HYDRODECHLORINATION OF AROMATIC COMPOUNDS

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DECLARATION

I declare that this dissertation is my own. It is being submitted for the Degree of Master of Science at the University of Witwatersrand, Johannesburg.
It has not been submitted before for any degree or examination in any other University.

(Signature of candidate)

_______ day of ________ 1998

To my father, Alexander Kostov

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ABSTRACT

It is well known that chlorinated organic compounds behave as highly toxic substances in the environment. Catalytic hydrodechlorination is one of the more convenient approaches used to treat chlorinated organic substances with the aim of obtaining compounds with lower or null toxiciy. Further, the selective cleavage of the C-Cl bond plays a key role in processes related to the manufacture of fine chemicals. These reactions can be performed over noble-metal catalysts, either in the gas or liquid phase.

In this project the catalytic hydrodechlorination of a tri-substituted chlorinated benzene ring has been studied. At present no technical route is available to convert 1,2,4-trichlorobenzene into partially or fully dechlorinated compounds. Many catalysts were examined to assess their capability in the hydrodechlorination of chlorinated benzenes. Reactions were performed using a variety of reaction conditions (flow rate, reactor temperature, and % gas in the reaction). The selectivity in the hydrodechlorination reaction of 1,2,4-trichlorobenzene was found to be highest for on 5,7 % Ni/TiO_2 (to dichlorobenzene isomers) and lowest for 1 % Au/Al_2O_3 catalysts. Maximum conversions using the above catalysts were 54.1 and 8 % respectively with a dichlorobenzene product ratio meta/para/ortho - 2 : 2.9 : 1 and 0.42 : 0.49 : 1. Optimal conditions for hydrodechlorination of a 1,2,4-trichlorobenzene was found to be at 250°C temperature reaction, 100 ml/min flow rate, 2.5% 1,2,4-trichlorobenzene in H_2 over 5,7 % Ni/TiO_2.

A 1 % Pd/Al_2O_3 was found to be highly selective to complete hydrodechlorination of the reactant with a maximum conversion to benzene of 99% being achieved. Optimal conditions for complete hydrodechlorination of 1,2,4-trichlorobenzene was found to be at 250°C temperature reaction, 100 ml/min flow rate, 2.5% 1,2,4-trichlorobenzene in H_2 over 1 % Pd/Al_2O_3. On the other hand optimal conditions for complete hydrodechlorination of industrial trichlorobenzene was found to be at 350°C temperature reaction, 50 ml/min flow rate, 0.016% industrial trichlorobenzene in H_2 over 1 % Pd/Al_2O_3.

To shed light on the reaction, a series of related chlorinated complexes have also been studied over 1 % Pd/Al_2O_3, e.g. p-chlorotoluene, m-chloroaniline, chlorobenzene and various disubstituted chlorobenzenes.

In the light of the success achieved in the above study a preliminary investigation of the use of the Pd/Al_2O_3 for the hydrodechlorination of non-aromatic chlorinated hydrocarbons such as 1,2-dichloroethane was also initiated. The catalyst also proved to be successful in this reaction

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CHAPTER 1 GENERAL INTRODUCTION : THE ENVIRONMENTAL CONCERNS RELATING IN CHLORINATED COMPOUNDS

Much consideration is being given to reducing pollution of the environment by dangerous substances, and certain groups of compounds, which show toxicity, persistence and bio-accumulation in aquatic organism, have been identified for urgent action. In particular, legislation is being provided for controlling the release of such pollutants into the environment and methods for disposal are being developed for cases where their concentrations are above the legal limit. In addition, industry is becoming increasingly aware of the importance of adopting a holistic approach towards waste management and, accordingly, emphasis is shifting away from "end-of-pipe" solutions to overall waste-minimisation schemes (1).

One group of compounds which have been subjected to the process of remediation are chlorinated aromatics. They became commercially important in the 1930s, but were only recognised as environmental pollutants in the 1960s. The subsequent attempts to remedy the pollution caused by certain of these compounds- DDT (dichlorodiphenyltrichloroethane), PCP (pentachlorophenol), PCB (polychlorinated biphenyl), PCDF (polychlorodibenzofuran) and PCDD (polychlorodibenzodioxin) have been the subject of numerous reports but, in general, the scope of earlier reviews has been limited to a discussion of a single remediation technology or of applications relevant to only one industry. This review endeavours to give an overview of the diverse approaches towards chlorinated aromatic remediation, including representative examples from different industrial sectors. In particular, a survey is provided of the sources of contamination, the toxicity of the compounds, the relevant environmental legislation controlling their release and treatment, and the resulting disposal/ waste-minimisation methods (2,3).

1.1 Common Anthropogenic Sources of Contamination

Among the variety of chlorinated aromatic compounds which may be found in the environment, some compounds have been the subject of more attention than others. For example the chlorinated pesticide DDT was introduced as an insecticide in 1939. Partly because of its persistency in the environment, most of the chlorinated hydrocarbons in the sea and 80% of those in marine organisms are in the form of DDE (dichlorodiphenylethane), a derivative from the breakdown of DDT. PCP was also introduced in the 1930's as a preservative for timber and lumber. It is no longer used extensively for this purpose but it is sometimes used in a wide variety of agricultural and industrial applications as a fungicide, bactericide, herbicide, molluscicide, algicide and insecticide (3). Perhaps the most environmentally topical of all chlorinated compounds are the PCBs. These compounds have been used widely in electrical equipment, and in the manufacture of paints, plastics, adhesives, coating compounds and pressure-sensitive copying paper. Furthermore, because they are chemically very stable, they have been used as flame retardants. The last set of compounds to be discussed here are the dioxins (PCDD's and PCDF's) These are currently the subject of considerable debate concerning their toxicity. Unlike the other compounds mentioned, they are not useful but are by-products from the manufacture of other chlorinated compounds or from the incineration of chlorinated waste.

1.2 Natural Production of Chlorinated Aromatic Compounds

Although the presence of chlorinated aromatic compounds in the environment is commonly attributed to anthropogenic sources, in certain cases natural processes may be a significant contributor.

Some 2000 chlorinated and other halogenated chemicals are known to be discharged into the biosphere by plants, marine organisms, insects, bacteria, fungi and mammals, and by other natural processes. Although most of the aromatic compounds are phenolic, a few examples of simple chlorinated aromatics such as 1,2,3,4-tetrachlorobenzene are known. Many of these are produced during volcanic eruptions, when it is surmised that rapid, but incomplete, high-temperature combustion of chloride-containing plant material occurs. Similarly, forest and brush fires are a major source of polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs). The relatively poor efficiency and incomplete oxidation when damp vegetation and wood are burned in the presence of high chloride concentrations are conditions conducive to their formation (1).

1.3 Distribution of Contaminants in the Environment

In general, hazardous waste is commonly found at the industrial site at which it was manufactured because it was typically disposed of in on-site lagoons, underground storage tanks and dump sites. In these cases, problems arise when the surrounding soil underlying ground water aquifers become contaminated. However, another concern of particular importance to chlorinated aromatic waste is subsequent delocalisation of the waste over the long lifetimes of these compounds. Even in the troposphere, where these compounds are subject to photolysis and attack by hydroxyl radicals, they are still sufficiently long-lived that they can be transported far from their industrial sources. In the sea, they will resist degradation for years. The most common input of these pollutants to the sea is by deposition from the atmosphere, but other common inputs are from:

a) rivers - e.s. 3 tonnes y^{-1} of PCBs enter the North Sea by this route mainly from the dumping of dredging spoil or sewage sludge;

b) agricultural uses, such as aerial spraying, river run-off and blown dust;

c) dumping of unwanted industrial products;

Once in the sea, these compounds are highly insoluble in water, and thus are absorbed strongly onto particles. Therefore, their distribution is far from uniform. Most are adsorbed onto inorganic particles or onto micro-organisms. If they are adsorbed onto inorganic particles they may ultimately be carried to the seabed which then acts as a sink. However, suspended or resuspended particles, if they of a suitable size or density, are commonly ingested by filter-feeding animals and chlorinated hydrocarbons may enter food chains by this route. Additionally, birds such as petrels skim off the fat from the surface layer of the sea which is rich in chlorinated aromatics.

PCP residues also occur widely in the environment. For example, PCP was detected in over 80% of urine specimens analysed during a US

Environmental Protection Agency (EPA) survey of both occupationally exposed workers and the general public. However in contrast to DDT, PCBs, PCDDs and PCDFs, PCP is rapidly degraded by UV light and by most living things. The widespread distribution of PCP in man may not therefore be attributed to a long lifetime, but contamination rather results from continual inhalation of the vapours, which are slowly released from preserved wood (1).

1.4 Toxicity of contaminants

Many chlorinated hydrocarbons accumulate in fats rather than other tissues because of their lipid solubility and this introduces two risks:

i) in times of poor feeding, animals metabolise and use fat reserves, so increasing the concentration of chlorinated hydrocarbons circulating in the body;

ii) as with other bio-accumulating contaminants, there is a strong possibility of transmission through food webs and biomagnification, as indeed has been established in a number of animals.

Accumulation rates for chlorinated aromatics, measured by residues in the body divided by residues in the food or the environment, vary widely between species. The actual concentrations acquired relate to the lipid content of the animal and its position in the food chain. Because chlorinated hydrocarbons are stored in fatty tissues of the body, they become biologically available and exert their influence only when the fat tissues are metabolised. Animals may therefore acquire a considerable body-burden of halogenated hydrocarbon, but do not reveal their presence except in conditions of starvation when fat reserves are metabolised.

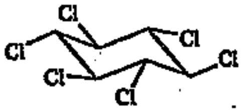
There have been numerous incidences in which contamination by DDT or PCBs has been accompanied by a dramatic increase in toxicity. In particular, in the 1960s, cases of contamination of seawater with DDT were associated with a sudden decrease in marine life and the death of seabirds. Also high rates of abortions were found in California sea lions, which were observed to have high levels of PCBs and DDT in their livers. Cases of toxicity to humans are less common, but in 1968, an outbreak of yusho disease in Japan was associated with PCB contamination of rice oil. In all, 1200 people were affected and suffered darkening of the skin, enlargement of their hair follicles, and eruptions of skin resembling acne. A majority developed respiratory difficulties which persisted for several years. The rice oil was found to contain 2·3 g/l of a 48% chlorinated hydrocarbon. The minimum dose that produced the disease symptoms was about 0.5 g of PCBs ingested over 120 days. Similar symptoms to those of yusho disease have been observed in workers at a Japanese condenser factory. This was thought to be due to local contact with PCBs and the symptoms disappeared when the use of PCBs ceased. It is not clear, though, that PCBs alone were responsible for the yusho incident because workers in Finland, who had been occupationally exposed to the PCBs and who had high concentration of PCBs in their blood and body fat, showed no sign of the adverse effects.

Some of the toxic effects associated with chlorinated pesticides and PCB contamination may originate from the traces of PCDDs and PCDFs present in the industrial samples. For example, the technical grade of the pesticide

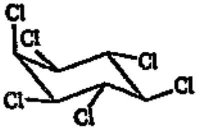
PCP, which contains traces of PCDDs and PCDFs, has widely different toxic properties when compared to the purified compound. Whereas the former is corrosive to skin and produces chloro-acne and significant liver damage, the latter has been shown to cause only mild biochemical and physical effects that do not alter life span or tumour incidence. Recently such fears concerning the toxicity of PCDDs and PCDFs would seem to have been confirmed by an EPA study that has shown that PCDFs are not only probable carcinogens but that they also cause a variety of non-cancer effects (4). These include disruption of the endocrine, reproductive and immune systems. The study also points to incidence of decreased sperm count in men.

1.5 Application of the aromatic compounds

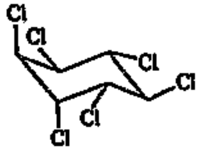
Hexachlorocyclohexane is ordinarily produced by reacting benzene in the liquid phase with chlorine in such a manner as to promote the addition of the chlorine to benzene. This reaction gives rise to the formation of five isomeric forms of hexachlorocyclohexane known as alpha, beta, gamma, delta and epsilon isomers, these isomers being present in varying quantities, possessing different properties and utilities.



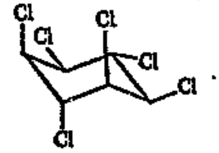
beta



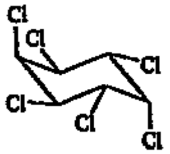
delta



(+−)alpha



gamma



epsilon

To date the most important use of the hexachlorocyclohexane as insecticides, parasiticides etc. Unfortunately, however only the gamma isomer is particularly effective for this purpose. One of the most successful commercial methods of recovering the gamma isomer, or lindane, comprises a separation based upon the solubility of the gamma isomer in lower aliphatic alcohol's (3). When it is recognised that the gamma isomer of hexachlorocyclohexane occurs to the extent of only 10 to 15 % of the crude hexachlorocyclohexane, it may be appreciated that isolation of this isomers results in the accumulation of large quantities of chlorinated material, which has no utility in itself. As a result many proposals have been made for utilising such waste products with only limited acceptance. One of the processes comprises the controlled hydrodechlorinatiom of a fraction of the waste products obtained by the recovery of lindane from crude hexachlorocyclohexane (5,6).

The crude hexachlorocyclohexane can be used to produce 1,3,5-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobiphenyl and hexachlorobiphenyl. Of these reactant products, 1,3,5-trichlorobenzene is the most unique and important since it can be utilised as a dye intermediate. It is more reactive than 1,2,4-trichlorobenzene. 1,2,4- and 1,2,3-trichlorobenzene are used as starting material for fungicides synthesis. 1,2,4,5-tetrachlorobenzene is an intermediate in the production of certain germicides and selected herbicides (7,8).

Chlorobenzene is consumed in the manufacture of phenol, DDT insecticide, and dyestuff intermediates; it also has extensive application as a solvent.

o-dichlorobenzene is also used in the manufacture of dye intermediates and as a special-purpose solvent; it has minor application as an insecticide (9). p-dichlorobenzene is used principally as a pest control agent, particularly against moths, and as an air purifier. Several of the higher chlorobenzenes have limited industrial applications (9).

The ring-chlorinated derivatives of toluene form a group of stable, industrially important compounds. Mono- and dichlorotoluene are used chiefly as chemical intermediates in the manufacture of pesticides, dyestuffs, pharmaceuticals, and peroxides, and as a solvent (10).

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CHAPTER 2 : EXPERIMENTAL

2.1 SURFACE CHARACTERISATION TECHNIQUES

2.1.1 Surface area measurement

The method used for surface area measurements is that of Brunauer-Emmett-Teller (BET). N_2 gas is brought into contact with the surface being determined at a temperature close to the condensation temperature of the N_2 (77 K). The gas then adsorbs onto the solid surface. The total volume of gas adsorbed onto the surface can be related to the volume of a single layer covering the catalyst surface (monolayer) according to an equation. The equation relates the volumes to the pressure of N_2 at the temperature at which the experiment was performed, and the enthalpy of adsorption of N_2.

Various assumptions involving condensation forces, molecular vibrations, and energies of adsorption, are made to derive the equation. Once the volume of a monolayer is known, this can be used, along with the size of an N_2 molecule, to determine the surface area of the solid. Provided an accurate calibration curve is available, this method consistently gives satisfactory results.

It is important to note that the BET method of surface area determination, measures the external surface areas of a solid, and possibly the areas of larger pores, but due to limitations (the size of the N_2 molecule) smaller pores may be missed.

2.1.2 Temperature programmed reduction

Temperature programmed reduction (TPR) supplies information about the reducibility of species. The substance being studied is reduced under a gas, usually H_2, as the temperature is increased from 0°C to 950°C. The amount of hydrogen consumed and the temperature at which it is consumed are recorded. For each peak, the temperature at which the most hydrogen is consumed (T_{max}) is considered to be the temperature at which a specific reduction takes place. T_{max} can be used to find the activation energy of a reduction step provided the heating rate is known.

2.1.3 X-ray powder diffraction

This method can be used to determine crystallinity, crystal size, crystal disorder, and unit cell sizes of crystalline samples. Planes of atoms within a crystal structure can be described by their intercepts with 3 symmetry axes, the Miller indices, which are reciprocal values of these intercepts and denoted h, k, and l.

When X-rays pass through a crystal structure they are scattered by the different atoms within the crystal. These reflected X-rays interact, producing a characteristic interference pattern for that crystalline substance. The lines of constructive interference are detected and recorded. The angle at which the X-rays strike the crystal and are reflected (θ), and the wavelength (λ) of the X-ray, can be related by the Bragg equation to give a measure of the distance between 2 planes within the crystal (d_{hkl}):

Bragg equation: $n\lambda = 2d_{hkl} \sin \theta$

By altering the angle, and plotting the observed diffraction intensity against the many different d values within a crystal, d can be found. The d values of a crystal are characteristic and can be matched using the Joint Committee on Powder Diffraction Standards (JCPDS) mineral powder diffraction file. The intensity of a peak can be used quantitatively, but for this a calibration curve, specific to the crystalline substance being studied, is necessary. Peak width can provide information about crystallite size and structural strain due to defects, provided that the effects of instrument broadening are neglected. Instrument broadening can be measured by determining the peak widths of a purely crystalline form of the substance being tested (if possible).
The peak widths are then used in the Scherrer formula:

$$\text{crystallite size} = \frac{\kappa\lambda}{\beta\cos\theta}$$

k = between 0.9 and 1.0, we have chosen to fix it at 0.9
θ = Bragg angle
λ = wavelength of X-ray
$\beta = B - b$ = (width of broadened peak) - (width of a nearby standard peak)

2.1.4 Thermogravimetric analysis

The weight loss measured on 10 - 20 mg used catalyst on a Du Pont TGA analyzer using linear temperature programming (10° C/min) under inert and oxygen atmospheres (30 ml/min) enabled determination of the level of carburization that took place during the synthesis runs.

2.1.5 Chemisorption

The ASAP 2010 is a sorption instrument used for collecting, analysing and processing physisorption and chemisorption data. It is the latest in technology for catalyst analysis.

The instrument can determine surface area, pore volumes and size distributions and is upgradable to chemisorption. It has multigas adsorbate capacity and can therefore analyse a wide range of adsorbate gases. A major advantage of the instrument is that it is operated by computer allowing for simultaneous WINDOWS and DOS processing.

The ASAP 2010 analyser contains two sample degassing ports and one analysis port. In-line cold traps are located between the vacuum pump and the manifold in both the analysis and the de-gas system. The sample saturation pressure tube is located next to the sample analysis port. The analysis fluid bath dewar resides on an automatically-operated elevator. Controls and indicators located on a control panel operate the vacuum systems, degas valves, and heating mantles.

2.2 EXPERIMENTAL PROCEDURES

2.2.1 Catalyst preparation

The γ–Al_2O_3, TiO_2 or MgO supports were mixed with deionised water and dried at 120°C for 6-8 h. The dried support was crushed and sieved to 0.5 and 1.0 mm particles for use as a catalyst support. A solution of $Ni(NO_3)_2.6H_2O$ was impregnated to the point of incipient wetness onto the support pellets. The impregnated system was thereafter dried at 120°C in an oven for not more than 8 h.

2.2.2 Reactor and GC studies

The reaction vessel comprised a heating bath to vaporise reagents and heated connections between the heating bath, the reactor and the GC. Reactions were carried out in a glass reactor placed in a heating jacket, which was connected to a GC as shown in Fig. 2.1.

Catalyst (0.1 g) was added into the reactor. Before starting the reaction each catalyst was reduced in hydrogen heated at 400-450°C for 2 h. A GC fitted with a FID detector was used for determining the activity and selectivity of the catalyst. The GC was calibrated with samples of the various products anticipated in the reaction. Response factors were assumed for the different materials. A Hewlett Packard capillary column (five meters) was used for separating the products of the reaction.

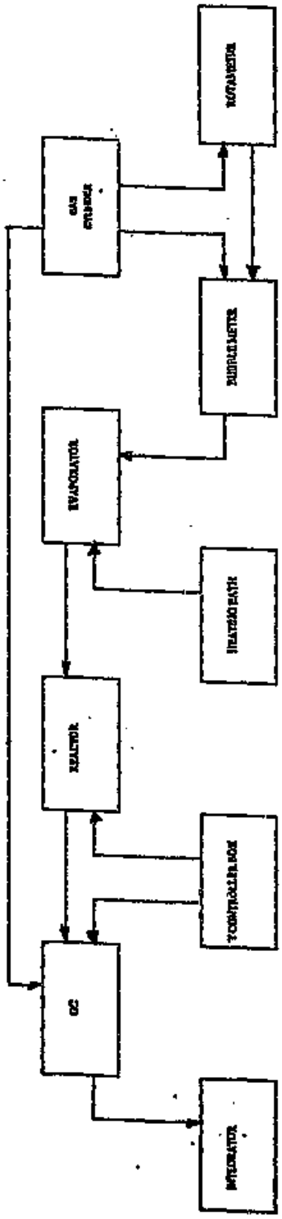

Fig. 2.1 Reactor Design

A PPQ column was installed when 1,2-dichloroethane starting materials were investigated.

