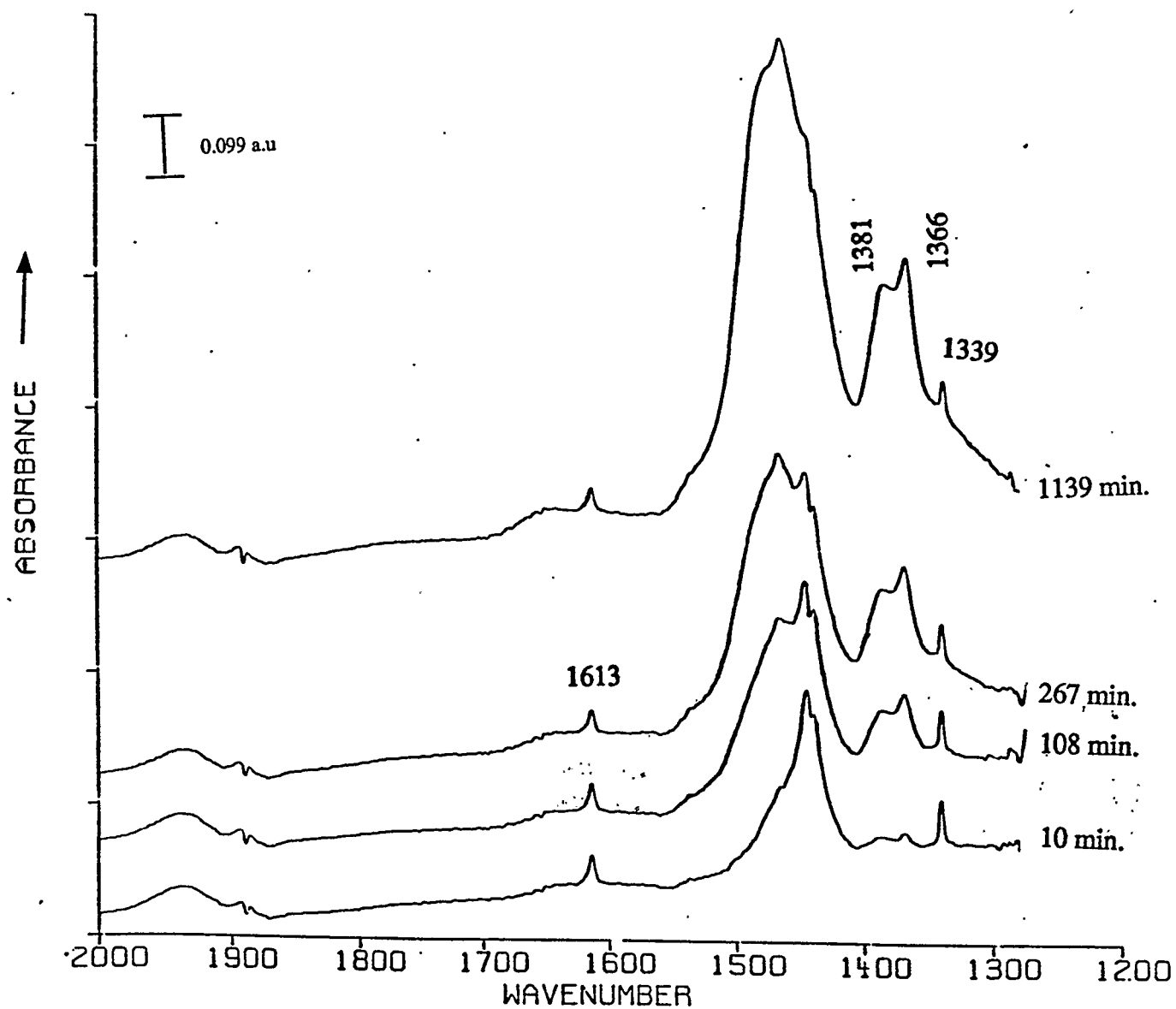


Fig. 6.7. Spectra showing the reaction of ethene on calcined HY at 75 °C. Spectra taken at different stages of the reaction.

Activity of catalyst for ethene reaction.

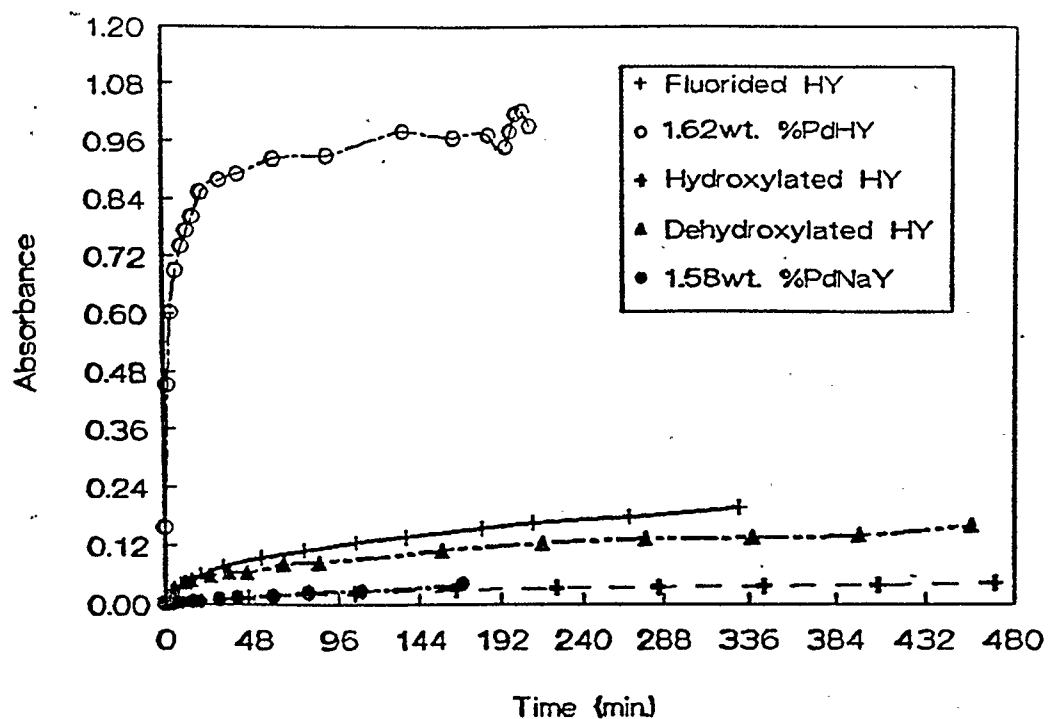


Fig. 6.9 Activity of catalyst for dimerization

Oxidized PdHY and PdNaY samples (75 °C).

