OXIDE SUPPORTED ORGANIC LAYER CATALYSTS.

Thesis Submitted To The University Of Glasgow
In Fulfilment Of The Requirement Of The
Degree Of Doctor Of Philosophy.

Fiona McMonagle.

Department Of Chemistry,
University Of Glasgow.
Glasgow.
May, 1995.

ACKNOWLEDGEMENTS.

I would like to thank my supervisor, Dr.J.M.Winfield, for his help and guidance throughout this work.

I would also like to express my appreciation for the invaluable help I have received from the technical staff, in particular Stuart Johnstone, glassblower, for his many talents, Larry McGhee and Rose " Shuffle Off To Buffalo" Millar for technical advice and entertainment. I would also like to thank staff at I.C.I., Runcorn for their help, in particular with B.E.T. and G.C.M.S. analysis and also Dr.J.Whitley and A.Wilson at S.U.R.R.C. for all their assistance.

Thanks also go to all of my colleagues, past and present, in the Fluorine, Catalysis and Inorganic Groups - Isobel, Bob, Colin, Nicky, Mark, Elaine, David, Rosie, Alan, Campbell, Ron, Graham, Paul, Norman, Paul, Peter, Dave, Larry, Billy, Irene, Phil, Vicky and Stuart - You all made it a pleasure to come to work each day!

Finally, I am of course indebted to my parents and my family for all their help and support throughout my studies - I couldn't have done it without you.

TABLE OF CONTENTS.

PAGE.

Acknowledgements. i.

Table Of Contents. ii.

Summary. iii.

Chapter 1. Introduction.

1.1. Background: CFCs And The Environment. 1.

1.2. Catalytic Routes To CFCs And CFC Alternatives. 5.

1.3. Heterogeneous Catalysts For Halogenation Reactions. 10.

1.4. Definition Of Acid And Base Concepts. 14.

1.5. Halogenation Of Chromia And Alumina Catalysts For Halogen Exchange Reactions. 18.

1.6. Oxide Supported Organic Layer Catalysts For Room Temperature Catalytic Halogenation Reactions. 25.

1.7. Aims. 27.

Chapter 2. Experimental.

2.1. Equipment.

2.1.1.The Vacuum System. 30.

2.1.2.Pyrex Glass Vacuum Line. 30.

2.1.3.Monel Metal Vacuum Line. 31.

2.1.4.Flow Line For Conditioning Reaction And Catalytic Reaction. 32.

2.1.5.Inert Atmosphere Box. 33.

2.2. Preparation And Purification Of Reagents.

2.2.1. Radioisotopes. 33.
2.2.2. Preparation Of [^{18}F]-Fluorine Labelled Caesium Fluoride. 34.
2.2.3. Preparation Of [^{18}F]-Fluorine Labelled Boron Trifluoride And Sulphur Tetrafluoride. 35.
2.2.4. Preparation And Purification Of [^{36}Cl]-Chlorine Labelled Hydrogen Chloride. 37.
2.2.5. Preparation And Purification Of [^{36}Cl]-Chlorine Labelled 1,1,1-Trichloroethane. 38.
2.2.6. Purification Of 1,1,1-Trichloroethane. 39.
2.2.7. Purification Of 1,1-Dichloroethene. 39.
2.3. Preparation Of Catalysts. 40.

2.4. Catalyst Pretreatment.

2.4.1. Calcination Of Catalysts. 41.
2.4.2. Room Temperature Reaction Of Sulphur Tetrafluoride With Calcined Catalysts. 42.
2.4.3. Room Temperature Reaction Of SF_4 Fluorinated Catalysts With 1,1,1-Trichloroethane. 42.

2.5. Infrared Spectroscopy.

2.5.1. Transmission Infrared Spectroscopy In The Vapour Phase Over Surface Reactions. 43.
2.5.2. Identification Of Gaseous Samples. 43.

2.5.3. Diffuse Reflectance Infrared Fourier Transform Spectroscopy. (D.R.I.F.T.S). 44.
2.6. Gas Chromatography. 45.

2.7. Radiochemical Counting.

2.7.1. Geiger Müller Counters. 45.
2.7.2. Plateau Regions. 47.
2.7.3. Background. 47.

2.8. Direct Monitoring Geiger Müller Counting Technique.

2.8.1. Equipment. 48.
2.8.2. Experimental Method. 49.
2.9. Scintillation Counters. 49.
2.10. Counting Vessels. 50.
2.11. Statistical Errors. 51.
2.12. Decay Correction. 52.

Chapter 3. Comparisons Of γ-Alumina And Chromias With Respect To Fluorination And Conditioning Reactions.

3.1. Introduction. 54.

3.2. Experimental.

3.2.1. Infrared Analysis of The Volatile Materials From The Sulphur Tetrafluoride Fluorination Process On γ-Alumina Under Static Conditions. 57.

3.2.2. Analysis Of Sulphur Tetrafluoride Fluorination Process By Pressure Changes. 57.
3.2.3. Analysis Of The Volatile Materials From The 1,1,1-Trichloroethane Conditioning Process Of SF$_4$ Fluorinated γ-Alumina Under Static Conditions. 58.
3.2.4. Analysis Of 1,1,1-Trichloroethane Conditioning Process On SF$_4$ Fluorinated γ-Alumina Under Flow Conditions In A Monel Metal Reactor. 59.
3.2.5. Infrared Study Of The Reaction Of 1,1,1-Trichloroethane With SF$_4$ Fluorinated γ-Alumina With Time. 60.
3.2.6. B.E.T. Surface Analysis. 60.
3.2.7. D.R.I.F.T.S. Study Of Adsorbed Pyridine Species On Calcined, Fluorinated And Conditioned γ-Alumina. 61.

3.3. Results.

3.3.1. I.R. Analysis Of Volatile Material From The SF$_4$ Fluorination Process. 62.
3.3.2. Analysis Of Sulphur Tetrafluoride Fluorination Process By Pressure Changes. 62.
3.3.3. I.R. Analysis Of The Volatile Material From The 1,1,1-Trichloroethane Conditioning Process. 63.
3.3.4. G.C. Analysis Of The Volatile Material From The 1,1,1-Trichloroethane Conditioning Process In Monel Metal Reaction Vessels. 63.

3.3.5.G.C.Analysis Of The Volatile Material From The 1,1,1-Trichloroethane Conditioning Process In Pyrex Glass Reaction Vessels. 65.

3.3.6.G.C.Analysis Of The Volatile Material From The 1,1-Dichloroethene Conditioning Process In Monel Metal Reaction Vessels. 67.

3.3.7.Analysis Of The Mass Changes Of The Solids From The 1,1,1-Trichloroethane Conditioning Process In Pyrex Glass Reaction Vessels. 68.

3.3.8.Analysis Of The Volatile Material From The 1,1,1-Trichloroethane Conditioning Process By *In Situ* Gas Infrared Spectroscopy. 70.

3.3.9.Analysis Of The Volatile Material From The 1,1-Dichloroethene Conditioning Process By *In Situ* Gas Infrared Spectroscopy. 72.

3.3.10.Analysis Of The Volatile Material From The Interaction Of Anhydrous Hydrogen Chloride With 1,1,1-Trichloroethane Conditioned, SF_4 Fluorinated Materials. 74.

3.3.11.Analysis Of The 1,1,1-Trichloroethane Conditioning Process On SF_4 Fluorinated γ-Alumina Under Flow Conditions. 74.

3.3.12.B.E.T Surface Area Analysis. 76.

3.3.13.D.R.I.F.T.S. Study Of Adsorbed Pyridine Species On Calcined, Fluorinated And Conditioned γ-Alumina. 77.

3.4. Discussion.

3.4.1.SF_4 Fluorination Reactions. 79.

3.4.2.BF_3 Fluorination Reactions. 82.

3.4.3.1,1,1-Trichloroethane Conditioning Reaction. 83.

3.4.4.D.R.I.F.T.S. Study Of Adsorbed Pyridine Species. 90.

Chapter 4. Interaction Of [^{18}F]-Fluorine Labelled Gases With Oxide Surfaces: Uptake And Exchange Reactions.

4.1. Introduction. 93.

4.2. Experimental.

4.2.1.Exchange Reactions At Room Temperature Of [^{18}F]-Fluorine Labelled Sulphur Tetrafluoride With SF_4 Fluorinated γ-Alumina And CH_3CCl_3 Conditioned, SF_4 Fluorinated γ-Alumina. 97.

4.2.2.Fluorine Uptake Reactions At Room Temperature Of [^{18}F]-Fluorine Labelled Boron Trifluoride With Calcined γ-Alumina. 98.

4.2.3.Fluorine Uptake Reactions At Room Temperature Of [^{18}F]-Fluorine Labelled Boron Trifluoride With SF_4 Fluorinated γ-Alumina And CH_3CCl_3 Conditioned, SF_4 Fluorinated γ-Alumina. 99.

4.2.4. Determination Of Specific Count Rate Of

[^{18}F]-Fluorine Labelled Sulphur Tetrafluoride And

Boron Trifluoride. 100.

4.2.5. Exchange Factors. 101.

4.3. Results.

4.3.1. Exchange Reactions At Room Temperature Of

[^{18}F]-Fluorine Labelled Sulphur Tetrafluoride With

SF_4 Fluorinated γ-Alumina And CH_3CCl_3 Conditioned,

SF_4 Fluorinated γ-Alumina. 103.

4.3.2. Exchange Reactions At Room Temperature Of

[^{18}F]-Fluorine Labelled Boron Trifluoride With

SF_4 Fluorinated γ-Alumina And CH_3CCl_3 Conditioned,

SF_4 Fluorinated γ-Alumina. 105.

4.3.3. Exchange Reactions At Room Temperature Of

[^{18}F]-Fluorine Labelled Boron Trifluoride With

SF_4 Fluorinated Chromia And Volcano Chromia And

CH_3CCl_3 Conditioned, SF_4 Fluorinated Chromia

And Volcano Chromia. 107.

4.3.4. Exchange Reactions At Room Temperature Of

[^{18}F]-Fluorine Labelled Boron Trifluoride With

BF_3 Fluorinated γ-Alumina And Volcano Chromia. 109.

4.3.5. Fluorine Uptake Reactions At Room Temperature Of

[^{18}F]-Fluorine Labelled BF_3 With Calcined

γ-Alumina And Volcano Chromia. 110.

4.3.6.Fluorine Uptake Reactions At Room Temperature Of [^{18}F]-Fluorine Labelled BF_3 With SF_4 Fluorinated γ-Alumina And CH_3CCl_3 Conditioned, SF_4 Fluorinated γ-Alumina. 113.

4.3.7.Fluorine Uptake Reactions At Room Temperature Of [^{18}F]-Fluorine Labelled BF_3 With SF_4 Fluorinated Chromia And Volcano Chromia And CH_3CCl_3 Conditioned,SF_4 Fluorinated Chromia And Volcano Chromia. 116.

4.4. Discussion.

4.4.1.[^{18}F]-SF_4 and [^{18}F]-BF_3 Fluorine Exchange Reactions. 120.

4.4.2.[^{18}F]-BF_3 Fluorine Uptake Experiments. 125.

4.4.3.[^{18}F]-BF_3 Fluorine Exchange Reactions With BF_3 Fluorinated Materials. 127.

Chapter 5. Interaction Of [^{36}Cl]-Chlorine Labelled Hydrogen Chloride And 1,1,1-Trichloroethane With γ-Alumina, Chromia and Volcano Chromia.

5.1.Introduction. 129.

5.2.Experimental.

5.2.1.Interaction At Room Temperature Of [^{36}Cl]-Chlorine Labelled Anhydrous Hydrogen Chloride With Calcined γ-Alumina. 132.

5.2.2. Interaction At Room Temperature Of [^{36}Cl]-Chlorine Labelled 1,1,1-Trichloroethane With SF_4 Fluorinated γ-Alumina. 133.

5.3. Results.

5.3.1. Interaction At Room Temperature Of [^{36}Cl]-Chlorine Labelled Hydrogen Chloride With Calcined, SF_4 Fluorinated And CH_3CCl_3 Conditioned, SF_4 Fluorinated γ-Alumina And Chromia Samples. 135.

5.3.2. Interaction At Room Temperature Of [^{36}Cl]-Chlorine Labelled 1,1,1-Trichloroethane With SF_4 Fluorinated And CH_3CCl_3 Conditioned, SF_4 Fluorinated γ-Alumina, Chromia And Volcano Chromia. 139.

5.4. Discussion.

5.4.1. [^{36}Cl]-Chlorine Labelled Hydrogen Chloride Adsorption Studies. 144.

5.4.2. Treatment Of Fluorinated Materials With [^{36}Cl]-Chlorine Labelled 1,1,1-Trichloroethane. 148.

5.4.3. Treatment Of Conditioned Materials With [^{36}Cl]-Chlorine Labelled 1,1,1-Trichloroethane. 152.

Chapter 6. Reaction Of Anhydrous HF And 1,1,1-Trichloroethane Over Oxide Supported Organic Layer Catalysts.

6.1. Introduction. 155.

6.2. Experimental.

6.2.1. Catalytic Fluorination Of 1,1,1-Trichloroethane With Anhydrous HF Over Oxide Supported Organic Layer Catalysts Under Static Conditions. 158.

6.2.2.Extraction And Analysis Of Organic Layer Material From 1,1,1-Trichloroethane Conditioning Of SF_4 Fluorinated γ-Alumina And Volcano Chromia Samples. 159.

6.3.Results.

6.3.1.Catalytic Fluorination Of 1,1,1-Trichloroethane With Anhydrous HF Over Oxide Supported Organic Layer Catalysts Under Static Conditions. 160.

6.3.2.Extraction And Analysis Of Organic Layer Material From 1,1,1-Trichloroethane Conditioning Of SF_4 Fluorinated γ-Alumina And Volcano Chromia Samples. 163.

6.4.Discussion.

6.4.1.Catalytic Activity Of Organic Layer Material. 168.

6.4.2.Extraction Of Organic Layer Material. 170.

Chapter 7. Discussion And Conclusions.

7.1.Discussion.

7.1.1.Fluorination Process. 174.

7.1.2.Conditioning Process. 178.

7.1.3.Comparisons Between The Reactions Of γ-Alumina, Chromia And Volcano Chromia. 183.

7.2.Conclusions. 186.

References.

SUMMARY.

A study has been made of the production of oxide supported organic layer catalysts at room temperature. The preparation involves the fluorination of the oxide surface with SF_4, which enhances the Lewis acidity of the surface. This is followed by conditioning with CH_3CCl_3, a reaction in which CH_3CCl_3 is dehydrochlorinated to $CH_2=CCl_2$ and HCl. The dehydrochlorination product, $CH_2=CCl_2$ undergoes further dehydrochlorination resulting in the laydown of an oligomeric organic layer on the surface. This organic layer is active, at room temperature, as a catalyst for fluorination of CH_3CCl_3 with HF. Comparisons have been made among γ-alumina, chromia prepared by hydrolysis of chromium nitrate and "volcano chromia" prepared by pyrolysis of ammonium dichromate. The catalytic properties of chromia-based materials have been demonstrated in, for example the reaction between HF and CH_3CCl_3 at temperatures >600K.

[^{18}F]-Fluorine radiotracer studies have been used to examine the behaviour of fluorine species on these materials. This aspect of the work indicates that γ-alumina, chromia and "volcano chromia" behave similarly. A "pool" of labile fluorine exists on these materials. The large values determined for fluorine exchange indicate that not only surface fluorine, but also bulk fluorine species are involved in the exchange process.

Examination of the conditioning process by G.C. and in situ I.R. analysis of the volatile products indicates that SF_4 fluorination of γ-alumina, chromia and volcano chromia creates Lewis acid sites capable of dehydrochlorinating

CH_3CCl_3. Hydrofluorination reactions are also observed, producing CH_3CCl_2F, CH_3CClF_2 and CH_3CF_3, with the product distribution dependent on the support material.

[^{36}Cl]-Chlorine radiotracer studies were used to examine the conditioning process. It is demonstrated that $H^{36}Cl$ is adsorbed on fluorinated materials and that the conditioning process has little effect on $H^{36}Cl$ adsorption. Studies of the reactions of [^{36}Cl]-CH_3CCl_3 indicate that chlorine containing organic material is laid down on SF_4 fluorinated γ-alumina, chromia and volcano chromia. Treatment of fluorinated materials that had been pretreated with CH_3CCl_3 with [^{36}Cl]-CH_3CCl_3 also results in incorporation of [^{36}Cl]-chlorine containing material on the surfaces: it is suggested that this material is adsorbed on the surface and also incorporated into the organic layer material. Introduction of HCl to [^{36}Cl]-CH_3CCl_3 treated materials indicates that a portion of the [^{36}Cl]-chlorine containing material can be displaced. *In situ* I.R. analysis of the reaction of HCl with conditioned materials indicates that hydrochlorinated and hydrofluorinated materials can be displaced from the oligomeric organic layer.

Determination of the activity at room temperature of the oxide supported organic layers as catalysts in the reaction of CH_3CCl_3 with HF indicate that both γ-alumina and "volcano chromia" are effective supports for these catalysts. Reactions on both surfaces result in hydrofluorination reactions, producing CH_3CCl_2F and also other fluorinated products. From the results obtained, it appears that "volcano chromia" is more active initially, but

γ-alumina is able to sustain the reaction over a longer time.

The organic material has been removed from the solid supports by solvent extraction. GCMS studies indicate that this material is based on C_2 units and contains fluorine and chlorine, although the chlorine is lost by hydrolysis on exposure to atmosphere.

INTRODUCTION.

"Humanity is conducting an enormous, unintended, globally pervasive experiment whose ultimate consequence could be second only to global nuclear war. It is imperative to act now"

"The Changing Atmosphere" Conference, Toronto May 1988.

1.1 BACKGROUND : CFCS AND THE ENVIRONMENT.

Commercial fluorocarbon chemistry dates from the 1890s, when F.Swarts discovered that antimony trifluoride and pentafluoride reacted with C-Cl bonds to form C-F bonds and was developed by Midgley and Hennes in the 1920s and 1930s (1). Chlorofluorocarbon compounds (CFCs) were developed jointly by General Motors and Dupont in the 1930s as an alternative, non-toxic, non-flammable refrigerant to replace SO_2 and NH_3 that were in use at that time (2). CFCs have no natural counterparts and are only manufactured by human industrial activities.

It was the chemical inertness of chlorofluorocarbon compounds that made them attractive for various industrial uses, such as aerosol propellants, foam blowing agents, solvents, refrigerants and carrier gases. For simplicity a numerical nomenclature is used for CFCs: From left to right, first digit = no of C atoms minus 1(not included for C_1 compounds where it = 0), second digit = no of H atoms plus 1 and the third digit = no of F atoms.Isomer rules: most symmetrical has no suffix, increasing asymmetry denoted by alphabetical suffixes a,b,c etc (8). In 1981, CFC production was a world wide industry with production of CFC-11 estimated as 3.1 x 10^8 kg and CFC-12 at 4.5 x 10^8 kg (2). By 1988 the annual consumption of these CFCs had risen to more than 11.4 x 10^8 kg. The use of CFCs leads ultimately to their release into the atmosphere. Comparisons of the rate of emission of CFCs with estimates of the rate at which they were being destroyed indicated that in effect five-sixth of the CFCs released each year stayed in the atmosphere (2). The chemical inertness that industry found so appealing proved to be the root of the greatest environmental problems caused by these compounds.