2.2.3 Calculations

% H_2 gas used for carrying out the hydrodechlorination reactions :

$$\% H_2 = \frac{\text{Psample}}{\text{Patm - Psample}} * 100$$

% Conversion (X_R) of each reagent used in the hydrodechlorination reaction:

$$\% X_R = \frac{\text{moles prods. out}}{\text{moles prods out - moles remained reag.}} * 100$$

% Selectivity of the product Pi in the hydrodechlorination reaction :

$$\% Pi = \frac{\text{moles prods Pi}}{\text{moles prods out - moles reag. remaining}} * 100$$

2.2.4 Analytical techniques used to characterise the catalysts

2.2.4.1 BET surface area determination

Each of the catalysts, uncalcined, were screened to between 0.5 and 1.0 mm particle size before determining their surface areas. Approximately 0.1 g of catalyst was placed on a quartz frit in a glass reactor. A mixture of N_2 and He gas (diluted in N_2) was passed over the catalyst while it was heated to 300°C for 1 hour to remove any traces of water or volatile impurities from the surface of the catalyst.

After allowing the catalyst to cool to room temperature, a mixture of N_2 and He gas (30%) was then passed over its surface. The levels of N_2 leaving the reactor were continuously monitored using gas chromatograph.

The reactor was then immersed in liquid nitrogen to lower its temperature to the condensation temperature of N_2 gas. The level of N_2 gas leaving the reactor dropped, as N_2 adsorbed onto the surface of the catalyst, and then increased as less of the N_2 was able to adsorb. After being immersed for between 6 to 10 minutes (depending on the catalyst), the reactor was removed from the liquid nitrogen and heated to expel the adsorbed nitrogen from the catalyst surface. This N_2 was subsequently detected using a gas chromatograph fitted with a thermal conductivity detector. The procedure was repeated for each catalyst to obtain at least 4 sets of data that agreed to within about 12%. The volumes of N_2 detected were then used in the BET calculations to obtain surface area values.

2.2.4.2 Temperature programmed reduction (TPR)

Fresh catalyst was subjected to TPR analysis. Approximately 0.05 g of catalyst particles, screened to between 0.5 and 1.0 mm in size, were placed inside a glass reactor upon a quartz frit. Inert N_2 gas was passed over the catalyst, which was heated at 300°C for 30 minutes in order to remove any volatile surface impurities. After this an N_2/H_2 (%) reducing gas mixture was passed over the catalyst while it was heated from room temperature to 950°C, over 90 minutes. Data sampling took place every 3 seconds which was recorded by a computer. Final output was generated with Hyperplot software.

2.2.4.3 X-ray powder diffraction (XRD)

A portion of each of the used or fresh catalysts was ground by hand to a fine powder, using a pestle and mortar. This powder was placed into a sample holder, such that the sample would not fall out of the container. This was achieved without forcing a preferred orientation on the particles. A Phillips PW1830 goniometer and optical system were used, with a Cu source (40kW and 20 MA).

The angle, 2θ was increased from 10° to 140° over the space of approximately 1 hour. Background noise was high since Cu Kα radiation is strongly adsorbed by Pd and induces Pd to emit fluorescent radiation. The XRD patterns obtained were compared to a reference database within the syst [illegible] attempt to identify the main structural components of the sample.

2.2.4.4 Thermogravimetric analysis (TGA)

TGA was performed on a 1% Pd/Al_2O_3 used catalyst after a reaction with monochlorobenzene as starting material to assess whether carbonisation had taken place.

2.2.4.5 Chemisorption

Approximately 1,5 g fresh 1% Pd/Al_2O_3 catalyst particles, screened to between 0.5 and 1.0 mm in size, was placed inside a glass reactor upon a quartz frit. Owing to the strongly bonded chemical-water of the initial metal solution, high heating temperature (300 °C) was used.

Metallic surface area was determined using CO chemisorption on an ASAP 2010 Chemi Instrument. The catalyst was reduced `in-situ` for 16 hours, whereafter CO adsorption was measured at 35 °C. An equilibration interval of 100 seconds was found to be optimal during CO adsorption in order to achieve a tolerance of 5.000 mmHg at pressures ranging from 100 to 450 mmHg.

CHAPTER 3 A SURVEY OF THE LITERATURE: CHLORINATED AROMATIC COMPOUNDS

3.1 General

A large number of chlorinated molecules are environmental hazards by reason of their toxic, and sometimes carcinogenic, effect on living organisms. There is therefore a need for a cheap and effective means for their destruction by conversion into less harmful products. A number of papers have appeared in recent years, reporting methods for the catalysed destruction of chlorinated molecules. These include dehydrochlorination, hydrogenolysis and oxidation.

The pollution of groundwater and soils by industrial chemicals is a cause of significant environmental concern. Such contaminated water is typically the legacy of past practices in which chlorinated degreasing solvents were discharged to the soil following use. These solvents have been used in dry-cleaning, all aspects of metals manufacturing, metal plating, engine maintenance, and in many other cleaning and fabrication applications. Consequently, thousands of sites have been affected. Other common chlorinated hydrocarbon pollutants include pesticides and herbicides, chlorophenols used in the wood-treatment industry, and polychlorinated biphenyl's (PCBs) which were used in electrical capacitors and as heat transfer fluids (1).

Since 1974 much research has been devoted to the problem of redressing the destruction of the ozone in the stratosphere. Aliphatic chlorocarbons and chlorofluorocarbons have found widespread commercial use as refrigerants, industrial solvents, and blowing agents for the preparation of rigid polyurethane foams. Recently, however, the environmental problems that are being posed by these compounds are causing their use to be restricted or eliminated. In the case of the chlorofluorocarbons (CFC's), the particular hazard is that they are sufficiently inert that they travel into the stratosphere before they are photodecomposed (2). This photodecomposition reaction in the stratosphere involves the cleavage of a carbon-chlorine bond in the CFC to give a chlorine atom, which then undergoes a chain reaction with ozone present at this altitude, resulting in a depletion of the ozone layer. Two groups of compounds that are being introduced as replacements for CFCs are hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). The HCFCs are considered to be less of a potential threat to the ozone layer because the presence of a carbon-hydrogen bond allows them to react with hydroxyl radicals present lower in the atmosphere, resulting in their chemical decomposition before they reach the stratospheric ozone layer. The HFCs cause no significant threat to the ozone layer because they do not contain carbon-chlorine bonds that can undergo photohomolysis (3). As a result "the Montreal Protocol on Substances that Deplete the Ozone Layer" was proposed in September 1987. Agreement was reached, at first for a freeze, and later for a scaled reduction to 50% in the production of several CFCs by 1999. Moreover a large reduction in allowed emission of CFCs will be introduced by legislation, and hence methods of collection, disposal and destruction will become important. Chemical processes for the destruction or substitution of CFCs include pyrolysis, photochemistry, incineration, and catalytic conversion over oxides or supported metal catalysts. Among them, the catalytic conversion of CFCs by hydrogen to hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) is a challenging task for heterogeneous catalysis. Many researchers have studied various kinds of treatment techniques for chlorofluorocarbons (CFCs) (4). These include the supercritical water method, plasma destruction method, chemical destruction method, UV photolysis method, high-energy radiation method, incineration decomposition method, and catalytic decomposition methods (hydrolysis and oxidation) (5).

3.2 REDUCTIVE DEHYDROCHLORINATION

One of the main reactions used to remove chlorine from chlorine containing materials, the dehydrochlorination process, can be formulated as:

$$\text{-CH}_2\text{CHCl-} \longrightarrow \text{-CH=CH-} + \text{HCl}$$

Depending on whether a catalyst is used and the reaction conditions the products are aromatics (or hydrocarbons) with a reduced number of chlorine substituents.

The dehydrochlorination of hexachlorocyclohexane (HCCH) has been traditionally carried out by thermal treatment at temperatures in the range 275-500°C, usually in the presence of a catalyst, such as iron or ferric chloride (6). This is a suitable method for the preparation of aromatic compounds such as trichlorobenzenes. However, this procedure is inefficient in that the desired 1,2,4-isomer is produced in poor yield. Large quantities of 1,2,3-trichlorobenzene, are produced. The 1,3,5- isomer is also produced in negligible amounts (7). Another method used for the dehydrochlorination of HCCH consists of heating HCCH with a basic solution, such as sodium or potassium hydroxide. This procedure is extremely inefficient in that the valuable hydrogen chloride produced in the dehydrochlorination reaction is converted by the action of the alkali into relatively valueless sodium or potassium chloride respectively (8).

It was discovered that HCCH and related compounds, such as heptachlorocyclohexane and octachlorocyclohexane can be readily and efficiently catalytically dehydrochlorinated at a high reaction rate. This reaction yields mixtures of isomeric polychlorobenzenes by contacting the polychlorocyclohexane with a selective, highly specific catalyst such as silica (9). Further, as described in the Crowder method (10), HCCH may be pyrolyzed over activated carbon at a temperature of at least 300 °C to produce a product which generally contains 80% 1,24-trichlorobenzene; 11% 1,3,5-trichlorobenzene, 4% 1,2,3-trichlorobenzene, 2% 1,2-dichlorobenzene, 4% 1,3-dichlorobenzene and 3% 1,2,4,5-tetrachlorobenzene (10).

The normal procedure for conversion of HCCH involves the catalytic thermal treatment of HCCH in the liquid phase at 250-300 °C in the presence of a catalyst, such as ferric chloride or metal iron. The pyrolysis reaction is slow. The product produced by this process typically contains 78% 1,2,4-trichlorobenzene, 0.6% 1,2-dichlorobenzene, 0.4% 1,4-dichlorobenzene, 1.6% 1,2,3,4-tetrachlorobenzene and 1.2% 1,2,4,5-

tetrachlorobenzene.

A process for the pyrolysis of by-product HCCH isomers allows for the removal of the valuable gamma isomer of HCCH. This involves reaction over a catalyst comprising activated carbon containing 5-10% of cupric chloride at 400-500°C to give the products: 63.6% 1,2,4-trichlorbenzene; 11% 1,2,3-trichlorobenzene; 7.9% 1,2-dichlorobenzene; 5.5% 1,4-dichlorobenzene and 12% 1,2,4,5-tetrachlorobenzene (11).

The dehydrochlorination of HCCH is typically carried out in the vapour state. However, vaporisation of the HCCH results in undesired coking which causes fouling of the process equipment and the build-up of a heat insulating surface layer. In general, it has been found desirable to melt and vaporise the HCCH, and then dehydrochlorinate the vapours in a separate step (12).

A process for the manufacture of pentachlorocyclohexane and hexachlorocyclohexane relates to subjecting a mixture, (consisting essentially of gamma HCCH, delta-HCCH and hepta-chlorocyclohexane) to a temperature of between 150-500°C for not more than 30 min. Immediate cooling of the reaction products to prevent further dehydrochlorination, allows recovery of the pentachlorocyclohexane, hexachlorocyclohexane (30% gamma and 40% delta HCCH isomers) and 30% heptachlorocyclohexane (13).

Variation of the reaction velocity can also influence the product distribution. HCCH can be de dehydrochlorinated at a high reaction velocity to yield a mixture of isomeric trichlorobenzenes (in which the proportion of 1,2,4-trichlorobenzene predominates over 1,2,3-trichlorobenzene) together with 2,3,4,5,6-pentachlorocyclohexane. The catalysts found to be suitable were certain inorganic and organic compounds containing nitrogen (triethylamonium chloride, triethanolamine, dimethylamine, triamylamine, quinoline, pyridine, triethylamine); ferric chloride and powdered iron. The reaction was performed at 200-500°C (8).

An iron barrier has been used to break down toxic trichloroethene into benign products, yielding water that meets Environmental Protection Agency requirements. This permeable barrier cleanup method exploits zero-valent metals and is a new topic in environmental chemistry. The concept is a variation on the corrosion process. When metal corrodes, the corrosive agents undergo reactions as well. These reactions may be used to remediate a slew of environmental chemicals from chlorinated solvents to radionuclides (14). In the early 1970s Sweeney and Fisher studied the phenomenon, even obtaining a patent for reductive dechlorination of halogenated pesticides. Gillham and colleagues tested the idea by using turnings from a machine shop at a contaminated site and found that water contaminants in the ground did indeed disappear. Iron alone, however, suffers from relatively slow reaction rates and does not dechlorinate important compounds, such as dichloromethane and PCBs. By chemically plating iron filings with palladium to approximately 0.05% (w/w), the dechlorination rate for trichloroethene is increased by one to two orders of magnitude, and the dechlorination reaction is extended to include less reactive compounds, such as PCBs (15).

3.3 CATALYTIC HYDRODECHLORINATION

This reaction type entails the removal of a halide (e.g. chlorine) atom with simultaneous replacement by a hydrogen atom viz.

$$CH{=}CCl + H_2 \longrightarrow CH{=}CH + HCl$$

or $$CHCl_3 + H_2 \longrightarrow CH_4 + HCl$$

This reaction is known as a hydrodechlorination reaction. The source of the H atom used in the reaction does not have to derive from H_2, but could come from any hydrogen source.

A wide range of reactions of this type have been reported:

a) Hydrodechlorination of aromatic compounds

1,2,4- and 1,3,5-trichlorobenzenes or other bromine and fluorine substituted benzenes have been used as starting materials, and reductive hydrodechlorination gives good yields of the halobenzene products (16). The 1,3,5-trichlorobenzene can be reacted with hydrogen in the presence of a platinum-on-carbon catalyst for an appropriate time until reaction occurs to produce a dichlorobenzene fraction of substantially meta-dichlorobenzene (17). However, if the starting material is 1,2,3-trichlorobenzene the products are only ortho-dichlorobenzene and a trace of meta-dichlorobenzene (16).

Numerous examples of hydrodechlorination catalysts are described in the literature many of which emphasise the superior performance of palladium supported on various high surface area materials. Several factors have been identified which influence the activity and selectivity of hydrodechlorination catalysts. These factors include support material, metal particles size and reaction conditions. Reduction of 1,2,4,5-tetrachlorobenzene (TeCB) in isooctane and n-dodecane as internal standard, gave complete hydrodechlorination to benzene. However less chlorinated benzenes are more reactive (18). A multiphase system consisting of a hydrocarbon solvent, a strong alkaline solution and a quaternary onium salt, in the presence of Pd/C catalyst with hydrogen and sodium hypophosphite at atmospheric pressure, allows for the rapid and progressive displacement of the chlorine atoms from polyhalogeneted benzenes (19). A highly active polymer anchored palladium catalyst (PVP-$PdCl_2$) exhibited very high catalytic activity for the hydrodehalogenation of organic halides under mild conditions in the presence of a base (20).The kinetics of hydrodechlorination of chlorobenzene was investigated over Pd/Al_2O_3 and Rh/Al_2O_3 catalysts of varying dispersion. Chlorobenzene interacted with the surface to form a surface chloride and benzene; hydrogen restored an H-covered surface. HCl competed with the reactant in the chlorination step. The lower reactivity of the rhodium catalyst was attributed to a greater inhibition of the surface by chlorine (21).

On PdRh and PdSn bimetallic catalysts, a marked decrease of C-Cl hydrogenolysis is observed, the factor being 10^2-10^3 upon rhodium addition, and larger than 10^6 when tin is added. There is an interaction of the palladium surface with the second metal. A geometric effect is proposed to be responsible for the observation (22), enhanced by a surface enrichment of the modifier. The driving force for this segregation is the higher affinity of rhodium or tin for the chlorine produced in the reaction and (23) an electronic interaction between palladium and rhodium or tin, which decreases the reducibility of the chlorine-covered palladium surface by hydrogen (2).

A hydrodehalogenation catalyst can be prepared by impregnating a C support of ash content, 0.2 wt. % with a combination of a metal consisting of 5-95% wt.% Au and 95.5% of at least one metal selected from Ru, Pd, Rh, Os, Ir, and Pt, at 350°C (24). The carbon is dried in air at 130-150 °C, and heated in a reducing atmosphere at 350 °C to provide metal in a reduced state. The addition of Au prevents sintering and increases the durability and mechanical strength of the catalyst (24).

The conversion of chlorinated alkanes into less chlorinated alkenes involves reaction of the alkane with H_2 in the presence of a supported bimetallic catalyst containing 0.05-10 wt.% Pd with respect to a support, such as activated C, and 0.05-10 wt.% Ag, Ga, In, Tl, Ge, Sn, Pb or Bi, or their mixture, at 150-450°C and 1-30 bar. The weight ratio of Pd : metal is 0.5-20. The conversion rate is high and selectivity is also good; especially for allyl chloride conversion (25).

Suzdorf and Morozov studied $Ni/\gamma-Al_2O_3$ catalysts in the gas phase hydrodechlorination of substituted chlorobenzenes (26). The results revealed that the catalysts activity could be determined by the Ni content when Ni concentrations greater than 3% were used. They are also showed that

$Ni/\gamma-Al_2O_3$ catalysts are not deactivated in reaction mixtures containing hydrogen chloride and chlorobenzene. The electron-donor substituents increased the reactivity of substituted chlorobenzenes, while electron-acceptor groups decreased the reactivity (26).

b) Hydrodechlorination of aliphatic compounds

Supported and unsupported metal carbide catalysts were studied for the dehalogenation of CCl_2F_2 (CFC 12). Their catalytic properties were compared to those of a standard palladium catalyst. The Pd-metal catalysts were prepared by impregnating a solution of $PdCl_2$ onto the carbide by the incipient wetness technique. The sample was dried at 423 K for 1 h and heated to 773 K for 3 h at 0.17 K/s with a H_2 flow of 680 mmol/s. The catalyst was cooled in He and passivated with 0.5 % O_2/He. The unsupported carbides had lower initial conversions than the supported carbides and the only product formed was CH_2F_2. All carbide catalysts have lower activity than the supported palladium catalyst, possibly due to coking (27). The hydrodechlorinationxz of CCl_4 was tested over several silica-supported $PdCl_2$-containing molten salt catalysts. The base catalyst was $PdCl_2$-$(C_4H_9)_4NCl/SiO_2$, while $CoCl_2$, $CuCl_2$, or both were used as promoters to modify the catalyst activity, product selectivity, and catalyst longevity. The catalysts converted CCl_4 into C_1-C_5 paraffins and C_2-C_4 olefins, CH_2Cl_2, $CHCl_3$, CCl_2CCl_2, and $CHClCCl_2$. Doping $CoCl_2$ into the $PdCl_2$-$(C_4H_9)_4NCl/SiO_2$ catalyst also enhanced its initial CCl_4 conversion from 85 to 99.3%, and shifted the reaction products towards more hydrocarbons, and also prolonged the life of the catalyst. Addition of $CuCl_2$ to the base catalyst also improved the initial CCl_4 conversion to 94.5 %. The copper had an even stronger stabilising effect on the catalytic activity and shifted the reaction products towards C_1-chlorocarbons. When both $CoCl_2$ and $CuCl_2$ were added to the $PdCl_2$-$(C_4H_9)_4NCl/SiO_2$, the promoted catalyst exhibited even higher conversions (99.5%) (28).

Destruction of chlorinated methane (CH_2Cl_2, $CHCl_3$ and CCl_4) with water vapour over γ-Al_2O_3 or TiO_2 (rutile) gave CO_2 and HCl at temperatures between 673-773 K. The activities of these two catalysts are about the same, and reactivity of the chlorinated molecules increased with the number of Cl atoms (29). A Pt catalyst supported on MgO was found to be a stable and selective catalyst for the hydrodechlorination of CCl_4 to give chloroform. XRD spectra of a Pt/MgO after the reaction indicated that 40% of MgO was transformed into $MgCl_2$ after the reaction (30). Hydrochlorination of CCl_4 has been studied over 1% Pt/Al_2O_3 prepared from various Pt precursors. A Pt/Al_2O_3 catalyst prepared from Pt(II) precursors showed stable high conversion of CCl_4 (> 99%) and selectivity of $CHCl_3$ (78%) at the reaction temperature of 393 K. The catalyst, prepared from $Pt(NH_3)_2(NO_2)_2$ gave retarded coke formation compared to the catalyst prepared from H_2PtCl_6. The difference between the catalyst prepared from Pt(II) and Pt(IV) precursors is due to the different oxidation states of Pt (30). Pt/MgO is an effective catalyst for the selective hydrodechlorination of CCl_4 to $CHCl_3$. Catalyst deactivation due to coking of the Pt surface was noted. The active phase of Pt in the Pt/MgO catalyst is Pt(0), in the form of metal particles. The surface area of the catalyst decreased due to a phase change of MgO to $MgCl_2 . H_2O$ during the reaction (30).

Carbon tetrachloride was transformed into chloroform and dichloromethane in a catalytic transfer hydrodehalogenetion reaction in a closed system at 80 °C using an aqueous solution of sodium formate as hydrogen donor and the water soluble ruthenium complexes $Ru(H_2O)_3(PTA)_3(tos)_2$ (PTA = 1,3,5-

triaza-7-phosphaadamantane and tos = tosylate) as catalyst (3).

Several other liquid halides were studied using the same conditions. While benzyl chloride was transformed cleanly, other alkyl halides gave low yields for water soluble ruthenium complexes ($Ru(H_2O)_3(PTA)_3(tos)_2$). Cyclohexyl halides gave similar results to their open chain analogues (5).