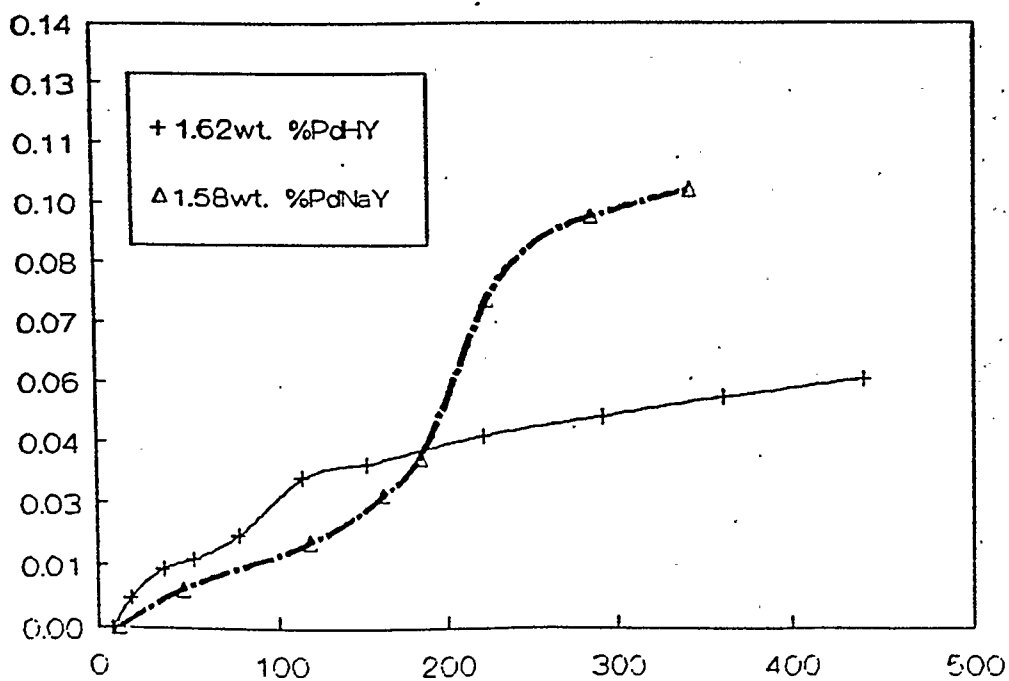
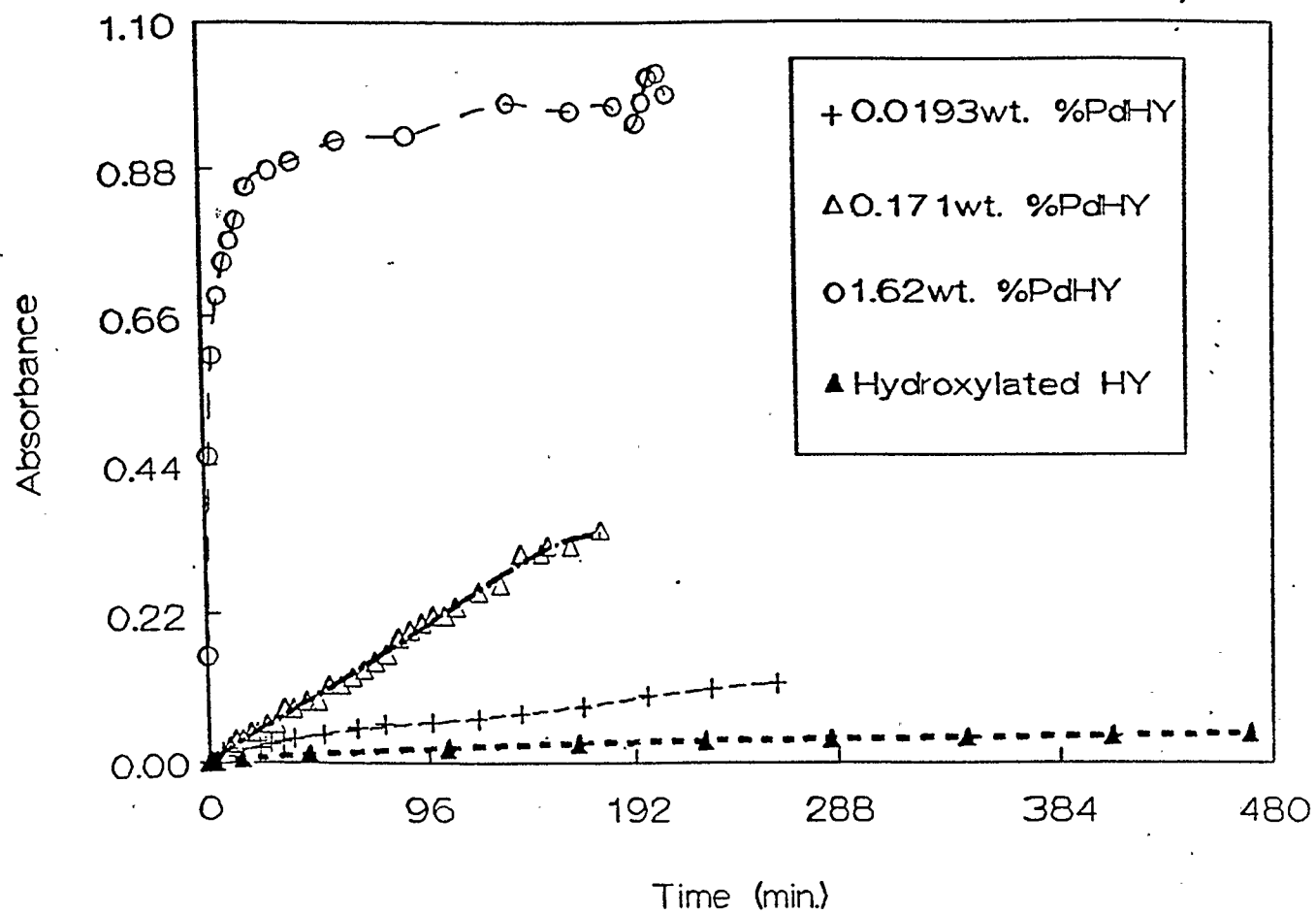


Fig. 6.10 Measurement of catalyst activity
Ethene reaction on oxidized samples.



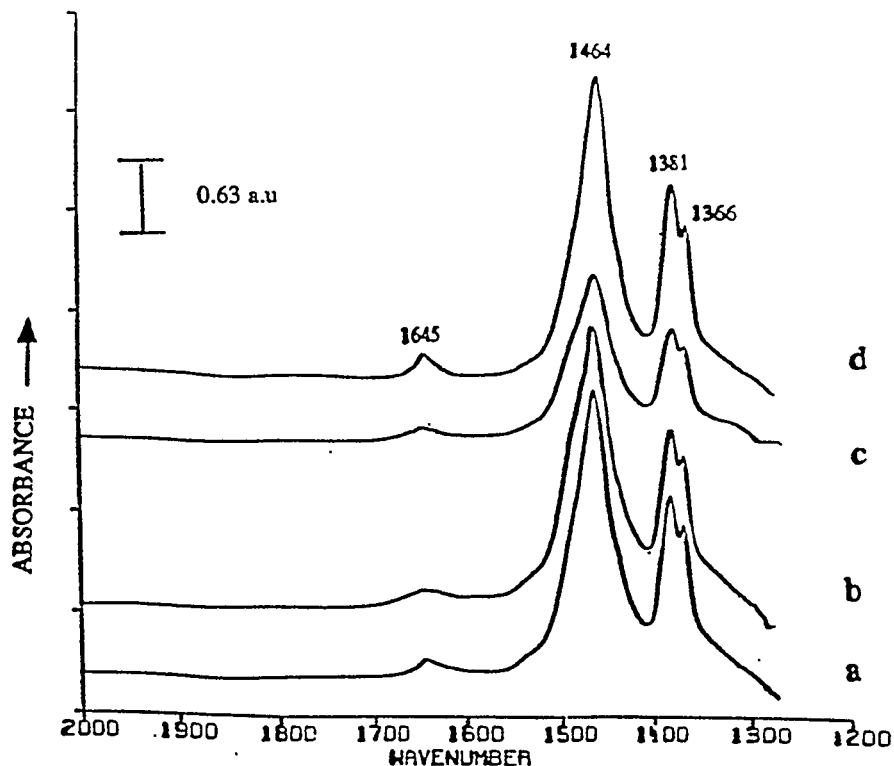


Fig. 6.11. Spectra showing the adsorbed species of trans-2-butene on acidic catalysts. a= 1.62wt. %PdHY b= 1.48wt. %PdHY c= fluoridated HY sample d= HY.

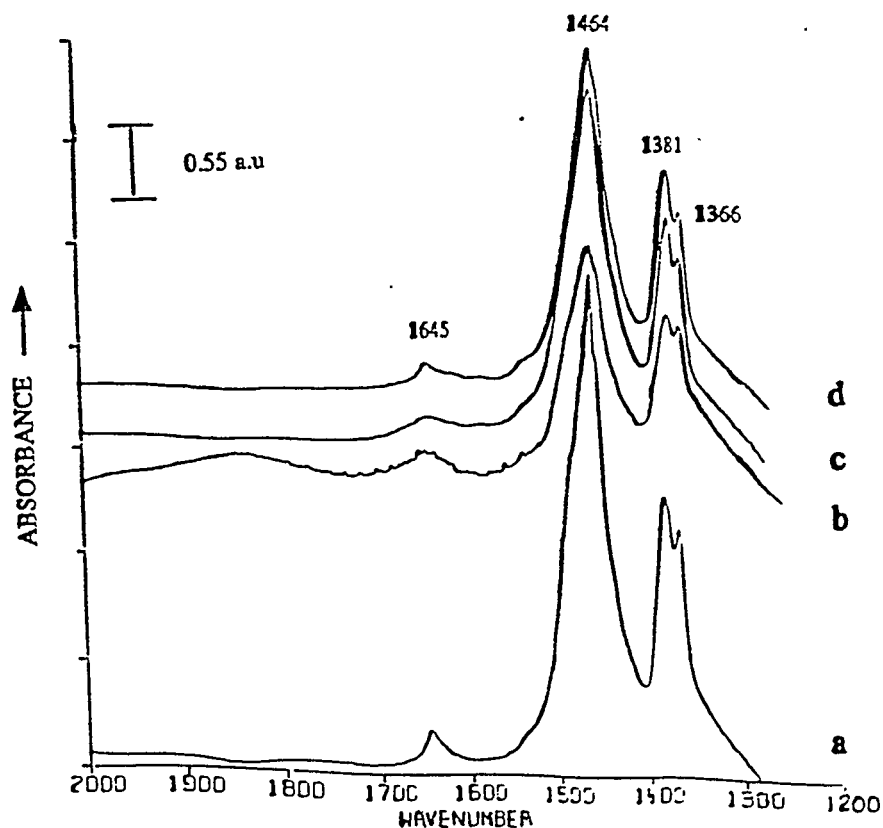


Fig. 6.12 Spectra showing the adsorbed species of cis-2-butene on acidic catalysts. a= HY b= fluoridated HY sample c= 1.48wt. %PdHY sample d= 1.62wt. %PdHY.