In 1973 Jim Lovelock and co-workers (3) reported the presence of halogenated hydrocarbons in the troposphere. The quantities of CFCs were equal, within experimental error, to the amounts ever manufactured. Tropospheric inertness of CFCs was thus confirmed and lifetimes of hundreds of years were indicated. Molina and Rowlands (4) realised that chlorine atoms from such reactions were a serious threat to the ozone layer because of their long atmospheric lifetimes. It is not until CFCs reach the stratosphere that enough energy is supplied by the increasing ultraviolet radiation to cause breakdown of the molecules by photolysis of the C-Cl bonds:

e.g. $CF_2Cl_2 \xrightarrow{h\nu} {}^{\cdot}CF_2Cl + Cl^{\cdot}$ Eqn.1.1.

The formation of ozone molecules occurs by the mechanism:

$O_2 \xrightarrow{h\nu} 2O^{\cdot}$ Eqn.1.2.

$O^{\cdot} + O_2 \rightarrow O_3$ Eqn.1.3.

The chlorine radicals produced by the breakdown of the CFC molecules disrupt the formation of ozone by the mechanism:

$$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2 \qquad \text{Eqn.1.4.}$$

$$ClO^{\cdot} + O^{\cdot} \rightarrow Cl^{\cdot} + O_2 \qquad \text{Eqn.1.5.}$$

So, the overall effect of CFCs on ozone is :

$$O^{\cdot} + O_3 \rightarrow 2O_2 \qquad \text{Eqn.1.6.}$$

The chlorine radical sets off a chain reaction which can involve the destruction of hundreds of thousands of ozone molecules before the chlorine radical joins with another radical and terminates the chain reaction. The main "sink" for chlorine radicals is HCl, which can be transported across the troposphere and subsequently "rained out".

Ozone in the stratosphere is constantly being created and constantly destroyed by photochemical reactions. A natural balance had been established between the two processes which ensured that the amount of ozone in the stratosphere remained virtually constant. However, the action of CFCs has increased the rate at which ozone is destroyed without any compensating increase in the rate of its production. The resultant reduction in the ozone layer is proving to have a dramatic effect on the environment, plants, animals and humans (5). Ozone protects living systems from the full intensity of solar ultraviolet radiation. Ozone has a strong absorption at wavelengths 230nm-290nm and is the only species in the atmosphere which is capable of reducing the sun's radiation at this wavelength. Macromolecules such as nucleic acids and proteins are damaged by radiation of wavelength shorter that 290nm. Therefore, decrease in the ozone allows the entering radiation to damage natural vegetation and crops and cause skin cancer.

In view of the growing scientific evidence of the effect of chlorine from chlorofluorocarbon compounds and also bromine from bromofluorocarbon compounds (Halons) on the seasonal loses of ozone, The Montreal Protocol on Substances That Deplete The Ozone Layer in 1987, called for a decrease in chlorofluorocarbon production to 50% of the 1986 level by 1988 and a freezing of the production of Halons at the 1986 level by 1992. Subsequent legislation due to social and political pressure has called for an end to the production of chlorofluorocarbons and chlorocarbons in the U.S. by the end of 1995, with the European deadline at the start of 1995. The production of Halons was halted in 1994. Manzer (6) refers to a Dupont report which estimated that about 60% of the projected CFC demand in the year 2000 will be satisfied by non fluorocarbon alternatives or will be eliminated by better conservation practices. The ban of ozone depleting substances has necessitated the search for alternatives to chlorofluorocarbons for the remaining 40% of applications which has been undertaken with unprecedented speed. The ideal replacement from an industrial viewpoint would be a "drop-in" replacement where little alteration would be required in the production methods and the practical applications. Any alternatives to CFCs will have to have properties very close to those of the CFCs they replace. The most feasible alternatives at present are hydrofluorocarbon (HFC) and hydrochlorofluorocarbon (HCFC) compounds, for example CH_2FCF_3 (HFC-134a), $CClFHCClF_2$ (HCFC-123) and CH_3CCl_2F (HCFC -141b). The suggested replacements have shorter lifetimes, generally less than twenty years, as they are broken down in the lower atmosphere and therefore the tropospheric concentration will be lower than that of the compounds they are replacing. However, as HCFCs contain chlorine and therefore have ozone depletion potential they are viewed as transition compounds to allow the rapid phase out of CFCs until better alternatives can be developed. HCFCs are to be phased out by 2030. Hydrofluorocarbons contain no chlorine and therefore have zero ozone depletion potential. However, another environmental problem caused by the release of gases into the atmosphere is global warming. Most of the HCFCs and HFCs and their final decay products are "greenhouse gases" which contribute to global warming and could affect the climate if concentrations became too large and are therefore not entirely environmentally friendly.

1.2. CATALYTIC ROUTES TO CFCs AND CFC ALTERNATIVES.

The industrial production of CFCs was dominated by two routes: homogeneous catalytic fluorination using liquid HF and $SbCl_5$, especially used in the synthesis of C_1 compounds and heterogeneous catalytic fluorination by HF vapour using chromia catalysts, used for compounds in the $C_2Cl_{6-n}F_n$ ($n=3$-5) series.

There are a variety of routes and starting materials for HCFC and HFC production and also many potential problems, such as selectivity and catalytic deactivation. The production of HFCs and HCFCs uses chlorocarbon or chlorohydrocarbon feedstocks and HF as the fluorinating agent. The use of anhydrous HF as a fluorinating agent has its obvious problems due to its toxicity and highly corrosive nature (7,8). There is little direct information regarding the adsorption behaviour of HF in this area of heterogeneous catalysis, although a two site model for the adsorption of HF on CrF_3 has been reported (9). There is also little information regarding the adsorption of CFCs onto catalytic surfaces. Studies of adsorption of chlorofluoromethanes on aluminium (III), chromium (III), iron (II) and (III) fluorides (10), chloroethanes on alumina (11) and CCl_2FCClF_2 on UO_2 (12) indicate that CFCs and related molecules are weakly adsorbed on metal oxide and fluoride surfaces. As further evidence, transmission I.R. spectroscopy has been used to detect CFC compounds adsorbed on lanthanide (III) halides (13) and DRIFTS has been used to detect physically adsorbed CFCs on chromia surfaces (14).

The two distinct routes in production of CFCs and related compounds will now be considered in more detail:

(i) Homogeneous Catalytic Fluorination.

As stated earlier, homogeneous fluorination of chlorine containing compounds using antimony halides was developed by Swarts. This procedure is still important in, for example, the preparation of perhalogenated chlorofluoropropanes (15) using SbF_3/Cl_2. The route for large scale catalytic preparation of CFC-12 and other C_1 CFCs employs liquid HF and $SbCl_5$ as a catalyst. This route has recently been developed to produce HCFCs (18).

The nature of the Sb^V species active for catalytic fluorination reactions is complicated and depends on the exact reaction conditions used. Kolditz (16) suggested that $SbCl_4F$ and $SbCl_2F_3$ were the active species for the fluorination of CCl_4 and that the reaction proceeds by fluorine-bridged binuclear intermediates. $SbCl_4F$ was also indicated to be the catalytically active species in the fluorination of $CHCl_3$ by Santacesaria et al (17), where the mechanism of the process was described as a rapidly established equilibrium step:
$HF + SbCl_5 \rightleftharpoons SbCl_4F + HCl$ followed by F-for-Cl nucleophilic substitution reactions on the carbon, with the rate decreasing as the fluorine content increases. Blanchard and co-workers (18-20) have studied the fluorination of CH_3CCl_3 with $HF/SbCl_5$ under a variety of conditions. The reaction of $SbCl_5$ with HF results in antimony mixed halides, the exact composition depending on the reaction temperatures and the molar ratios used. At 233K the catalytically active species is $SbCl_5.4HF$ and the reaction of CH_3CCl_3 produces CH_3CCl_2F. At 333K the catalytically active species is $SbCl_4F.4HF$ and the catalytic fluorination of CH_3CCl_3 results in CH_3CCl_2F, CH_3CClF_2 and CH_3CF_3. The reaction is accompanied by the formation of a purple organic material and is thought to proceed via a dehydrochlorination-hydrofluorination route. The selectivity is better at low temperatures since the first C-Cl bond in CH_3CCl_3 is the easiest to break. The strength of this bond increases in

conjunction with the number of fluorine atoms bonded to the carbon (19) and so for further substitutions a higher temperature is required.

(ii) Heterogeneous Catalytic Fluorination.

Catalytic fluorination of hexachloroethane (C_2Cl_4/Cl_2) or chlorofluoroethanes by hydrogen fluoride has been one of the most commonly used methods for the production of CFCs

$C_2Cl_6 \rightarrow C_2Cl_5F \rightarrow C_2Cl_4F_2 \rightarrow C_2Cl_3F_3 \rightarrow$ etc. Eqn.1.7.

The catalysts most widely used in this process include aluminium trifluoride and alumina-based or chromia-based catalysts. The reaction has been studied widely for many years (21) due to its importance in the production of CFCs. There has been great emphasis on determining the reaction conditions necessary for maximizing the yield of a particular compound (22,23). The reactions in this system were initially described as a combination of catalytic fluorination and chlorination reactions, dismutation and isomerization reactions (21,40,115).

e.g. Fluorination: $C_2Cl_3F_3 + HF \rightarrow C_2Cl_2F_4 + HCl$ Eqn.1.8.
Isomerisation: $CCl_2F\text{-}CClF_2 \rightarrow CCl_3\text{-}CF_3$ Eqn.1.9.
Dismutation: $2C_2Cl_3F_3 \rightarrow C_2Cl_4F_2 + C_2Cl_2F_4$ Eqn.1.10.

From a mechanistic standpoint, an ionic model explained the exchange of fluorine and chlorine in terms of acidic catalytically active sites. The CFC dissociates into the chloride ion and its respective carbocation. The chloride ion bonds to an acid centre on the catalyst whilst halogen transfer takes place. However, radiotracer techniques indicated a different mechanism and the Halogen Exchange Model was developed (24-26). The use of radiotracers allows for direct observation of the surface adsorbed species and allows a detailed study of the interactions to establish the relevant reaction mechanisms. Initially it was thought that halogen exchange involved a concerted dismutation process in which halogen is transferred between molecules rather than between a molecule and the catalyst surface. In the case of isomerisation, transfer within the molecule occurs and the acid sites adsorb the molecule whilst rearrangement takes place: it is an intramolecular rearrangement in the sense that it does not involve the surface halogen containing species that are involved in the catalytic fluorination and chlorination reactions. Isomerisation should be regarded as distinct from other reactions and therefore it is probable that different active sites are involved. Evidence has now been provided (26) to show that as well as a catalytically active fluorine species, there is also a catalytically active chlorine species present. Therefore, halogen exchange need not be a concerted mechanism. This idea of halogen exchange involves transfer of halogen from the catalyst surface to reactant molecule: an intermolecular reaction. The catalytically active chlorine which is used in chlorine-for-fluorine step originates from the fluorine-for-chlorine step.

This model involves both Bronsted and Lewis acid sites and incorporates the idea of active fluorine and chlorine species (27).

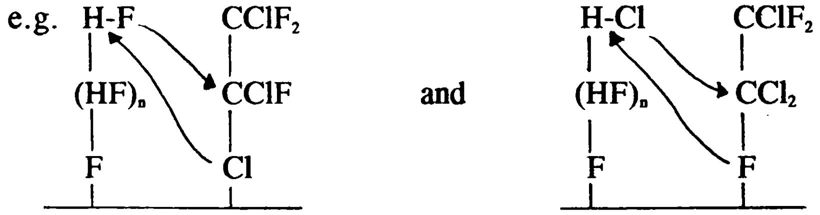


Fig.1.1. Model Mechanism for Fluorination and Chlorination Reactions.

The use of [^{36}Cl]-chlorine radiotracers supported the previous idea that isomerisation process was intramolecular. But it is now suggested that the molecule is adsorbed onto the surface in a dissociative manner such that the adsorbed fluorine species is not equivalent to any other surface fluorine species.

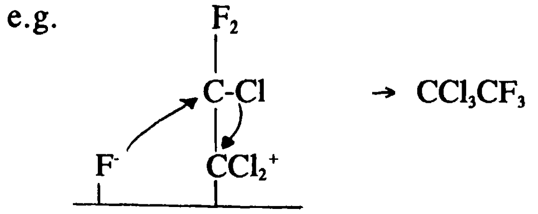


Fig.1.2. Model Mechanism for Isomerisation Reaction.

1.3. HETEROGENEOUS CATALYSTS FOR HALOGENATION REACTIONS.

(i) Chromia Catalysts.

Chromia catalysts have been used extensively in the production of chlorofluorocarbon compounds. The normal method of preparation is slow hydrolysis of $[Cr(NO_3)_3]^{3+}$ (28) or by pyrolysis of $(NH_4)_2Cr_2O_7$ (29).

Chromia has the ideal formula Cr_2O_3. It can exist in an amorphous or crystalline state. Crystalline or α-chromia has the corundum structure, where the oxide ions are hexagonally closely packed and chromium ions fill two thirds of the octahedral interstitial sites. Crystalline chromia displays little catalytic activity. However, amorphous chromia is used widely as a catalyst in reactions such as ethene polymerization (30), cyclopropane isomerization (31), dehydration of secondary alcohols (32) and dechlorination of chloroethanes (33). The exact nature of the active catalytic sites and the effects of various pretreatments on them has been the source of much speculation. Several authors have described adsorption at coordinately unsaturated sites on the chromia surface (28,34), exposed Cr^{3+}-Cr^{3+} pair sites (30,35) or at strained sites formed by elimination of H_2O from two adjacent surface hydroxyl groups (35).

Chromium oxidation states other than +3 are thought to exist in chromia. The importance of oxidation states greater than +3 in determining the activity of the catalyst has been reported. T.P.R. studies of chromia catalysts indicated the presence of Cr^{VI} and Cr^{IV} species. After extensive use in catalytic fluorination reactions, Cr^{IV} was not detected (25). An E.P.R. study of chromia has been interpreted on the basis of an electron exchange interaction between Cr^{III} and higher oxidation states (36). The presence of Cr^{VI} is necessary to promote catalytic activity towards, for example secondary alcohol dehydrogenation (32) and n-butane dehydrogenation (37).

Temperature programmed desorption and temperature programmed oxidation (T.P.D. and T.P.O.) studies determined that the catalytic activity of chromia in the fluorination of CF_3CH_2Cl to form CF_3CH_2F can be linked to the number of chromium atoms that can be reversibly oxidised (38). The results of I.R. studies on crystalline and amorphous chromia (39) suggested that dehydration of a catalyst created coordinatively unsaturated Cr^{3+} ions on the surface with coordination number of 4 or 5, as compared with the fully coordinated value of 6. As the water content of chromia decreases the activity increases. Since passage of HF over chromia dehydrates the catalyst (25), an interaction between HF and coordinatively unsaturated Cr^{3+} is possible. The presence of Cr in an oxidation state of > III is characteristic of the best chromia catalysts used in vapour-phase fluorination of chlorofluoroethanes.

The formation of crystalline α-Cr_2O_3 in catalysts used for the vapour phase fluorination of chlorofluoroethanes is an undesirable effect since it exhibits little catalytic activity (40). The difference in activity between crystalline and amorphous chromia may in part be attributable to the more open structure of the amorphous form.

(ii) Alumina Catalysts.

γ-Alumina is used as a support in many industrial catalytic processes (41,42). Transition metals (e.g. Mo, W, Co, Ni etc) supported on alumina are active towards dehydroxygenation, hydronitrogenation or hydrosulphurisation reactions (43). These catalysts are termed bifunctional since both the metal and the oxide components play an active role. Alumina is not a passive, inert support in these catalysts (43,44).

The catalytic behaviour of alumina is dependent on how it is prepared (45-50). Aluminium oxide has only one stoichiometric form (51), Al_2O_3. This simple form includes both the polymorphs and several hydrated species (52-54).

Three series of alumina have been determined, based on the close-packed oxygen lattices with aluminium ions in octahedral and tetrahedral interstices. The three series are:

The α-series: hexagonally closed-packed oxide lattices,
schematically ABAB....
The ß-series: alternating close-packed oxide lattices,
schematically ABAC-ABAC or ABAC-CABA...
The γ-series: cubic packed oxide lattices,
schematically ABC ABC....

The α-series is represented only by α-alumina, with aluminium atoms in the octahedral interstices. This is obtained in the form of stable corundum or as the decomposition product of Diaspore (55). The ß-series is represented by alkali or alkaline earth oxides containing ß-alumina and the decomposition products of Gibbsite which have related structures (56). The γ-series is prepared from the decomposition of the hydroxides bayerite, nordstandite and boehmite or by the flame hydrolysis of aluminium (III) chloride. In this work, the low temperature phase of γ-alumina was used (57). γ-Alumina is a support material that is widely used due to its high surface area and thermal stability. One of the most important structural characteristics is the cubic close-packing of the oxygen which forms a lattice that is strongly related to spinel ($MgAl_2O_4$) (58).

The unit cell of a spinel (AB_2O_4) is formed by a cubic closed packing of 32 oxygen atoms with 16 trivalent atoms in half of the octahedral interstices and 8 divalent atoms in tetrahedral holes (58). Powder X-ray diffraction has established that γ-alumina crystallizes with a spinel-related structure (55) in which 32 oxygen atoms per unit cell are arranged exactly as in a spinel, but with 21⅓ aluminium atoms distributed over the 24 available cation positions (59), giving, on average, 2⅔vacant cation sites per unit cell. The occurrence of these vacant sites contributes to the achievement of electrical neutrality. The crystallite surface containing hydroxyl groups, in place of oxygen ions, further contributes to electrical neutrality of the γ-alumina. The surface structure of γ-alumina has been discussed extensively (57,60-62). In the model for the [110] face of γ-alumina there are six distinct aluminium environments that may occur for terminal hydroxyl groups (Figs.1.3 and 1.4).

1.4. DEFINITIONS OF ACID AND BASE CONCEPTS.

(i) Brϕnsted-Lowry Definition.

In 1923 the Brϕnsted-Lowry definition of acids and bases was proposed by the Danish chemist J.N.Brϕnsted (63) and British chemist T.M. Lowry (64). This definition extended the range of acid/base systems to cover all protonic solvents. Acids are defined as proton donors and bases as proton acceptors.

Fig. 1.3.(i). [110] FACE OF SPINEL STRUCTURE.