Various functional groups on substituted chlorobenzene; eg Me (3- and 4-chlorotoluene) or NH_2 (4-Chloroaniline) can be successfully dechlorinated with hydrogen in the presence of the rhodium complex, $Rh(H)Cl_2L_2$ (L = Cy_3P, i-Pr_3P), as catalyst (1).

Hydrodehalogenation of the carbon-halogen bond over selected metal catalysts seems a promising method for environmenal remediation (2). The conversion of difluorodichloromethane was studied in the gas phase between 433 and 523 K at atmospheric pressure over Pd black and Pd supported on alumina, graphite, or AlF_3. In CF_2Cl_2 hydrogenation, CH_2F_2 and CH_4 represented more than 95% of the products. The catalytic properties of Pd/AlF_3 samples are unchanged with time, but Pd/graphite, Pd/Al_20_3, and Pd black suffered changes of activity or selectivity during the first few hours on stream. This is ascribed to the diffusion of halide species into the bulk of palladium, and transformation of Al_2O_3 to AlF_3. At steady state, the kinetics of CF_2Cl_2 hydrogenation can be described either by a dehalogenation of the Pd surface by CF_2Cl_2 and H_2, respectively, or by a classical Langmuir-Hinshelwood mechanism. The CH_2F_2/CH_4 selectivity ratio is lowest on Pd/graphite and highest on Pd/AlF_3. It is proposed that adsorbed halide species are responsible for the loss of CH_2F_2 selectivity. The high selectivity ratio on Pd/AlF_3 is ascribed to a co-operative effect between Pd and AlF_3 (23).

The hydrodechlorination reaction of dichlorodifluoromethane (CF_2Cl_2) was investigated at atmospheric pressure at 130-210 °C over a Pd/AlF_3 catalyst. The major products were found to be CH_2F_2 and CH_4. The formation of these products could be explained by the direct hydrogenation of the intermediate species, CF_2, rather than the consecutive scheme of CF_2Cl_2--->CHF_2Cl--->CH_2F_2--->CH_3- CH_4 (4).

Conversion of difluorodichloromethane under hydrogen was studied in the gas phase between 413 and 473 K at atmospheric pressure over graphite supported Pd, PdK, PdFe, PdCo and PdAg catalysts reduced at 523 K. Neither a stoichiometric phase, nor a solid solution was detected in this catalyst. In CF_2Cl_2 hydrogenation at low CF_2Cl_2 pressure ($p(CF_2Cl_2)/p(H_2) < 0.3$), CH_2F_2 and CH_4 represent more than 95% of the products. However, at high CF_2Cl_2 pressure ($p(CF_2Cl_2)/p(H_2) < 2$), and use of PdFe/graphite or PdCo/graphite catalysts, high selectivities for the coupling product CF_2CF_2 was obtained. This is probably due to the occurrence of some mixed sites between Pd and Fe or Co. The kinetics of the reaction indicates adsorption competition between CF_2Cl_2 and H_2 for the active sites which can be described by an halogenation/dehalogenation mechanism of the palladium surface by CF_2Cl_2 and hydrogen respectively (28).

More than 80% selectivity in the hydrodechlorination of 1,1,2-trichlorotrifluoroethane (CFC-113) is observed over Pd catalysts containing selected metal additives such as Ag, Bi, Cd, Cu, Hg, In, Pb, Sn, Tl. The products obtained were chlorotrifluoroethene (3FCl) and trifluoroethene

(3FH). In particular, a bismuth modified palladium catalyst supported on SiO_2 and a thallium modified catalyst supported on active carbon provided 3FH and 3FCl in > 90% yield at 500-600 K. Kinetic studies suggest that the reaction route is CFC-113---->3FCl---->3FH and that the role of the metal additive is to suppress the hydrodechlorination of 3FCl to 3FH (31). Karpinski and Early obtained catalytic hydrodechlorination of 1,1-dichlorotetrafluoroethane over a Pd/γ–Al_2O_3 catalyst. This gave three main products : 1,1,1,2-tetrafluoroethane, 1-chloro-1,2,2,2-tetrafluoroethane, and 1,1,1-trifluoroethane, with approximately 85% selectivity toward the desired CF_3CFH_2 (32). Catalytic hydrodechlorination of 1,1,2-trichloroethane (TCE) at 250 °C over CsCl supported on silica gels gave high conversions (90 %) of dichloroethylene and traces of vinylchloride using both pulse and flow reactors (33). An Au/Co_3O_4 catalyst was found to be significantly more active than platinum group metal catalysts. The Au/Co_3O_4 catalyst selectively oxidised CH_2Cl_2 to CO_2 and HCl, and the catalysts were found to be stable at 350°C in the presence of the oxidation products. The addition of the small gold particles to the Co_3O_4 significantly improved the activity of the oxide (34). Furthermore the decomposition of CCl_2F_2 and CH_3Cl was conducted over Au/Co_3O_4 and Au/Al_2O_3 and the supports showed quite different behaviors. Traces of COF_2 and COClF were observed by mass spectoctroscopy. The yield of CCl_2F_2 was similar to that for CH_3Cl when Au/Al_2O_3 was the catalyst. In contrast, Au/Co_3O_4 showed a very high activity for CH_3Cl synthesis but very low production of CCl_2F_2.

The mechanism of carbon-halogen hydrodechlorination is still controversial (21). The reaction has been described either as an interaction between two adsorbed species (22) or as the interaction between a gaseous molecule and a surface compound.

3.4 CATALYTIC OXIDATIVE DECOMPOSITION

In this reaction type, halogenated complexes are destroyed in the presence of oxygen. This can result in the complete breakdown of a molecule to ultimately give CO_2 and other products.

Oxidative incineration methods are employed for polychlorinated biphenyl (PCB) and 2,4,5-trichlorophenoxyacetic acid (35). However, the incineration-decomposition of CFC-115 requires very high temperature (over 1300 K). A new class of combustion catalysts $CuCl/KCl/SiO_2$ Cr_2O_3/SiO_2, CuO/SiO_2, Co_3O_4/SiO_2 and MnO_2/SiO_2 give high activity for the total oxidation of chlorinated hydrocarbons such as CH_2Cl_2, CH_2ClCH_2Cl, CCl_4 and 1,2-dichlorobenzene into carbon oxides (CO and CO_2) and HCl or Cl_2, in the presence of excess air at 300-500°C (36). Liu and Cheng (37) have reported the effects of the addition of silica to titania for the oxidative incineration of chlorinated hydrocarbons to chloroform. The results revealed that the addition of silica enhanced the dispersion of titania by forming Ti-O-Si bonds. The activity of TiO_2 increased to about 60% on incorporation of 43 wt.-% SiO_2 (37). Gordon and Gaur presented results (38) regarding the evaluation of bulk metal oxides as catalysts for the low temperature incineration of mixed carbonaceous residues which are typical by-products of the fluidized bed combustion of mixed wastes under oxygen-lean conditions. Results indicated that metal oxides which are p-type semiconductor materials, are suitable as catalysts for this application (38). Oxides of cobalt, molybdenum, vanadium and manganese are found to be particularly stable and active catalysts under conditions specific to this process. Stenger and Buzan have described (39) a treatment process, involving a catalyst-sorbent that simultaneously destroys the halogeneted hydrocarbons and captures the halogens produced In this process Cu and Mn oxides are supported on sodium carbonate.

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CHAPTER 4 RESULTS and DISCUSSION

4.1 General Introduction

The removal of chemical waste streams that contain chlorinated aromatics is a technological problem of some concern (1,2). In the introductory chapters in this thesis the general issue of the removal of chlorine from chemicals was discussed. Numerous options were presented. In this chapter attempts to catalytically hydrodechlorinate chlorobenzenes will be described. This was brought about by the desire to specifically remove chlorine from a tri-substituted benzene ring. At present no technical route is available to convert 1,2,4-trichlorobenzene into partially or fully dechlorinated complexes. This chapter specifically addresses this issue. Further, to shed light on the reaction a series of related chlorinated complexes have been investigated in the catalytic hydrodechlorination reaction e.g. p-chlorotoluene, m-chloroaniline, chlorobenzene and various disubstituted chlorobenzenes. Prior to the presentation of the data a brief review of the literature of this area of study will be given.

The catalytic thermal hydrodechlorination of polychlorinated chlorobenzenes has been described in the literature and catalysts such as powdered iron, ferric chloride (in the presence of triethylamonium chloride) (3), triethanolamine, dimethylamine, triamylamine, quinoline, pyridine, triethylamine (4), and silica (5) have been used in the reaction.

Further, as described in the Crowder method (6), polychlorinated benzenes may be pyrolyzed over activated carbon at a temperature of at least

300 °C. Another method used for the hydrodechlorination of polychlorinated benzenes consists of heating them with a basic solution, such as sodium or potassium hydroxide (7).

The liquid phase approach to the catalytic removal of chlorine from aromatics has been extensively described. Catalysts employed include Ni (8), Pd (8,9,10,11), Pt (10), Ru (10), Rh (10) and Ti (8). Of more significance to our study however are the earlier reports on reactions in the gas phase.

One of the earlier comprehensive studies in this area was the report by Bodnariuk et al. on the use of Pd and Rh catalysts (12). In this investigation the reaction of chlorobenzene over Pd/Al_2O_3 and Rh/Al_2O_3 was reported. The role of catalyst dispersion (particle size) permitted an evaluation of the reaction mechanism. From the study it was proposed that the data was consistent with a Mars-van Krevelen mechanism.

$$\text{Pd-H} + C_6H_5Cl_{(g)} \xrightarrow{k_1} \text{Pd-Cl} + C_6H_{6(g)}$$

$$\text{Pd-H} + HCl \xrightarrow{k_2} \text{Pd-Cl} + H_2$$

$$\text{Pd-Cl} + H_2 \xrightarrow{k_h} \text{Pd-H} + HCl$$

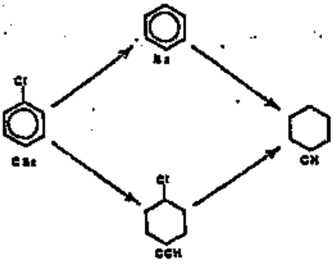

Fig.1 Hydrodechlorination of chlorobenzene. k_1, k_2 and k_h are the rate constants for the various reaction steps.

In a later related study (12) the authors studied the effect of alloying on the reaction using PdRh, PdSn catalysts. Reduced activity was noted. This was brought about both by dilution of the active metal component (Pd) and an electronic interaction between the Pd and the second metal.

Numerous papers have appeared on the use of NiMo supported catalysts. Hagh and Allen have investigated the kinetics of the reaction of the chlorobenzene family of reagents over NiMo/Al_2O_3 (13-15). In these studies the kinetic parameters for the complete range of hydrodechlorination recations (from hexachlorbenzene to chlorobenzene) were determined.

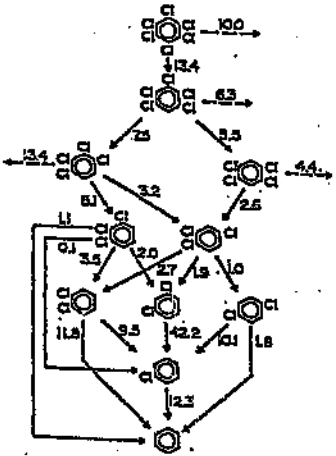

Fig. 2 Pseudo-first order kinetic rate constants for dechlorination of chlorinated benzenes (liter/g cat-min)x 10^3 (15).

These same catalysts, and variants thereof, have also been studied by other workers. Thus, Ni/C, NiMo/C, Mo/C and NiMo/Al_2O_3 catalysts have been studied for the *parallel* reactions of hydrodechlorination and hydrodesulfurisation (16). While good dechlorination was generally achieved the same cannot be a said for the parallel desulfurisation reaction.

In a more recent study these authors have investigated other catalysts and reported the excellent behaviour of a PdS/C catalyst (17). This work is similar to that described in this thesis. However, this article only appeared after the study described in this thesis was well underway. The role of sulfiding on the NiMo catalysts has also been reported (18-21).

To further understand the action of the above catalysts a recent study has investigated the use of a bulk Ni catalyst on the conversion of o-dichlorobenzenes to benzene in the presence of H_2. The reaction was proposed to occur via the Mars-van Krevelen mechanism (22).

Zeolitic supports have also been used in the catalysed reaction. Thus Pt/H-BEA zeolite has been studied. While the influence of the acidic sites resulted in less coke deposition, when compared to a Pt/Al_2O_3 catalyst, poorer activity was also observed (23).

This review would not be complete without some mention of the liquid hydrogenation reactions of p-chloronitrobenzene. In the catalysed reaction to synthesise the p-chloraniline from p-chloronitrobenzene, over-hydrogenation frequently occurs. This leads on occasion to the hydrodechlorination reaction and the synthesis of aniline (24-29).

4.1.1 Project objectives

This project describes the synthesis and study of a range of metal supported catalysts for the hydrodechlorination of chlorinated benzenes. It was hoped that this study would lay the groundwork for the development of a process for generating either valuable dichlorobenzene isomers or less valuable chlorobenzene and benzene from 1,2,4-trichlorobenzene.

From the previous interaction data, see Fig. 2 a comparison of the effect of different catalysts on the o/m/p ratio of the of the disubstituted products is possible. This aspect was throughly investigated in the study.

To assist with an understanding of the above reaction the hydrodechlorination of chlorobenzene, 1,2- and 1,4-dichlorobenzene, 1,2,4-trichlorobenzene from an alternative source, 3- and 4-chlorotoluene, as well as 2-chloroaniline over 1% Pd/Al_2O_3 catalyst was also studied.

In the light of the success achieved with the above study a preliminary investigation of the use of the Pd/Al_2O_3 for the hydrodechlorination of non-aromatic chlorinated hydrocarbons such as 1,2-dichloroethane was also investigated.

Physical characterisation of the catalysts used in the above reactions was achieved using a range of techniques that included TPR, XRD, BET, TGA, chemisorption etc. Analysis was performed both before and after the catalysed reactions.

4.2 Experimental

The reaction vessel consisted of a heating bath to vaporise reagents and heated connections between the heating bath, the reactor and the GC.

The hydrodechlorination reaction was carried out in a glass reactor placed in a heating jacket, which was connected to a GC fitted with a FID detector, which was used for determining the activity and selectivity of the catalyst (Chapter 2). The catalyst (0.1 g) was placed in the reactor. Before starting the reaction each catalyst was reduced in hydrogen at 450°C for 2 h.

Each support was mixed with deionised water and dried at 120°C for 6-8 h. The dried support was crushed to 0.5 and 1.0 mm particles for use as a catalyst support. A solution of a salt was impregnated to the point of incipient wetness onto the support pellets. The impregnated system was thereafter dried at 120°C in an oven for 8 h.

4.3 Results

Reactor studies were performed on the equipment described in Chapter 2. The results of the numerous studies are discussed in the next section.

Catalyst characterisation was carried out via TGA, XRD, chemisorption and BET studies. XRD spectra for a series of Ni, Au and Pd unused catalysts are shown in Figs 4.1 to 4.4. BET surface areas for 1% Pd/Al_2O_3 and 5,7% Ni/TiO_2 catalysts, after drying at 120°C overnight, were found to be 345.8 m^2/g and 63.6 m^2/g respectively. A Pd metallic surface area of 52.8 m^2/g was measured, which gives a Pd metal dispersion of 13.9 %.

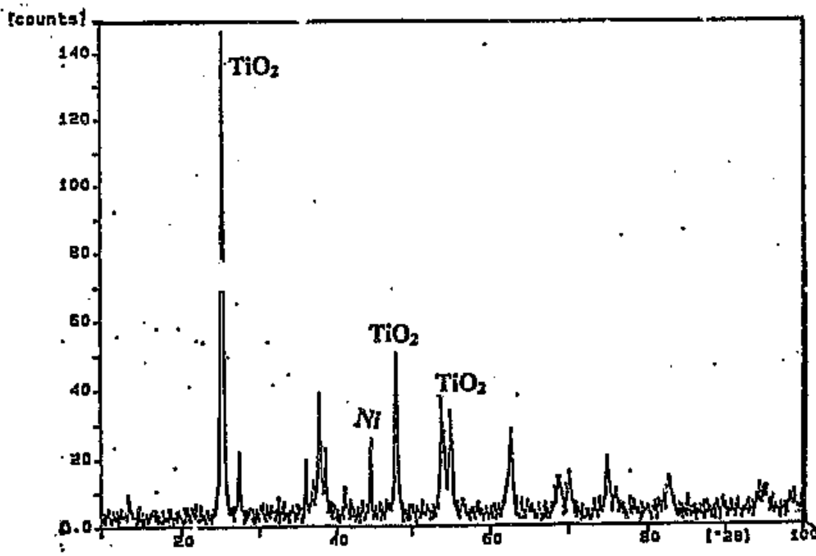

Fig 4.1 XRD data of 5.7% Ni/TiO_2 unused catalyst

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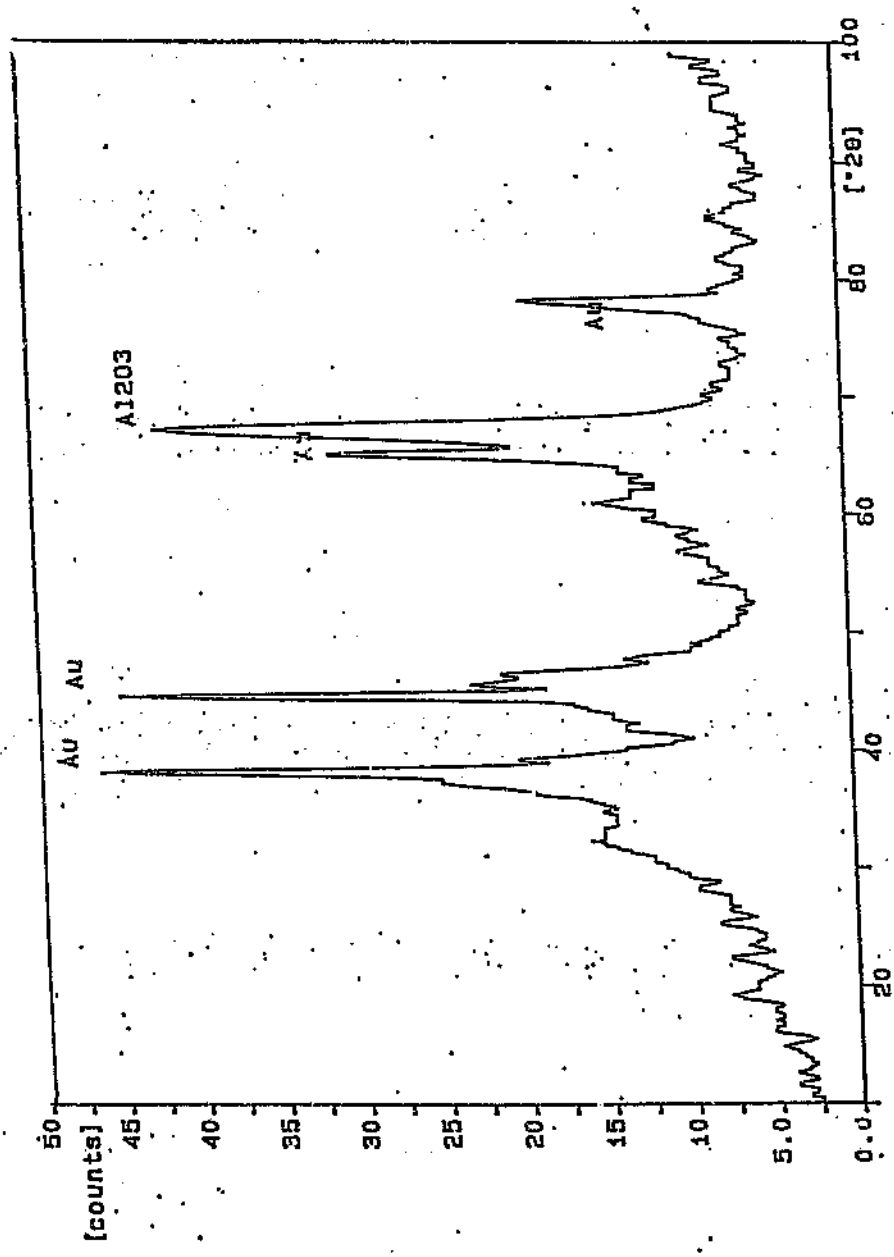