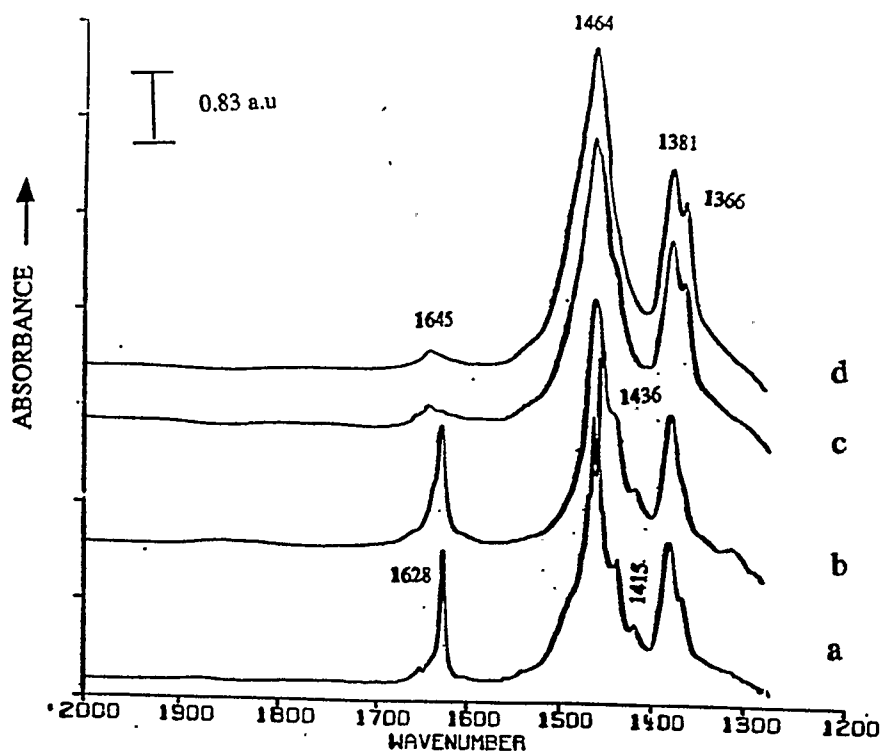


Fig. 6.13. Spectra showing the adsorbed species of 1-butene on acidic catalysts. a= HY b= highly dehydroxylated HY c= 1.62wt. %PdHY d= spectra showing adsorbed species of trans-2-butene on PdHY (shown for comparison).

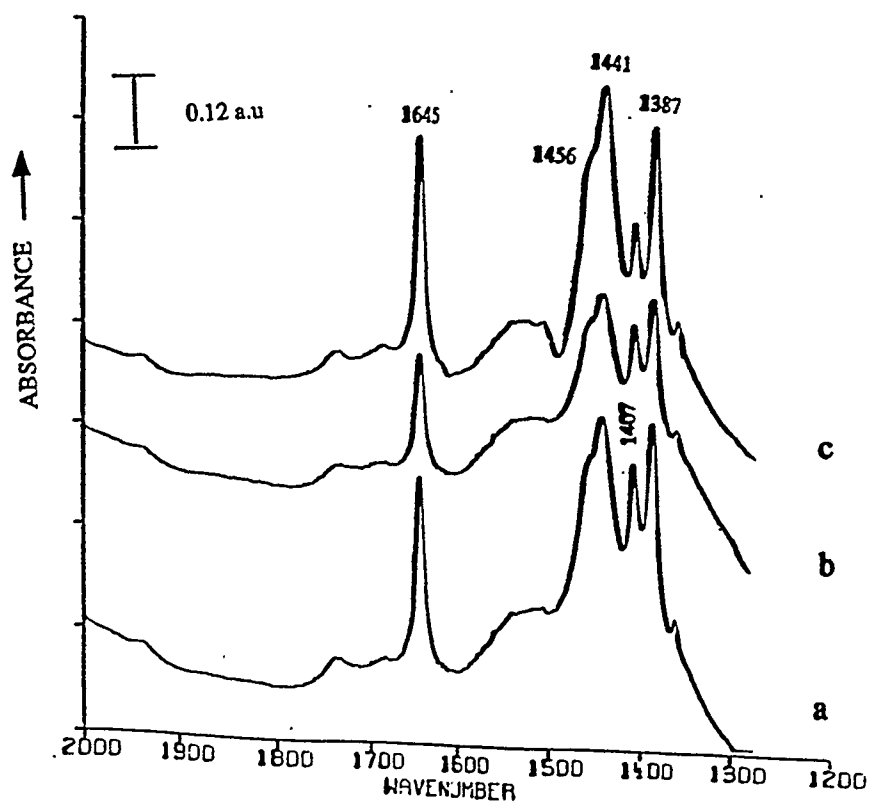


Fig. 6.14. Spectra showing the adsorbed species of cis-2-butene on non-acidic catalysts. a= 1.50wt. %PdFNaY b= 1.58wt. %PdNaY c= NaY.

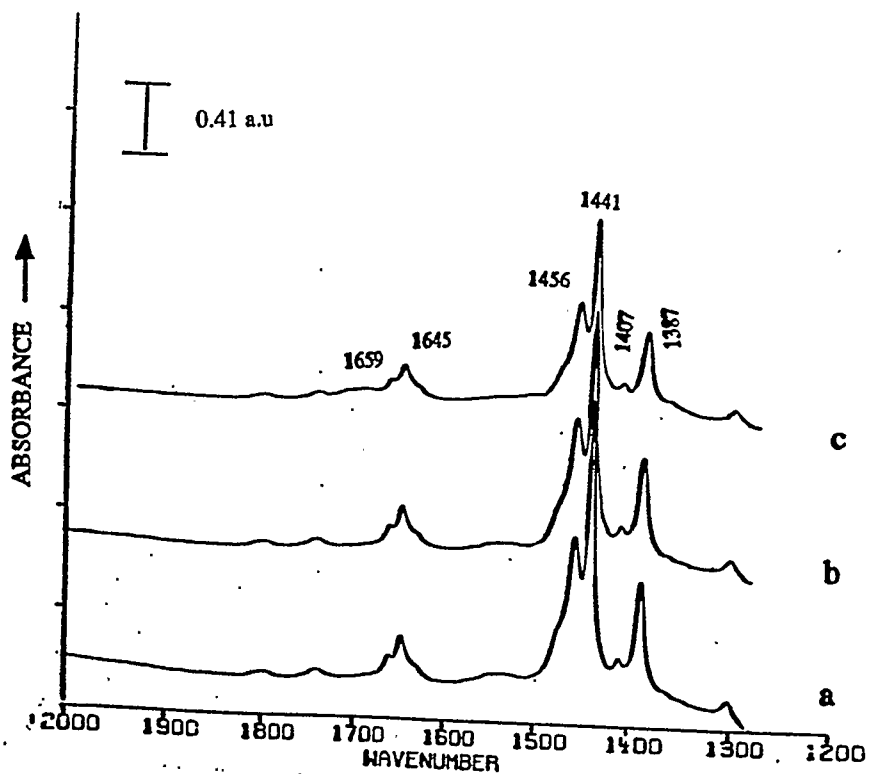


Fig. 6.15. Spectra showing the adsorbed species of trans-2-butene on non-acidic catalysts. a=1.50wt. %PdFNaY b=1.58wt. %PdNaY c=NaY.

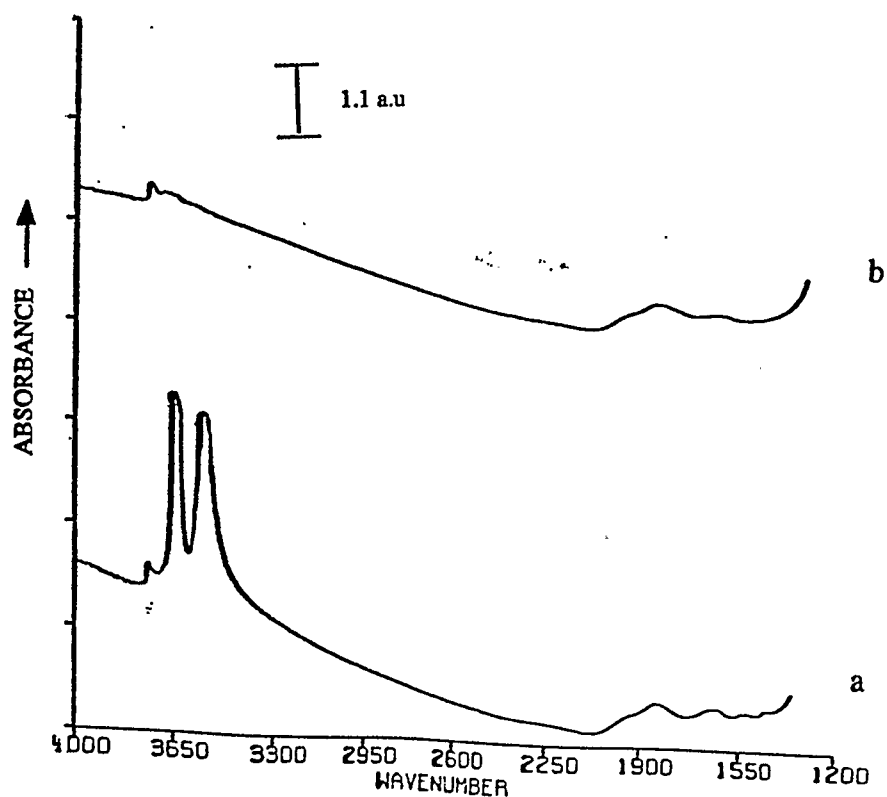


Fig. 6.16. IR spectra of calcined zeolite samples. a=HY b= highly dehydroxylated HY.