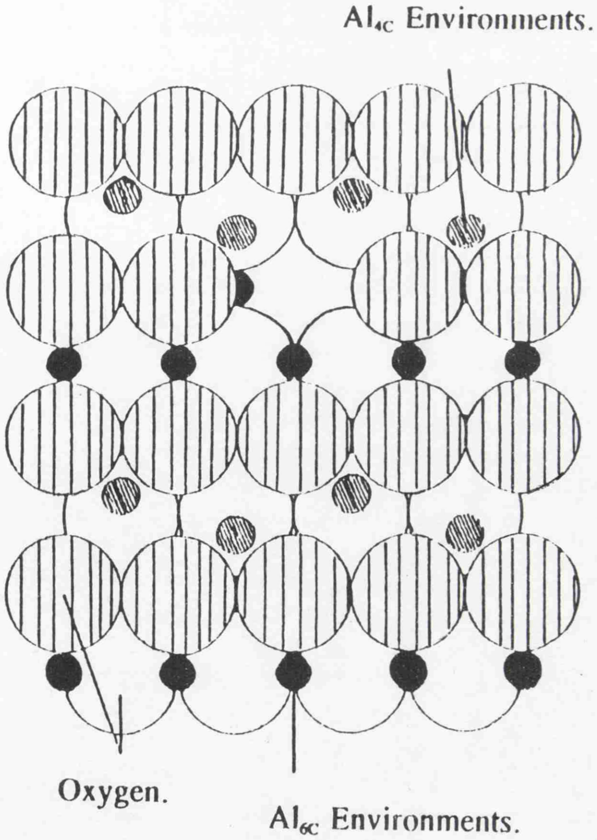
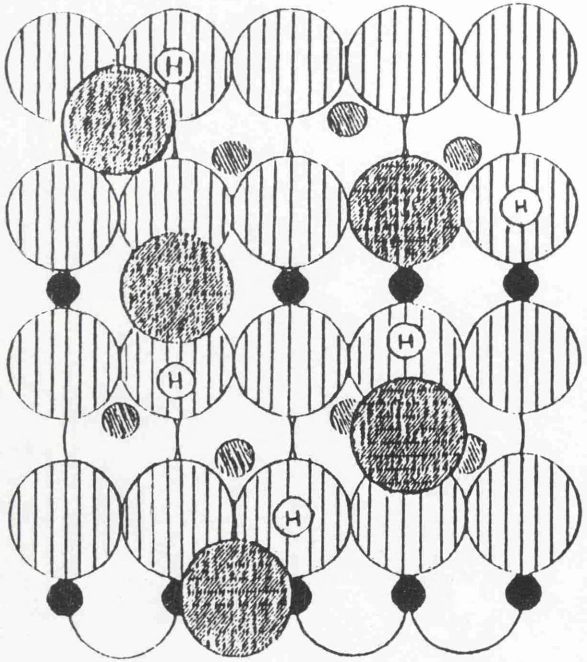
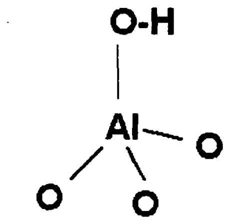
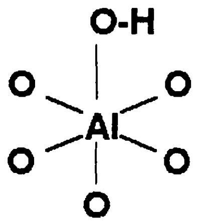


Fig. 1.3.(ii). HYDROXYL ENVIRONMENTS OF γ-ALUMINA.

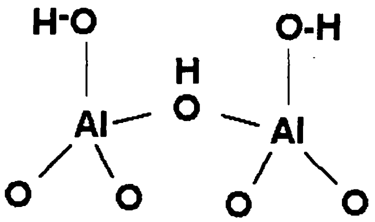




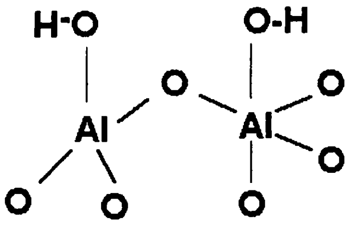
1. Tetrahedral.



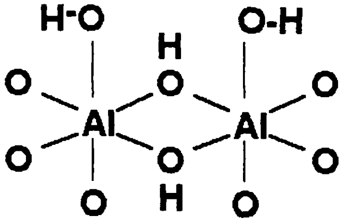
2. Octahedral.



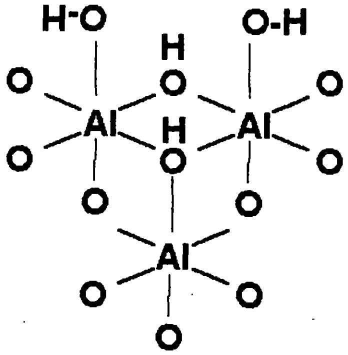
3. Tetra-O-Tetra.



4.Tetra-O Octa.



5. Octa-O-Octa.



6.Octa-O-Octa
|
Octa.

Fig.1.4. 6 Distinct Aluminium Environments For Terminal Hydroxyl Groups.

Thus, every acid will have a conjugate base:

$$\text{ACID} \rightarrow \text{CONJUGATE BASE}^- + H^+ \qquad \text{Eqn.1.11.}$$

The ionization of HCl in water is an example of a Brφnsted-Lowry acid/base system. Hydrogen chloride is a Brφnsted acid since it donates protons and Cl^- is its conjugate base. In an aqueous medium H_2O accepts protons and therefore is a base and H_3O^+ is its conjugate acid. A strong acid has a weak conjugate base and vice versa.

$$\text{e.g. } \underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightarrow \underset{\substack{\text{Conjugate}\\ \text{Acid}}}{H_3O^+} + \underset{\substack{\text{Conjugate}\\ \text{Base}}}{Cl^-} \qquad \text{Eqn.1.12.}$$

In a solid acid, the base is a site which accepts a proton and the protonated surface site is its conjugate acid. The catalytic activity of a Brφnsted acid depends on its ability to lose a proton, which is related to the dissociation constant of the acid. The dissociation constant is the equilibrium constant for the deprotonation of an acid into a proton and a conjugate base. Since the dissociation constants of Brφnsted acids are measured in aqueous medium they do not apply directly to heterogeneous systems. For a Brφnsted acid site on γ-alumina the ratio of the equilibrium constants shown in equation 1.13 is equal to K_a, equation 1.14.

e.g.

$$\text{-O-Al-O-H} \underset{k'}{\overset{k}{\rightleftharpoons}} H^+ + \text{-O-Al-O}^- \qquad \text{Eqn.1.13.}$$

$$K_a = \frac{k}{k'} = \frac{\text{Specific Rate Of Reaction Of O-Al-O-H}}{\text{Specific Rate Of Reaction Of } H^+ + \text{O-Al-O}^-}$$

Eqn.1.14.

Since the specific forward and reverse reaction rates k and k' are inseparable, Brϕnsted (65) proposed the approximate relationship:

$$K_{HA} = GK_a^x$$ Eqn.1.15.

where K_{HA} is the catalytic coefficient of the Bronsted acid, K_a is the dissociation constant and G and x are constants for a given reaction.

In homogeneous catalytic reactions (66), stronger acids result in greater catalytic activity and this can be extended to solid acids containing Brϕnsted acid sites. Enhancement of Brϕnsted acidity in a solid catalyst will enhance the catalytic activity towards reactions that require a protonation step in a catalytic process.

(ii) Lewis Acid-Base Definition.

In 1923 G.N. Lewis proposed the role of the electron lone pair as the basis of the definition of acids and bases. The Lewis definition of an acid substance is a compound "which can employ a lone pair of electrons from another molecule in completing the stable group of its own atoms" and a basic substance as a compound "which has a lone-pair of electrons which may be used to complete the stable group of another atom" (67). Therefore neutralisation corresponds to the formation of a coordinate bond. The reaction is shown in equation 1.16, where A is the acid species and B is the base:

$$A + :B \rightarrow A:B \qquad \text{Eqn.1.16.}$$

Lewis also proposed that the main functional criterion of an acid is that a stronger acid will displace a weaker acid from its acid-base complex. The related heterolytic processes, which follow from the fundamental relationship outlined in Eqn 1.16 are expressed in equations 1.17 - 1.19.

$$A^1 + A^2{:}B \rightarrow A^2 + A^1{:}B \qquad \text{Eqn.1.17.}$$

$$B^1 + A{:}B^2 \rightarrow B^2 + A{:}B^1 \qquad \text{Eqn.1.18.}$$

$$A^1{:}B^1 + A^2{:}B^2 \rightarrow A^1{:}B^2 + A^2{:}B^1 \qquad \text{Eqn.1.19.}$$

The Lewis acid/base concept can be used for a typical Brφnsted-Lowry acid/base definition, as outlined in equation 1.16, where the proton in equation 1.20 represents the Lewis acid:

$$B^1 + H^+{:}B^2 \rightarrow B^2 + H^+{:}B^1 \qquad \text{Eqn.1.20.}$$

The advantage of the Lewis acid/base concept is that it can classify aprotic acids and bases. The disadvantage is that this is not a quantitative approach since the Lewis acid/base approach is made variable by its dependence upon the reaction or method for evaluation.

Although originally based on homogeneous systems, the Lewis acid/base concepts can be applied to gas/solid reactions if the definitions are restated as follows:

A Lewis acid site on a solid surface is a site which has an unoccupied orbital with a high affinity for an electron pair. When such a site shares an electron-pair donated by an adsorbed Lewis base molecule there is a decrease in the orbital energy of the system. Lewis base sites on the surface are those which have electron-pairs available and a decrease in the orbital energy results if they share this electron pair with an adsorbed electron-pair acceptor.

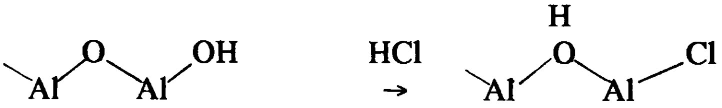
1.5. HALOGENATION OF CHROMIA AND ALUMINA CATALYSTS FOR HALOGEN EXCHANGE REACTIONS.

The promotion of Brϕnsted and/or Lewis acidity on the surfaces of metal oxide catalysts by halogenation is of considerable importance in for example bifunctional catalysis (41-43) and is a well documented process (68-73). The use of different halogenating agents results in different effects, for example treatment of γ-alumina with anhydrous HCl results in enhanced Brϕnsted acidity whereas both Brϕnsted and Lewis acidity are enhanced by treatment with CCl_4 or $OCCl_2$ (69-70). This will be discussed more fully later. The catalysts under investigation in this work display similarities in, for example, the fact that they have extensively hydroxylated surfaces, acidic surface sites and are of high surface area. The nature of the halogenated catalysts will now be considered.

(i) γ-Alumina Catalysts.

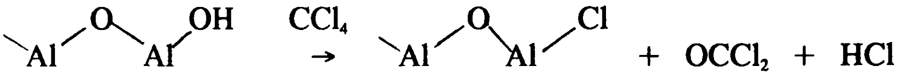
The activity of alumina for adsorption and catalysis is revealed by partial dehydroxylation of its surface which results in both acid and basic sites (74-76). The presence of these sites has been demonstrated by adsorption of basic or acidic molecules or by the poisoning effect of those molecules on various reactions (77-79). Use of pyridine to investigate the nature of the acidic sites indicated the presence of Lewis acid sites and weak Brϕnsted sites but the absence of strong Brϕnsted sites. The acidity can be enhanced by halogenation of the surface, for example fluorination with BF_3 leads to enhanced Brϕnsted acidity (80,81) and aqueous NH_4F treatment followed by calcination promotes Brϕnsted and Lewis acidity (82,83). Solid state [^{18}F]-NMR indicated the presence of Al-F species in such materials (84). Kemnitz et al (85-87) have made extensive studies of γ-alumina using chlorofluoromethanes or hydrochlorofluoromethanes as the source of fluorine to promote the surface acidity. Halogenated alumina catalysts have been used extensively as acid catalysts and as supports in hydrocarbon chemistry (88-90).

One of the fundamental goals of studies of halogenated catalysts has been to establish the nature of the active sites involved. Studies of chlorinated γ-alumina provided probable models of the active sites. Chlorination of γ-alumina generates enhanced acidity on the surface of the material. As stated previously the nature of the acidity is dependent on the chlorinating agent used: chlorination of γ-alumina with CCl_4 or $OCCl_2$ at temperatures above 473K leads to enhanced Brϕnsted and Lewis acidity (69,70,72), whereas treatment with anhydrous HCl at room temperature leads to enhancement of Brϕnsted acidity (71). Use of [^{36}Cl]-chlorine radiotracer reactions indicated differences in the lability of chlorine species and these are the basis for the proposals regarding the nature of Brϕnsted and Lewis sites on chlorinated γ-alumina (69). Chlorine exchange studies with anhydrous HCl on γ-alumina chlorinated with anhydrous [^{36}Cl]- HCl resulted in the removal of >90% of the [^{36}Cl] surface activity. In contrast, similar studies with anhydrous HCl on [^{36}Cl]-CCl_4 chlorinated γ-alumina resulted in *ca.*70% exchange of activity. Therefore it is clear that chlorination with CCl_4 results in two types of chlorine, one which is labile with respect to [^{36}Cl]-exchange with HCl and the other which is inert. Chlorination with $OCCl_2$, which, as stated previously, is an intermediate in CCl_4 chlorination, produced similar results. Previous studies have indicated that there is no observable exchange between [^{36}Cl]-HCl and the strong Lewis acid $AlCl_3$. Thus, chlorine associated with Brφnsted sites is labile with respect to [^{36}Cl]-chlorine exchange with $H^{36}Cl$ at room temperature, whereas chlorine associated with Lewis sites is inert to exchange with $H^{36}Cl$. The enhancement of Brφnsted acidity by treatment of γ-alumina with anhydrous HCl is explained as due to formation of new acid sites by dissociative adsorption of the HCl. This involves the replacement of a terminal hydroxyl group by a chlorine atom and the protonation of a neighbouring bridged oxygen species (72), equation 1.21.



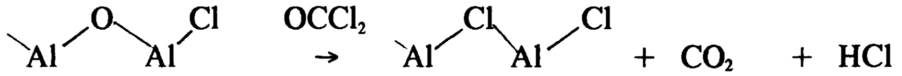
Eqn.1.21.

The reactions involving CCl_4 and $OCCl_2$ with γ-alumina are similar, which is not unexpected as $OCCl_2$ is a reaction intermediate in the CCl_4 chlorination reaction. The initial stage is thought to involve the replacement of terminal hydroxyl groups by chlorine, with formation of $OCCl_2$ and HCl, equation 1.22.



Eqn.1.22.

The carbonyl chloride is then able to react further to give CO_2 and HCl, equation 1.23

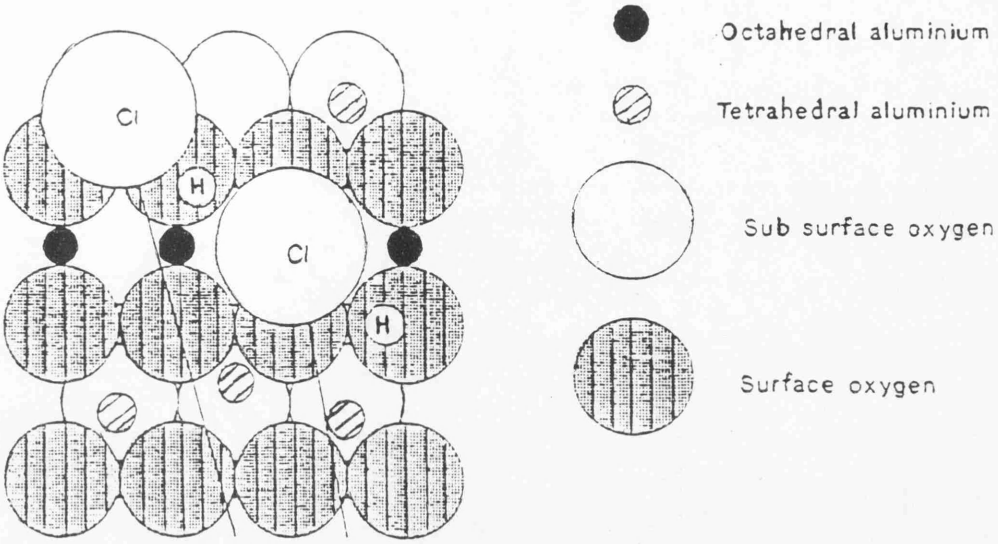


Eqn.1.23.

The hydrogen chloride formed in these reactions can also react with the surface as indicated above.

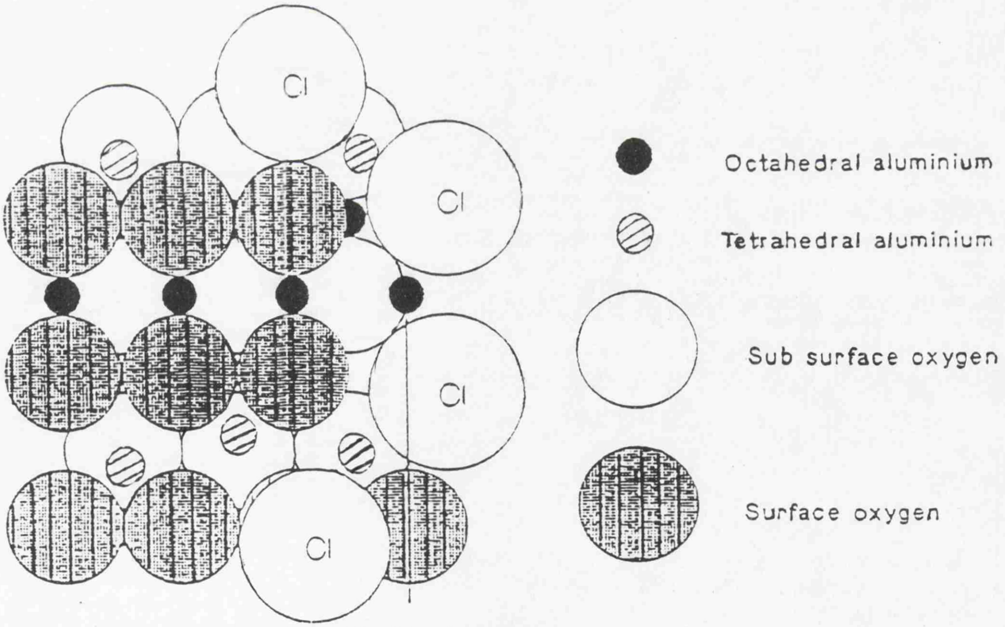
As stated previously, chlorination of γ-alumina with anhydrous HCl results in replacement of a terminal hydroxyl group on Al(III) by Cl and protonation of a bridging oxygen. Replacement of the terminal hydroxyl group by the chlorine is possible for tetrahedral and octahedral Al^{III} environments.(Fig 1.5) The Brϕnsted acidity is enhanced due to the protonation of the bridged oxygen species. Lewis acidity is not expected since the chlorine atom is larger than the OH and thus the Al^{III}_{oct} surface species are effectively saturated.