Fig 4.3 XRD data of 1% Au/Al_2O_3 unused catalyst

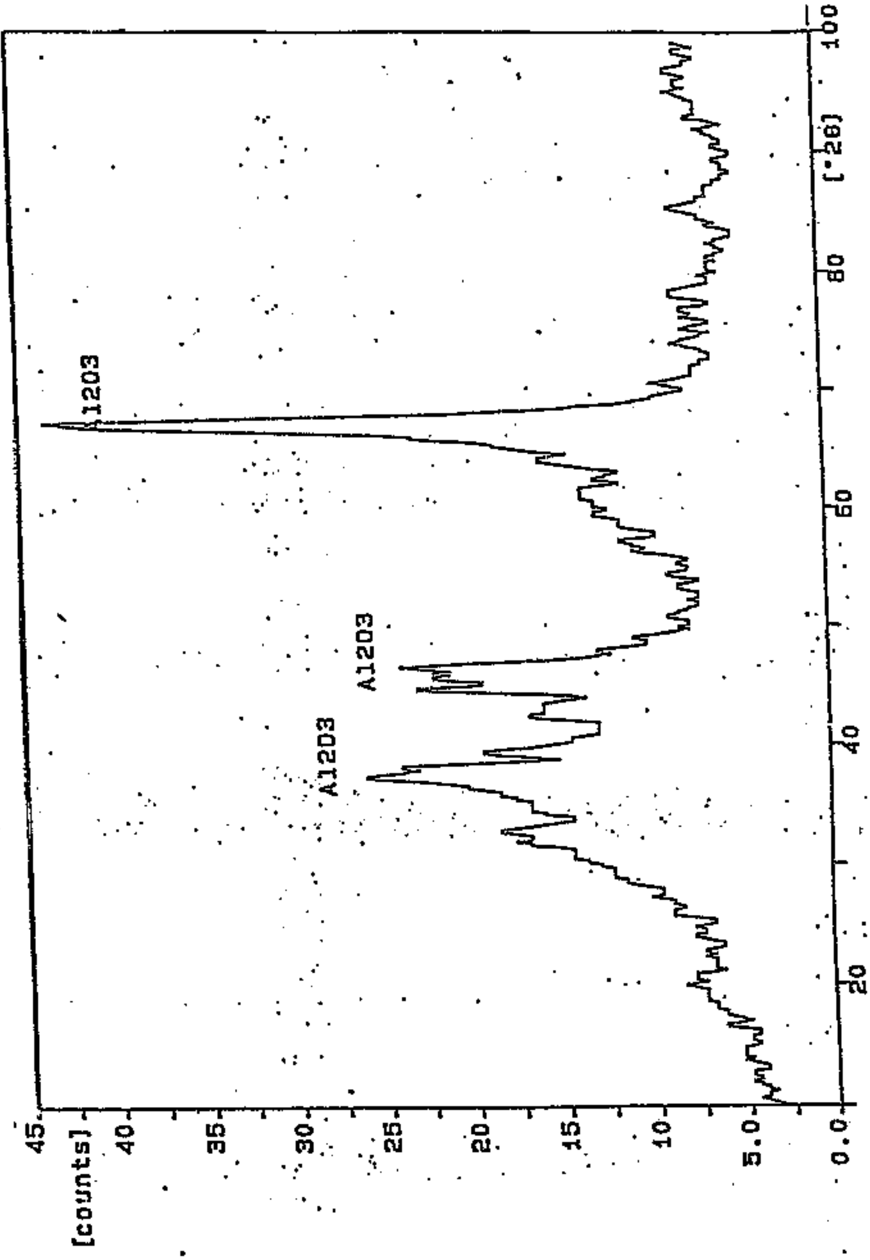

Fig 4.4 XRD data of 1% Pd/Al_2O_3 unused catalyst

The TPR spectrum of the unused 1 % Pd/Al_2O_3 catalyst is shown in Fig 4.5 while the TPR spectrum of the unused 1% $Pd/Al_2O_3/C$ is shown in Fig 4.6. Both spectra are similar with reduction peaks occurring at 100 °C (presumably due to Pd reduction) and at about 470 °C (due to C reduction). The C containing support also shows a peak at 470 °C (due to carbon reduction). It thus appears that the carbon could affect the reducibility properties of the Pd.

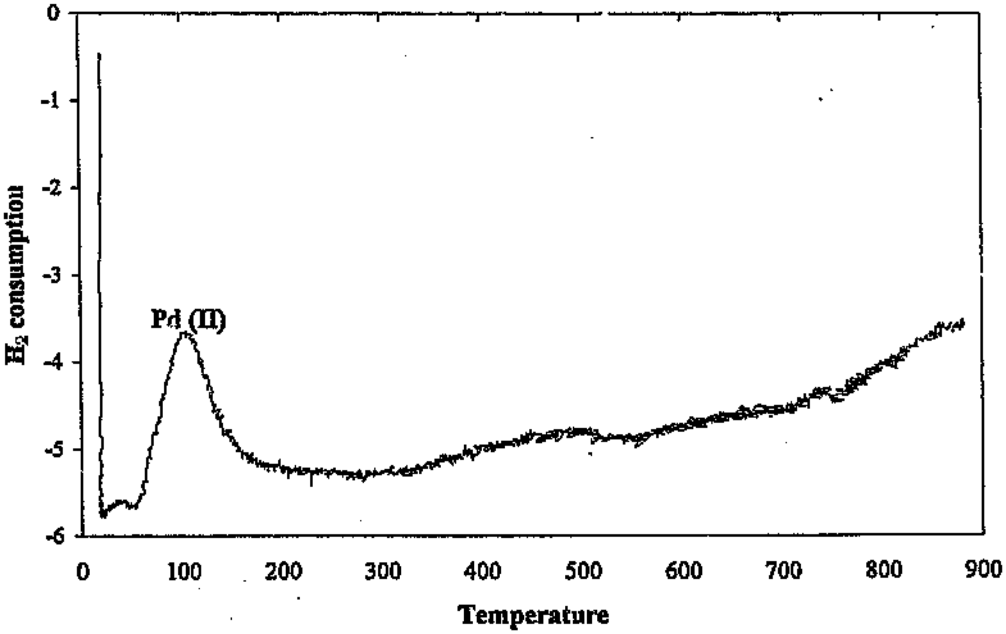

Fig 4.5 TPR data of 1% Pd/Al_2O_3 unused catalyst

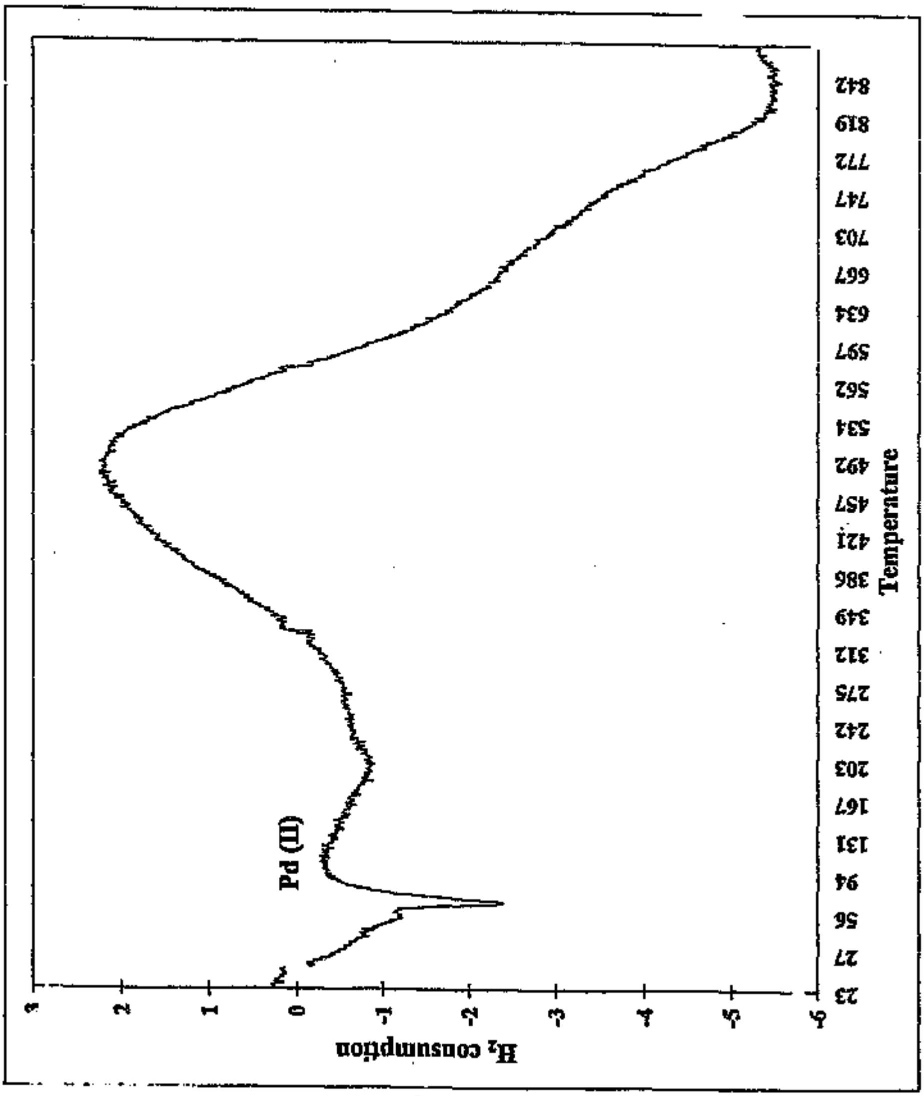

Fig 4.6 TPR data of 1% Pd/Al_2O_3/C unused catalyst

TGA analysis was performed on a used Pd/Al_2O_3 catalyst, after reaction with monochlorobenzene as starting material (Fig 4.7). The major weight loss occurs at T < 100 °C and is suggestive of water loss. Above 100 °C some mass loss is to be seen and this could be due to removal of surface species. No carbonisation was detected suggesting that no carbon had been deposited on the catalyst under the reaction conditions.

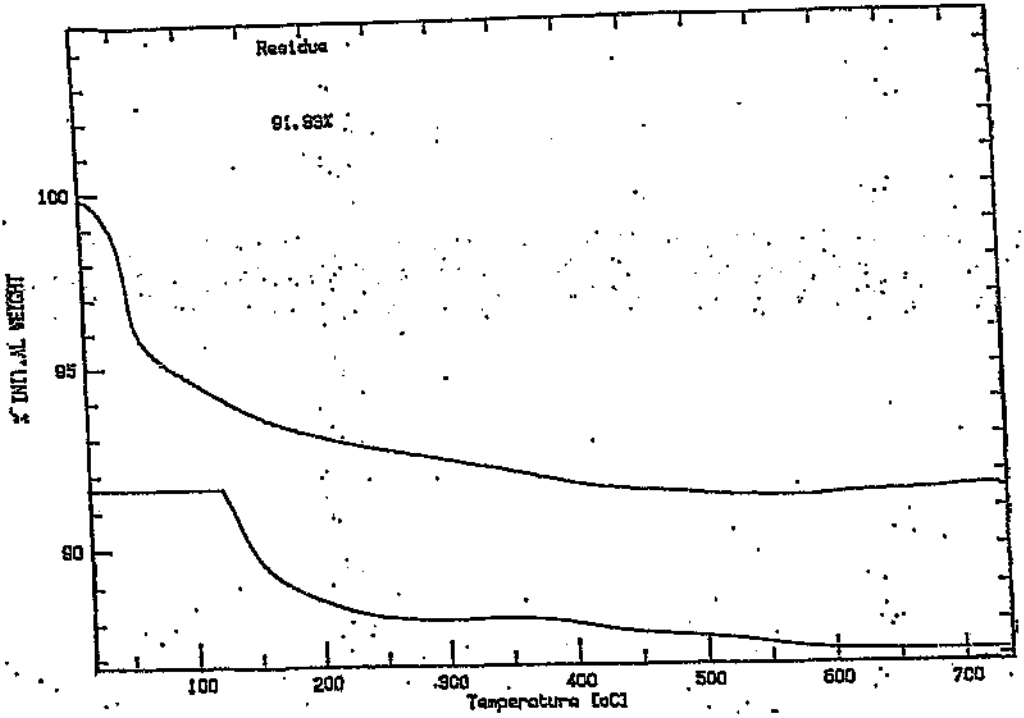

Fig 4.7 TGA data of 1% Pd/Al_2O_3 used catalyst after reaction with Chlorobenzene as starting material at 450°C

The XRD spectra of the used 1 % Pd/Al_2O_3 catalyst are shown in Figs 4.8 to 4.10. The XRD spectrum of the used 1 % Pd/Al_2O_3 catalyst after reaction with monochlorobenzene as starting material is shown in Fig 4.8 while the XRD data of the used 1 % Pd/Al_2O_3 catalyst after reaction with dichlorobenzene as starting material is shown in Fig 4.9. The XRD spectrum of the used 1 % Pd/Al_2O_3 catalyst after reaction with 1,2-dichloroethane as starting material is shown in Fig 4.10. The results revealed more amorphous material when compared to the fresh catalyst. The results are to be compared with 1 % Pd/Al_2O_3 fresh catalyst and pure Al_2O_3. XRD data suggest the presence of carbon. Indeed carbonisation would be predicted to occur at T > 350 °C but little if any weight loss is indicated by the data.

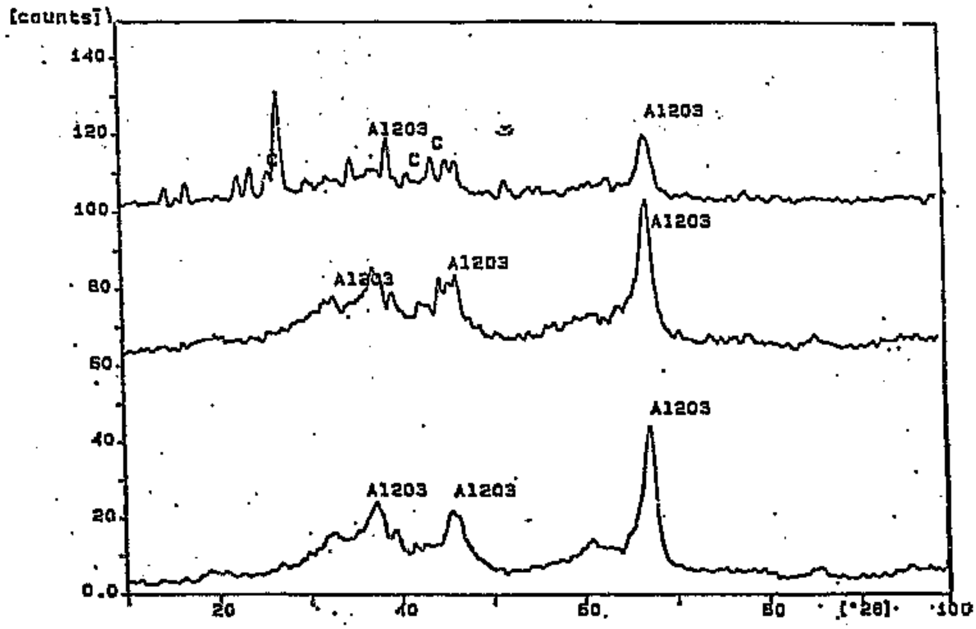

Fig 4.8 XRD data of 1% Pd/Al_2O_3 used catalyst after reaction with Chlorobenzene as starting material compared with 1% Pd/Al_2O_3 unused catalyst and pure Al_2O_3

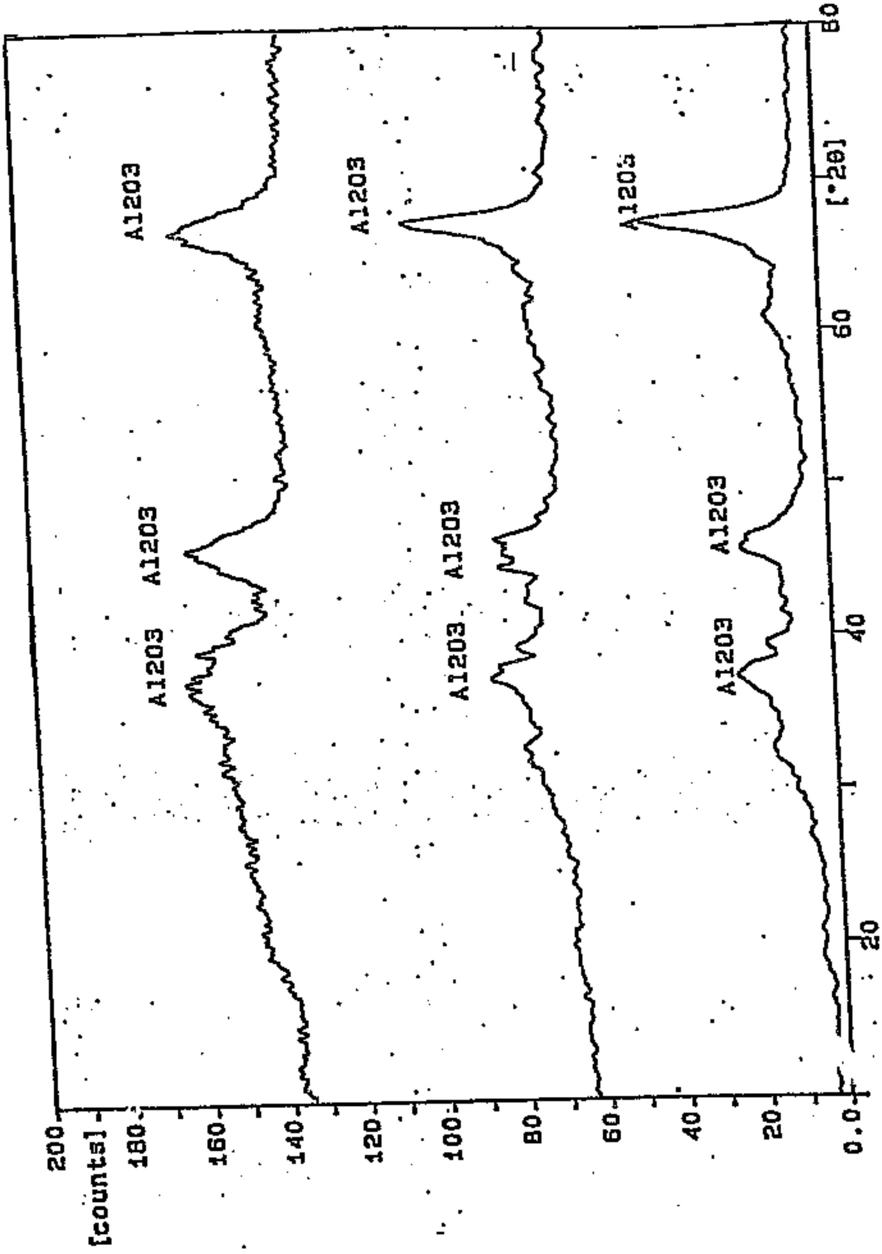

Fig 4.9 XRD data of 1% Pd/Al_2O_3 used catalyst after reaction with 1,2-Dichlorobenzene as starting material compared with 1% Pd/Al_2O_3 unused catalyst and pure Al_2O_3

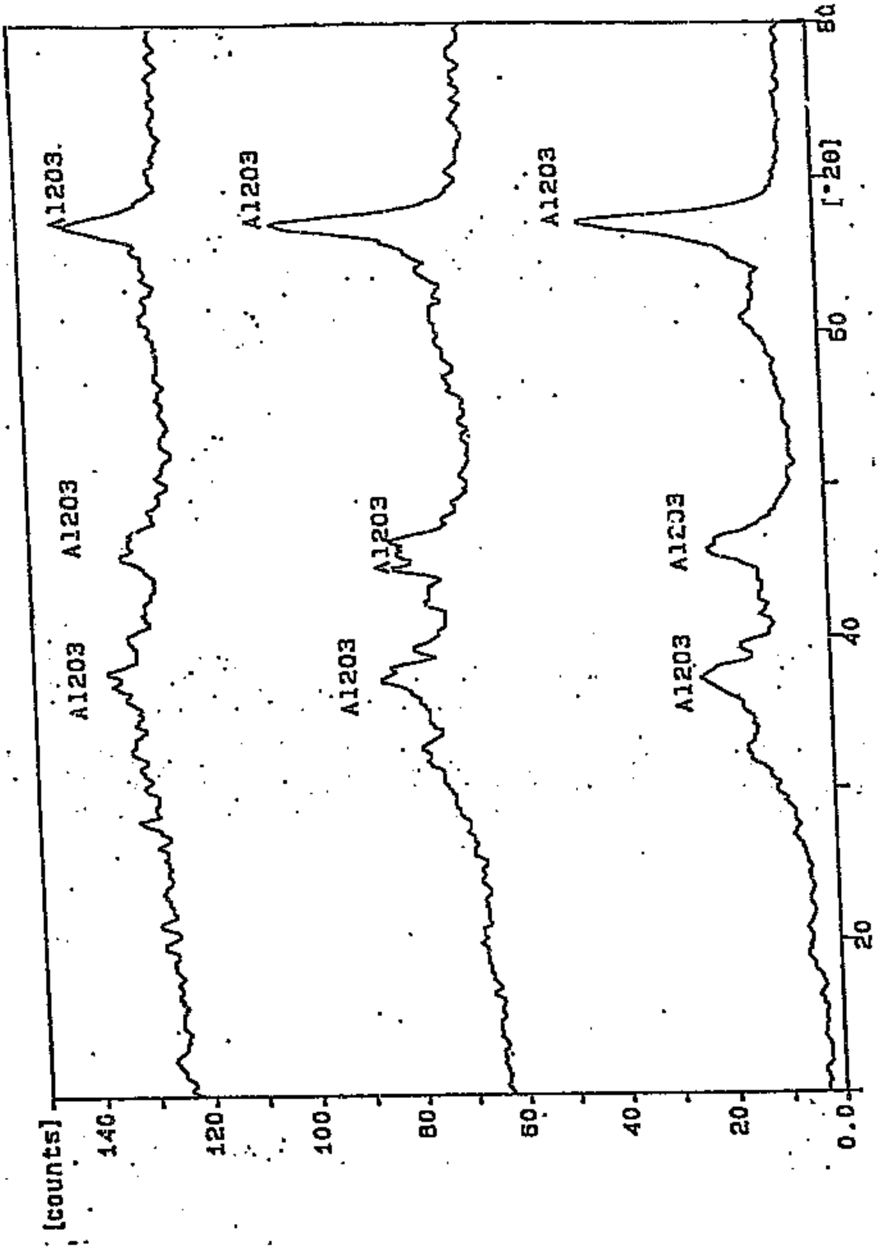

Fig 4.10 XRD data of 1% Pd/Al_2O_3 used catalyst after reaction with 1,2-Dichloroethane as starting material compared with 1% Pd/Al_2O_3 unused catalyst and pure Al_2O_3

4.4 Catalytic hydrodechlorination of chlorinated benzenes

4.4.1 Initial Experiments

a) Blank study

Preliminary experiments were performed to determine the catalytic effect of the reactor and the support on the hydrodechlorination reaction. Thus, when 2.5 % and 0.16 % 1,2-dichlorobenzene (amounts determined by the evaporator temperature) were passed through the reactor at flow rates (50 – 200 ml/min), and temperatures (250 – 350 °C) to be used in the study, less than 6 % conversion was achieved (see Table 4.1).

b) G.C. separation of reactants and products

The conditions for separation of the three dichlorobenzenes on a gc column were established and a typical gc spectrum which shows this separation is shown in Fig 4.11. The disubstituted isomers eluted as follows: meta/para/ortho. It is also to be noted that the other chlorinated aromatics are well separated on the column. Identification of the various components was established with samples of the materials purchased from various suppliers.