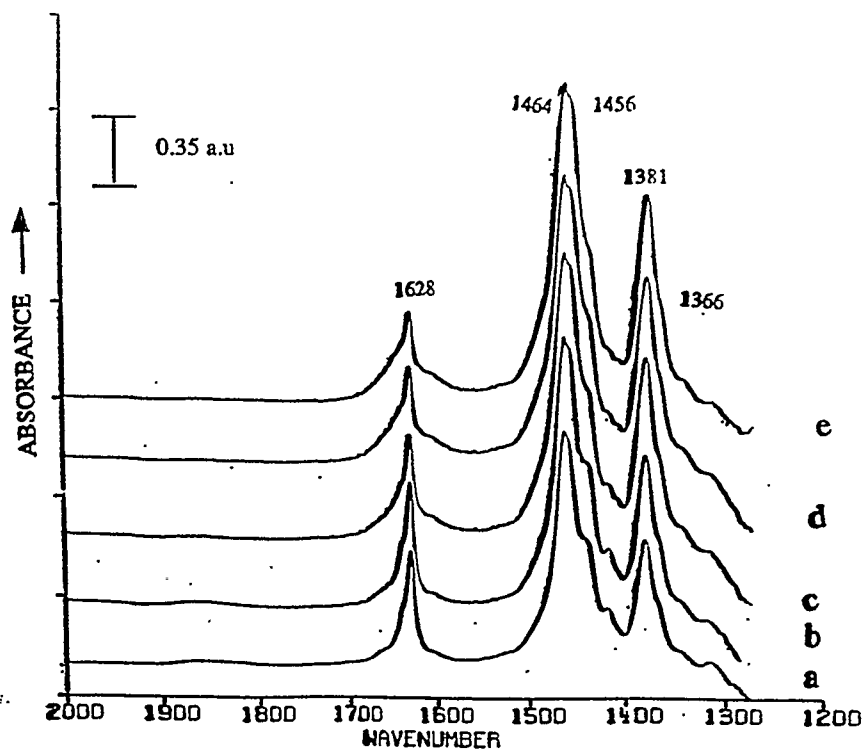


Fig. 6.17. Spectra showing the reaction of 1-butene on a highly dehydroxylated HY sample at 25 °C. Spectra taken at different stages of the reaction. a= 1 min. b= 17 min. c= 176 min. d= 282 min. e= 411 min..

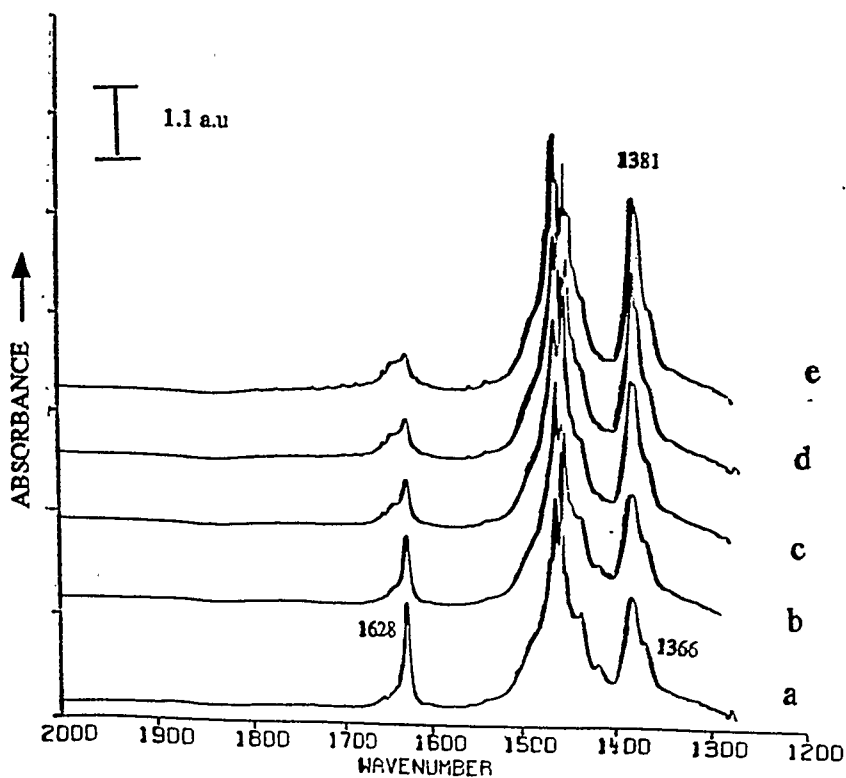


Fig. 6.18. Spectra showing the reaction of 1-butene on a calcined HY sample at 25 °C. Spectra taken at different stages of the reaction. a= 2 min. b= 15 min. c= 90 min. d= 150 min. e= 305 min..

Fig. 6.19 Effect of reduction time on activity

Peaks from ethene reaction (0.171wt. %PdHY).

130

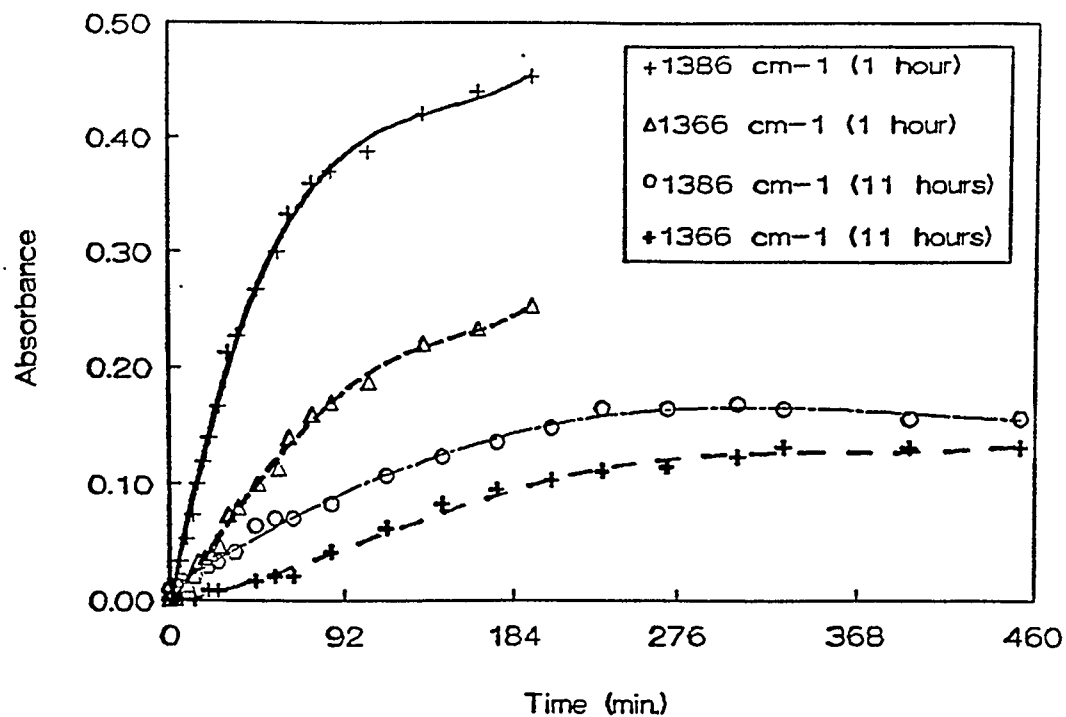


Fig. 6.20 Oxidized and reduced 0.0193wt. %PdHY

Peaks from ethene reaction (25 °C).

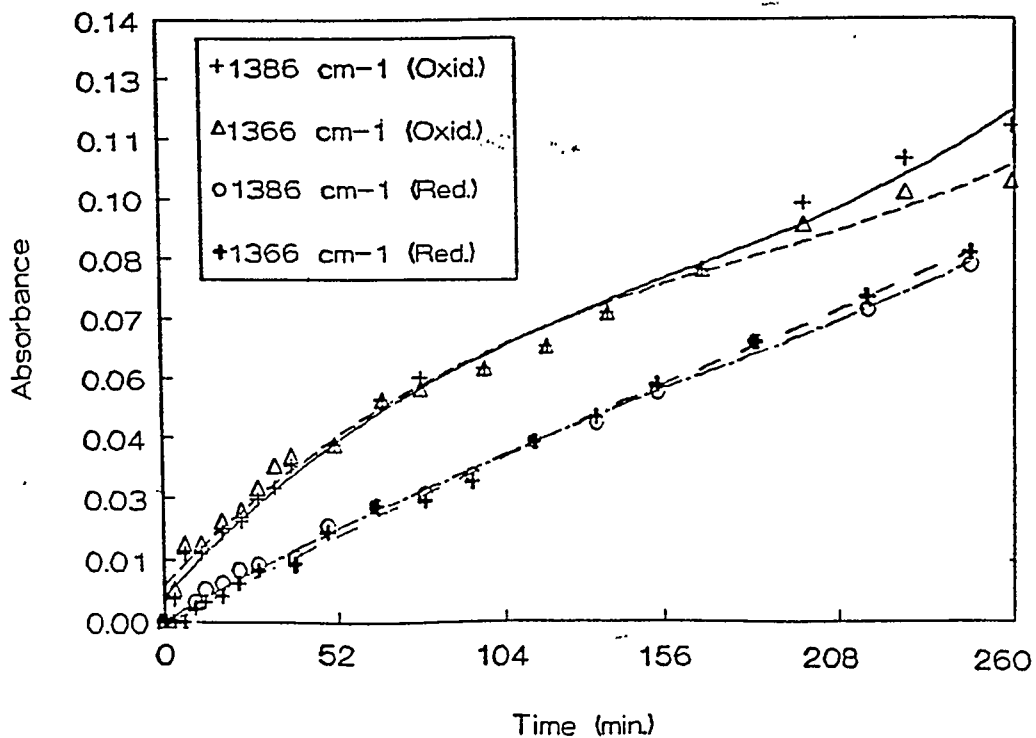


Fig. 6.21 Oxidized and reduced 0.171wt. %PdHY
Peaks from ethene reaction.