It has been proposed (69) that the chlorination process involving CCl_4 and $OCCl_2$ involves both terminal hydroxyl groups and in-plane oxygens that bridge three Al(III): Two surface Al(III) atoms and one immediately below the



Coordinatively Saturated Al_{4c} and Al_{6c} Environment.

FIG.1.5. BRΦNSTED SITES ON CHLORINATED γ-ALUMINA.



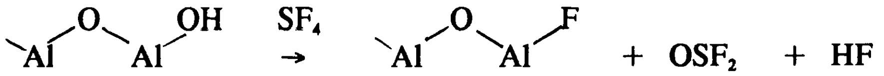
Coordinatively Unsaturated Al_{6c} Environment.

FIG.1.6. LEWIS SITES ON CHLORINATED γ-ALUMINA.

surface (Fig 1.6). This model suggests that the site involves an octahedral Al(III), two tetrahedral Al(III) and four chlorines: the coordinatively unsaturated Al(III) is bound to two chlorines, each acting as a bridge to a neighbouring tetrahedral Al(III) and to an Al(III) beneath the plane. Each tetrahedral Al(III) also has a terminal chlorine atom.

It should be noted that Figs 1.5 and 1.6 are based on the assumption that the surface is a perfect spinel whereas in fact γ-alumina is a defect spinel. However, it is clear that replacement of an in-plane oxygen bridge by two chlorines, one terminal and one bridging, has considerable disruptive effect on the lattice and hence requires a greater expenditure of energy than is required for chlorination using HCl.

Attempts have been made to extend this model for halogenation of γ-alumina surfaces for the fluorination reaction. Surface Lewis acidity was probed by the room temperature dehydrochlorination behaviour of 1,1,1,-trichloroethane. The behaviour of γ-alumina chlorinated with CCl_4 or $OCCl_2$ towards 1,1,1-trichloroethane is analogous to that observed with the strong Lewis acid, solid anhydrous aluminium(III) chloride (91): CH_3CCl_3 is rapidly dehydrochlorinated to give 1,1-dichloroethene and HCl. 1,1-dichloroethene undergoes further reaction at the surface to give a purple, oligomeric, organic layer. The significance of the organic layer will be discussed later. (It should be noted that γ-alumina that has not been halogenated is not active for room temperature dehydrochlorination). Temperatures of $>$400K are required for dehydrochlorination of CH_3CCl_3 to occur on γ-alumina (11)). Unexpectedly, carbonyl fluoride does not behave in an analogous fashion to carbonyl chloride. Instead of promotion of Lewis acidity, OCF_2 is rapidly hydrolysed on the surface of the γ-alumina and the Brφnsted acidity is increased, probably due to the hydrolysis product HF. The OCF_2 fluorinated γ-alumina has been shown to isomerize but-1-ene to but-2-ene, a reaction that is known to be dependent on Brφnsted acidity (92). Treatment of γ-alumina with HF or OSF_2 does not enhance Lewis acidity. However, treatment of γ-alumina with SF_4 at room temperature creates a surface with strong Lewis acid sites, possibly by a similar route to CCl_4 and $OCCl_2$ (Eqn.1.24).



Eqn.1.24.

It has not yet been established whether the models proposed for the active sites on chlorinated γ-alumina can be extended to fluorinated γ-alumina. This is one of the aims of this work.

(ii) Chromia Catalysts.

Chromia is a more complicated solid than γ-alumina due to the variety of oxidation states present and models for the active sites are still debatable. The fluorination of chromia with either HF at 623K (93,94) or chlorofluoromethanes (29) is a well established and studied process. An important feature of fluorinated chromia catalysts is that the extent of fluorination increases with the catalysts lifetime and ultimately results in catalyst deactivation. This has been correlated to the slow conversion of Cr^{III}-OH and Cr^{III}-O groups to Cr^{III}-F groups (95,24), which are known to be catalytically inactive. Use of [^{18}F]-fluorine radiotracer experiments has established the presence of three types of fluorine containing species on the chromia surface (24,95). The first type accounts for *ca.* 15% of the total fluorine content and is easily lost, for example by inert gas flow at 623K. This fraction is considered to be present as weakly adsorbed HF. The second type of fluorine containing species is inert to exchange with or displacement by HF at 623K. It is fluorine in this category that is involved in the slow deactivation of chromia catalyst by conversion to CrF_3. The proportion of fluorine in this section increases with increasing use of the catalyst. The third fluorine containing species is labile with respect to exchange with HF. This fluorine is involved in the halogen exchange reactions with chlorofluoroethanes that occur over fluorinated chromia catalysts. The exact nature of the catalytically active fluorine has not been determined but Cr^{VI} sites have been indicated. Radiotracer studies have also suggested that hydrogen bonded $(HF)_n$ oligomers may be the source of catalytically active fluorine and that incorporation of HCl to such oligomers could provide catalytically active chlorine species (25). The organic substrate is thought to adsorb at an adjacent Lewis site with enhanced acidity due to fluorination. These studies gave rise to the mechanistic models for halogen exchange reactions discussed in Section

1.2(ii). Vapour phase fluorination of chlorocarbon compounds with HF at temperatures of 600K in the presence of chromia catalysts has been one of the main routes for CFC production and therefore there have been extensive studies of the products from these reactions and substantial work to determine conditions required for maximizing the yields of specific products. However there is less evidence regarding the exact nature of active sites and reactive species although the models presented in Section 1.2(ii) involving halogen exchange and isomerisation are perhaps the most convincing advances to date.

1.6. OXIDE SUPPORTED ORGANIC LAYER CATALYSTS FOR ROOM TEMPERATURE CATALYTIC HALOGENATION REACTIONS.

As discussed in Section 1.5(i) studies of the strong Lewis acid aluminium (III) chloride indicated that the dehydrochlorination of 1,1,1-trichloroethane could be used as a specific probe reaction for Lewis acidity (91). The dehydrochlorination reaction produces 1,1-dichloroethene and HCl with further polymerization . of the 1,1-dichloroethene to produce an oligomeric organic layer on the surface. The exact nature of the organic layer has not been established conclusively, but the organic layer appears to be derived from partially dehydrochlorinated -CH_2CCl_2- groups and contains additional chlorinated derivatives. Figure.1.7 (96-98) demonstrates the dehydrochlorination of 1,1,1-trichloroethane on γ-alumina pretreated with CCl_4 or $OCCl_2$:

$$\begin{tikzcd}
CH_3CCl_3(g) \arrow[d, shift left] \arrow[d, leftarrow, shift right] & CH_2CCl_2(g) \arrow[d, shift left] \arrow[d, leftarrow, shift right] & & \\
CH_3CCl_3(ads) & CH_2CCl_2(ads) \arrow[dd] & + & HCl(ads) \arrow[d, shift left] \arrow[d, leftarrow, shift right] \\
 & & & HCl(g) \arrow[d, shift left] \arrow[d, leftarrow, shift right] \\
 & {[CH_{2-x}CCl_{2-x}]_n} & + & HCl(ads) \\
 & (x = 1, 0) & &
\end{tikzcd}$$

Fig.1.7.Dehydrochlorination Of 1,1,1-Trichloroethane On CCl_4 or $OCCl_2$ Chlorinated γ-Alumina.

Studies of the dehydrochlorination reaction on SF_4 fluorinated γ-alumina (96-98) revealed that the formation of the organic layer was accompanied by formation of fluorinated products, $CH_3CCl_{3-n}F_n$ (n=1-3), by halogen exchange reaction with the fluorinated surface. At room temperature the organic layer is capable of catalysing the reaction of 1,1,1-trichloroethane with anhydrous HF (mole ratio 3:1) to give a mixture of fluorinated products $CH_3CCl_{3-n}F_n$ (n=1-3) (96-98). Similar halogen exchange reactions have been observed with other C_2 and C_3 chlorocarbons, such as $CH_3CCl_2CH_3$, CH_2ClCCl_3, $CHCl_2CHCl_2$ and $CHCl=CCl_2$ (98). Although these reactions can be described formally as replacement of C-Cl bonds by C-F bonds, there is no evidence to determine whether the mechanisms involved are similar to those described in Section 1.2(ii) for the halogen exchange reactions between HF and chlorofluorocarbons in the presence of a fluorinated chromia catalyst. The most obvious difference is that the catalytic reaction observed on SF_4 fluorinated γ-alumina occurs at room temperature whereas for the halogen exchange reactions on fluorinated chromia catalyst require temperatures of $>600K$. Also, although organic material is adsorbed on to the surface of the fluorinated chromia catalyst there is no evidence of an active organic layer, whereas the organic material deposited on the SF_4 γ-alumina plays an integral role in the catalytic activity and no such activity is observed in the absence of the supported organic material. It is obvious that in the study of oxide supported organic layer catalysts an understanding of the reactions occurring in the conditioning step and in the catalytic reaction and the development of mechanisms for these reactions is of vital importance. It is also important to extend the scope of such catalysts by establishing if organic layers are produced only on γ-alumina or whether oxides such as chromia can be used as an alternative support for such layers.

1.7. AIMS.

As discussed, the need to develop effective routes for the production of alternatives to chlorofluorocarbons is an important and urgent requirement for industry in view of the international regulations requiring the introduction of more environmentally friendly substances. Clearly, a reaction which could be performed at room temperature would be favourable to industry in terms of both cost and environmental considerations. Thus the realisation of the catalytic activity at room temperature of the organic layer on CH_3CCl_3 conditioned, SF_4 fluorinated γ-alumina was extremely important. In view of this, a detailed understanding of the catalytic organic layer material is essential. This was one of the aims of this work. In order to understand the catalytic activity of the organic layer material it is essential to have a detailed knowledge of the reactions occurring in its production. In view of this, [^{18}F]-fluorine radiotracer studies have been undertaken to examine the fluorination process and the activity of the surface fluorine species. From these studies it may be possible to determine if the models for halogenated sites derived from chlorination processes can also be applied to the fluorinated materials.

[^{36}Cl]-Chlorine radiotracer studies have been performed to examine the conditioning reaction and the subsequent reactivity of the chlorine containing organic layer material. These studies have allowed the development of model reactions for these processes.

As stated earlier in the study of oxide supported organic layer catalysts it is important to determine if such organic layers are unique to γ-alumina or if it is possibly to use other oxides as alternative supports. One of the aims of this present work was to extend the study of organic layer materials, using chromia, the most obvious alternative to γ-alumina in view of the extensive work carried out on chromia catalysts for halogen exchange reactions at elevated temperatures. Direct detailed comparisons have been made in the fluorination and conditioning steps of the catalyst production process on γ-alumina and chromia samples to establish if these materials behave similarly: is an organic layer laid down on chromia surfaces in an identical manner to that on γ-alumina. Comparisons have also been made in the room temperature reaction of HF with 1,1,1-trichloroethane in the presence of conditioned materials to establish if chromia, pretreated with SF_4 and CH_3CCl_3, in an identical way to γ-alumina, is also active as a catalyst for room temperature hydrofluorination reactions.

EXPERIMENTAL.

It was important in this work to ensure that all air and moisture were excluded from the reactions being examined, due to the hygroscopic nature of the calcined and halogenated materials. All work was therefore carried out under vacuum (10^{-4} Torr) or in an inert atmosphere box.

2.1. EQUIPMENT.

2.1.1. THE VACUUM SYSTEMS.

Two separate types of vacuum system were used to manipulate volatile materials:- a Pyrex glass system for handling organic materials and Monel metal lines for handling sulphur tetrafluoride and hydrogen chloride. (Monel is an alloy of nickel and copper and is used because of its resistance to corrosive chemicals.).

Rotary pumps were used to evacuate both systems. A series of waste traps cooled in liquid nitrogen was used to protect the pump from any volatile materials in the system. The pump and the waste traps could be isolated from the other parts of the line.

2.1.2. PYREX GLASS VACUUM LINE.

This was an enclosed Pyrex glass structure consisting of a manifold, a Heise Bourdon Gauge or manometer and a mercury Vacustat (Fig.2.1). A mercury diffusion pump was used in conjunction with the

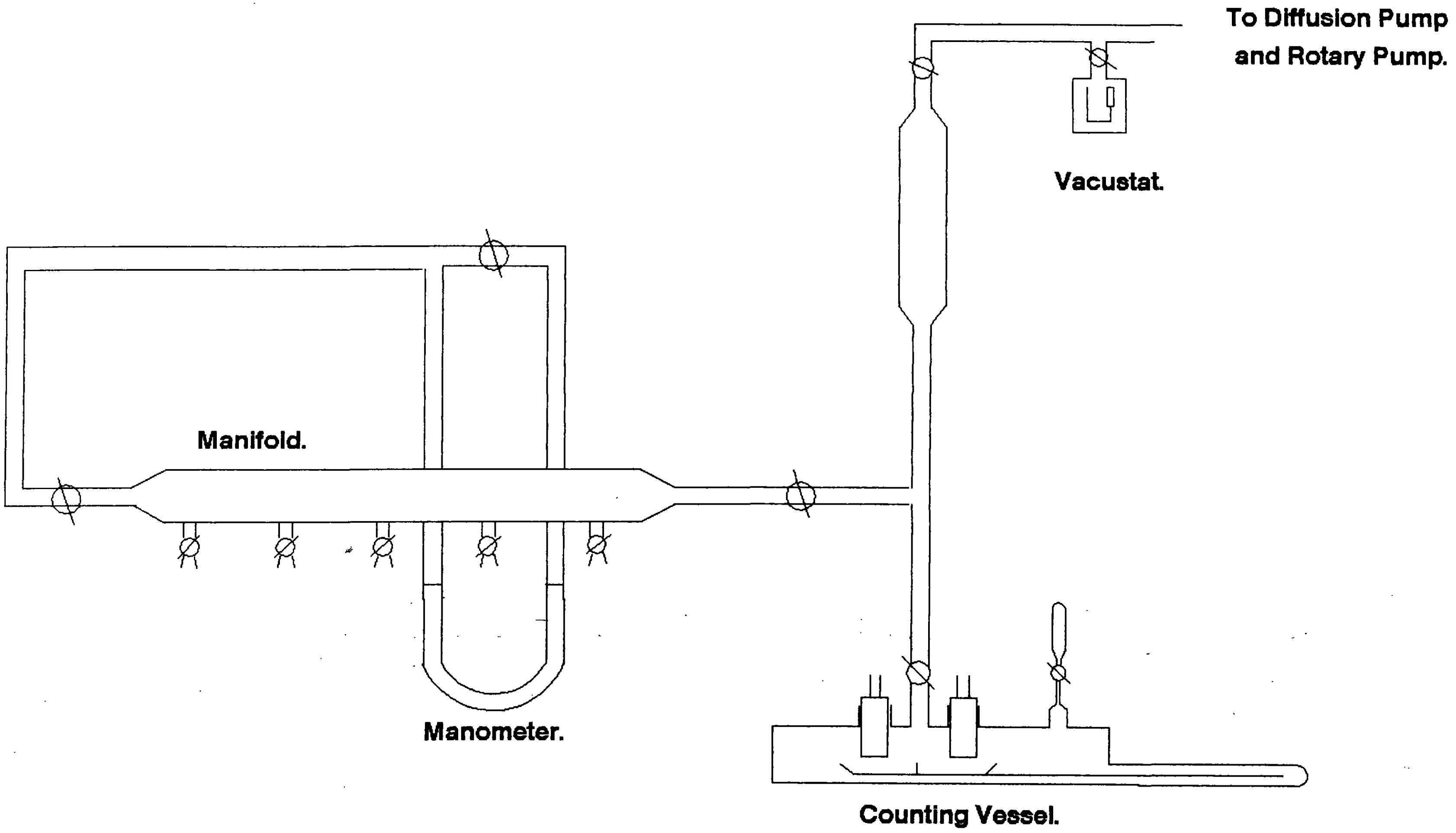


Fig.2.1. Pyrex Glass Vacuum System.

rotary pump to achieve a vacuum of 10^{-4} Torr. The Vacustat was used to measure the vacuum achieved by the pumps. The Heise Bourdon gauge or the manometer was used to measure pressures of gases in the line to an precision of ± 0.5 Torr.The manifold had several B14 sockets which could be isolated from the line by means of high vacuum stopcocks (J. Young or Rotaflow). Vacuum flasks and ampoules, also equipped with high vacuum stopcocks and B14 cones were attached to the manifold to introduce and withdraw reactants. All vessels and the line itself were flamed out, while the system was pumped, in order to reduce the amount of moisture adsorbed on the surface of the glass (99).

2.1.3. MONEL METAL LINE.

This was of a similar design to the Pyrex system but was constructed using 2/5 inch o.d. Monel tubing and Monel metal valves. (Autoclave Engineers). Monel metal or stainless steel pressure vessels were connected to the line by means of nipple and collar screw couplings (Autoclave Engineers). A lecture bottle of sulphur tetrafluoride and a Monel metal waste trap were also connected to the SF_4 - line. Pressure in the line was determined using a Budenberg gauge (Fig 2.2).

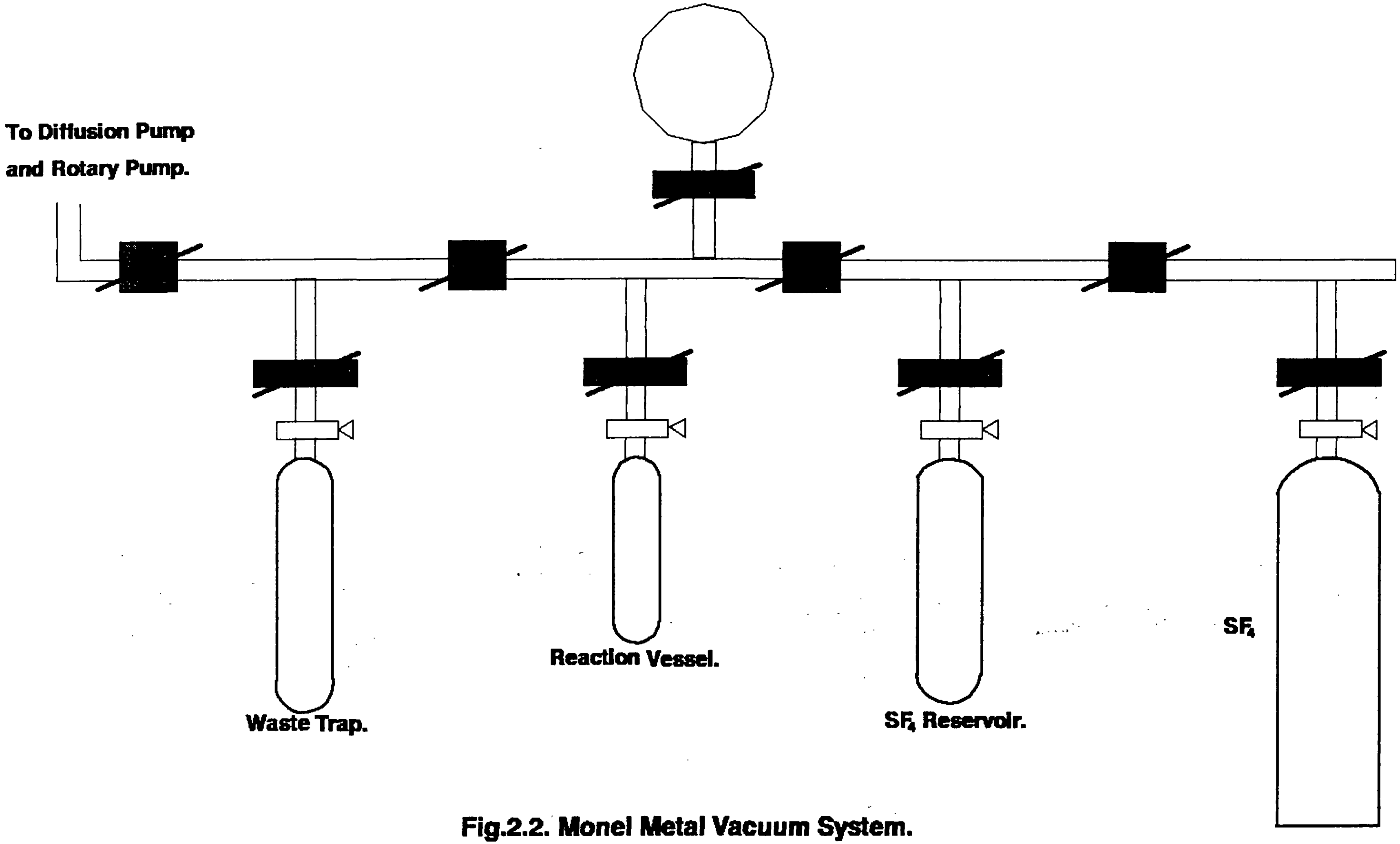


Fig.2.2. Monel Metal Vacuum System.