The actual ratio of the disubstituted isomers formed was determined from both their rate of production as well as their rate of reaction by gc analysis. The reaction sequence for hydrodechlorination of 1,2,4-trichlorobenzene can be seen below (Fig 4.12).

Table 4.1

Blank gas-phase hydrodechlorination of 2.5% and 0.16% 1,2-Dichlorobenzene in H_2

Flow rate	T reactor	T evaporation	Conversion	Selectivity		%
ml/min	°C	°C	%	Benzene	Clbenzene	DiClbenz
50	250	85	3.3	1.23	2.09	96.7
100	250		1.6	0.38	1.17	98.4
200	250		1.3	0.39	0.92	98.7
50	350	85	1.9	0.61	1.28	98.1
100	350		1.3	0.35	0.88	98.7
200	350		0.85	0.2	0.64	99.15
50	250	20	1.9	0.74	1.16	98.1
100	250		2.06	0.81	1.25	97.9
200	250		1.8	0.73	1.11	98.2
50	350	20	5.3	2.07	3.19	97.7
100	350		5.8	2.39	3.48	94.2
200	350		4.4	1.88	2.59	95.6

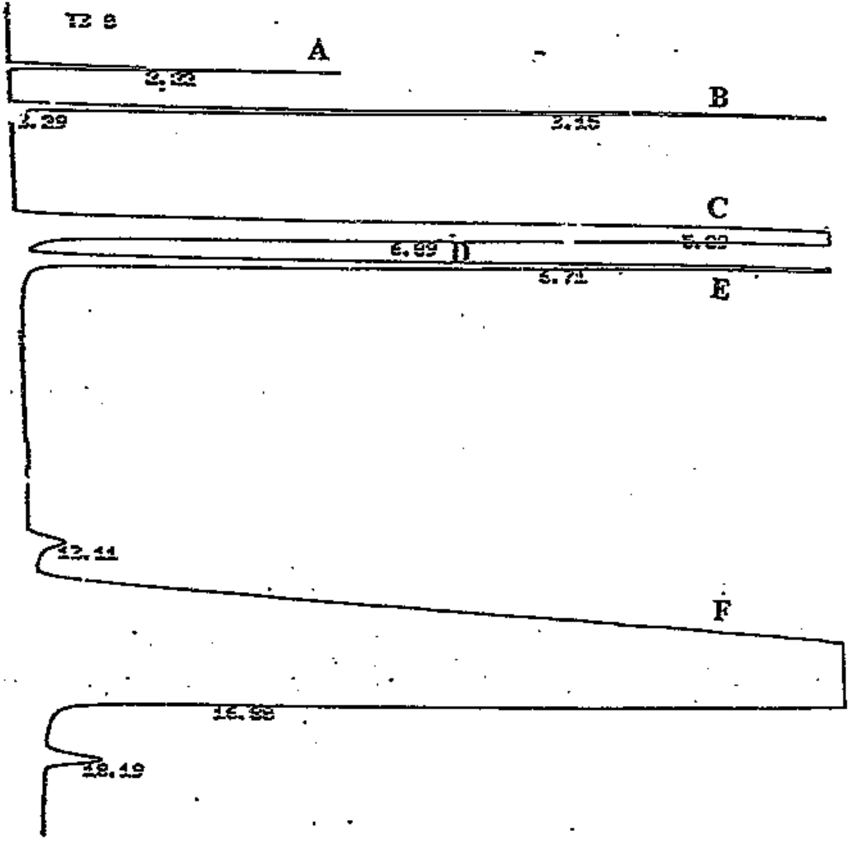

Fig. 4.11

Gas-phase hydrodechlorination of 8% ind.Trichlorobenzene in H_2 at 250°C, over 5,7% Ni/TiO$_2$ catalyst 100 ml/min H_2 flow rate
when : A- Benzene; B- Chlorobenzene; C- m-Dichlorobenzene;
D- p-Dichlorobenzene; E- o-Dichlorobenzene; F- Trichlorobenzene

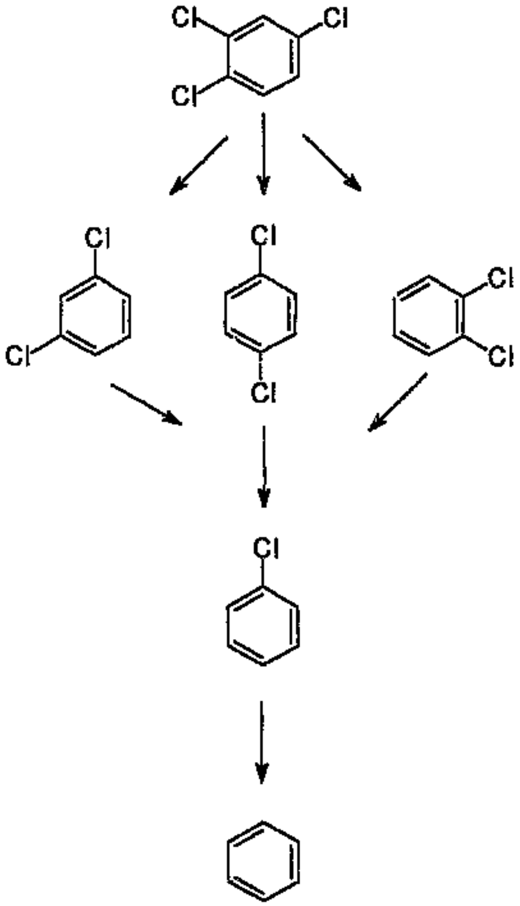

Fig.4.12 Reaction sequence for hydrodechlorination of 1,2,4- Trichlorobenzene

Ratios for the isomers have been reported in the literature. Hagh and Allen (14) found that an ortho/meta/para ratio 2.7:1.9:1 was detected over a Ni/Mo/Al_2O_3 catalyst. Balko(11) also mentioned similar results to those obtained by Hagh and Allen with an ortho/meta/para ratio of 4.4:1.8:1 for their catalyst. As will be seen in this work, this ratio can vary. For example 5.7% Ni/TiO_2, which exhibited the highest conversion to m/p/o dichlorobenzene products revealed a ratio of 2.23:3.72:1 (Tables 4.2; 4.2.1, 2, 3). This issue is discussed more fully below.

c) Data reproducibility

A further issue of importance was the reproducibility of the reactor data. Data were found to be reproducible as indicated by results recorded in Tables 4.3 and 4.3.1. Duplicate runs for 5.7 % Ni/TiO_2 catalysts recorded at a reaction temperature of 250 °C were performed at two different flowrates. It can be seen from the tables that p-dichlorobenzene isomer is in the highest yield at 85°C evaporation temperature (2,5 % reagent in H_2). The intensity ratio of m/p/o is as follow: 2:2.9:1.

It is to be noted that the highest yield depends on the evaporation temperature. Use of a 115-120°C evaporation temperature (4.8 and 8% reagent in H_2) gave the highest yield of m and o-dichlorobenzene isomers with a ratio of m/p/o dichlorobenzene products: 1.1:0.92:1 ; 1.15:0.76:1 respectively (Table 4.2.3).

d) Effect of support

The hydrodechlorination of 1,2,4-trichlorobenzene was attempted over various supports (TiO_2, C/Al_2O_3 and Al_2O_3) used in the study and the data are shown in Table 4.4. As can be seen, up to 10 % conversion is possible in the absence of a metal catalyst under the most extreme conditions to be used The data further suggest that the carbon support does not affect the reaction (see data at reactor temp = 350 °C and 100 ml/min flow rate). The m/p/o dichlorobenzene isomers exhibited a ratio 0.32:0.28:1 on Al_2O_3 support, 0.33:0.36:1 on Al_2O_3/C support and 0.35:0.37:1 on TiO_2 support. This can be compared to the data of the blank hydrodechlorination reaction (Table 4.2.2).

Table 4.2

A comparison of the Dichlorobenzene products distribution in the hydrodechlorination of Trichlorobenzene over various catalysts

Catalyst	T reactor	H_2 in TriClb	Flowrate	Dichlorobenzene isomers-results			Ratios		
100 mg	°C		ml/min	meta	para	ortho	p/m	p/o	m/o
1% Ni/TiO_2	250	2,5% in 1,2,4-	50	10.5	17.5	4.71	1.67	3.72	2.2
	250		100	9.1	14.54	4.61	1.59	3.15	2
	450		100	0.54	0.93	0.24	1.72	3.87	2.3
5,7% Ni/TiO_2	250	2,5% in 1,2,4-	100	12.65	18.29	6.35	1.44	2.85	2
	250		100	10.37	14.7	4.82	1.41	3.06	2.2
1% Ni/Al_2O_3	250	2,5% in 1,2,4-	100	0.85	1.02	0.84	1.19	1.21	1
	450		100	6	7.15	5.45	1.19	1.31	1.1
1% Ni/Al_2O_3/C	450	2,5% in 1,2,4-	200	3.14	3.3	2.77	1.06	1.18	1.1
1% Pd/Al_2O_3	100	2,5% in 1,2,4-	50	0.82	0.44	6.76	0.54	0.07	0.1
	100		100	1.62	0.87	11.86	1.86	0.07	0.1
1% Pd/Al_2O_3/C	100	2,5% in 1,2,4-	100	3.56	1.58	23.61	0.44	0.07	0.2
	450		100	0.28	0.22	1.74	0.79	0.13	0.2
1% Pd/Al_2O_3 + quartz beads	250	2,5% in 1,2,4-	200	0.63	0.45	2.74	0.71	0.16	0.2
	450		200	1.38	0.04	1.55	0.03	0.03	0.9
8.6% Ni/Al_2O_3	350	2,5% in 1,2,4-	50	0.24	0.22	1.05	0.92	0.21	0.2
	450		50	1.09	1.01	6.93	0.93	0.15	0.2
Blank	150	2,5% in 1,2,4-	50	0.76	0.62	3.44	0.82	0.18	0.2
	350	2,5% in 1,2,4-	50	1.48	1.07	7.62	0.72	0.14	0.2
1% Au/Al_2O_3	450	2,5% in 1,2,4-	50	1.55	1.8	3.63	1.16	0.49	0.4
	450		100	0.81	0.97	1.82	1.19	0.53	0.4
1% Au/Al_2O_3/C	450	2,5% in 1,2,4-	50	1.22	1.56	2.37	1.28	0.66	0.5
	450		100	0.5	0.66	0.96	1.32	0.68	0.5
1%Ni/Al_2O_3 + quartz beads	450	2,5% in 1,2,4-	100	0.63	0.66	2.71	1.05	0.24	0.2
0.8% Ni/MgO	450	2,5% in 1,2,4-	100	0.35	0.42	1.2	2.5	0.4	0.3
Al_2O_3	350	2,5% in 1,2,4-	100	1.47	1.31	4.56	0.89	0.29	0.3
Al_2O_3/C	350	2,5% in 1,2,4-	100	1.53	1.67	4.62	1.09	0.36	0.3
TiO_2	350	2,5% in 1,2,4-	50	0.91	0.95	2.56	1.04	0.37	0.4

Table 4.2.1

A comparison of the Dichlorobenzene products distribution in the hydrodechlorination of Trichlorobenzene over various catalysts

Catalyst	T reactor	H_2 in TriClb	Flowrate	Dichlorobenzene isomers-results			Ratios		
100 mg	°C		ml/min	meta	para	ortho	p/m	p/o	m/o
0,5% Ni/TiO_2	250	8% in 1,2,4-	100	5.22	8.15	3.63	1.56	2.3	1.4
1% Ni/TiO_2	250	8% in 1,2,4-	50	8.17	12.15	5.53	1.19	2.2	1.5
	250		100	8.04	10.04	5.69	1.25	1.8	1.4
	250		200	3.97	6.06	1.53	1.53	2.1	1.4
5,7% Ni/TiO_2	250	8% in 1,2,4-	200	8.26	9.48	4.62	1.14	2.1	1.8
	250		100	7.94	8.14	4.35	1.03	1.9	1.8
5,7% Ni/TiO_2	250	2.5% in ind	100	8.83	13 42	4.54	1.52	3	1.9
5,7% Ni/TiO_2	250	4,8% in ind	100	10.3	9.35	10.13	0.91	0.9	1
5,7% Ni/TiO_2	250	8% in ind	50	7.56	5	6.63	0.66	0.8	1.1
	250		50	7.13	4.7	6.24	0.66	0.8	1.1
	250		100	5.66	4.21	4.41	0.74	1	1.3
	250		100	5.49	4.06	4.56	0.73	0.9	1.2

Table 4.2.2

A comparison of the Dichlorobenzene products distribution ratio m : p : o in the hydrodechlorination of Trichlorobenzene over various catalysts

Catalyst	T reactor	%H_2 in TriCl	Flowrate	Dichlorobenzene isomers-results			Product ratio
100 mg	°C		ml/min	meta	para	ortho	m : p : o
1% Ni/TiO_2	250	2,5% in 1,2,4-	50	12.65	18.29	6.35	2 / 2.9 / 1
	450		100	0.54	0.93	0.24	1.72 / 3.92 / 1
5,7% Ni/TiO_2	250	2,5% in 1,2,4-	100	10.5	17.5	4.71	2.23 / 3.72 / 1
	250		100	10.37	14.7	4.82	2.15 / 3.04 / 1
1% Ni/Al_2O_3	250	2,5% in 1,2,4-	100	0.85	1.02	0.84	1.2 / 1.2 / 1
	450		100	6	7.15	5.45	1.2 / 1.3 / 1
1% Ni/Al_2O_3/C	450	2,5% in 1,2,4-	200	3.14	3.3	2.77	1.1 / 1.2 / 1
1% Pd/Al_2O_3	100	2,5% in 1,2,4-	50	0.82	0.44	6.76	0.12 / 0.06 / 1
	100		100	1.62	0.87	11.86	0.14 / 0.07 / 1
1% Pd/Al_2O_3/C	100	2,5% in 1,2,4-	100	3.56	1.58	23.61	0 15 / 0.07 / 1
	450		100	0.28	0.22	1.74	0.16 / 0.12 / 1
1% Pd/Al_2O_3 + quartz beads	250	2,5% in 1,2,4-	200	0.63	0.45	2.74	0.23 / 0.16 / 1
	450		200	1.38	0.04	1.55	0.89 / 0.02 / 1
8.6% Ni/Al_2O_3	350	2,5% in 1,2,4-	50	0.24	0.22	1.05	0.22 / 0.21 / 1
	450		50	1.09	1.01	6.93	0.15 / 0.14 / 1
Blank	150	2,5% in 1,2,4-	50	0.76	0.62	3.44	0.22 / 0.18 / 1
	350	2,5% in 1,2,4-	50	1.48	1.07	7.62	0.19 / 0.14 / 1
1% Au/Al_2O_3	450	2,5% in 1,2,4-	50	1.55	1.8	3.63	0.42 / 0.49 / 1
	450		100	0.81	0.97	1.82	0.44 / 0.53 / 1
1% Au/Al_2O_3/C	450	2,5% in 1,2,4-	50	1.22	1.56	2.37	0.51 / 0.65 / 1
	450		100	0.5	0.66	0.96	0.52 / 0.68 / 1
1%Ni/Al_2O_3 + quartz beads	450	2,5% in 1,2,4-	100	0.63	0.66	2.71	0.23 / 0.24 / 1
0.8% Ni/MgO	450	2,5% in 1,2,4-	100	0.35	0.42	1.04	0.33 / 0.4 / 1
Al_2O_3	350	2,5% in 1,2,4-	100	1.47	1.31	4.56	0.32 / 0.28 / 1
Al_2O_3/C	350	2,5% in 1,2,4-	100	1.53	1.67	4.62	0.33 / 0.36 / 1
TiO_2	350	2,5% in 1,2,4-	50	0.91	0.95	2.56	0.35 / 0.37 / 1

Table 4.2.3

A comparison of the Dichlorobenzene products distribution ratio m : p : o in the hydrodechlorination of Trichlorobenzene over various catalysts

Catalyst	T reactor	H_2 in TriClb	Flowrate	Dichlorobenzene isomers-results			Product ratio
100 mg	°C		ml/min	meta	para	ortho	m : p : o
0,5% Ni/TiO_2	250	8% in 1,2,4-	100	5.22	8.15	3.63	1.6 / 2.3 /1
1% Ni/TiO_2	250	8% in 1,2,4-	50	8.17	12.15	5.53	1.5 / 2.2 / 1
	250		100	8.04	10.04	5.69	1.4 / 1.8 /1
	250		200	3.97	6.06	2.89	1.5 / 2.1 / 1
5,7% Ni/TiO_2	250	8% in 1,2,4-	100	8.26	9.48	4.62	1.8 / 2.1 / 1
	250		100	7.94	8.14	4.35	1.8 / 1.9 / 1
5,7% Ni/TiO_2	250	2.5% in ind	100	8.83	13.42	4.54	1.9 / 3 / 1
5,7% Ni/TiO_2	250	4,8% in ind	100	10.3	9.35	10.13	1.1 / 0.92 / 1
5,7% Ni/TiO_2	250	8% in ind	50	7.56	5	6.63	1.15 / 0.76 / 1
	250		50	7.13	4.7	6.24	1.14 / 0.75 / 1
	250		100	5.66	4.21	4.41	1.3 / 0.95 / 1
	250		100	5.49	4.06	4.56	1.2 / 0.89 / 1

Table 4.3

Gas-phase hydrodechlorination of 2.5%, and 8% 1,2,4-Trichlorobenzene in H_2 over Ni/TiO_2 catalyst with different loadings

Catalyst	T	flowrate	Convers	Selectivity %					
100 mg	°C	ml/min	%	Benzene	Clbenz	m-DiClbenz	p-DiClbenz	o-DiClbenz	TriClbenz
2,5% 1,2,4-Trichlorobenzene in H_2									
1% Ni/TiO_2	250	50	45.1	6.95	5.38	10.5	17.5	4.71	54.9
	250	100	35.28	1.27	5.77	9.10	14.54	4.61	64.72
	250	200	25.36	0.70	3.32	6.80	11.09	3.45	74.64
	450	50	99.11	96.14	1.25	0.54	0.93	0.24	0.89
	450	100	97.83	89.51	3.81	1.42	2.49	0.60	2.17
5,7 % Ni\TiO_2	250	100	54.11	4.17	12.66	12.65	18.29	6.35	45.89
	250	100	40.40	3.88	6.62	10.37	14.70	4.82	59.6
	250	100	39.1	3.77	6.31	10.06	14.29	4.70	60.9
8% 1,2,4-Trichlorobenzene in H_2									
0,5% Ni\TiO_2	250	100	8.52	0.08	0.88	2.20	3.60	1.87	91.48
	250	100	19.80	0.26	2.53	5.22	8.15	3.63	80.2
1 % Ni\TiO_2	250	50	33	1.04	6.11	8.17	12.15	5.53	67
	250	100	22.78	0.36	3.4	6.14	8.52	4.36	77.22
	250	100	28.87	0.54	4.21	8.04	10.4	5.69	71.13
	250	200	14.60	0.15	1.52	3.97	6.06	2.89	85.40
5,7 % Ni\TiO_2	250	100	26.99	0.90	3.74	8.26	9.48	4.62	73.01
	250	100	23.72	0.61	2.69	7.94	8.14	4.35	76.28

Table 4.3.1

Gas-phase hydrodechlorination of 2,5, 4,8, 8% ind. Trichlorobenzene in H_2 over Ni/TiO_2 catalyst.