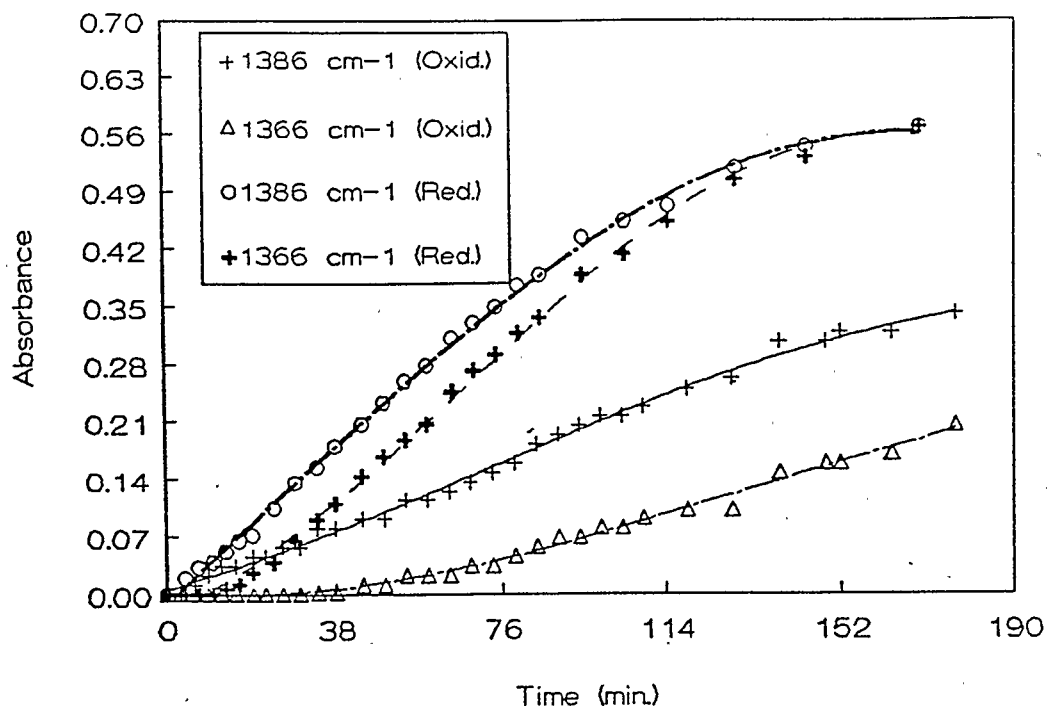
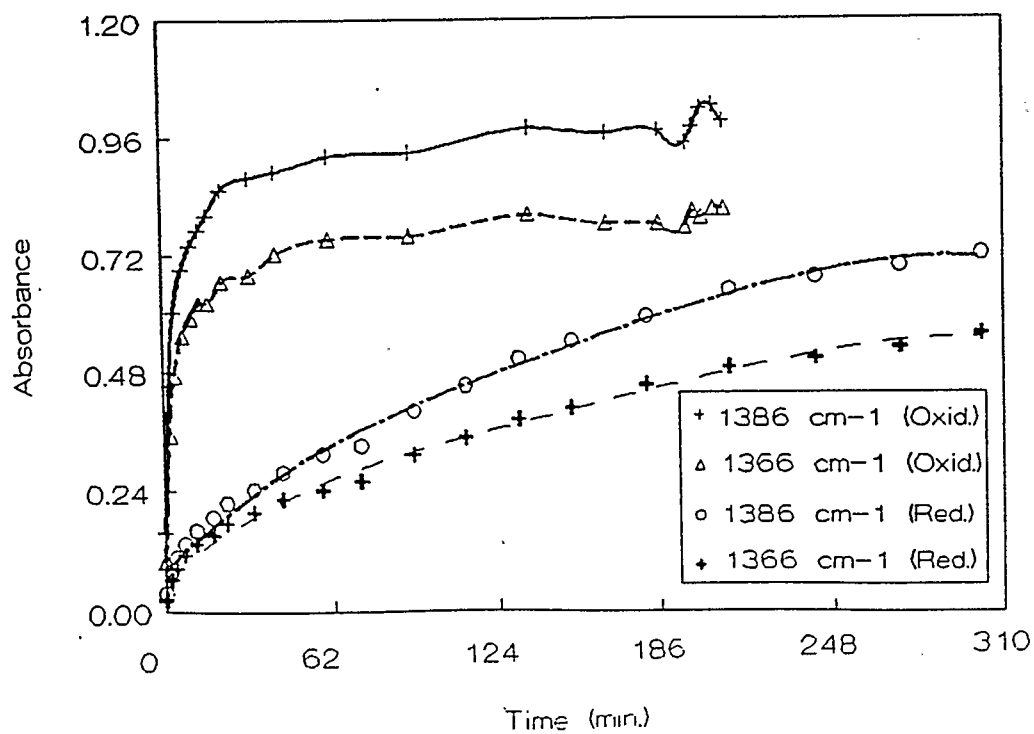


Fig. 6.22 Oxidized and reduced 1.62wt. %PdHY
Peaks from ethene reaction.



6.4 DISCUSSION

6.4.1 ADSORPTION OF ETHENE

There are twelve possible vibrations of gaseous ethene (C_2H_4) and only five of these vibrations are active in the infrared.

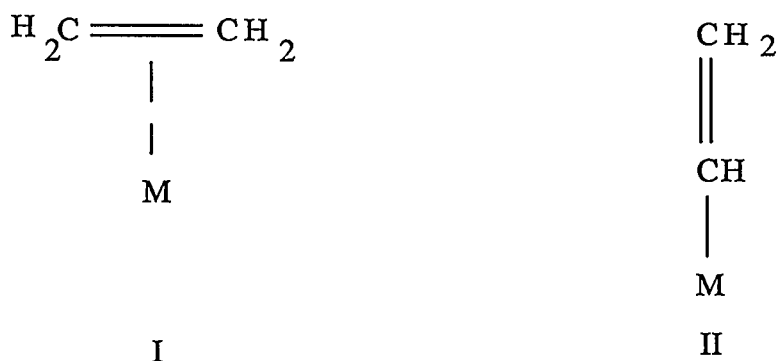
Of the four C—H vibrations of C_2H_4 , ν_1, ν_5, ν_9 and ν_{11} , only ν_9 (3105 cm^{-1}) and ν_{11} (2889 cm^{-1}) are accompanied by a change in dipole moment and are infrared active, while ν_1 (3019 cm^{-1}) and ν_5 (3075 cm^{-1}) are symmetrical and are accompanied by a change in polarizability and are thus Raman active. A distortion of the symmetry of the electronic structure of the C_2H_4 molecule so that it no longer has D_{2h} symmetry, can lead to activation of the ν_1 and ν_5 vibrations in the infrared. Also, the valence vibration of the C=C bonds, ν_2 , and ν_3 (CH_2 scissoring) which are IR-forbidden in gaseous C_2H_4 can also be seen after adsorption on zeolite samples (26,27).

On adsorption of ethene on PdNaY and PdHY samples (fig. 6.2 and 6.3), peaks due to adsorbed C_2H_4 were initially observed at $1613\text{ cm}^{-1}(\nu_2)$, $1444\text{ cm}^{-1}(\nu_{12})$, $1339\text{ cm}^{-1}(\nu_3)$, $2974\text{ cm}^{-1}(\nu_{11})$. On the hydroxylated HY sample, we observed a peak at about $3094\text{ cm}^{-1}(\nu_9)$ due to adsorbed C_2H_4 . This 3094 cm^{-1} band was also observed in the spectrum of an HY zeolite that has been completely dehydroxylated to give only Lewis sites on the zeolite.

For gaseous C_2H_4 , the ν_2 and ν_3 vibrations are infrared inactive but occur in the Raman at a frequency of 1623 cm^{-1} and 1342 cm^{-1} respectively. The observation of infrared bands due to adsorbed C_2H_4 on the catalyst at 1613 cm^{-1} and 1339 cm^{-1} shows that the catalyst has perturbed the C_2H_4 molecule. The presence of the 1613 cm^{-1} band also shows that the C_2H_4 molecule interacts with the zeolite without loss of the double bond.

Two possible species can be proposed for the adsorbed state of C_2H_4 based on

the infrared bands observed :



Species II is not very likely since one would expect that the frequency of the ν_2 and ν_3 vibrations for this species should be very different from that of the gas phase C_2H_4 , which is not what was observed. Also, one would not expect room-temperature evacuation to remove species II as we observed in our studies (the 1613 and 1339 cm^{-1} bands disappear on evacuation). This means that ethene is associatively adsorbed (species I) on the zeolite.