2.1.4. FLOW LINE FOR CONDITIONING REACTION AND CATALYTIC REACTION.

A Monel metal flow system was used to study the conditioning and the catalytic reaction under flow conditions - that is where the reactants pass through the reactor as a continuous flow - to give a clearer model of an industrial system and to allow comparisons between static and flow conditions for the reactions.

The main constituents of the catalytic rig were a hydrogen fluoride reservoir, a 1,1,1-trichloroethane reservoir and a catalytic reaction vessel (Fig 2.3).

The hydrogen fluoride reservoir was a double-ended sample cylinder, housed in an insulated bath and cooled to 0°C or below by means of a chiller unit fitted with a temperature controller,to allow greater control of HF flow. The tubing from the reservoir could be heated to prevent HF condensing in the line.

The 1,1,1-trichloroethane reservoir was a double ended sample cylinder. The reservoir and the feed line could be heated by using the appropriate Variac and thermocouple.This allows the concentration of CH_3CCl_3 in the feed gas to be varied and prevents its condensation in the line.

Separate feed lines for HF and CH_3CCl_3 allowed the catalyst to be treated with CH_3CCl_3 alone for the conditioning reaction or with HF and CH_3CCl_3 for the catalytic reaction. A nitrogen carrier gas was used

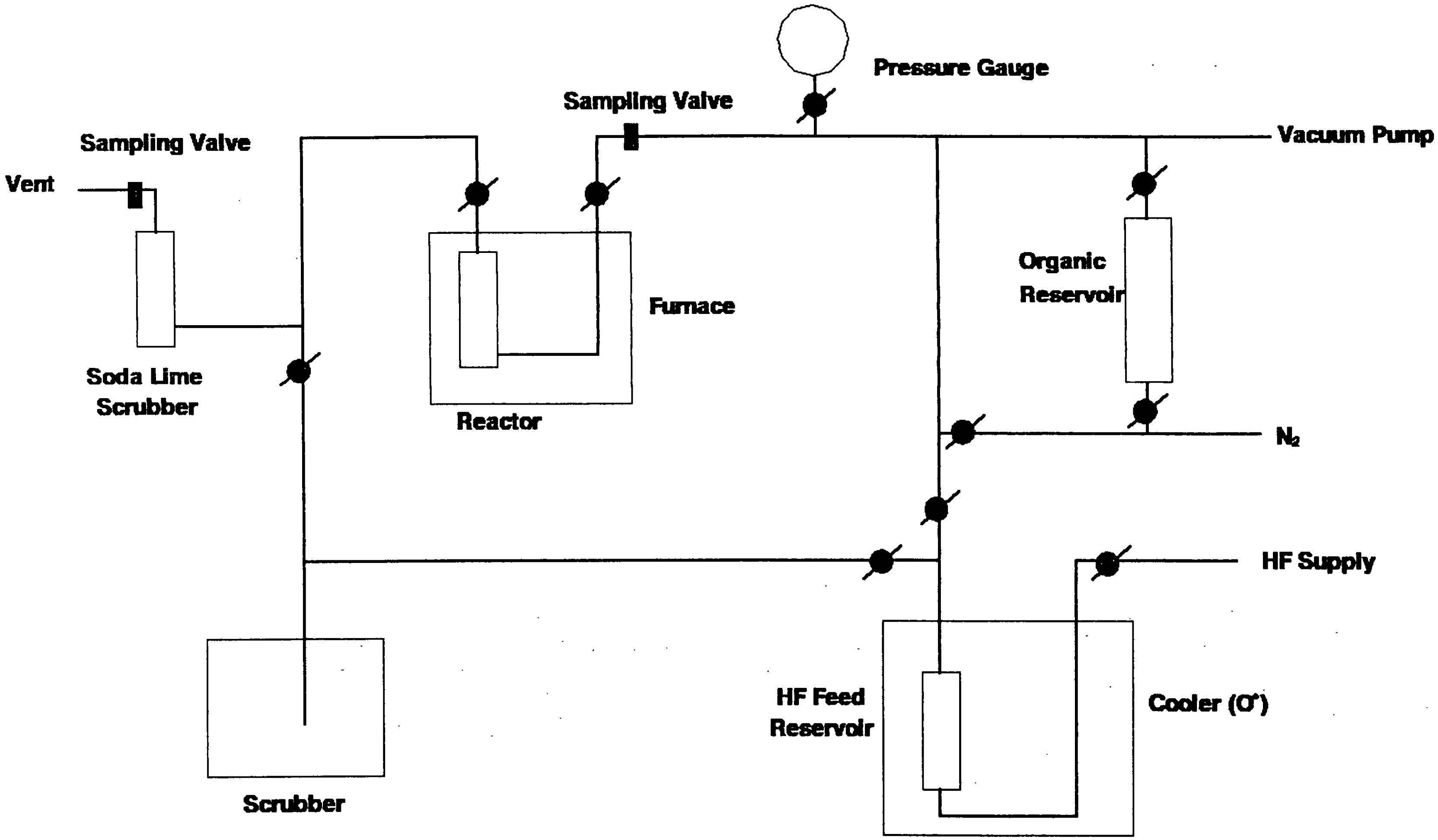


Fig.2.3. Catalytic Flow Rig.

to flow the feed gases over the catalyst.

The catalytic reactor was a U-shaped vessel, with the catalyst loaded into the larger left-hand side, so that the feed gases flowed from the bottom to the top of the reactor. The catalytic reactor was housed in an oven, allowing the reactor to be heated if required.

The Rig Off Gases (ROG) could be passed through the main scrubber (KOH) to remove excess HF, or through a smaller HF scrubber (soda lime) to a gas sampling outlet to allow for monitoring of the products of the reaction by gas chromatography. The 1,1,1-trichloroethane feed could also be sampled to ensure continuity of flow and determination of extent of reaction.

2.1.5. INERT ATMOSPHERE BOX.

A nitrogen atmosphere glove box (Lintott) (H_2O < 10ppm) was used when handling and storing all samples. Glass vessels were evacuated and flamed out before being transferred to the box. The box contained an analytical balance, allowing samples to be weighed precisely in a dry, inert atmosphere.

2.2. PREPARATION AND PURIFICATION OF REAGENTS.

2.2.1. RADIOISOTOPES.

Extensive use has been made of radiotracer techniques in this work. The radioisotopes used were:-

(i) [^{18}F]-FLUORINE.

The isotope [^{18}F]-fluorine is a β^+ emitter. Annihilation of β^+ particles with negative electrons releases energy in the form of γ-radiation, which is readily detected from both the surface and the bulk of the material. The maximum γ-emission energy is 0.51 MeV and the half-life is 109.72 ± 0.6 min. (100).

The relatively short half-life means that experimental work must be completed in one day. After 11 hours (6 half-lives) less than 2% of the original activity remains.

(ii) [^{36}Cl]-CHLORINE.

The [^{36}Cl]-chlorine isotope has a half-life of 3×10^5 years (101) and decays by β^- emission and, although moderately energetic, self adsorption considerations dictate that emission from the solid is limited to the surface alone. The isotope was supplied as an aqueous solution of Na^{36}Cl (Amersham International plc.) and was diluted with concentrated hydrochloric acid to give a solution with a specific [^{36}Cl]-chlorine activity of *ca.*9.3×10^5 Bq cm^{-3}.

2.2.2 PREPARATION OF [^{18}F]-FLUORINE LABELLED CAESIUM FLUORIDE.

The method used for the preparation of [^{18}F]-fluorine was by irradiation of lithium carbonate (*ca.*2g) in the central core of the

S.U.R.R.C. reactor at East Kilbride, using the sequence :-

$^{6}Li(n,\alpha)^{3}H, \quad ^{16}O(^{3}H,n)^{18}F$ (102)

The irradiation conditions were typically 30 minutes at a flux of 3.6×10^{12} neutrons cm^{-2} s^{-1}. The [^{18}F]-LiF produced in the irradiation was converted to [^{18}F]-HF by reaction with sulphuric acid (conc. H_2SO_4 : H_2O 1:1 by volume). The [^{18}F]-HF was distilled into a solution of caesium hydroxide at 273K. The solution was neutralised by addition of aqueous hydrogen fluoride and this was followed by evaporation to dryness to give [^{18}F]-CsF as a finely divided white powder.

2.2.3. PREPARATION OF [^{18}F]-FLUORINE LABELLED BORON TRIFLUORIDE AND SULPHUR TETRAFLUORIDE.

Simple exchange between $Cs^{18}F$ and SF_4 does not produce sufficient activity in $SF_3{}^{18}F$ to carry out subsequent reactions. The procedure used in this work was developed previously in Glasgow (102) and involves the following reactions:

$$Cs^{18}F + 2BF_3 \rightarrow CsBF_3{}^{18}F + BF_2{}^{18}F \qquad \text{Eqn.2.1.}$$

$$BF_2{}^{18}F + SF_4 \rightleftharpoons [^{18}F]\text{-}[SF_3^+][BF_4^-] \qquad \text{Eqn.2.2.}$$

$$[^{18}F]\text{-}[SF_3^+][BF_4^-] + Et_2O \rightarrow SF_3{}^{18}F + Et_2O.BF_2{}^{18}F. \qquad \text{Eqn.2.3.}$$

All the reactions were carried out in stainless steel bombs , attached to the calibrated Pyrex vacuum system . In a typical preparation, $Cs^{18}F$ (2.00g.) was activated by treatment with $(CF_3)_2CO$ (20.0mmol.) at room temperature for 20min., then volatile material was removed and the bomb heated at 300K for a further 15min. to remove any remaining volatile material. This activation step, which involves the formation and thermal decomposition of $Cs(OCF(CF_3)_2)$, results in enhanced surface area and probably enhanced porosity of the CsF and hence increases the [^{18}F]-specific activity of the $SF_3{}^{18}F$ that is finally obtained.

Boron trifluoride (20.0mmol.), previously treated with activated sodium fluoride to remove any traces of hydrogen fluoride, was added to the activated $Cs^{18}F$, and heated at 300K for 30min. to allow ^{18}F exchange to occur (Eqn.2.1.). The labelled $BF_2{}^{18}F$ (10.0mmol.) was distilled into a second stainless steel bomb and SF_4 (8.0mmol.) added. This was held at 195K for 20min. The adduct $[SF_3^+][BF_4^-]$ formed (Eqn.2.2.) has a large dissociation pressure at room temperature and under the conditions used, [^{18}F]-exchange is complete. The reaction vessel was cooled to 195K and material volatile at this temperature, a mixture of $^{18}FSO_2$, SO_2 and unreacted $BF_2{}^{18}F$ was removed. Dried diethyl ether (2.0mmol.) was added to the reaction bomb and allowed to react at room temperature for 20min. to decompose the adduct (Eqn.2.3.). The vessel was then cooled to 195K and $SF_3{}^{18}F$ (2.0mmol.) removed by distillation. An aliquot of the labelled vapour was removed and the specific count rate determined by counting in dry pyridine (0.5ml.), with which SF_4 forms a weak adduct.

In principle, the $SF_3{}^{18}F$ and $BF_2{}^{18}F$ labelled by this procedure should have equal specific count rates when allowance is made for the different number of F atoms involved. However, in practice it was found that the specific count rate of $BF_2{}^{18}F$ was greater than that of $SF_3{}^{18}F$. This may be accounted for by the lower stability constant of $[SF_4.py]$ compared with $[BF_3.py]$, resulting in a significant concentration of SF_4 in the gas phase. The counting efficiency is dependent on the phase of the material,with solid being more efficient than liquid which in turn is more efficient than gas phase.

2.2.4.PREPARATION AND PURIFICATION OF [^{36}Cl]-CHLORINE LABELLED HYDROGEN CHLORIDE. (103,104).

[^{36}Cl]-Chlorine labelled hydrogen chloride was generated in an apparatus consisting of a reaction vessel with a dropping funnel and a pressure equilibrating arm, to which a series of cooled traps were attached (Fig 2.4).

Traps (i), (ii), and (iv) contained phosphorus pentoxide as a drying agent. Traps (i) and (ii) were cooled to 213K in dichloromethane/dry ice baths. The collection vessel, (iii), was equipped with high vacuum stopcocks, so it could be isolated from the rest of the apparatus and was cooled to 153K in an isopentane/liquid N_2 bath.

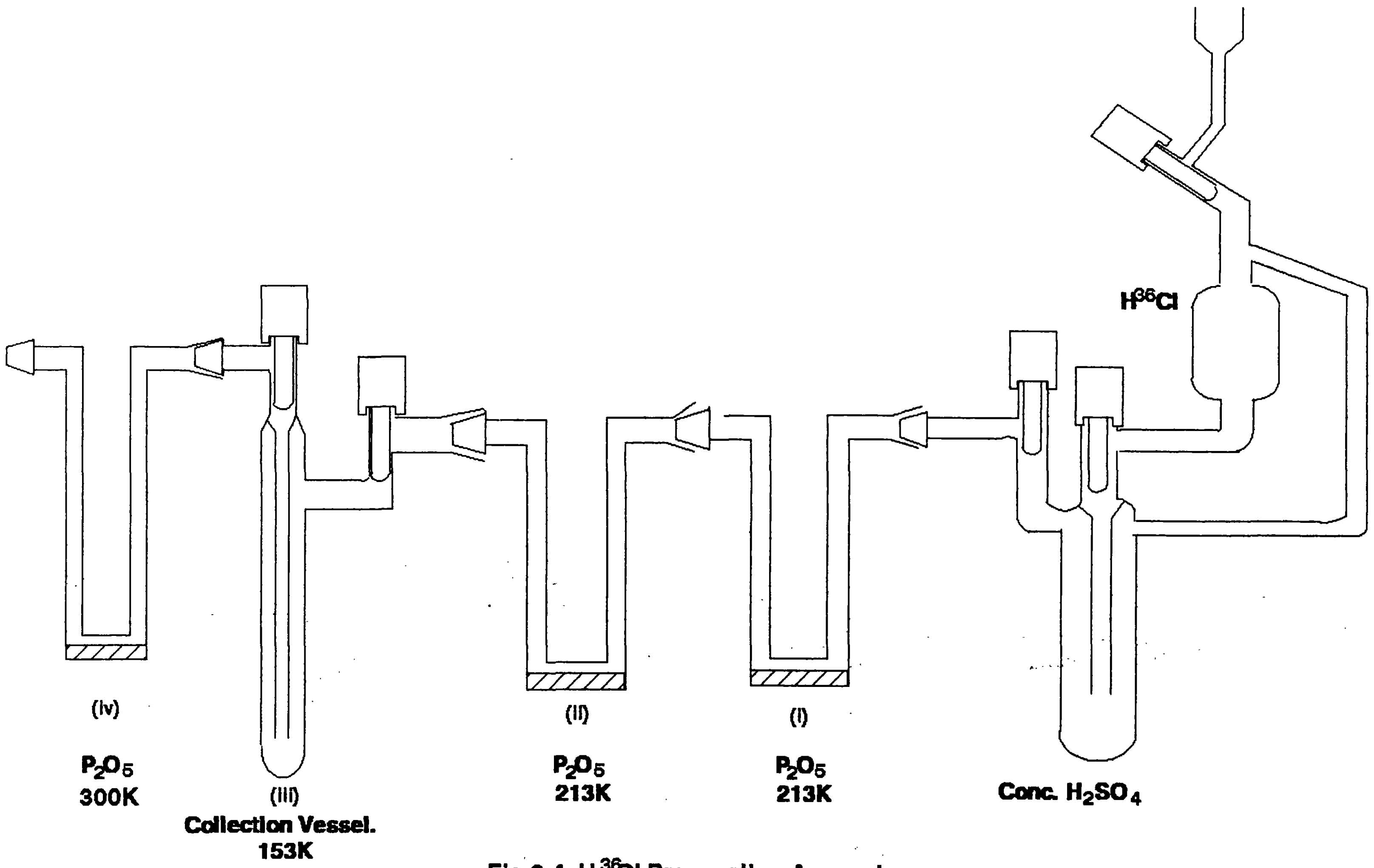


Fig.2.4. $H^{36}Cl$ Preparation Apparatus.

Aqueous [^{36}Cl]-chlorine labelled sodium chloride (2.0ml, 40uCi, Amersham International.) was diluted with conc. HCl (10ml), as described in Section 2.2.1, and this solution added dropwise to concentrated sulphuric acid. The [^{36}Cl]-chlorine labelled hydrogen chloride generated was distilled through traps (i) and (ii) and collected in the collection vessel (iii), then transferred to a vacuum line where the [^{36}Cl]-HCl was degassed and vacuum distilled into a Monel metal bomb, containing phosphorus pentoxide.

2.2.5. PREPARATION AND PURIFICATION OF [^{36}Cl]-CHLORINE LABELLED 1,1,1-TRICHLOROETHANE. (105).

[^{36}Cl]-Chlorine labelled 1,1,1-trichloroethane was prepared by hydrochlorination of 1,1-dichloroethene over an iron (III) chloride catalyst.

$$CH_2{=}CCl_2 \ + \ [^{36}Cl]\text{-}HCl \ \xrightarrow[FeCl_3]{293K} [^{36}Cl]\text{-}CH_3CCl_3 \qquad \text{Eqn.2.4.}$$

Anhydrous $FeCl_3$ (>99.0% pure, Aldrich) was loaded into a Monel metal bomb and attached to a vacuum line.Then $CH_2{=}CCl_2$ (34.0mmol, 99% pure, Aldrich) and [^{36}Cl]-HCl (35.0mmol) were introduced. The reaction occurred at room temperature over 48h.