Catalyst	T	flowrate	Convers	Selectivity %					
100 mg	°C	ml/min	%	Benzene	Clbenz	m-DiClbenz	p-DiClbenz	o-DiClbenz	TriClbenz
2,5% industrial Trichlorobenzene in H_2									
5,7 % Ni\TiO$_2$	250	100	33.36	1.26	5.28	8.83	13.42	4.54	66.64
	250	100	27.26	0.75	2.33	8.60	9.26	6.32	72.74
	250	100	26.24	1.35	1.73	7.22	9.88	6.06	73.76
4,8% industrial Trichlorobenzene in H_2									
5,7 % Ni\TiO$_2$	250	100	35.60	0.70	5.12	10.30	9.35	10.13	64.40
8% industrial Trichlorobenzene in H_2									
5,7 % Ni\TiO$_2$	250	50	21.54	0.19	2.53	7.08	5.16	6.58	78.46
	250	50	21.41	0.16	2.07	7.56	5.00	6.63	78.59
	250	50	20.20	0.14	1.99	7.13	4.70	6.24	79.80
	250	100	15.45	0.08	1.09	5.66	4.21	4.41	84.55
	250	100	15.2	0.22	1.02	5.49	4.06	4.56	84.8
	250	100	15.02	0.09	1.06	5.31	4.21	4.35	84.98

Table 4.4

Gas-phase hydrodechlorination of 2.5% 1,2,4-Trichlorobenzene in H_2 over different supports

Support	T reactor	Flow rate	T evapor	Convers	Selectivity %					
100 mg	°C	ml/min	°C	%	Benzene	Clbenz	m-DiClbenz	p-DiClbenz	o-DiClbenz	TriClbenz
C/Al_2O_3	350	100	85	9.6	0.81	0.96	1.53	1.67	4.62	90.4
	450	100	85	5.6	0.29	0.45	1.17	1.4	1.28	94.4
Al_2O_3	250	20	85	6.1	0.23	0.39	0.9	0.76	3.86	93.9
	350	100	85	9.4	0.88	1.13	1.47	1.31	4.56	90.6
	450	100	85	0.88	0.07	0.07	0.15	0.14	0.44	99.12
TiO_2	250	100	85							100
	300	50	85							100
	350	50	85	4.97	0.09	0.45	0.91	0.95	2.56	95.03
	450	100	85	3	0.08	0.11	0.74	0.98	2.16	97

4.4.2 Preliminary reactor studies

Preliminary studies were performed using 1,2,4-trichlorobenzene as reagent and these studies revealed that Pd/Al_2O_3 was an excellent catalyst for the *complete* conversion of the reagent to benzene (see below Figs 4.13 and 4.14). For this reason, studies of the hydrodechlorination of mono- and dichlorobenzenes were undertaken with this catalyst. These studies will be discussed first; then the studies with the different metal catalysts and their effect on the dichlorobenzene isomer ratios will be described.

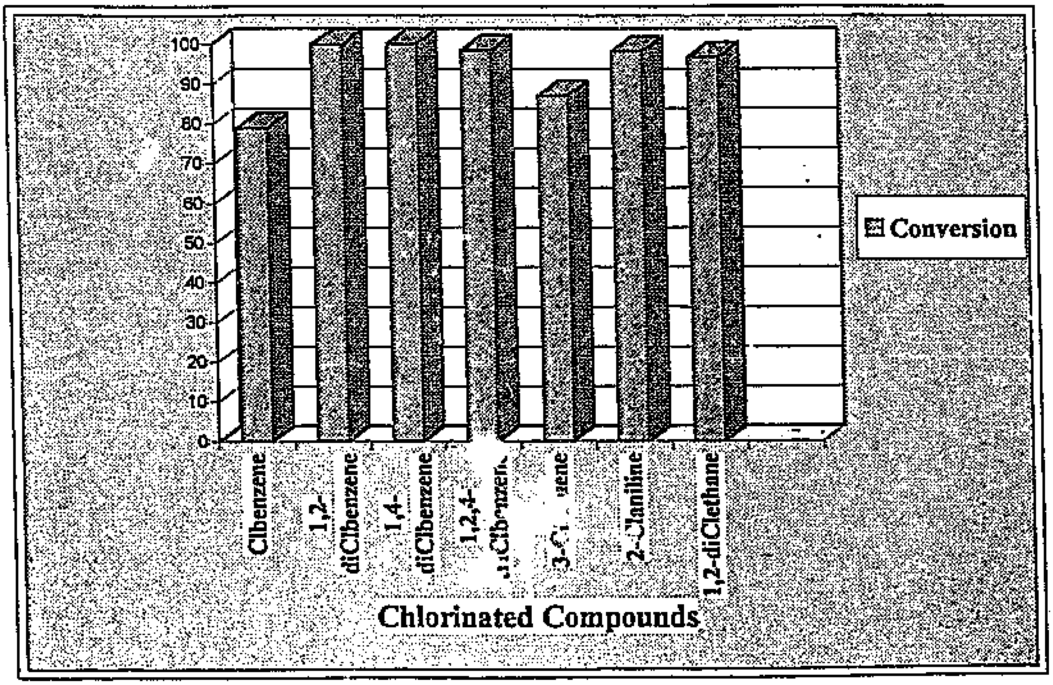

Fig 4.13

A comparison of the conversion of the chlorinated compounds in the hydrodechlorination reaction over 1%Pd/Al_2O_3 catalyst.

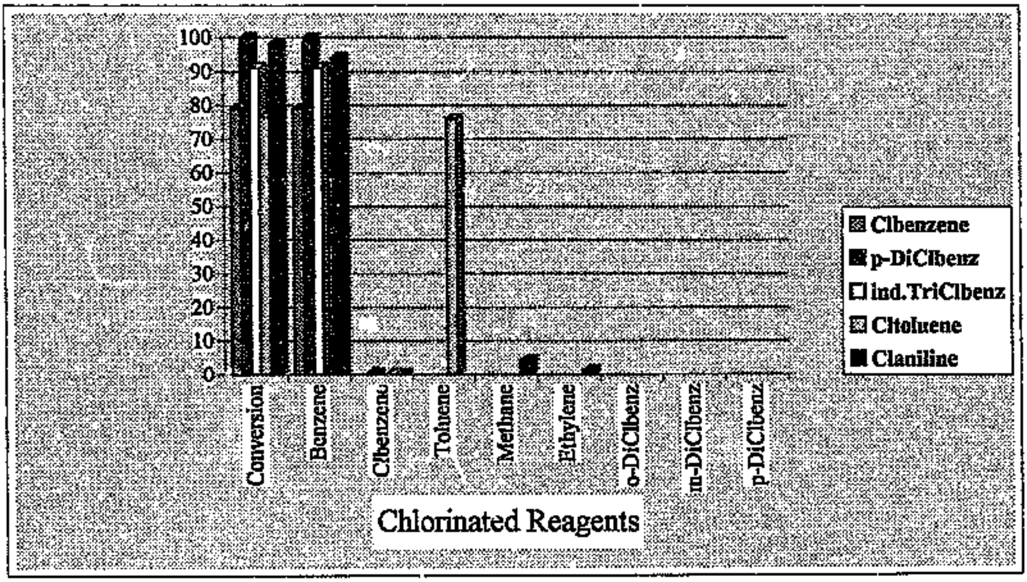

Fig. 4.14

A comparison of the conversion and selectivity of the reaction in the hydrodechlorination of chlorinated reagents at 350°C over 1% Pd/Al_2O_3 catalyst

4.4.3 Hydrodechlorination of chlorobenzene

The gas-phase hydrodechlorination of 1,6% chlorobenzene in H_2 over a 1 % Pd/Al_2O_3 catalyst was attempted and the results are displayed in Table 4.5. A range of reaction conditions was used in an attempt to optimize the product yield. Increasing flow rate gave the expected decrease in product yield. More interesting was the effect of reaction temperature on the benzene yield. The yield increased up to a temperature of 350 °C and then *decreased.* This later effect can be attributed to carbon deposition on the catalyst (see Fig.4.8). This is also suggested by the results at higher temperature and higher flowrates where a slower than expected decrease in rate is to be noted. It is also to be noted that in no reaction was complete conversion to benzene achieved.

Previous reports have appeared in the literature on the above reaction. In particular the gas phase reaction of Pd/Al_2O_3 and Rh/Al_2O_3 have been reported and their activities contrasted (10). Issues that were pertinent and have bearing on this study are the following:

- No cyclohexane or chlorinated cyclohexane was detected in our study. This in agreement with (10)
- Self poisoning by HCl was identified as a deactivation pathway in the work by Coq et al. (24).

Our data, under different reaction conditions are consistent with carbon deposition, an issue not discussed by Coq et al. Kinetic data suggest that the removal of Cl is rapid (14).

Table 4.5

Gas-phase hydrodechlorination of 1.6% Chlorobenzene in H_2 over 1% Pd/Al_2O_3 catalyst

Catalyst	T evapor	T reactor	Flowrate	Convers	Selectivity	%
100 mg	°C	°C	ml/min	%	Benzene	Clbenzene
1%Pd/Al_2O_3	22	100	20	1,3	1,31	98.7
			50	0,7	0.67	99.3
		150	20	6.4	6.43	93,6
			50	3.3	3.33	96.7
			100	2.2	2.19	97.8
		250	20	39.4	39.35	60,6
			50	22,5	22,48	77.5
			100	22.7	22.72	77.3
		350	20	78.9	78.95	21.1
			50	40.3	40.32	59.7
			100	40.6	40.64	59.4
		400	20	66,3	66.25	33.7
			50	45.5	45.48	54.5
			100	40.9	40.88	59.1
		450	20	67.8	67.77	32.2
			50	57.5	57.53	42.5
			100	46.1	46.12	53.9

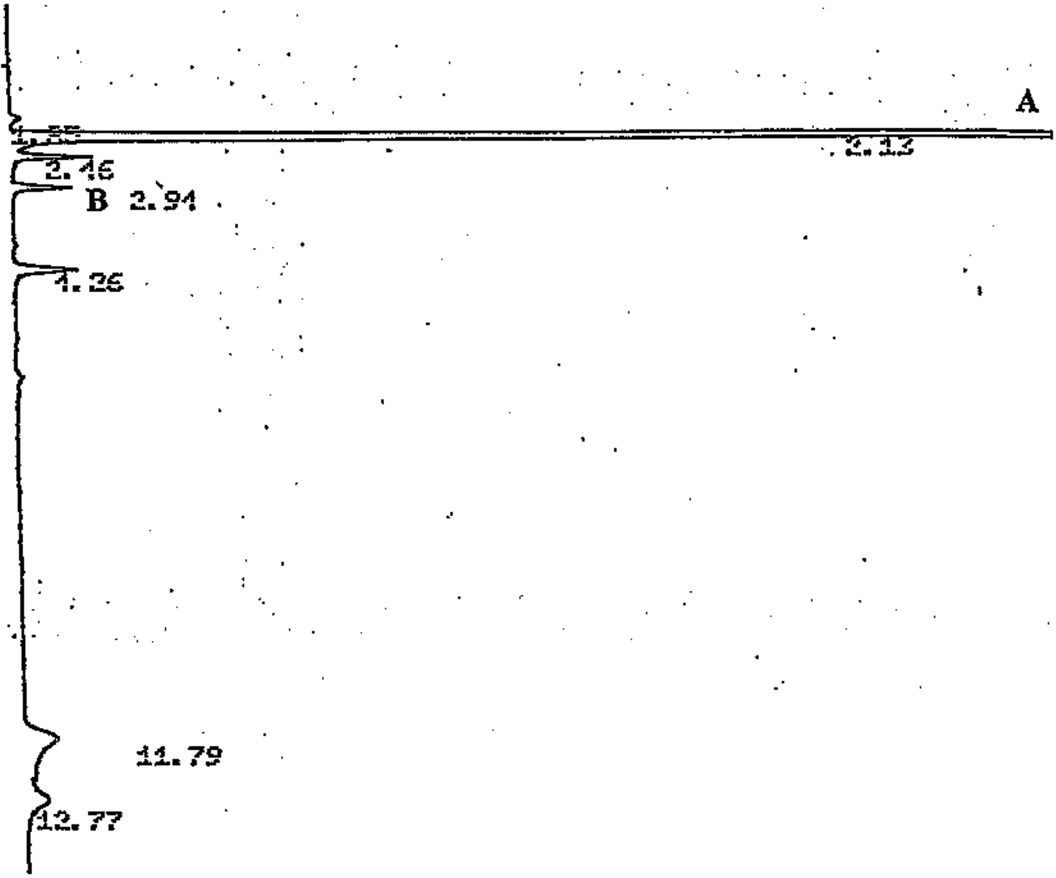

Fig 4.15

Gas-phase hydrodechlorination of 1,6% Chlorobenzene in H_2 over 1% Pd/Al_2O_3 catalyst 20 ml/min H_2 flow rate, when A- Benzene; B- Chlorobenzene.

4.4.4 Hydrodechlorination of dichlorobenzene

1,2-dichlorobenzene

Data for the gas-phase hydrodechlorination reaction of 0,16 % 1,2-dichlorobenzene in the presence of 1 % Pd/Al_2O_3 catalyst is shown in Table 4.6. At the lower flow rate (compared to the data obtained for the monchlorobenzene hydrodechlorination reaction) complete conversion to benzene is possible as can be seen in the gc spectra - Fig 4.16. The expected trend of yield increase with reactor reaction temperature and decrease with flow rate are to be noted. As can be seen, mild reaction conditions
(ca. 250 °C) will give the fully dechlorinated product.

1,4-dichlorobenzene

Data using this reagent are shown in Table 4.7. Again the typical trends are to be noted – increased yield with increased reaction temperature and decreased yield with flow rate, although it appears that catalyst poisoning is occurring at 450 °C. Of more significance is the observation that complete conversion to benzene is not possible even at the highest reaction temperature. It is also to be noted that some (< 1 %) chlorobenzene is always detected. This result indicates that the different dichlorobenzenes are dechlorinated at different rates.

These reactions have previously been studied and results have been reported in the literature (10,14)

The key literature result is that the three dichlorobenzene isomers are dechlorinated at different rates (14). The ortho and para isomers react four times slower than the meta isomer,with the 1,2 isomer reacting some 10 % more rapidly than the 1,4 isomer. Here we see the typical effect of ring substitution on reactivity – in this case the Cl/H substitution reaction. Our own data suggest a more significant difference in reaction ratio, presumably due to the difference in the synthesis/type of catalyst. The data suggest that the isomer ratio can thus be affected by catalyst (and reactor) control.

Table 4.6

Gas-phase hydrodechlorination of 0.16 % 1,2-Dichlorobenzene in H_2 over 1% Pd/Al_2O_3 catalyst

Catalyst	Flowrate	T reactor	Convers	Selectivity %		
100 mg	ml/min	T°C	%	Benzene	Clbenz	DiClbenz
1% $Pd//Al_2O_3$	20	100	30.3	14.52	15.79	69.7
	50	100	30.5	16.38	14.11	69.5
	100	100	28.1	16.68	11.39	71.93
	20	150	64	49.31	15	35.68
	50	150	50.6	36.37	11.22	52.[illegible]
	100	150	44.4	30.9	9.04	60.05
	200	150	37.8	24.31	7.2	68.53
	20	250	99.5	98.78	0.51	0.49
	50	250	99.4	98.63	0.76	0.57
	100	250	99.7	99.61	0.12	0.27
	200	250	99.2	98.69	0.42	0.88
	50	350	100	100		
	100	350	100	100		
	200	350	100	100		
	50	450	100	100		
	100	450	100	100		

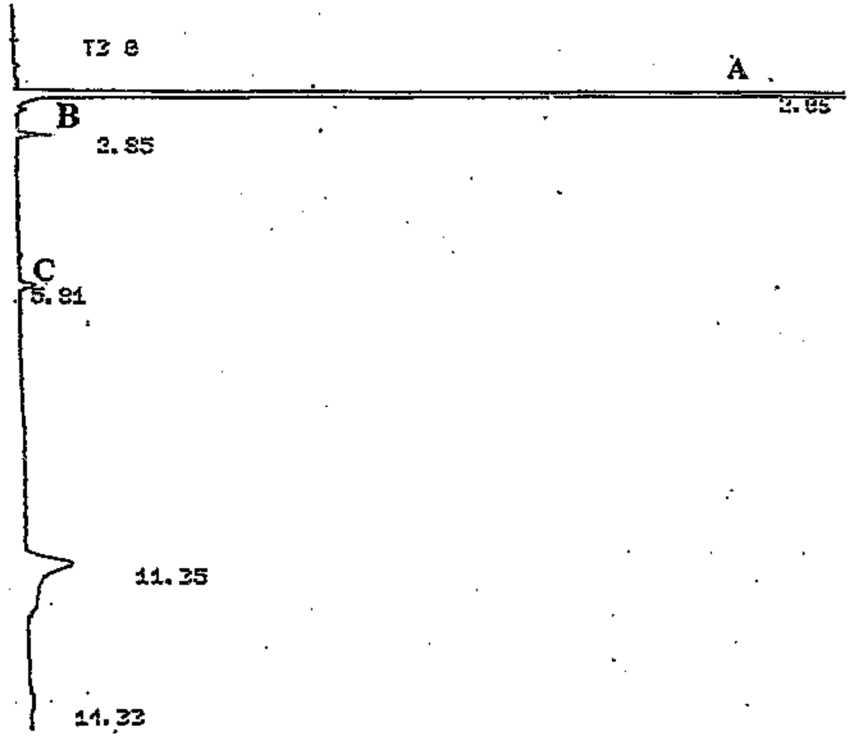

Fig 4.16

Gas-phase hydrodechlorination of 0,16% 1,2-DiClbenzene in H_2 over 1% Pd/Al_2O_3 catalyst 50 ml/min H_2 flow rate when: A- Benzene; B- Chlorobenzene; C- o-Dichlorobenzene.

Table 4.7

Gas-phase hydrodechlorination of 1.6% 1,4-Dichlorobenzene in H_2 over 1% Pd/Al_2O_3 catalyst

Catalyst	Flowrate	T reactor	Conver	Selectivity %		
100 mg	ml/min	T°C	%	Benzene	Clbenz	DiClbenz
1% Pd/Al_2O_3	20	100	66,2	56.5	9,81	33,7
	50	100	48.5	37.7	10.78	51.5
	100	100	37,7	27,2	10.47	62,3
	20	150	53.2	26.8	26.49	46.7
	50	150	37.5	21.9	15,66	62.4
	100	150	37,6	18,1	19,51	62.4
	20	250	99.2	97,5	1,66	0.75
	50	250	97.8	93.7	4.16	2,23
	100	250	95,9	90.3	5.84	4,04
	20	350	99.8	99.7	0.18	0.16
	50	350	98,1	96.6	1,56	1.9
	100	350	88.6	81.1	7.37	11.5
	20	450	97.9	97.7	0,96	2.16
	50	450	95,3	95,6	1.77	4.8
	100	450	95,3	94,6	2.28	4,8

4.4.5 Hydrodechlorination of trichlorobenzene

The approach to be followed here will be to discuss the effect of the various metals on the above reaction and then to draw conclusions from the findings. **Gold catalysts.** The gold catalysts were supported on both C/Al_2O_3 and Al_2O_3 (Table 4.8). Poor conversions were noted as is presented in Fig 4.17. Indeed the data are suggestive of a reaction that is not influenced by the gold (compare yield given in Table 4.4). An increase in the ortho isomer selectivity has occurred with a ratio of m/p/o dichlorobenzene products: 0.42:0.49:1 and 0.51:0.65:1. The dichlorobenzene ratios can be seen in Table 4.2.2. However the low yield does not make this an attractive procedure for making high yields of the ortho isomer.

Nickel catalysts. Data from this study are shown in Tables 4.3, 4.3.1 and 4.9. If the data from Tables 4.9 are compared with the blank data and to those with supports (Tables 4.4 and 4.10) it can be seen that there is very poor conversion in the presence of the metals as is also presented in Fig 4.18. Conversion at 450 °C over Ni supported on MgO, Al_2O_3 and C/Al_2O_3 at flowrates of 50 - 300 ml/min are all poor. Both the addition of quartz beads and carbon as a catalyst diluent results in poorer conversions.

An increase in the ortho isomer selectivity has occurred with a ratio of m/p/o dichlorobenzene products : 0.23:0.24:1 (1% Ni/ Al_2O_3+quartz beads) but the addition of carbon results in a decrease in the ortho and an increase in the meta and para isomers - 1.13:1.19:1. The dichlorobenzene ratios can be seen in Table 4.2.2. Some change in the m/p/o dichlorobenzene product ratio is to be noted. The reason for this relates to the use of the different supports, loadings and different reaction conditions applied. For example, 8.6 %

Ni/Al_2O_3, which exhibits very poor conversion to m/p/o dichlorobenzene products revealed a product ratio as follows : 0.22:0.21:1 (350°C reaction temperature, 50 ml/min flow rate). However 1 % Ni/Al_2O_3 catalyst, which also exhibited very poor conversion to m/p/o dichlorobenzene products gave a different ratio (1.1:1.31:1; at 450°C reaction temperature, 100 ml/min flow rate). On the other hand 5,7 % Ni/TiO_2 catalyst treated in 8% industrial trichlorobenzene in H_2, which revealed a high conversion to m/p/o dichlorobenzene products, demonstrated the highest m-isomer yield with a product distribution ratio m/p/o 1.3:0.95:1 (250°C reaction temperature, 100ml/min flow rate). This means that the catalyst influences the product ratio.