Since the fundamental frequencies of the adsorbed molecules were not shifted appreciably from the gas-phase values, the adsorbed molecule could not have been greatly perturbed electronically.

Ethene must be adsorbed on these PdNaY and PdHY catalysts by a kind of weak chemisorption or strong physisorption since evacuation at room temperature usually removes the 1613 and 1339 cm^{-1} from the spectrum, while the 1444 cm^{-1} band is reduced in intensity.

It was also observed that C_2H_4 interacts with the OH groups of the zeolites and a broad band develops at 3300 cm^{-1} due to the perturbation of the zeolitic OH groups by ethene. This perturbation is due to hydrogen bonding of ethene with the OH groups (15). On the samples used in our studies, ethene interacted with the OH groups which give the 3643 cm^{-1} peak while the 3545 and 3740 cm^{-1} OH groups are only slightly perturbed.

It should also be remembered that ethene was observed to adsorb associatively

on HY zeolite containing only Lewis sites.

This means that there are three modes of adsorption of ethene on metal loaded zeolites :

- 1) Associative adsorption on the metal cation
- 2) Hydrogen bonding interaction with the OH groups
- 3) Associative adsorption on Lewis acid sites.

On adsorption of ethene on 1.58wt. %PdNaY, 1.62wt. %PdHY and HY catalysts, some differences were observed between the 1613 and 1339 cm^{-1} peaks due to adsorbed C_2H_4 on the pellet surface. On PdNaY, the 1339 cm^{-1} peak was more intense than the 1613 cm^{-1} band, but on the HY pellet, the 1613 cm^{-1} band was more intense. On PdHY, both bands are usually of equal intensity.

The differences between the behaviour of adsorbed ethene on PdNaY and HY samples might indicate that C_2H_4 is adsorbed differently on these catalysts. It appears as if C_2H_4 is just physically adsorbed on PdNaY while the adsorption involves the double bond on the HY catalyst. It was also observed that the 1339 cm^{-1} band disappears more rapidly on PdHY than on PdNaY which is an indication of observed rate of reaction on these catalysts.

6.4.2 REACTIONS OF ETHENE

6.4.2(a) NaY SUPPORT

On adsorption of ethene on NaY zeolite support, no reaction was observed. From chapter five (pyridine study), we know that this catalyst does not contain any Bronsted or Lewis site. This indicates, as expected, that this support does not catalyze ethene reactions; that is, the monovalent sodium cation is not catalytically active.

The three isomers of butene were adsorbed on the Pd-exchanged form of the zeolite (fig.6.5) to help in the identification of the products seen on all the catalyst samples used in our study, since these species have been identified in various studies as products in the reaction.

The identification of these isomers is not easy since their spectra are very similar, but certain characteristic peaks can be used to differentiate these isomers. Adsorbed 1-butene has a very intense peak at 1628 cm^{-1} which is not present on the other isomers; adsorbed cis-2-butene has a characteristic peak at 1407 cm^{-1} which is relatively intense compared to the band at 1387 cm^{-1} , which is not the case with trans-2-butene. Adsorbed trans-2-butene has peaks at 1456 and 1441 cm^{-1} which have a characteristic ratio of intensities that is not observed on the other isomers. The intensity of the 1441 cm^{-1} is greater than the 1456 cm^{-1} band.

6.4.2(b) PdNaY CATALYST

On reacting ethene on this catalyst at 75°C (fig. 6.6), the intensity of the 1444 cm^{-1} band (adsorbed C_2H_4) increased initially and was subsequently shifted, over a matter of 26 minutes, to 1441 cm^{-1} (ν_{17} of trans-2-butene). Other bands due to adsorbed trans-2-butene at 1456 cm^{-1} (ν_{25}), 1387 cm^{-1} (ν_{26}) and 1298 cm^{-1} (ν_{27}) were also observed growing at the same time as the 1444 cm^{-1} band was shifting to 1441 cm^{-1} . As the reaction progressed, bands appeared at 1407 cm^{-1} (ν_{26} of cis-2-butene) and at 1628 cm^{-1} (ν_7 of 1-butene).

This seems to indicate that trans-2-butene is the first species formed in ethene reaction on this catalyst (compare fig. 6.6 (after 147 minutes) to 6.5), although the possibility exists that an adsorbed 1-butene-like species forms first, which then reacts instantaneously to form trans-2-butene. However, it is clear that no significant concentration of 1-butene forms initially, and in fact, infrared bands from cis-2-butene

and 1-butene can only be seen after 5 hours at 75°C. This result appears to be in contradiction to the results from ESR and GC studies which suggest that 1-butene forms first (3,4). However, it is difficult to be certain that trans-2-butene forms first, because the isomerization is very rapid under this condition.

It is also possible to have underlying bands in the 1380 - 1460 cm^{-1} region from larger oligomers or polymers on this catalyst although they cannot be present in large amounts since this would modify the intensities and widths of these bands; also, bands seen for C_2H_4 reaction on acid catalysts at 1367 and 1465 cm^{-1} which are attributed to oligomers are not seen on PdNaY. These results indicate that oligomerization does not occur to a large extent on PdNaY catalyst; dimerization seems to be the main reaction.

6.4.2(c) HY SUPPORT

Reaction of ethene at 75°C is surprisingly very slow on this highly acidic zeolite (fig. 6.7). Adsorbed ethene (peaks at 1613, 1444 and 1339 cm^{-1}) can still be seen after carrying out the reaction overnight. The weak 1439 and the small 1387 cm^{-1} bands which are also present may represent a small amount of dimerization to form trans-2-butene. The 1367 and 1464 cm^{-1} bands also grow very slowly and they probably represent oligomers formed on the zeolite (17). The presence of the 1367 cm^{-1} band usually represents a branched chain oligomer (28) while the 1464 cm^{-1} band usually represents both methyl asymmetric deformation and methylene scissoring vibrations (29).

The ratio of the intensities of the CH_3 and CH_2 stretching vibrations can be used to estimate the extent of branching on the oligomer (30,31); a linear oligomer has an intensity ratio of 0.42 (30). On reacting C_2H_4 on HY at 25°C, the intensity ratio was found to decrease from 2.80 to 2.05 as the reaction progressed. This result indicates that the oligomers formed on this catalyst are highly branched and that the sites for branching

are used up as the reaction progresses (since the ratio is not constant).

6.4.2(d) PdHY CATALYST

Reaction of C_2H_4 at $75^\circ C$ on the 1.62wt. %PdHY sample was so fast that it was not possible to see the development of the surface species; the reaction was almost complete in 48 minutes. In order to slow the reaction down to study the process better, ethene dimerization was carried out at a lower temperature.

On doing the reaction at $25^\circ C$ (fig. 6.2), the same bands (1628, 1456, 1441, 1387 and 1298 cm^{-1}) due to butenes as on PdNaY were observed, except that bands at 1367 and 1464 cm^{-1} also showed up. It is obvious that both dimerization and oligomerization to give branched products are occurring simultaneously. The oligomerization reaction was much faster than observed on PdNaY (see fig. 6.8) and this shows that Pd is more accessible on PdHY than PdNaY as identified in chapter three.

The rate of dimerization was followed at $75^\circ C$ by measuring the intensity of the gas phase peak at 2865 cm^{-1} due to trans-2-butene; the dimerization rate was initially higher on PdHY than on PdNaY, but as the reaction progressed, the activity of PdNaY became greater (fig. 6.9). The initial higher rate of PdHY is probably due to the better accessibility of Pd on the HY support as compared to Pd on NaY as identified in chapter three (CO study); it was proposed that on NaY support, the Pd is mostly stabilized in the hexagonal prisms while on HY support, the Pd is mostly stabilized in sodalite cages. So one would expect the Pd on HY to be more accessible for catalysis than on NaY, since it will take longer for the Pd on the latter support to migrate to accessible sites. The subsequent decrease in dimerization activity on PdHY could be due to the poisoning of these active Pd sites by the oligomerization occurring simultaneously and/or it could be due to the fact that the dimer is being used up to form the oligomer. From the gas-phase spectra of PdHY, 27% of the initial ethene was used up in the reaction, while on PdNaY,

about 56% of the initial ethene gas was used up in the reaction cell when the reaction was observed to have stopped on both catalysts. This might indicate that the poisoning of the active Pd site can explain the subsequent decrease in dimerization activity that was observed on PdHY.

It can also be seen (fig. 6.8) that the rate of the oligomerization reaction was much faster on PdHY than on HY. This observed higher rate on PdHY could be due to the strengthening of the active acid sites on HY by Pd or it could be due to the presence of trans-2-butene which was formed on the Pd. Trans-2-butenes were not easily formed from ethene on HY, but the presence of Pd in PdHY catalyzed this dimerization.

The study of ethene reactions on PdHY samples with increasing loadings of Pd was not particularly informative. At the lowest loading of PdHY (0.0193wt. %Pd), the catalyst behaved similarly to HY while the 0.171wt. %PdHY gave the same products as the 1.62wt. %PdHY sample but the rate was much slower (fig. 6.10).

6.4.2(e) ACTIVE SITES FOR OLIGOMERIZATION

To explain the exact effect of Pd on the reaction of ethene, various other studies were done. The three isomers of butene were adsorbed on acid catalysts HY, 1.62wt. %PdHY and the fluorided samples (figs. 6.11 - 6.13) to identify the products from these isomers. Cis- and trans-2-butenes were also adsorbed on NaY, 1.48wt. % PdNaY and 1.50wt. %PdNaFY samples as shown in figs. 6.14 - 6.15). 1-butene adsorption on the 1.48wt. %PdNaY sample is shown in fig. 6.5.