Purification was achieved by low temperature vacuum distillation of the reactant material, CH_3CCl_3 being retained at 195K. The material volatile at this temperature was isolated and condensed into a vessel held at 77K. This procedure was repeated until an infrared spectrum showed that HCl and $CH_2{=}CCl_2$ were absent.

2.2.6. PURIFICATION OF 1,1,1-TRICHLOROETHANE.

1,1,1-Trichloroethane (99% pure, Aldrich) was stored over activated 3Å molecular sieves, under subdued light to inhibit photopolymerisation. The stabilizer, 1,4 dioxane, present to inhibit polymerization and oxidation, was removed by vacuum distillation and the CH_3CCl_3 was degassed prior to use.

2.2.7. PURIFICATION OF 1,1-DICHLOROETHENE.

1,1-Dichloroethene (99% pure, Aldrich) was stored over activated 3Å molecular sieves, under subdued light to inhibit photopolymerisation.This material contained a stabilizer,hydroquinone monomethyl ether, to inhibit oxidation and polymerisation.

1,1-Dichloroethene was vacuum distilled to remove the stabilizer and degassed prior to use.

2.3. PREPARATION OF CATALYSTS.

Three catalysts have been used in this work:-

(i) γ-ALUMINA

A high purity commercial alumina (Degussa "C"), which was received as a very fine powder. To facilitate the handling of this material a sample (500g) was mixed with deionized water (350cm^{-3}) until a smooth paste was formed. This was then heated,. in an evaporation dish, on a hot-plate until dry. The "cake" was broken up and sieved to give particle size of 400-1680μm.

(ii) AN INDUSTRIAL CHROMIA. (106).

A sample of a chromia catalyst used in industrial halogen exchange reactions using hydrogen fluoride and elevated temperatures (700°C). This catalyst was used as a standard for comparison purposes.

The industrial chromia catalyst was prepared by slow addition of aqueous ammonia to a solution of chromium nitrate. The chromium hydroxide obtained is dried in air at 373K then calcined in an inert atmosphere at 500-700K.

The catalyst was received in the form of pellets which were ground before use.

(iii) "VOLCANO CHROMIA." (107).

This catalyst was prepared from the $(NH_4)_2Cr_2O_7$ volcano reaction:-

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O \qquad \text{Eqn.2.5.}$$

Ammonium dichromate (30g) (99% pure, Aldrich) was ignited. After lighting the reaction was self sustaining. The product was a fine green powder.

2.4. CATALYST PRETREATMENT.

The catalysts were all pretreated using identical procedures:-

2.4.1. CALCINATION OF CATALYSTS.

The catalyst (typically 10g) was loaded into a dry Monel metal or stainless steel bomb and fitted with a cone and valve. The bomb was attached to the vacuum system and degassed by pumping. An electrical heater fitted with a vertical thermo-couple pocket was fixed around the bomb and the bomb was heated to 523K and allowed to calcine for 6h.under dynamic vacuum,to remove water and some hydroxyl groups, dehydrating the surface.The calcined samples were stored under nitrogen in the dry box.

2.4.2 ROOM TEMPERATURE REACTION OF SULPHUR TETRAFLUORIDE WITH CALCINED CATALYSTS.

A sample of the calcined material (0.5g) was loaded into a Monel metal bomb in the dry box.The bomb was transferred to a Monel vacuum line and degassed by pumping. An aliquot of sulphur tetrafluoride (3mmol) (99% pure, Fluorochem.) was condensed onto the calcined material and allowed to react at room temperature for 2h. The volatile material was removed and examined by infrared analysis, and the contents of the bomb were pumped for 5mins to remove any remaining volatile material. This process was repeated twice, to give a total of 9mmol SF_4.

2.4.3 ROOM TEMPERATURE REACTION OF SF_4-FLUORINATED CATALYSTS WITH 1,1,1-TRICHLOROETHANE.

An aliquot of unstabilized 1,1,1,-trichloroethane (3mmol) was condensed onto the fluorinated material in a Monel metal bomb and allowed to react at room temperature for 3h. The volatile material from the conditioning step was removed and examined by infrared and G.C. analysis.

2.5. INFRARED SPECTROSCOPY.

2.5.1. TRANSMISSION INFRARED SPECTROSCOPY IN THE VAPOUR PHASE OVER SURFACE REACTIONS.

Infrared spectroscopic analysis of the vapour phase in gas/solid systems were performed using an *in situ* gas i.r. cell (Fig 2.5), which could be attached to the vacuum system. The i.r. cell was fitted with AgCl windows and was of path length 10cm. B14 sockets allow the introduction, under vacuum, of solid samples via a dropping vessel and a trough prevented the solid impinging on the spectrometer beam. Vapour was expanded into the gas cell to the desired pressure (usually 60 Torr). The gas cell was then fitted to the spectrometer, using a specially designed holder to ensure reproducible positioning of the cell in the spectrometer beam. The solid was then introduced to the cell containing the vapour and the reaction monitored with time.

2.5.2. IDENTIFICATION OF GASEOUS SAMPLES.

In all infrared spectroscopic analysis species were assigned by comparison with standard vapour phase spectra obtained from the Aldrich Library of Infrared Spectra or vapour phase spectra from pure standard samples.

Analytically useful peak positions of gaseous species are presented in Table 2.1

Fig.2.5. *Insitu* **Infrared Gas Cell.**

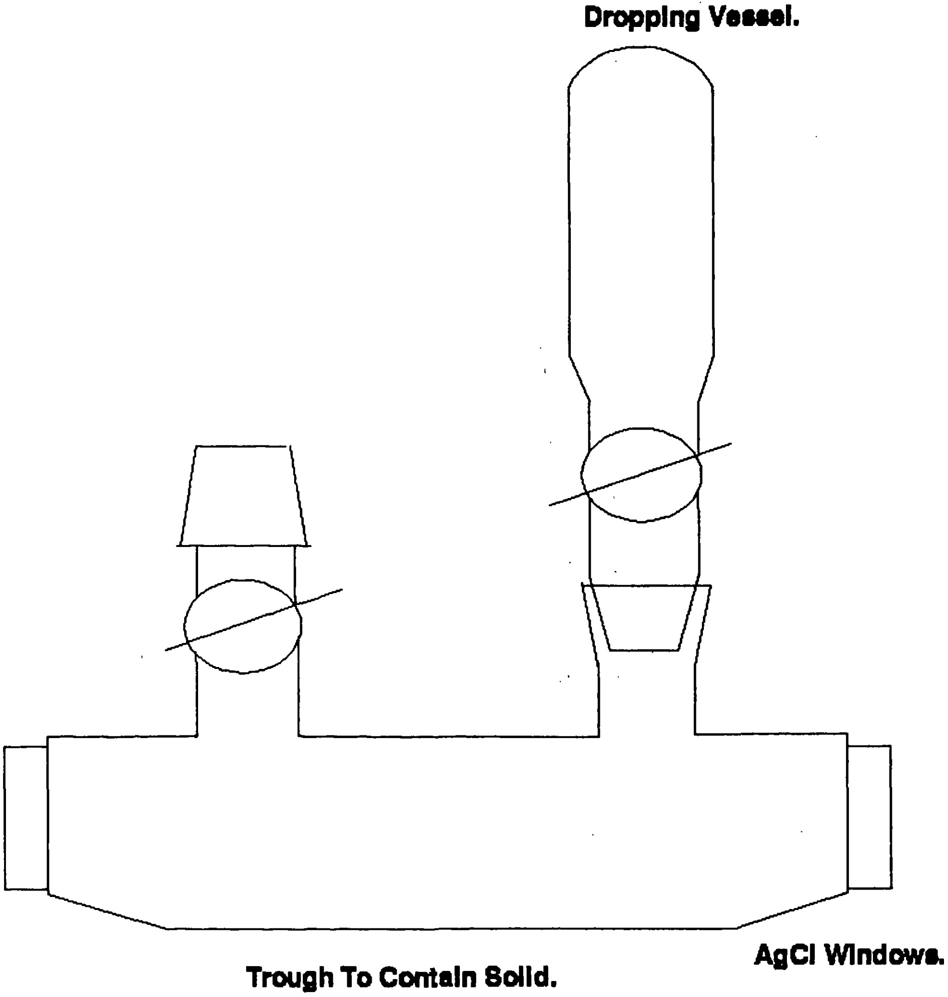


Table.2.1. Principal I.R. Peaks For Possible Reaction Products.

COMPOUND.	WAVELENGTH (cm^{-1})
SF_4	892, 860, 730, 550, 530
SOF_2	1308, 801, 721, 526, 393
SO_2	1362, 1151
SiF_4	1030
CH_3CCl_3	3010, 2950, 1440, 1385, 1085, 1010, 720, 520
CH_2CCl_2	1730, 1620, 1570, 1139, 1090, 865, 790, 595
CH_3CCl_2F	3015, 2940, 1450, 1400, 1089, 1030, 745, 580
HCl	2900-2800

2.5.3. DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY. (D.R.I.F.T.S.)

In reflectance spectroscopy the radiation being analyzed is reflected from the surface of the sample (Fig 2.6).

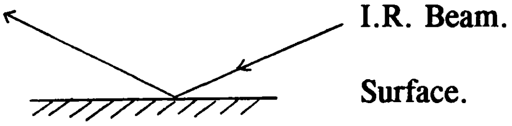


Fig.2.6. Reflectance Spectroscopy.

This is different from transmission spectroscopy, where the radiation passes completely through the sample.

In diffuse reflectance spectroscopy the infrared beam is reflected from an ellipsoid mirror onto the sample (Fig 2.7).

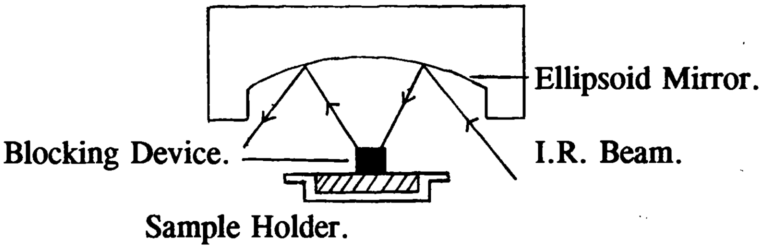


Fig.2.7. Diffuse Reflectance Spectroscopy.

Radiation that is reflected without penetrating the sample is prevented from reaching the collection mirror by a blocking device. The diffusely reflected radiation penetrates the sample and is able to reach the collection mirror.

To obtain a DRIFT spectrum the sample holder was first loaded with

KBr to obtain a background spectrum. The KBr was replaced by the sample being examined and several scans (usually 50) obtained. Attempts were made to use an inert atmosphere shroud to prevent the exposure of the moisture sensitive samples to the atmosphere, but the noise levels were unacceptably high with respect to signals, so handling and scanning times were kept as short as possible to minimise hydrolysis. The spectrometer used for DRIFTS analysis was a Nicolet 5DXC FTIR Spectrometer with a Nicolet Auxiliary Experiment Module attached.

2.6. GAS CHROMATOGRAPHY.

Samples were analysed by gas chromatography using a Varian 3400 G.C. fitted with an FID, a 50m capillary column with injection via gas sampling valve onto the column. Helium was used as carrier gas with a flow rate of $8cm^3min^{-1}$.

ANALYSIS METHOD.

Initial Column Temp: 35°C.   Column Hold Time: 7.5 min.

Final Temp: 150°C.   Hold Time: 2.2 min.   Ramp Rate: $50^\circ Cmin^{-1.}$

Injector Temp: 200°C.   Detector temp: 250°C.

2.7. RADIOCHEMICAL COUNTING.

2.7.1. GEIGER MÜLLER COUNTERS. (108, 111)

A Geiger-Müller tube consists of a metal tube with a thin gas-tight mica window at one end and a gas-tight insulated support for a thin central wire at the other (Fig 2.8). The tube is filled with a gas mixture, for example 90% argon and 10% methane, which becomes partially ionised when radiation enters the detector producing positive ions and free electrons. The inside wall of the tube forms the cathode and the central wire is the anode, which is held at a high positive potential with respect to the wall cathode. Hence the electrons formed move rapidly towards the central wire and the positive ions drift slowly towards the wall.

As the potential difference between the wall and the wire is increased, electrons gain sufficient energy to cause further ionisations as they collide with gas molecules and so the number of electrons collected on the wire becomes greater than the number created by the passage of radiation through the detector gas. This is called ion multiplication.

Increasing the wire voltage further increases the extent of ion multiplication until a finite limit is reached - the Geiger region, where the number of electrons produced by ion multiplication per primary electrons produced by radiation becomes so great that the "electron avalanche" created spreads along the entire anode wire. In this state the detector is said to be saturated; the number of electrons collected on the wire and hence the magnitude of the resultant voltage pulse is independent of the number of electrons created by the passage of radiation through the detector.

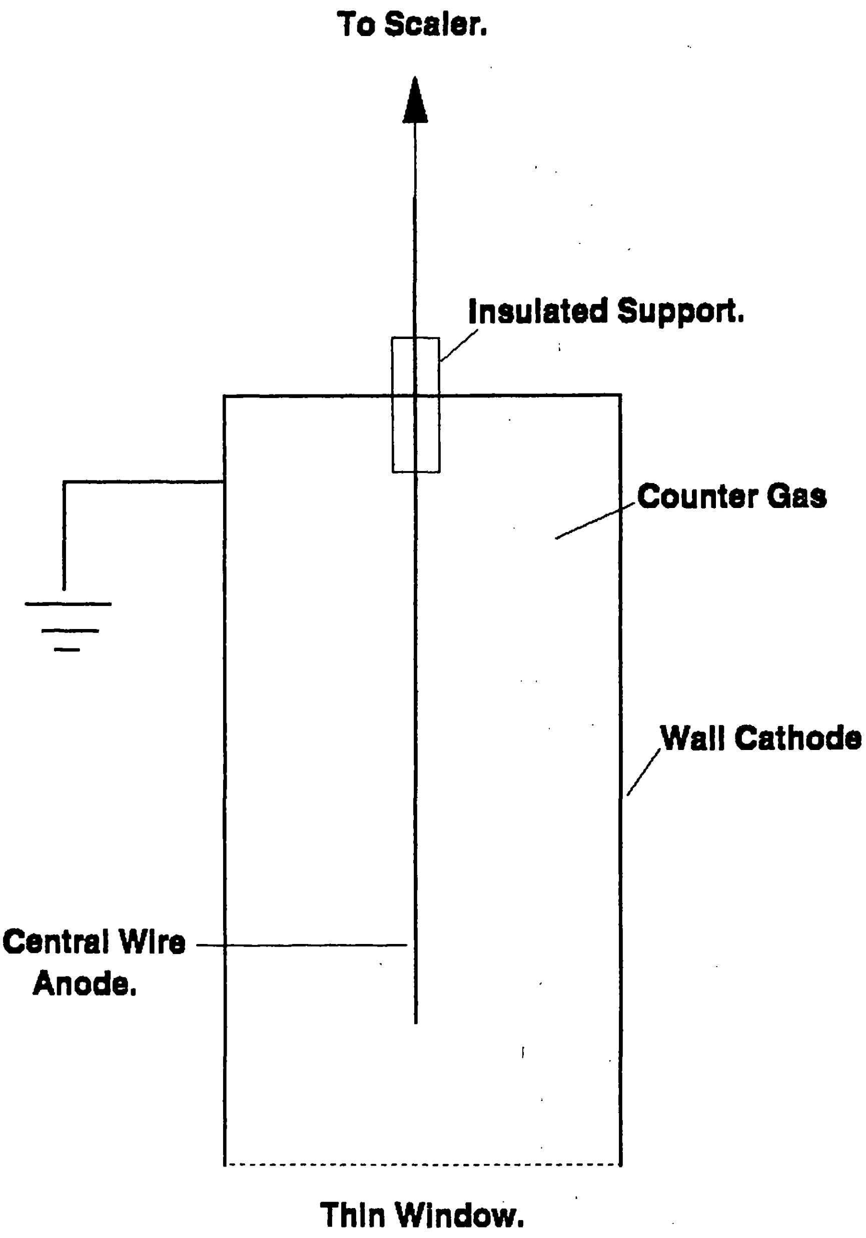


Fig.2.8. Schematic Diagram Of Geiger Müller Tube.

2.7.2 PLATEAU REGIONS.

When detecting ionising radiation using a Geiger-Müller counter no counts are registered until the voltage applied is large enough to attract the free electrons to the anode wire. Above this "Geiger threshold"(V_0) the count rate increases rapidly until the plateau region is reached where the count rate is independent of applied voltage. As the voltage is increased, further spurious discharges inside the counter cause an additional rapid increase in the count rate.It is desirable to work at a voltage in the middle of the plateau region where the counter is most stable.

The plateau region was determined for each Geiger-Müller counter used by constructing a plot of counts obtained from a solid ß-source against applied voltage. Fig 2.9. shows a plot of a typical plateau curve.

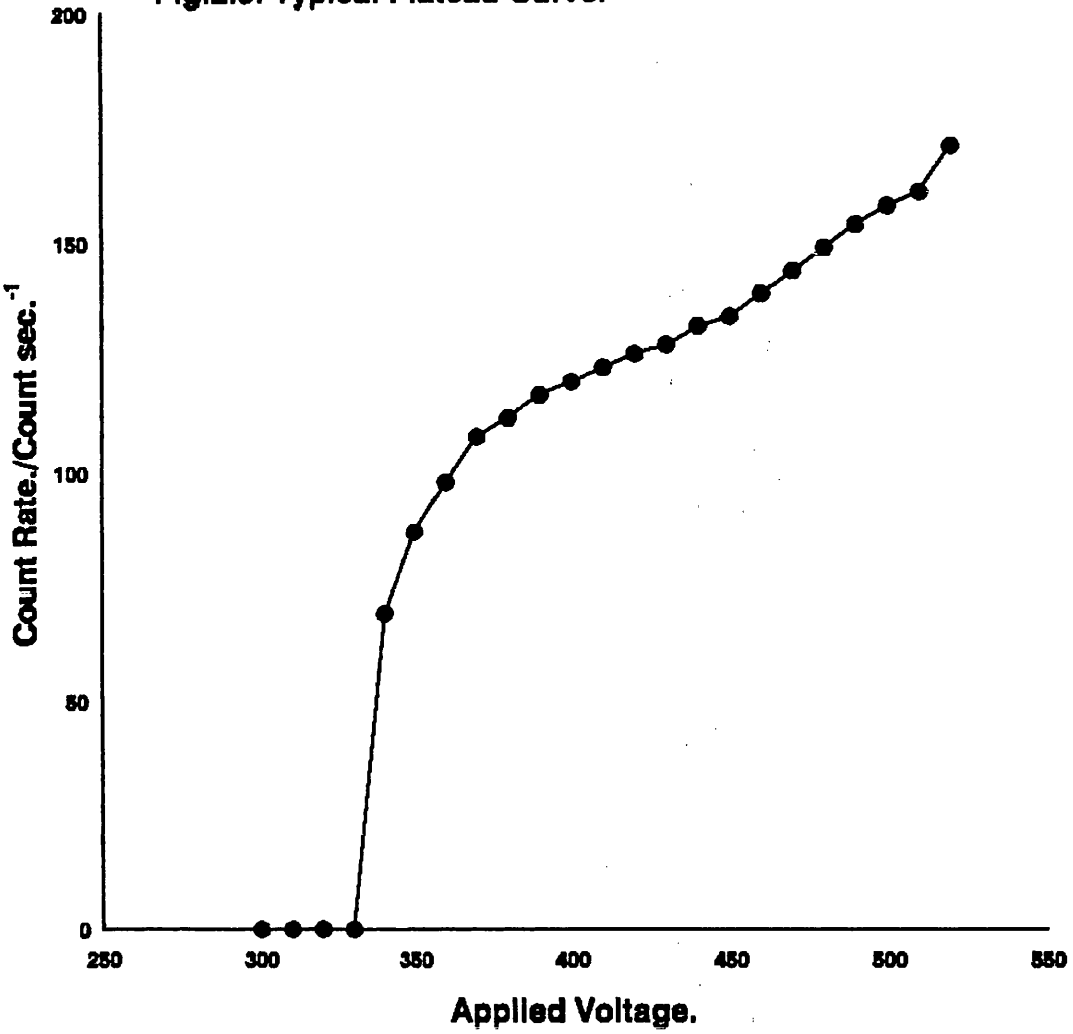
2.7.3 BACKGROUND.