Thus the following are to be noted:

1) Ni catalysts supported on Al_2O_3 and C/Al_2O_3 revealed the highest yields of the para isomer; however Ni supported on MgO, Al_2O_3 with quartz beads, (8,6% Ni) revealed more ortho isomer.

2) It can be seen that the isomer ratio can be affected by both the reaction conditions and the type of support.

3) The poor overall conversions do not make this a viable route to the dichlorobenzenes.

Table 4.8

Hydrodechlorination of Trichlorobenzene over 1% Au/Al_2O_3, 1% Au/Al_2O_3/C catalysts

Catalyst	T reactor	Flowrate	Convers	Selectivity %					
100 mg	°C	ml/min	%	Benzene	Clbenz	m-DiClbenz	p-DiClbenz	o-DiClbenz	TriClbenz
2.5% Trichlorobenzene in H_2									
1% Au/Al_2O_3	450	50	7.65	0.38	0.29	1.55	1.80	3.63	92.35
	450	100	4.17	0.20	0.36	0.81	0.97	1.82	95.83
	450	300	2.08	0.13	0.18	0.40	0.50	0.86	97.92
1% Au/Al_2O_3/C	450	50	5.86	0.17	0.54	1.22	1.56	2.37	94.14
	450	100	2.33	0.06	0.15	0.50	0.66	0.96	97.67
8% Trichlorobenzene in H_2									
1% Au/Al_2O_3/C	450	100	0.43	0.06	0.07	0.07	0.09	0.15	99.57

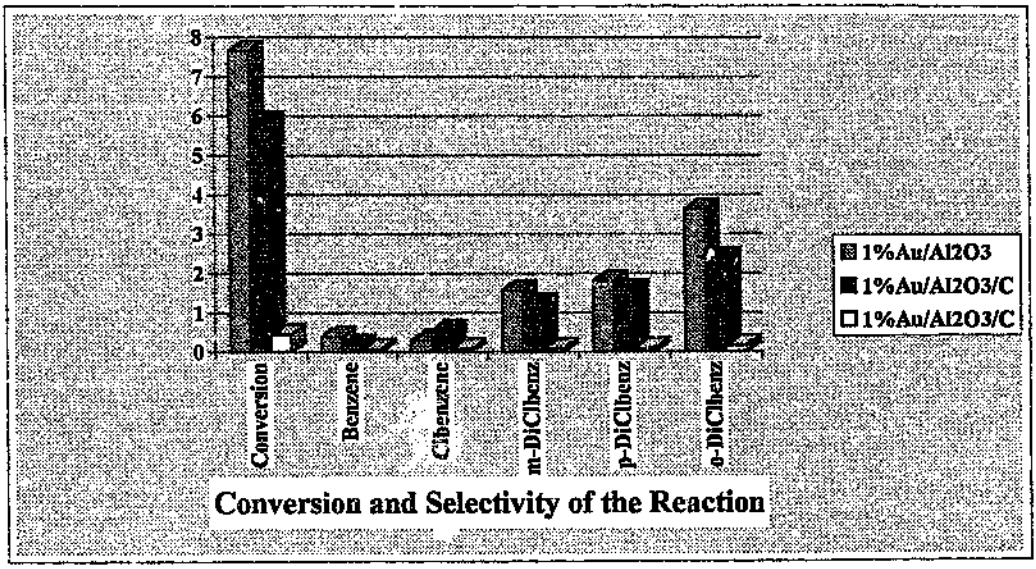

Fig.4.17
A hydrodechlorination reaction of trichlorobenzene over 1% Au/Al_2O_3 and 1% $Au/Al_2O_3/C$ catalysts.

Catalyst	% H_2 in triClb
1%Au/Al_2O_3	2,5 %
1%$Au/Al_2O_3/C$	2,5 %
1%$Au/Al_2O_3/C$	8,0 %

Table 4.9

Gas-phase hydrodechlorination of 1,2,4-Trichlorobenzene over Ni metal catalyst with different supports

Catalyst	T reactor	Flowrate	Convers	Selectivity %					
100 mg	°C	ml/min	%	Benzene	Clbenz	m-DiClbenz	p-DiClbenz	o-DiClbenz	TriClbenz
2,5% 1,2,4-TriClbenzene in H_2									
1% Ni/Al_2O_3/C	150	200	2.06	1.31	0.00	0.00	0.00	0.75	97.94
	250	100	0.38	0.19	0.03	0.00	0.00	0.17	99.62
	400	100	14.52	1.74	6.43	1.98	2.30	2.07	85.48
	450	200	12.62	1.06	2.36	3.14	3.30	2.77	87.38
	500	100	12.39	1.40	2.12	2.73	3.16	2.98	87.61
	500	200	[illegible].70	1.90	2.68	2.85	3.23	3.05	86.30
1% Ni/Al_2O_3	150	100	0.13	0.13	0.00	0.00	0.00	0.00	99.87
	250	100	2.96	0.08	1.71	0.85	1.02	0.84	97.04
	450	100	37.16	7.00	11.60	6.00	7.15	5.45	62.[illegible]
	450	200	28.46	1.71	6.63	6.37	7.36	6.38	71.54
	450	300	15.82	0.55	2.72	4.07	4.50	3.98	84.18
1% Ni/Al_2O_3+ quartz beads	450	100	7.08	1.72	1.36	0.63	0.66	2.71	92.92
	450	200	2.65	0.16	0.26	0.63	0.74	0.87	97.35
8,6% [illegible]l_2O_3	250	50	0.68	0.12	0.04	0.15	0.14	0.38	99.17
	350	50	2.14	0.66	0.2	0.24	0.22	1.05	97.63
	350	100	1.61	0.56	0.14	0.16	0.15	0.74	98.25
	450	50	26.63	14.45	3.15	1.09	1.01	6.93	73.37
	450	100	9.78	4.72	1.31	0.53	0.49	3.22	89.73
0.8% Ni\MgO	450	100	2.03	0.10	0.11	0.35	0.42	1.04	97.97
8%1,2,4-TriClbenzene in H_2									
1% Ni\Al_2O_3	450	50	0.97	0.01	0.05	0.27	0.31	0.33	99.03
	450	100	2.97	0.07	0.17	0.85	1.02	0.84	97.03

Table 4.10

Blank gas-phase hydrodechlorination of 2.5% 1,2,4-Trichlorobenzene in H_2

Flow rate	T reactor	T evapor	Convers	Selectivity %					
ml/min	°C	°C	%	Benzene	Clbenz	m-DiClbenz	p-DiClbenz	o-DiClbenz	TriClbenz
50	150	85	4.93		0.1	0.76	0.62	3.44	95.07
100	150		4.43		0.08	0.76	0.64	2.93	95.58
20	250	85	7.49	0.51	0.88	1.05	0.85	4.22	92.51
100	250		6.18	0.23	0.4	0.91	0.76	3.88	93.82
50	350	85	10.77	0.32	0.36	1.48	1.07	7.62	89.23
100	350		10.06	0.18	1	2.07	1.84	4.98	39.94
100	450	85	3	0.08	0.11	0.77	0.99	1.04	97

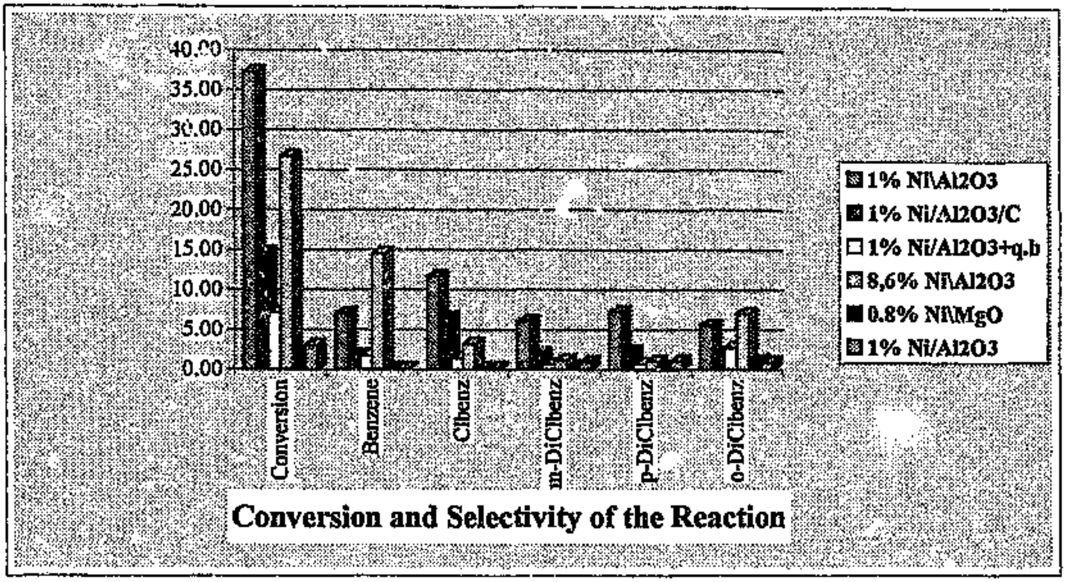

Fig 4.18

A comparison of the selectivity of the products in the hydrodechlorination of trichlorobenzene at 450°C over Ni metal with different supports

Catalyst	% H_2 in triClb
1% Ni\\Al_2O_3	2,5 in 1,2,4-
1% Ni/Al_2O_3/C	2,5 in 1,2,4-
1% Ni/Al_2O_3+q.b	2,5 in 1,2,4-
8,6% Ni\\Al_2O_3	2,5 in 1,2,4-
0.8% Ni\MgO	2,5 in 1,2,4-
1% Ni/Al_2O_3	8 in 1,2,4-

More success was achieved with the Ni/TiO_2 catalysts (see Table 4.3 and 4.3.1). Here good conversions to all products was achieved. Illustration of the conversion and selectivity of all products can be seen in Fig.4.19.

Effect of metal loading. As the metal loading is increased (1 % to 5.7 % the conversion increases, although the increase is marginal above 0.5 % Ni). This suggests the reaction is not limited by the number of metal sites but may be limited by diffusional issues at the higher loadings.

Effect of flow rate. The expected decrease in reaction yield with increased flow rate was observed. However, the yield of p-dichlorobenzene was twice that of the ortho isomer (as can be seen in Tables 4.2 and 4.2.1). The product ratio (p/o) for the hydrodechlorination reactions over 1% and 5.7 % Ni/TiO_2 catalysts treated with 2.5% and 8% 1,2,4-trichlorobenzene in H_2 at 250°C reaction temperature, and a 100 ml/min flow rate are 3.15; 3.72 (2.5%) and 1.76; 2.06 (8%) respectively.

The effect of flow rate is very clear (Tables 4.2 and 4.2.1). For example, setting the flow rate to 50 ml/min compared to 100 ml/min over 5.7 % Ni/TiO_2 catalyst in 2.5% 1,2,4-trichlorobenzene in H_2, showed a decrease in reactivity yielding product ratio (p/o) of 3.72 and 3.06 respectively. Similar results were detected when the same catalyst was treated in 8% 1,2,4-trichlorobenzene in H_2 with product ratios of 2.06 and 1.87 respectively. The observed product ratios were as follow : p/m 1.67; p/o 3.72 and m/o 2.23. However the 5.7 % Ni/TiO_2 catalyst treated with 8% industrial trichlorobenzene gave the highest yield of m-dichlorobenzene. In these experiments the product distribution of the three isomers are about the same. The product ratios are as follows : p/m 0.66; p/o 0.75 and m/o 1.14.

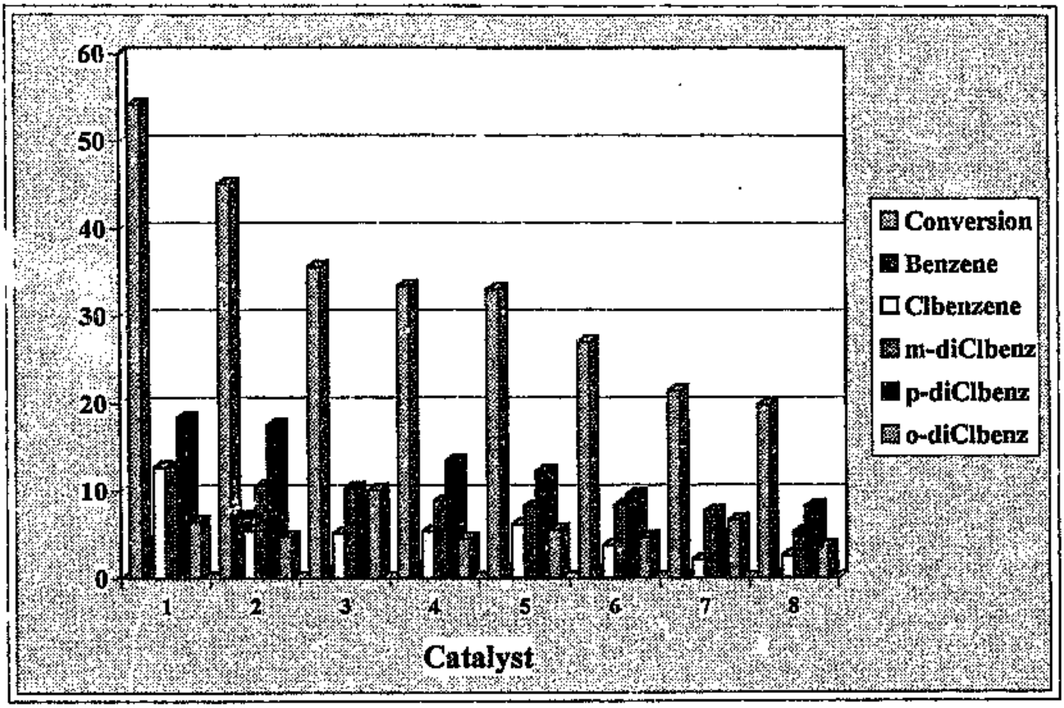

Fig 4.19
A comparison of the selectivity of the reaction in the hydrodechlorination of trichlorobenzene over Ni/TiO$_2$ catalyst with different loadings.

Seq	Catalyst	H$_2$ in triClbenz
1	5.7%Ni/TiO$_2$	%2.5 in 1,2,4-
2	1%Ni/TiO$_2$	%2.5 in 1,2,4-
3	5.7%Ni/TiO$_2$	%4.8 in ind
4	5.7%Ni/TiO$_2$	%2.5 in ind
5	1%Ni/TiO$_2$	%8 in 1,2,4-
6	5.7%Ni/TiO$_2$	%8 in 1,2,4-
7	5.7%Ni/TiO$_2$	%8 in 1,2,4-
8	0.5%Ni/TiO$_2$	%8 in 1,2,4-

Effect of Reagent Concentration. As expected the higher the reagent concentration the poorer the conversion.

Palladium catalysts. Data from this study are shown in Tables 4.11 and 4.12. The palladium catalysts were supported on C/Al_2O_3, Al_2O_3 and Al_2O_3/quartz beads. Both the addition of quartz beads and carbon as a catalyst diluent resulted in lower conversions. There is no change in the m/p/o dichlorobenzene product ratio to be noted.

A very high increase in the ortho isomer selectivity has occurred with a ratio of m/p/o dichlorobenzene products : 0.12:0.06:1, 0.15:0.07:1 and 0.89:0.02:1 on use of Pd/Al_2O_3, Pd/C/Al_2O_3, and Pd/Al_2O_3 catalysts. The dichlorobenzene ratios can be seen in Table 4.2. A comparison of the data from Tables 4.11 and 4.12 with the blank results (Tables 4.4 and 4.10) shows that there is a very high conversion (98.4-98.5 %; 150-250°C reaction temperature, 50-100 ml/min flow rate (Table 4.11)).

The complete conversion to benzene can also be seen in Fig 4.20.

Even at 100°C reaction temperature a high conversion to benzene (90.7 %; Table 4.11) was obtained.

The catalyst was also used in the hydrodechlorination reaction of industrial trichlorobenzene. The highest conversion of trichlorobenzene to benzene (91.7 to 93.7 %) can be obtained with 350-450°C reaction temperature, 20-50-100 ml/min flow rate (Table 4.12). As is evident, a complete hydrodechlorination reaction has occurred.

Effect of flow rate. The expected decrease in reaction yield with increased flow rate was observed.

Table 4.11

Gas-phase hydrodechlorination of 2.5% 1,2,4-Trichlorobenzene in H_2 over Pd/Al_2O_3 catalyst with different supports.

Catalyst	T reactor	Flowrate	Convers	Selectivity %					
100 mg	°C	ml/min	%	Benzene	Clbenz	m-DiClbenz	p-DiClbenz	o-DiClbenz	TriClbenz
1% Pd/Al_2O_3	100	50	90.76	80.43	2.31	0.82	0.44	6.76	9.24
	100	100	79.78	61.92	3.5	1.62	0.87	11.86	20.22
	150	50	98.40	98.40					1.60
	250	100	98.55	98.30	0.25				1.45
1% Pd/Al_2O_3+	250	200	14.99	9.46	1.72	0.63	0.45	2.74	85.01
quartz beads	450	200	26.91	21.71	2.23	1.38	0.04	1.55	73.09
1% $Pd/Al_2O_3/C$	100	100	67.18	30.36	8.07	3.56	1.58	23.61	32.82
	250	100	95.21	91.00	1.22	0.42	0.25	2.44	4.79
	450	100	95.12	92.04	0.83	0.28	0.22	1.74	4.88

Table 4.12

Hydrodechlorination of 0.016% industrial Trichlorobenzene in H_2 over 1% Pd/Al_2O_3 catalyst

Catalyst	Flow rate	T reactor	Conver	Selectivity %					
100 mg	ml/min	ToC	%	Benzene	Clbenz	m-DiClbenz	p-DiClbenz	o-DiClbenz	TriClbenz
1 % Pd/A_2O_3	100	100	37.3	10.5	5.31	2.84	1.54	17.4	62.7
	200	100	29.2	7.6	4.05	2.28	1.2	14.03	70.8
	20	150	83.2	77.9	1.27			1.41	16.8
	50	150	82.4	80.9	0.85			0.97	17.6
	100	150	82.4	74.8	2.99	0.72	0.64	3.48	17.6
	200	150	81.8	68.3	5.04	1.53	1.33	6.34	18.2
	20	250	79.1	79.1					20.9
	50	250	77.6	77.6					22.4
	100	250	86.5	85.6	0.68			0.37	13.5
	200	250	88.3	86.5	1.24			0.56	11.7
	20	350	91	91					9
	50	350	91.7	91.7					8.3
	100	350	79.5	79.2	0.19				20.5
	20	450	89.8	89.8					10.2
	100	450	93.7	93.7					6.3

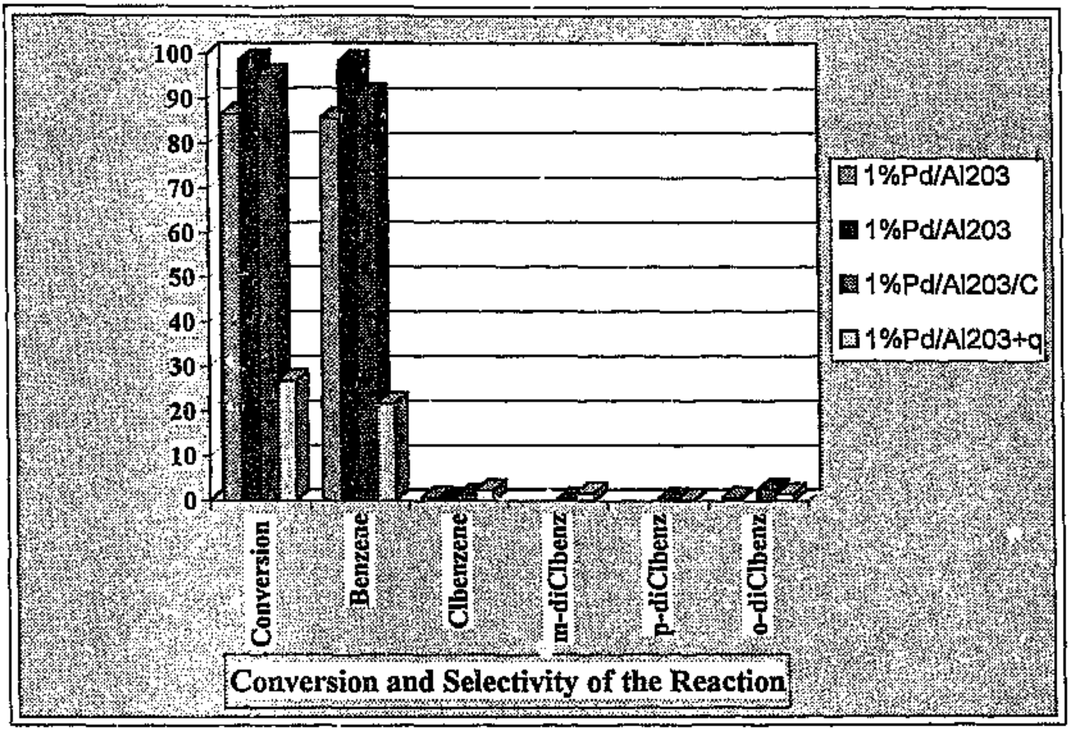

Fig 4.20

A comparison of the selectivity of the reaction in the hydrodechlorination of trichlorobenzene over 1%Pd metal catalyst with different supports.