From figs. 6.11 - 6.13, it can be seen that reactions of trans- and cis-2-butene on HY and PdHY give branched chain oligomers as seen by the bands at 1381 and 1366 cm^{-1} . These bands have an intensity ratio of 1.4 : 1, while 1-butene on HY gives mostly straight-chain oligomers as shown by the low intensity of the 1366 cm^{-1} band. The intensity ratio of the 1381 cm^{-1} to the 1366 cm^{-1} band for the oligomer product of

1-butene is 2.5 : 1. It was observed that on adsorption of 20 mm Hg of 1-butene on PdHY, all the 1-butene isomerized to trans-2-butene (fig. 6.13) in less than a minute and the subsequent reaction of the trans-2-butene was as observed above. On adsorption of 1-butene on a Pd-loaded HY zeolite which had been extremely dehydroxylated to remove all Bronsted acid sites (and leave only Lewis acid site), the same rate of isomerization was observed as seen on the hydroxylated HY (containing OH groups) and this indicates that isomerization occurs on the Pd rather than on the OH groups. This result supports the proposal by Ghosh and Kevan (3) that Pd is the active site for 1-butene isomerization while the proposal by Michalik (4) that OH groups constitute the active sites seems to be wrong. On adsorption of 1-butene on PdNaY, the isomerization reaction was found to be far slower than on PdHY and no oligomerization was observed. It was also observed that the oligomerization reaction of these butenes on PdHY zeolite was found to occur for a very short time and at a slow rate after an initial fast start. It should be remembered that ethene reaction on PdHY gives branched chain oligomers and that the reaction was very fast and went on for a longer period of time than observed with the butenes on PdHY; also, branching was found to become more extensive as the ethene reaction progressed; the intensity ratio of the 1381 and 1366 cm^{-1} peaks decreased from 1.75 to 1.2.

Although in section 6.4.2(b), peaks due to trans-2-butene were observed first in ethene dimerization, the extremely fast isomerization of 1-butene to trans-2-butene observed on PdHY means that it is possible that 1-butene is the first species formed in ethene dimerization. The rather slow isomerization of 1-butene observed on PdNaY is due to the inaccessibility of the Pd on this catalyst in comparison to the PdHY catalyst. The appearance of peaks due to 1-butene at the latter stages of the ethene dimerization (section 6.4.2(b)) is because equilibrium between the butene isomers has been attained in this reaction.

To establish whether the differences in reactivity between HY and PdHY for oligomerization were due to different active sites or the presence of 2-butenes on PdHY, cis- and trans-2-butenes were adsorbed on both catalysts (figs. 6.11 and 6.12) for the same extent of time, and it was observed that the same type of products were formed. This definitely shows that ethene oligomerization occurs on the same sites on these catalysts but the difference in ethene reactivity between HY and PdHY is because the PdHY can easily form 2-butenes which seem to react faster than ethene on the active acid site.

It has previously (section 6.2.2) been proposed that the active sites for the oligomerization reaction were acid sites, but these active sites could be Bronsted or Lewis acid sites or a combination of these sites.

To identify which type of acid sites are active for oligomerization on the acid catalysts, an HY zeolite was highly dehydroxylated at 650°C to leave only Lewis sites on this zeolite (fig. 6.16) and then 1-butene was adsorbed on it. It was observed that mostly linear oligomers were formed on this sample (6.17), which was what we observed on a hydroxylated HY sample (fig. 6.18), which contains mostly Bronsted sites with a small number of Lewis sites; the intensity ratio of the 1381 cm^{-1} to the 1366 cm^{-1} band on the highly dehydroxylated sample is 2.4 : 1 (2.5 : 1 for the hydroxylated sample). This seems to suggest that the same sites are active on both samples. On adsorption of ethene on a sample with only Lewis acid sites, products (branched chain oligomers) similar to that found on the HY sample were observed, and these observations strongly support the view that Lewis sites are the active sites for oligomerization. This view was also expressed by Turkevich (14) after studying ethene reactions. It should be remembered that from section 5.3.4(a), Lewis acid sites on HY were observed to be stronger than Bronsted acid sites in bonding to pyridine.

6.4.3 GAS PHASE SPECTRA

The gas phase product of the reaction over all Pd-containing catalysts was predominantly made up of trans-2-butene and smaller amounts of cis-2-butene and 1-butene as expected. From thermodynamic considerations, one would expect an equilibrium mixture of the butenes to contain approximately 75% and 22% of trans- and cis-2-butene respectively and 3% of 1-butene. Gas-phase butenes were observed at the same time they were seen on the catalyst surface; so it appears like the butenes are formed on the catalyst surface and some of them desorb rapidly into the gas phase while some are oligomerized on the catalyst surface.

On hydroxylated HY, the highly dehydroxylated HY and the fluoridated HY, there was no gas phase product and this definitely confirms that Pd is the active site for the dimerization reaction.

A peak at 2865 cm^{-1} (ν_3 of trans-2-butene) can be used to measure the rate of the dimerization reaction on the catalysts. The use of gas phase spectra to measure the rate of dimerization ensures that no underlying oligomer bands perturb the intensity. It was observed that this 2865 cm^{-1} band has a faster initial growth on PdHY than on PdNaY for ethene reaction at 75°C , but after 185 minutes, the intensity of the band on PdNaY became stronger than that on PdHY (fig. 6.9). The reason for this observation was explained in section 6.4.2(d).

On carrying out the reaction on 1.58wt. %PdNaY for about 27 hours, 56% of the gas phase ethene gas had been used up in the reactions on the catalyst; and by this time, the dimerization reaction was found to have stopped, as seen in fig. 6.9. This shows that dimerization reaction stopped because the active sites had been used up, rather than because the reactant had been used up.

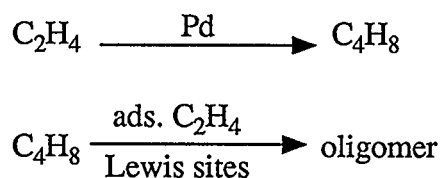
6.4.4 MECHANISM

Having identified Pd as the active site for ethene dimerization and Lewis sites as active sites for oligomerization, it is necessary to identify the reactant(s).

As said earlier, on adsorption of 2-butenes on HY and PdHY, branched oligomers were formed but the reaction stopped very quickly. Adsorption of ethene also gave branched oligomers but the reaction went on for a longer period of time and branching was more extensive. Since the presence of the 2-butenes has been identified as the reason for the differences in reactivity between HY and PdHY (section 6.4.2(e)), it might appear that the longer period of oligomerization observed with ethene as compared to 2-butene might indicate that adsorbed ethene is needed in the chain propagation stage of the oligomerization reaction. This proposal was tested by initially admitting trans-2-butene onto a PdHY pellet and subsequently adding ethene to the set-up after the reaction had stopped. It was observed that ethene was not adsorbed on this pellet since all the sites had been covered by trans-2-butene and the small amount of oligomer formed. The reaction did not start up again since there was no adsorbed ethene. But if ethene is initially adsorbed on a PdHY, the reaction was found to go on for a longer period of time as trans-2-butene is formed from the Pd site.

These results suggest that both ethene and butenes play a direct role in the oligomerization process. It does not appear that ethene simply dimerizes to butenes which then forms oligomers; the ethene also enters the second step (oligomer formation) as well.

The proposed mechanism is shown below :



6.4.5(a) EFFECT OF REDUCTION AND REDUCTION TIME

From chapter 3, reduction was found to convert Pd^{2+} into Pd^+ and Pd^0 on PdNaY and PdHY samples and as shown in section 5.3.6(b), reduction of PdHY decreased the number and strength of Bronsted sites and it created more strong Lewis acid sites by dehydroxylation. The increase in number of strong Lewis sites was shown not to be due to the removal of the polarizing effect of Pd^{2+} . On PdNaY (5.3.2(b)), reduction increased the number and decreased the strength of Bronsted sites; and it also increased the number and decreased the strength of Lewis sites.

From the above observations on the zeolite samples, it will be possible to identify the active oxidation state of Pd for dimerization and also one would expect based on the discussion in section 6.4.2(e) and the results from the pyridine study above that oligomer formation should increase on PdHY sample after reduction since Lewis sites are formed during reduction.

It was observed that the same products were formed on the oxidized and reduced samples, but the rate of reaction was different. It should also be remembered that since the dimer is subsequently used up in the oligomerization, the effect of reduction on the oxidation state of Pd will affect the rate of dimerization and subsequent oligomerization. This means that if the effect of reduction on oxidation states of Pd-loaded zeolites can be identified, then it will be possible to identify the active oxidation state of Pd for dimerization.

From a study of the effect of the extent of reduction on activity (fig. 6.19), it can be seen that the longer the reduction period, the lower the overall activity of the catalyst. The reason for this could be due to the increased number of Pd^0 formed if reduction is done for a long time; Pd^0 has been shown to be catalytically inactive for dimerization.