Since Geiger Müller counters detect individual ionizing events, they register some counts in the absence of a radioactive source, for example from naturally occurring radioisotopes in the environment. An average background count must be subtracted from all counts in radiochemical counting experiments to correct for this effect.

2.8. DIRECT MONITORING GEIGER-MÜLLER COUNTING TECHNIQUE.

This method was developed by Thomson and modified by Al-Ammar and

Fig.2.9. Typical Plateau Curve.



Webb (109,110) to determine surface radioactivity on solids exposed to radiolabelled gases. This technique has proved useful in the determination of mechanisms in heterogeneous catalysis by allowing *in situ* monitoring of the reaction between solids and radiolabelled gases.

2.8.1. EQUIPMENT.

The counting vessel consisted of an evacuable Pyrex reaction vessel (Fig 2.10) containing two Geiger-Müller tubes and was connected via a manifold to a constant volume manometer and gas handling facilities. A Pyrex "boat", with two sections, was placed inside the counting vessel and could be moved along the length of the vessel using a magnet. The counting vessel was fitted a B14 socket for the attachment of an ampoule containing the solid to be studied, thus enabling the solid to be introduced into the counting vessel under vacuum. The apparatus was calibrated before use. The Geiger-Müller tubes were calibrated by monitoring counts using varying pressures of radioactive gas. A plot of pressure against counts should give a straight line which passes through the origin. Fig 2.11 shows the result of a typical calibration. When the counts from the Geiger-Müller tubes were plotted against each other (Fig 2.12) a straight line was obtained. The gradient of this line is equal to the counting ratio between the two tubes.The counting rate should remain constant and was usually in the region of 0.85.

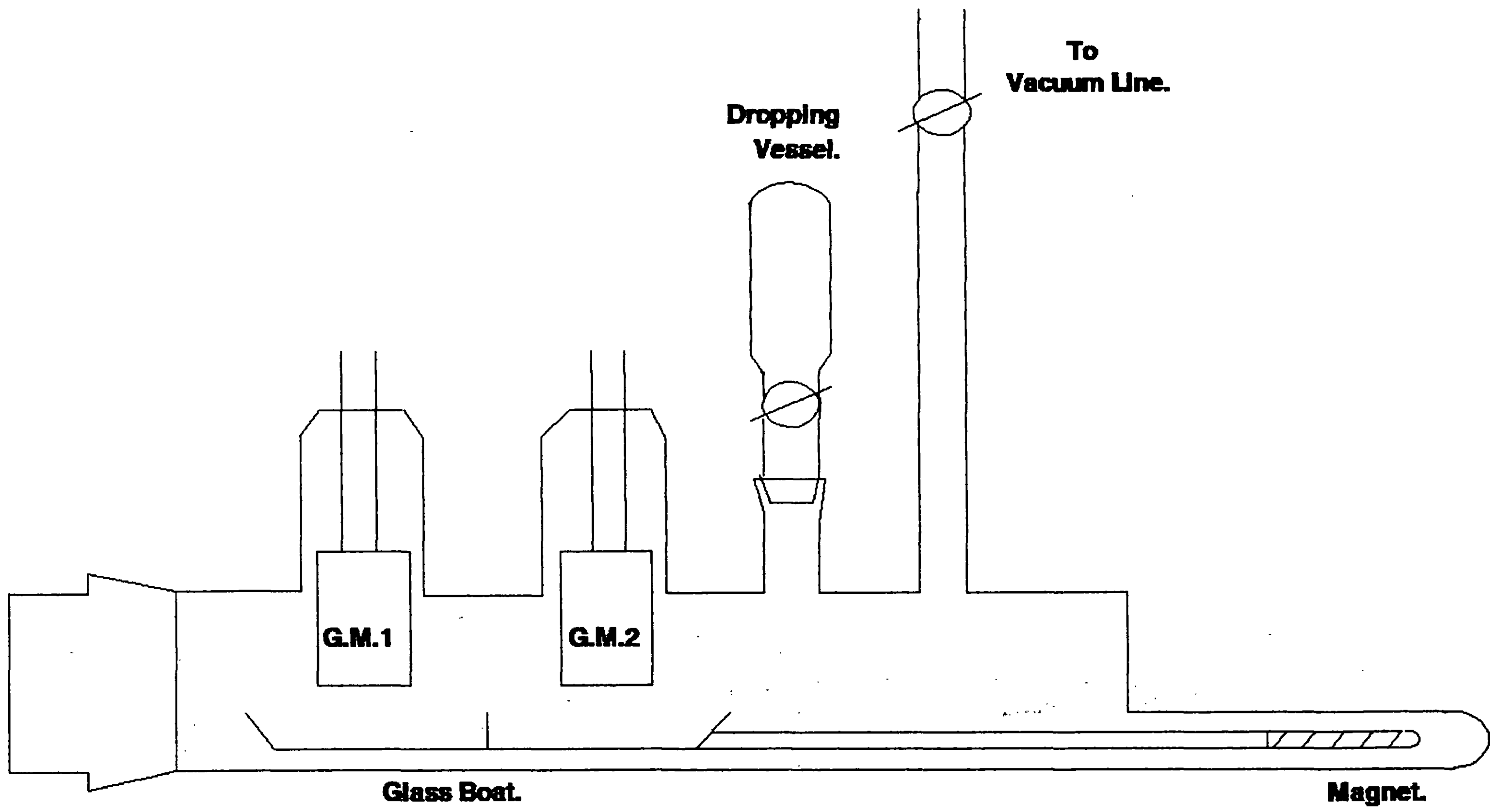


Fig.2.10. Direct Monitoring G.M. Counting Vessel.

Fig.2.11. Typical Calibration of G.M. Tube.

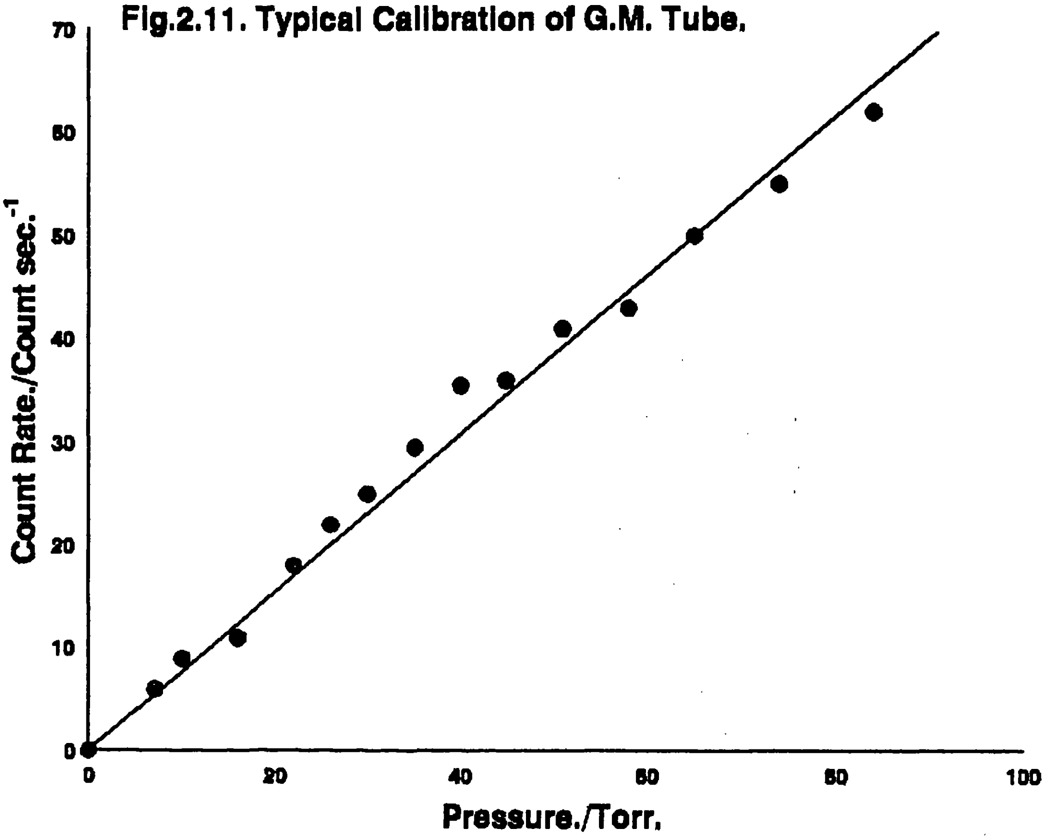
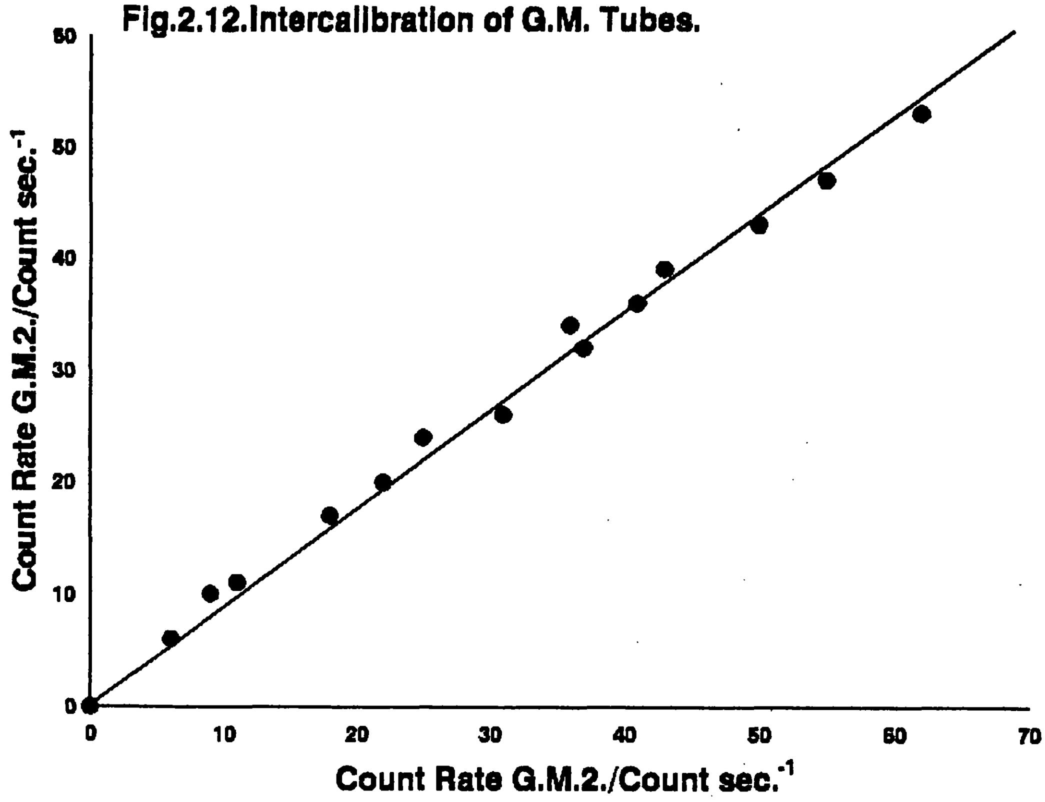


Fig.2.12.Intercalibration of G.M. Tubes.



2.8.2. EXPERIMENTAL METHOD.

A sample of the catalyst (0.5g) was transferred to a small dropping vessel in the dry box, degassed and attached to the evacuated, flamed out counting vessel. The solid was dropped from the ampoule into the right hand section of the "boat", which was then positioned so that the left hand section of the "boat" was directly under Geiger-Müller 1 and the right hand section was under Geiger-Müller 2. Thus, G.M.1. recorded counts from the gas alone and G.M.2. recorded counts from gas plus solid.

Radioactive gas was introduced to the counting vessel at a desired initial pressure. The reaction vessel was then isolated from the rest of the system and counts taken from both Geiger-Müller tubes for a measured time. All counts were corrected for background and intercalibration. The counts from G.M.1, gas alone, were subtracted from the counts from G.M.2, gas plus solid, to give values for surface counts alone.

2.9. SCINTILLATION COUNTERS. (111).

The technique used for detecting γ-radiation is based on the phenomena that when energetic photons enter certain crystals, short duration flashes, known as scintillations are observed. The most widely used crystal for γ-photon detection is sodium iodide containing small quantities of thallium (I) iodide (0.1-0.2 %). The high density of NaI ($3.7 gcm^{-3}$) and the high Z value of iodine makes this a very efficient γ-ray detector. Thus, the problem of detecting γ-photons is reduced to the problem of detecting visible light scintillations.

A photomultiplier tube (PMT) is the standard device used for detecting small numbers of visible light photons and essentially it converts light flashes into electrical impulses. When a γ-photon interacts with NaI/Tl crystal a scintillation, which consists of several visible light photons, is detected by the photomultiplier and is converted into a shower of electrons by accelerating them by an electrical potential gradient to an electrode which produces an approximately fourfold increase. These secondary electrons are similarly accelerated so that in a ten stage photomultiplier tube there is a gain of 10^4. These electrons are collected on the anode of the tube. This produces a negative pulse of short duration on the anode and these pulses are amplified and passed to a scaler ratemeter, where they are recorded. The magnitude of voltage pulses from scintillation detector is proportional to the energy of γ-photons giving rise to scintillations.

To achieve a maximum pulse, the scintillation crystal is surrounded by a reflector. The space between the crystal and the photomultiplier is filled with high viscosity paraffin or silicone oil, to improve light transmission. The scintillation counter and the scaler were calibrated before use, using a [^{60}Co] source which emits γ-rays of energy 1.33Mev. The γ-ray spectrum obtained by monitoring counts from a Cs^{18}F source while varying the applied threshold is shown in Fig 2.13.

2.10.COUNTING VESSELS.

Reactions involving [^{18}F]-fluorine were monitored using single limbed

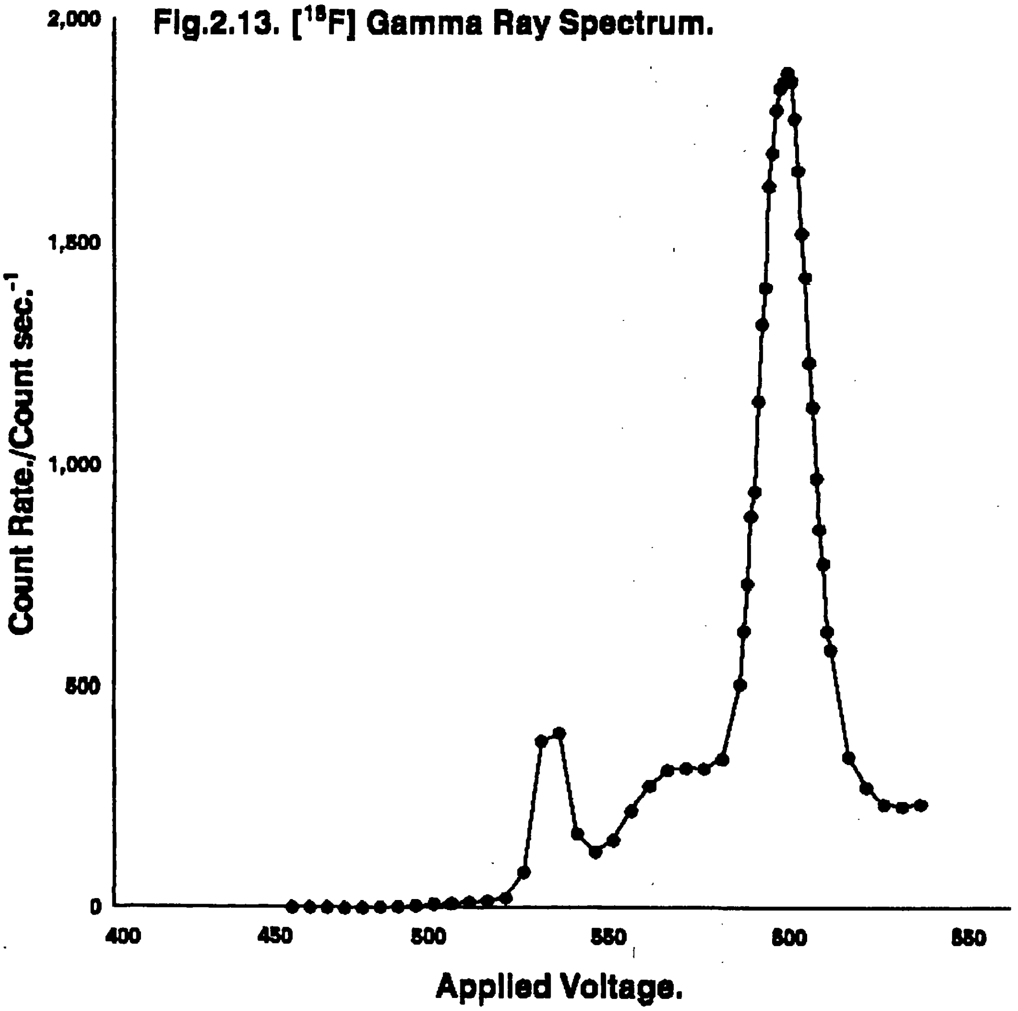


Fig.2.13. [^{18}F] Gamma Ray Spectrum.

counting vessels.(Fig 2.14). The specific count rate of [^{18}F]-fluorine samples were determined by introducing a known pressure of labelled vapour to a single limbed counting vessel containing dry pyridine (0.5ml). The efficiency of [^{18}F]- fluorine counting is dependent on the state of the sample;

solid > liquid > gas , so by forming an adduct between the gaseous [^{18}F]-fluorine sample and pyridine the counting is more efficient.