Catalyst	H_2 in triClbenz
1%Pd/Al$_2$0$_3$	%0.016 in ind
1%Pd/Al$_2$0$_3$	%2.5 in 1,2,4-
1%Pd/Al$_2$0$_3$/C	%2.5 in 1,2,4-
1%Pd/Al$_2$0$_3$+q.b.	%2.5 in 1,2,4-

4.5 Catalytic hydrodechlorination of substituted chlorinated benzene

To further understand the workings of the Pd/Al_2O_3 catalyst the effect of ring substituents on the hydrodechlorination of chlorinated benzenes was investigated.

4.5.1 Hydrodechlorination of chlorotoluene

The data for the hydrodechlorination reaction are shown in Table 4.13. The dominant reaction in this experiment was the removal of the Cl group with very little formation of chlorobenzene (< 0,6 %). Fig 4.21 presents the gc spectrum of the products from the chlorotoluene catalysed reaction. The reaction yield increased with temperatures less than 250 °C; above 250 °C there was a decrease in yield. This suggests a competing reaction is occurring in the reactor.

To evaluate the effect of the ring methyl group on the reaction the data for this experiment can be compared directly with the data in Table 4.5. The data in Table 4.5 clearly shows that the presence of the methyl group enhances the reaction (250 °C, all flowrates). Thus an electron donating group enhances the C-Cl bond cleavage in the presence of the Pd catalyst.

When the data in Table 4.13 is compared to the data in Tables 4.6, 4.11 and 4.14 the effect is different : chlorotoluene which contains a methyl group showed lower activity. This suggests that the methyl group causes a decrease in reactivity.

Table 4.13

Gas-phase hydrodechlorination of 1.6% 3-Cltoluene in H_2 over 1% Pd/Al_2O_3 catalyst

Catalyst	T evapor	Flow rate	T reactor	Conver		Selectivity	%	
100 mg	°C	ml/min	°C	%	Benzene	Toluene	Clbenz	3-Cltoluene
1% Pd//Al_2O_3	20	20	100	12.1		12.1		87.9
		50	100	8.9		8.9		91.1
		100	100	8.9		8.9		91.1
		200	100	6.7		6.7		93.3
		20	150	63,2	0,21	62,77	0.05	36.8
		50	150	49.2	0,17	49,02		50,8
		100	150	39,8	0,09	39,66		60,2
		200	150	32,2	0,07	32,14		67,8
		20	250	87	0,57	86,46		13
		50	250	68,8	0,36	68.4	0,1	31,2
		100	250	60,3	0,28	59,98		39.7
		200	250	51.3	0.19	51,06		48.7
		20	350	76,3	0,4	75,87	0,04	23.7
		50	350	63.9	0.27	63,63	0,05	36.1
		100	350	63.6	0.29	63,27	0,06	36,4
		200	350	47.5	0,17	47,32		52,5
		20	450	37,2		36.93	0.13	62.8
		50	450	17.8		17.66	0.07	82,2
		100	450	8,8		8,8	0,14	91,2
		200	450	6.3		6.29		93,7

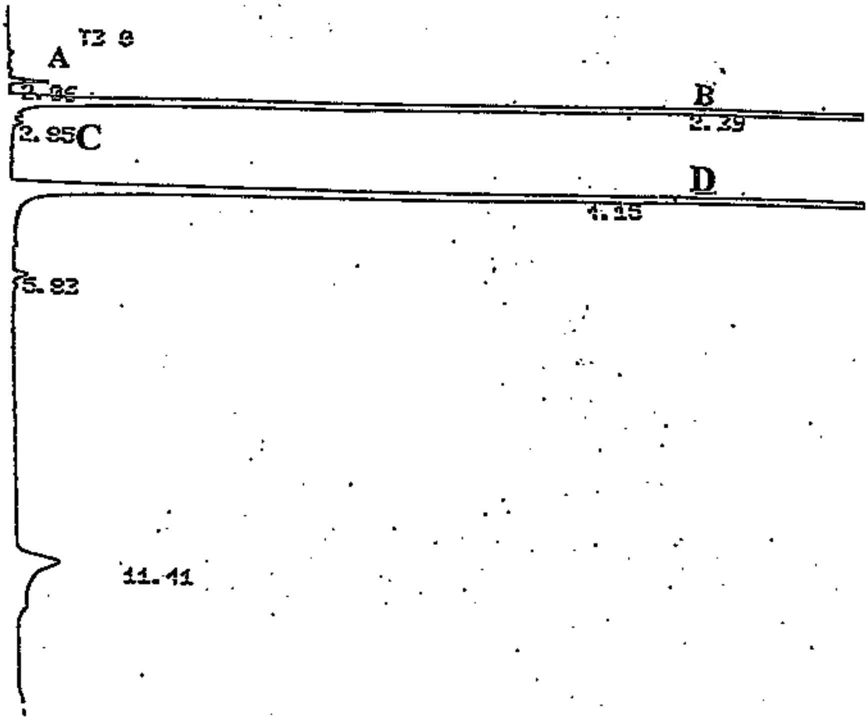

Fig 4.21

Gas-phase hydrodechlorination of 0,16% 3-Cltoluene in H_2 over 1% Pd/Al_2O_3 catalyst, 50 ml/min H_2 flow rate, when A- Benzene; B- Toluene; C- Chlorobenzene; D- Chlorotoluene.

4.5.2 Hydrodechlorination of chloroaniline

Data obtained from a study of the hydrodechlorination reaction are shown in Table 4.14. The remarkable feature of this reaction is that the presence of the NH_2 group results in the breakdown of the benzene ring in the presence of the Pd catalyst. Gc analysis revealed the presence of methane and ethylene in the product stream (see Fig 4.22).

The hydrodechlorination reaction is facile and reaches a maximum conversion (98.1% at 350 °C) of chloroaniline to benzene with a value of 93.86 % selectivity.

A comparison with the data shown in Table 4.14 (same reagent concentration, temperature etc.) reveals that the chloroaniline reacts faster than the chlorobenzene as can be seen in Table 4.5 (150 °C) but the substituent removed is different. The NH_2 is readily removed, even at 150 °C with a high conversion to products (85.4%).

Both the NH_2 and the Cl can be removed from the reagent. However they are removed in consecutive steps. Once the NH_2 group is removed the reaction merely becomes a hydrodechlorination reaction of chlorobenzene. Removal of the Cl group in preference to the NH_2 group is only a minor competing reaction at 450 °C.

The data thus indicate that the Pd catalyst can readily dehydrochlorinate the chloroaniline under mild reaction conditions, but that the product obtained is benzene.

Our studies do not at this stage provide a good explanation for the observations. Aniline, a weak base, is made even weaker by the presence of the Cl substituent. Whether the NH_2 portion of the molecule is now made more readily accessible to interaction with the Pd (or the support) and in this way yields the benzene cleavage reaction is not known. Further studies will be required to determine the factors responsible for the reaction.

Table 4.14

Gas-phase hydrodechlorination of 0.16 % 1,2-Claniline in H_2 over 1% Pd/Al_2O_3 catalyst

Catalyst	T evapor	T reactor	Flow rate	Convers	Selectivity %					
100 mg	°C	°C	ml\min	%	Methane	Ethylene	Benzene	Clbenz	Aniline	2-Claniline
1% Pd/Al_2O_3	50	150	20	85.4	3.43	0.67	41.29	39.82		14.6
			100	75.2	2.72	1.6	36.21	32.12		24.8
		250	20	97.4	2.88	0.85	93.43	0.19		2.6
			100	97.1	4.51	1.2	91.21	0.18		2.9
		350	20	98.1	3.92	0.97	93.86	0.13		1.9
			100	97.9	3.07	0.89	93.65	0.13		2.1
		450	20	98.9	2.25	0.56	92.1	3.04	0.91	1.1
			100	97.9	5.9	1.39	93.87	1.71	0.34	2.1

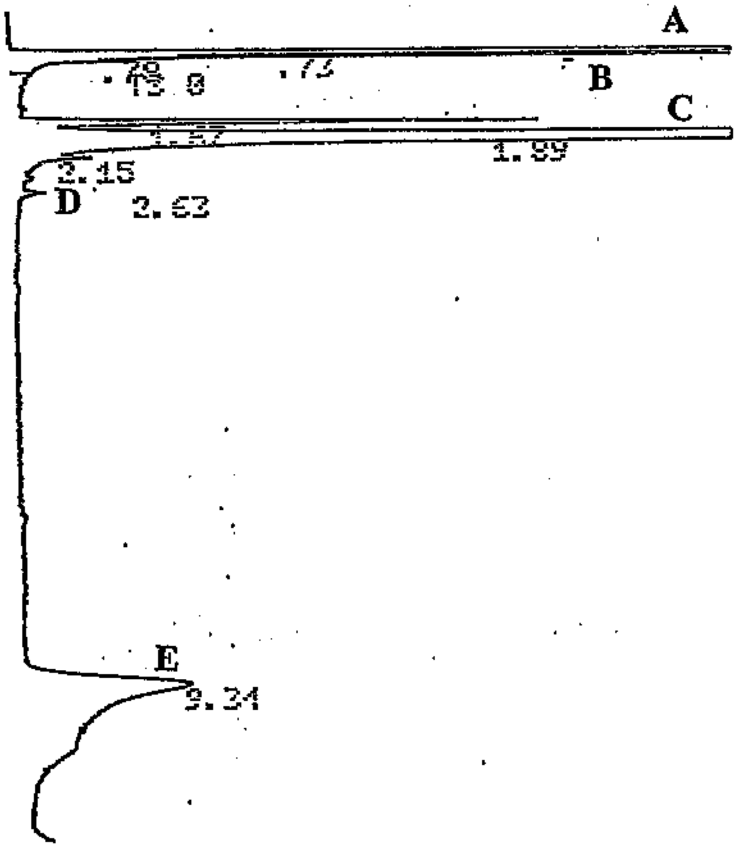

Fig 4.22

Gas-phase hydrodechlorination of 0,16 % 2-Chloroaniline in H_2 over 1% Pd/Al_2O_3 catalyst 100 ml/min H_2 flow rate, when A- Methane; B-Ethylene; C- Benzene; D- Chlorobenzene; E- Chloroaniline.

4.6 Catalytic hydrodechlorination of chlorinated hydrocarbons

The ability to hydrodechlorinate the aromatic complexes above suggested that hydrodechlorination of hydrocarbons with the Pd/Al_2O_3 catalyst should be feasible. 1,2 Dichloroethane was thus chosen for study. The reaction of 6% 1,2-dichloroethane in H_2 over a 1% Pd/Al_2O_3 catalyst was thus investigated. The results are displayed in Table 4.15. The products observed in the reaction were found (by gc procedures: see (Fig 4.23)) to be methane, ethylene, ethane, chloroethane, and vinyl chloride.

There was no starting material observed at 100 °C. There was no vinyl chloride observed either.

Under the low temperature conditions ethane and ethylene are the major products i.e. both Cl's are readily removed from the starting material. At the higher flow rates the ethene/ethane ratio increases suggesting that the hydrogenation reaction of ethene is a secondary reaction. The higher yields of chloroethane are consistent with this picture.

In the intermediate temperature range, i.e. 250 °C and 350 °C, a lower conversion is noted. At 450 °C a 100 % reaction of the starting material is to be seen. Two processes must be occurring as a function of temperature. The decrease, we suspect, is due to carbon build up on the catalyst through reagent or product decomposition. At the higher temperature this carbon is proposed to be removed by reaction with H_2. The large amount of methane formed would be consistent with this proposal.

In the reaction it is clear that a variety of atom removal steps take place. A possible network sequence to show these reactions is displayed below:

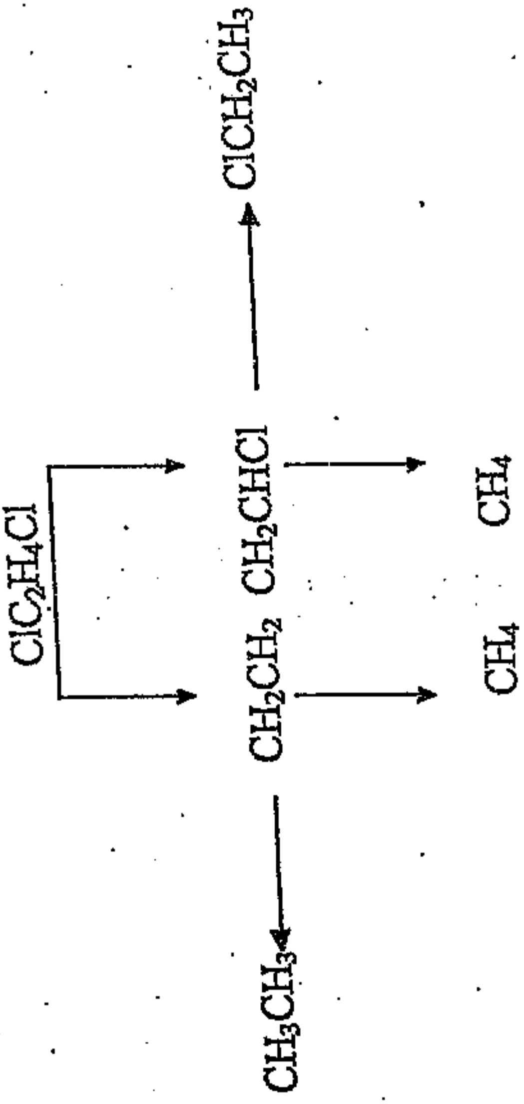
ClC_2H_4Cl
CH_2CH_2
CH_2CHCl
$ClCH_2CH_3$
CH_3CH_3
CH_4
CH_4

Table 4.15

Gas-phase hydrodechlorination of 6% 1,2-Dichloroethane in H_2 over 1% Pd/Al_2O_3 catalyst

Catalyst	T evapor	T reactor	Flowrate	Conver	Selectivity %					
100 mg	°C	°C	ml/min	%	Methane	Ethylene	Ethane	Clethane	Vinilchlor	DiClethane
1%Pd/Al_2O_3	20	100	20	100	0,34	50.74	40,9	10.31		
			50	100	2,45	52,45	31,95	13.12		
			100	100	2,26	54,79	31,6	11,27		
		250	20	88.1	0,26	44,7	27,61	12,02	3,4	11,9
			50	77,6	0,16	27,56	21,9	26,76	1,23	22,4
			100	74	0,25	37,09	11,62	20,79	4,27	26
		350	20	96,7	0,59	43,3	34,02	7.92	10,86	3,3
			50	95,9	0,54	44,09	29,68	9,11	12,26	4,1
			100	92.1	0,56	47,92	12,15	15,21	16,16	7,9
		450	20	100	0.6	38,39	43,2	6,53	11,28	
			100	100	4,84	50,96	28,73	8,14	7,33	

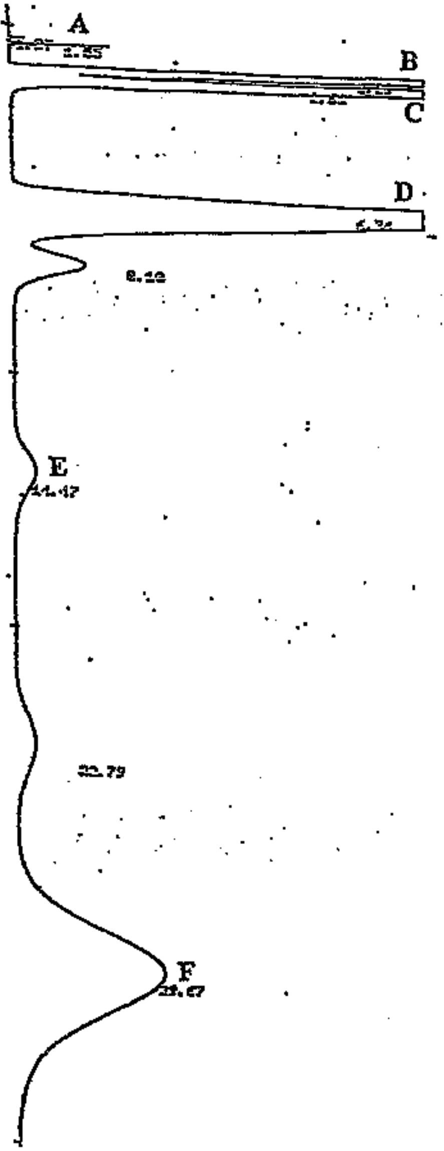

Fig 4.23

Gas-phase hydrodechlorination of 6% 1,2-Dichloroethane in H_2 over 1% Pd/Al_2O_3 catalyst 50 ml/min H_2 flow rate, when A.- Methane; B- Ethylene; C- Ethane; D- Chloroethane; E- Vinilchloride; F- Dichloroethane.

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CHAPTER 5 CONCLUSIONS

It is well known, that approximately 20 % of all waste streams contain halogenated aromatics, which are extremely hazardous to the environment.

Catalysed chlorine replacement by hydrogen of chlorinated benzenes such as 1,2,4-trichlorobenzene has been shown to be an effective method for resolving the above technological problem. Catalytic removal of chlorine was also found to apply to substituted chlorinated benzenes such as 3-chlorotoluene, 2-chloroaniline as well as to 1,2-dichloroethane.

The data obtained in the study has been summarised below.

A range of catalysts were found to hydrodechlorinate the above mentioned chlorinated reagents under a range of reaction conditions - flow rate, reactor temperature and % gas in the reagent stream. It was found that the presence of a metal (as Pd, Ni, Au, etc.) was required in the reaction.

The use of a 5,7 % Ni/TiO_2 catalyst was shown to give the highest conversion of 1,2,4-trichlorobenzene to m/p/o-dichlorobenzene isomers.

The selectivity in the hydrodechlorination reaction of 1,2,4-trichlorobenzene was found to be highest for on 5,7 % Ni/TiO_2 (to dichlorobenzene isomers) and lowest for 1 % Au/Al_2O_3 catalysts (Figs 4.19 and 4.17). Maximum conversions using the above catalysts were 54.1 and 8 % respectively with a dichlorobenzene product ratio meta/para/ortho - 2:2.9:1 and 0.42:0.49:1.

The optimal reaction conditions were found to be at 250 °C reaction temperature, 100 ml/min flow rate in H_2 and 2,5 % 1,2,4-trichlorbenzene in

H_2. This led to a 37 % conversion to the dichlorobenzenes. These dichlorobenzenes have vast potential commercial applicability in the dye, insecticide and parasiticide industries.

A 1 % Pd/Al_2O_3 catalyst has been found to be a catalyst which exhibits very high activity in the *complete* hydrodechlorination of 1,2,4-trichlorobenzene. The complete conversion of 1,2,4-trichlorbenzene to benzene (98.5 %) was obtained at 250° C (Fig 4.20).

The complete conversion was also obtained of industrial trichlorobenzene to benzene (91.7 to 93.7 %) at 350° and 450 °C.

Optimal conditions for complete hydrodechlorination of 1,2,4-trichlorobenzene was found to be at 250°C temperature reaction, 100 ml/min flow rate, 2.5% 1,2,4-trichlorobenzene in H_2 over 1 % Pd/Al_2O_3. On the other hand optimal conditions for complete hydrodechlorination of industrial trichlorobenzene was found to be at 350°C temperature reaction, 50 ml/min flow rate, 0.016% industrial trichlorobenzene in H_2 over 1 % Pd/Al_2O_3.

It is interesting to note that different ratios of dichlorobenzenes could be produced from the trichlorobenzene using different catalysts. For example 1% and 5,7 % Ni catalyst supported on TiO_2 gave more p-dichlorobenzene also supported on Al_2O_3. However 8,6 % Ni catalyst supported on Al_2O_3 gave more o-dichlorobenzene isomer. Furthermore Pd/Al_2O_3 also gave more o-dichlorobenzene isomer. A 5,7 % Ni catalyst supported on TiO_2 gave more m-dichlorobenzene when the temperature of evaporation was increased to 115-120 °C (4,8 and 8 % reagent in H_2)

The above catalyst was also found to be effective for the hydrodechlorination of substituted chlorinated benzenes, such as 3-chlorotoluene and 2-chloroaniline (Figs 4.13 and 4.14).
The 1 % Pd/Al_2O_3 was also found to catalytically hydrodechlorinate 1,2-dichloroethane (Fig 4.14).

The primary objectives of the project have thus been accomplished. Some attempt was made to characterise the catalysts both before and after reaction. However, this was not a primary objective of the study and consequently much more work will still be needed to correlate catalyst characteristics with the catalyst activity.

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