On 0.0193wt. %PdHY (fig. 6.20), reduction with H_2 at $300^\circ C$ does not seem to have an effect on the activity of the catalyst for oligomerization. This result agrees well with the observation in sections 3.3.1(a) and 3.3.2(a) of the CO study which showed that the Pd is in inaccessible cages at this level of loading and so the subsequent reduction at this temperature did not affect the valency or position of Pd. Also, section 5.3.6(b) (fig. 5.13) showed that reduction did not affect the overall strength of the Lewis sites at this level of loading of Pd. Only weak Lewis sites were formed by reduction on this catalyst as observed on the HY zeolite itself.

On 0.171wt. %PdHY (fig. 6.21), the reduced sample showed higher activity for oligomerization than the oxidized sample, but for the 1.62wt. %PdHY sample, the oxidized sample is more active (fig. 6.22). One possible explanation for these seemingly contradictory results involves the location of the Pd cation at different levels of loading. On 0.17wt. %PdHY sample, the Pd is still not as accessible as on 1.62wt. %PdHY and this means that reduction of the former catalyst will not be very efficient. So on reduction of 0.171wt. %PdHY, the Pd^{2+} is not reduced efficiently but more Lewis sites are formed and this will make the reduced sample more active than the oxidized sample if Pd^{2+} is the active oxidation state of Pd. On the 1.62wt. %PdHY sample, reduction is more efficient and will give Pd^+ and Pd^0 (and more Lewis sites), and if Pd^{2+} is the active valent state, it means the reduced sample will be of lower activity than the oxidized sample despite the increase in number of Lewis sites, which is what we observed. These results are consistent with Pd^{2+} as the active oxidation state for dimerization.

6.4.5(b) EFFECT OF FLUORIDE TREATMENT

From chapter 3 (CO study), the fluoridation of the NaY and HY has been shown not to affect the location or valent state of Pd loaded on these supports, and from chapter 5, it was shown that on PdFNaY samples, the fluoride seemed to have removed the sites for strong Bronsted and Lewis acid sites. On FHY catalyst, the fluoride was found to decrease the number and strength of the OH groups while it slightly increased the number of the Lewis sites.

On FHY and HY samples, the same products were formed in the ethene reaction but the reaction rates are different. From fig. 6.8, it can be seen that the activity of the FHY sample was greater than that of the HY sample which confirms once again that oligomerization is not catalyzed by Bronsted sites. The fact that fluoridation seemed to increase the number of Lewis sites shows again that oligomerization is being catalyzed by Lewis acid sites.

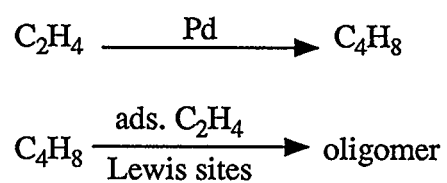
6.5 CONCLUSION

Ethene reaction on PdNaY catalyst was observed to give only dimers while on PdHY, the dimers were subsequently oligomerized. This difference in reactivity was explained by the presence of stronger acid sites on the latter catalyst. Branched chain oligomers were formed on the PdHY catalyst and Lewis acid sites were identified as the active sites for oligomerization.

Trans-2-butene was proposed as the first dimer formed during ethene reaction on PdNaY and PdHY catalysts and it was observed that the active sites for isomerization are Pd cations rather than the hydroxyl groups as proposed by some workers.

Pd^{2+} was proposed as the active site for dimerization on both PdNaY and PdHY catalysts since the reduction of the metal cation by hydrogen reduces the activity for dimerization.

The mechanism proposed for ethene reaction involved the formation and isomerization of dimers on the Pd cation and subsequent oligomerization of the dimers in the presence of adsorbed ethene on Lewis sites.



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CHAPTER SEVEN

7. CONCLUSION

In the work carried out for this thesis, infrared spectroscopy was used to study palladium-exchanged zeolite Y catalysts. It was hoped that it would be possible to understand how the use of the acidic form of the support (HY), instead of the conventional Na^+ - or Ca^{2+} -exchanged form, would affect the interaction between the metal and the support. Carbon monoxide and pyridine were used as probe molecules to study various properties of the catalyst surface. IR spectroscopy was also used to study the reaction of ethene on the catalysts. CO is useful for identifying the oxidation state of the metal, and pyridine can reveal information about the acidity of the surface. The ethene reaction has previously been studied on both non-acidic PdY zeolite and non-metal loaded HY zeolite, but it has not previously been studied on PdHY zeolite.

7.1 CARBON MONOXIDE STUDY

Using adsorption of CO on PdHY and PdNaY samples, it has been possible to establish that during cation exchange of the supports, the Pd cation is preferentially stabilized in the hexagonal prisms of the zeolite support at low loadings of Pd, but as the extent of cation loading is increased, the Pd cation spills over into sodalite cages and supercages. CO adsorption was not able to determine which of these sites the Pd occupies at the highest loadings used in our study since the CO can enter both cages. It was observed that on PdNaY and PdHY samples with equal loadings of Pd, the latter sample had more cations in accessible locations than the former. The NaY support seems to preferentially stabilize the majority of the loaded cations in inaccessible sites.

The CO study also showed that calcination in O_2 leaves the Pd cations in their high oxidation states, Pd^{2+} and Pd^{3+} . The Pd^{3+} cation was observed only on the PdHY

sample with the highest loading of Pd (1.62wt. %) which shows the easy accessibility of the cation on this sample. Oxidation was also observed to promote metal dispersion. It was observed that reduction in H_2 caused metal agglomeration and higher reduction temperatures were required to reduce the Pd cations if they were in inaccessible sites. Reduction converts the Pd^{2+} to Pd^+ and Pd^0 . Reduction at high temperatures was observed to favour the formation of well defined crystallite aggregates which shows that metal agglomeration increases with increasing reduction temperature. It was confirmed from the CO study that migration of reduced metal is more favoured on the HY support than the NaY support. Fluoridation of the support was observed not to affect the location or oxidation state of Pd on NaY, but on HY, the effect of fluoridation on cation location and oxidation state is not fully clear.

7.2 PYRIDINE STUDY

The adsorption of pyridine on the various catalysts and support has made it possible to identify the types and strength of acid sites on them.

The NaY support has been shown not to be cation deficient since there are no Bronsted or Lewis acid sites on it. The cation exchange of Pd on NaY created Bronsted and Lewis sites by cation hydrolysis and dehydroxylation respectively. Pyridine was observed bonded to two types of Lewis acid sites on PdNaY and PdHY giving peaks at 1450 and 1462 cm^{-1} . The 1462 cm^{-1} band has never previously been reported on a NaY-based catalyst; it has on occasion been observed on HY-based catalysts. Suggestions were made for the origin of this site in section 5.3.4(a).

Pyridine adsorption on calcined and reduced samples with the highest loading of Pd, PdNaY (1.58wt. %) and PdHY (1.62wt. %), has shown that Pd is not stabilized in the supercages on these catalyst.

It was identified that Lewis acid sites are stronger than Bronsted acid sites on

HY-supported samples while the reverse is true for the NaY-supported samples. There was some evidence to indicate that Pd^{2+} interacts with the Bronsted acid sites (OH groups) on PdHY and PdNaY catalysts; the Pd^{2+} was observed to have strengthened these sites by polarizing the OH bond.

Fluoridation of the support was also observed to have removed strong acid sites, which was not expected. The reason proposed for this was that the fluoride treatment leached out the lattice aluminium as fluoroaluminates and hence removed these strong acid sites.

On carrying out reduction on these catalysts, different behaviour of the OH groups was observed on HY and PdHY as compared to PdNaY. On HY and PdHY, reduction decreases the number of OH groups, but on PdNaY, the number of OH groups is increased by reduction. The explanation for this observation is that dehydroxylation occurs to a larger extent on HY samples than on NaY samples due to the higher concentration of OH groups present on the former samples.

7.3 ETHENE REACTION

Ethene was observed not to react on a NaY support since this support has no Bronsted or Lewis sites. The main reaction of ethene on PdNaY was dimerization to give butenes. It appeared that trans-2-butene is the first product to form and this isomerizes to give 1-butene and cis-2-butene, but because of the very rapid isomerization of the butenes, this conclusion has to be treated with caution.

On the HY support, slow oligomerization of ethene to give saturated branched chain oligomers was observed; but on a highly dehydroxylated Y zeolite (which had only Lewis sites), the oligomerization reaction was observed to occur at a faster rate to give the same product. This observation has confirmed that the oligomer is formed on Lewis sites rather than on Bronsted sites as usually proposed for this type of reaction.

On PdHY samples, dimerization and oligomerization reactions were observed and the oligomer products are similar to those formed on the HY support, which confirms that Lewis sites are the active sites for the oligomerization reaction.

By comparing the initial rates of the ethene reaction on reduced and oxidized Pd-loaded samples, it was proposed that the active sites for dimerization on PdHY and PdNaY samples are Pd^{2+} cations rather than the Pd^+ proposed elsewhere. It was also confirmed that isomerization of the butenes occurs on the Pd cation, rather than the OH groups as proposed by some workers.

A mechanism was proposed to explain the reaction of ethene on the Pd-loaded catalyst. The dimerization occurs on Pd^{2+} cations to give butenes and subsequent oligomerization of the butenes on the Lewis acid sites occurs in the presence of adsorbed ethene to give branched chain products. The proposed mechanism is :