To follow uptake experiments between solids and [^{18}F]-fluorine labelled gases double limbed counting vessels (Fig 2.15) were used, allowing the count rate from both the solid and the gas phase to be monitored with time. The solid was contained in one limb of the vessel and the vapour phase was allowed to expand throughout the vessel. Therefore one limb provided counts from gas phase alone while counts determined from second limb were from gas plus solid.

2.11.STATISTICAL ERRORS.

Decay of a radioisotope is a random process and therefore subject to fluctuations due to the statistical nature of the process.The number of disintegrations observed during a fixed time when a source is measured repeatedly will not remain constant, even when half-life decay is taken into consideration. The probability W(m) of obtaining m disintegrations in time t from N_o original radioactive atoms is given by the binomial expression (Eqn.2.6.):

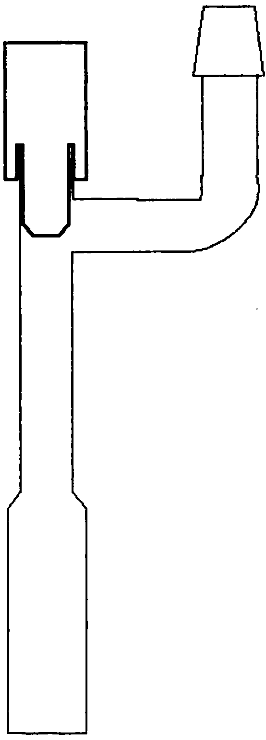


Fig.2.14. Single Limbed Counting Vessel.

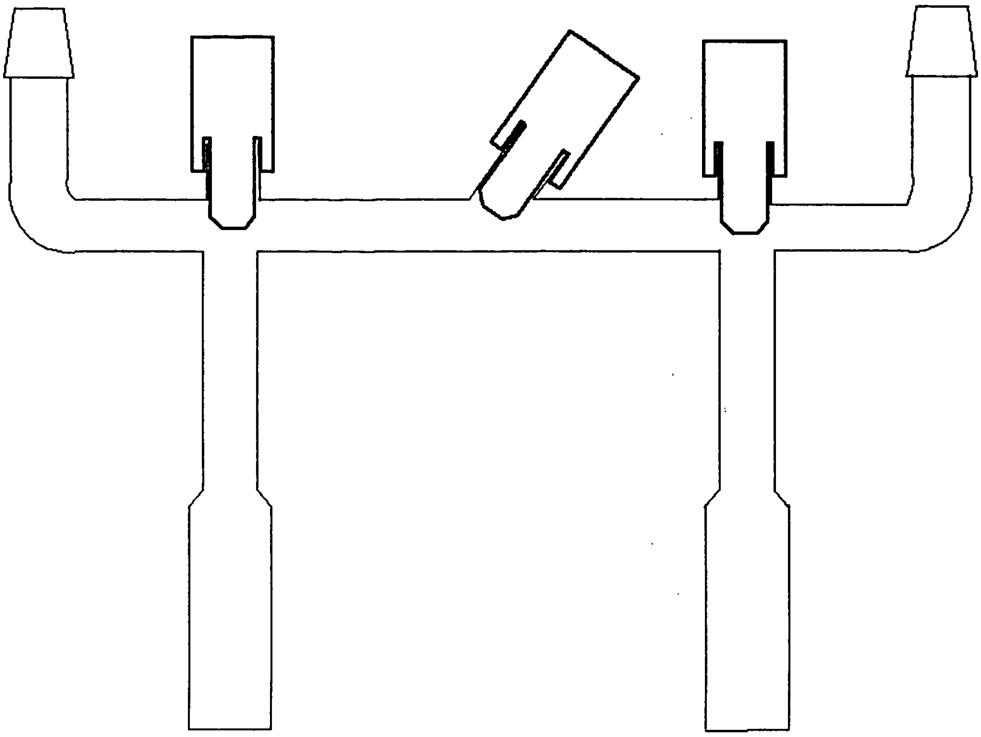


Fig.2.15. Double Limbed Counting Vessel.

$$Wm = \frac{No!}{(No-m)!m!} p^{m}(1-p)^{No-m} \qquad \text{Eqn.2.6.}$$

where p is the probability of a disintegration occurring within the time of observation (111).

It can be shown from this expression (112-114) that the expected standard deviation for radioactive disintegration, σ, is given by equation 2.7:

$$\sigma = \sqrt{me^{-\lambda t}} \qquad \text{Eqn.2.7.}$$

In practice the observation time t is short in comparison to the half-life so that equation 2.7.is reduced to :

$$\sigma = \sqrt{m} \qquad \text{Eqn.2.8.}$$

where m is the number of counts obtained.

In this work all errors quoted on radiochemical measurements are the combination of the uncertainty in the physical measurement, such as weight of sample and pressure of gas and the uncertainty in the count obtained.

2.12.DECAY CORRECTIONS.

Radioactive decay is a random process and so it is impossible to predict when a single atom will decay. However the characteristic rate of radioactive decay can be expressed in terms of the half-life, $t_{½}$, which is defined as the time required for the measured activity,A, to decrease by one half of its original value. The half-life can be conveniently determined from a plot of lnA against time.

The decay constant, λ, is related to the half-life by the equation:

$$t_{1/2}=\ln 2/\lambda \qquad \text{Eqn.2.9.}$$

The activity of a sample,A, is the number of events per second occurring within the sample.The decay process is described by the equation:

$$A_t = A_0e^{-\lambda t} \qquad \text{Eqn.2.10.}$$

where A_t is the count rate of the sample at time t

A_0 is the count rate of the sample at time 0

λ is the decay constant

Where significant decay occurred in the time taken to complete an experiment (i.e. when using short-lived isotopes such as ^{18}F-fluorine) all data obtained were corrected to zero time before being analysed.

COMPARISONS OF γ-ALUMINA AND CHROMIAS WITH RESPECT TO FLUORINATION AND CONDITIONING REACTIONS.

3.1 INTRODUCTION.

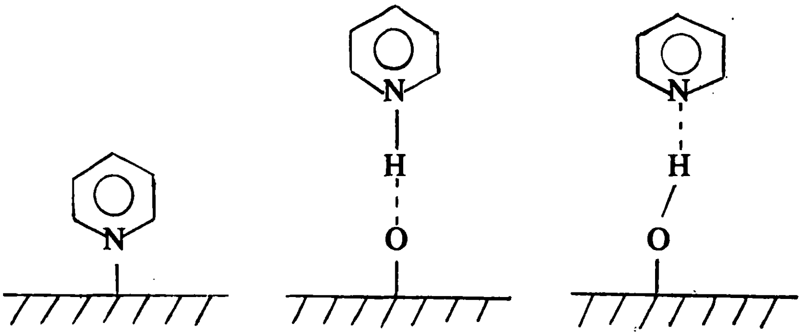
Catalytic fluorination of haloalkanes is one of the main processes used in the production of chlorofluorocarbon compounds and also hydrochlorofluorocarbon and hydrofluorocarbon compounds, which at present are the most viable alternatives to C.F.C s. The reaction involves vapour phase fluorinations at elevated temperatures in the presence of γ-alumina based (115), chromia based (22,23,115,116) or aluminium (III) fluoride catalysts (40,115,117) or liquid phase fluorinations in the presence of, for example, antimony pentachloride catalyst (16-20).

One of the principal catalysts that is used industrially in this process is chromia fluorinated with anhydrous hydrogen fluoride at 700K (93). Passing chlorofluoroethanes over this catalyst under similar conditions results in a mixture of chlorinated and fluorinated products within the series $C_2Cl_{6-n}F_n$, (n = 0 - 6). Radiotracer methods have been used to determine the routes to these products and indicate the occurrence of a series of catalytic halogen exchange reactions at the fluorinated chromia surface, involving catalytically active halogen and adsorbed chlorofluoroethane species (24-26).

Studies of the reactions of anhydrous hydrogen fluoride and chlorofluoroethanes using a γ-alumina catalyst indicated that this reaction did not result in the production of fluorinated products, as treatment of γ-alumina with HF does not create the strong Lewis acid sites required in a surface that is active for halogen exchange reactions (97). However, when sulphur tetrafluoride is used as a fluorinating agent at room temperature the Lewis acidity is enhanced (97). The dehydrochlorination reaction of 1,1,1-trichloroethane is used as a probe reaction for Lewis acidity. This characteristic reaction was determined on the strong Lewis acid aluminium (III) chloride (91) and the products are 1,1-dichloroethene and hydrogen chloride. The 1,1-dichloroethene formed undergoes further dehydrochlorination and polymerisation to give a purple organic layer on the solid. In the reaction of 1,1,1-trichloroethane with SF_4 fluorinated γ-alumina a similar dehydrochlorination reaction occurs with laydown of organic material but this is accompanied by the production of a mixture of hydrochlorofluoroethanes by hydrofluorination reactions (97,70). The resultant purple solid formed is described as an oxide supported organic layer catalyst and is active for further fluorination reactions involving chlorofluoroethanes and hydrogen fluoride. The formation of organic layers is not limited to SF_4 fluorinated γ-alumina and aluminium (III) chloride. It is also observed in γ-alumina chlorinated with CCl_4 or $OCCl_2$ (69,70) and $SbCl_{5-n}F_n$ (n = 0 - 5) with CH_3CCl_3 and HF (18-20), although further studies are required to determine the catalytic activity of these.

In order to examine how general the chemistry of the oxide supported organic layer catalyst is, comparisons have been made between the γ-alumina system and chromia treated in an identical manner. Studies have also been carried out to determine if fluorination with SF_4 occurs similarly on γ-alumina and on chromia samples in view of the differences observed in the HF fluorination process and also to establish a more detailed understanding of the conditioning process on γ-alumina and to determine if this extends to chromia.

For the dehydrochlorination reactions of 1,1,1-trichloroethane strong Lewis acid sites are essential. Analysis of Brφnsted and Lewis acid sites by direct spectroscopic techniques is difficult. The method used extensively is an indirect method which involves the adsorption of a basic probe molecule onto the acidic sites (118-135). The most common probe molecule for infrared studies is pyridine since its organic ring structure is ideal for infrared adsorption techniques. The I.R. spectrum of pyridine coordinately bonded to the surface is different from that of the pyridinium ion, permitting differentiation of the type of acid site on the surface.



Coordinatively Bonded Pyridine.

Pyridinium Ion.

H-Bonded Pyridine.

Fig.3.1. Adsorbed Pyridine and Pyridinium Species.

Comparisons between the acid sites on γ-alumina and chromias will provide information on the types and possibly the strengths of the acid sites on the solids and also on the effects of the fluorination and conditioning processes on the acid sites.

EXPERIMENTAL.

3.2.1. INFRA-RED ANALYSIS OF THE VOLATILE MATERIALS FROM THE SULPHUR TETRAFLUORIDE FLUORINATION PROCESS ON γ-ALUMINA UNDER STATIC CONDITIONS.

A sample (0.525g) of calcined γ-alumina was loaded into a Monel metal bomb in the dry-box. The bomb was then attached to the SF_4 dispensing line, degassed and the fluorination procedure using three aliquots of 3mmol SF_4 was performed as described in Section 2.4.2. After each addition the volatile material was removed and analysed by infra-red spectroscopy.

The procedure to study the volatile material from the SF_4 fluorination of chromia and volcano chromia was the same as described above.

3.2.2.ANALYSIS OF SULPHUR TETRAFLUORIDE FLUORINATION PROCESS BY PRESSURE CHANGES.

A sample (10.10g) of γ-alumina was loaded into a Monel metal bomb, calcined for 8h. at 500K and then attached to the sulphur tetrafluoride dispensing line. The γ-alumina was fluorinated using 15 aliquots of 12mmol of SF_4, resulting in a total of 180mmol SF_4 introduced to the γ-alumina. The reaction of each aliquot occurred at room temperature over two hours, during which time pressure readings were taken at regular intervals.

The procedure to study the SF_4 fluorination of volcano chromia under flow conditions was the same as described above.

3.2.3. ANALYSIS OF THE VOLATILE MATERIALS FROM THE 1,1,1-TRICHLOROETHANE CONDITIONING PROCESS OF SF_4 FLUORINATED γ-ALUMINA UNDER STATIC CONDITIONS.

A sample of γ-alumina was fluorinated as described in Section 3.2.1. Dry, unstabilised 1,1,1-trichloroethane was condensed into the bomb containing this material and allowed to react as described in Section 2.4.3. The volatile material from this conditioning step was removed and analysed by gas infrared spectroscopy and gas chromatography.

The same procedure was used to study the volatile material from the conditioning step on SF_4 fluorinated chromia and volcano chromia.

The conditioning process was also performed in Pyrex glass vessels to allow observations to be made with respect to colour changes during the reaction. After the removal of the volatile material the sample was reweighed to determine any mass changes and then a second aliquot of 3mmol of 1,1,1-trichloroethane was introduced and the reaction repeated to determine if further organic material could be laid down on the catalyst.

In order to gain further information concerning the conditioning reaction, this process was also studied using $CH_2=CCl_2$ as the starting material for the conditioning of fluorinated materials.

3.2.4. ANALYSIS OF 1,1,1-TRICHLOROETHANE CONDITIONING PROCESS ON SF_4 FLUORINATED γ-ALUMINA UNDER FLOW CONDITIONS IN A MONEL METAL REACTOR.

A sample of γ-alumina was fluorinated with SF_4 as described in Section 3.2.2 then transferred, in the dry box, to a Monel metal reaction vessel and fitted to the HF/CH_3CCl_3 flow line (Section 2.1.4).

The catalyst was purged with N_2, flow rate $10cm^3min^{-1}$, overnight. The conditioning reaction was achieved by flowing the nitrogen carrier gas through the 1,1,1-trichloroethane reservoir, flow rate 4.6mmol h^{-1}, and over the γ-alumina sample. The gas was vented through the sample point scrubber unit. Samples for analysis by gas chromatography were taken of the feed gas and the Rig Off Gas (ROG) at regular intervals to allow determination of product composition. The conditioning process was continued for 30h after which time the CH_3CCl_3 feed flow was stopped and the γ-alumina was purged with N_2 ($10cm^3min^{-1}$) for 2h.

This reaction was repeated using a Pyrex glass reaction vessel to allow observations to be made with respect to colour changes throughout the reaction process.

The same procedure was used to study the conditioning step on SF_4 fluorinated volcano chromia under flow conditions.

3.2.5. INFRA-RED STUDY OF THE REACTION OF 1,1,1-TRICHLOROETHANE WITH SF_4 FLUORINATED ALUMINA WITH TIME.

A sample of SF_4 fluorinated γ-alumina was prepared as described in Section 3.2.1 and loaded into an *in situ* gas I.R. cell and allowed to interact with 1,1,1-trichloroethane (1.0mmol) as described in Section 2.5.1. The data collected were reprocessed and the absorbance for the gas of interest determined. This was plotted with respect to time to examine changes in the gas phase composition above the solid during the conditioning reaction.

The procedure to study the gas phase material in the conditioning step on SF_4 fluorinated chromia and volcano chromia was the same as described above.

A similar method was employed to examine the materials in the gas phase when 1,1-dichloroethene was used to condition the fluorinated materials in order to study the conditioning process fully. *In situ* I.R was also used to study the reaction when anhydrous hydrogen chloride was introduced to conditioned plus fluorinated material. This provided information regarding labile chlorine containing species on the surfaces of conditioned materials.

3.2.6. B.E.T. SURFACE ANALYSIS.

B.E.T. analyses on calcined, fluorinated and fluorinated plus conditioned materials were performed at I.C.I. Runcorn, using Micromeritics 2400 gas adsorption equipment.

3.2.7. D.R.I.F.T.S STUDY OF ADSORBED PYRIDINE SPECIES ON CALCINED, FLUORINATED AND CONDITIONED γ-ALUMINA.

A sample of calcined γ-alumina (0.502g) was transferred into a reaction vessel in the dry box. The vessel was fitted to a vacuum line and degassed. The sample was then exposed to the vapour of dried pyridine for 10min after which the reaction vessel was isolated and left at room temperature for 24h. for the reaction to occur. The sample was then degassed and transferred to the dry box. A sample of this pyridine-treated γ-alumina (ca.0.05g) was analysed by diffuse reflectance I.R. spectroscopy as described in Section 2.5.3.

This procedure was also used for calcined chromias, SF_4 fluorinated γ-alumina and chromias and conditioned plus fluorinated γ-alumina and chromias.

3.3. RESULTS.

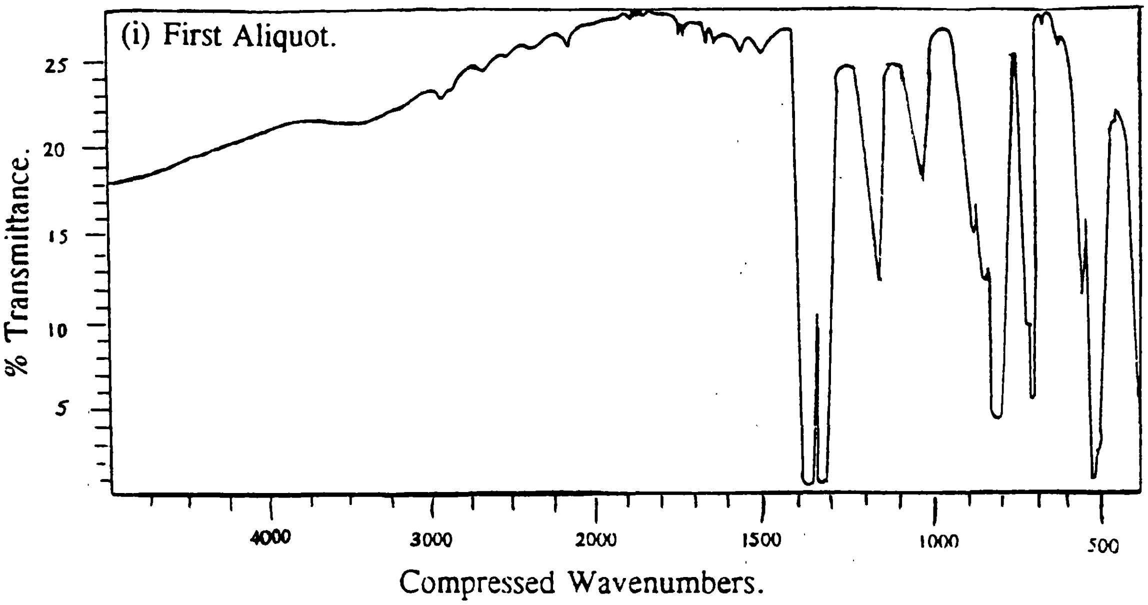
3.3.1. I.R. ANALYSIS OF VOLATILE MATERIAL FROM THE SF_4 FLUORINATION PROCESS.

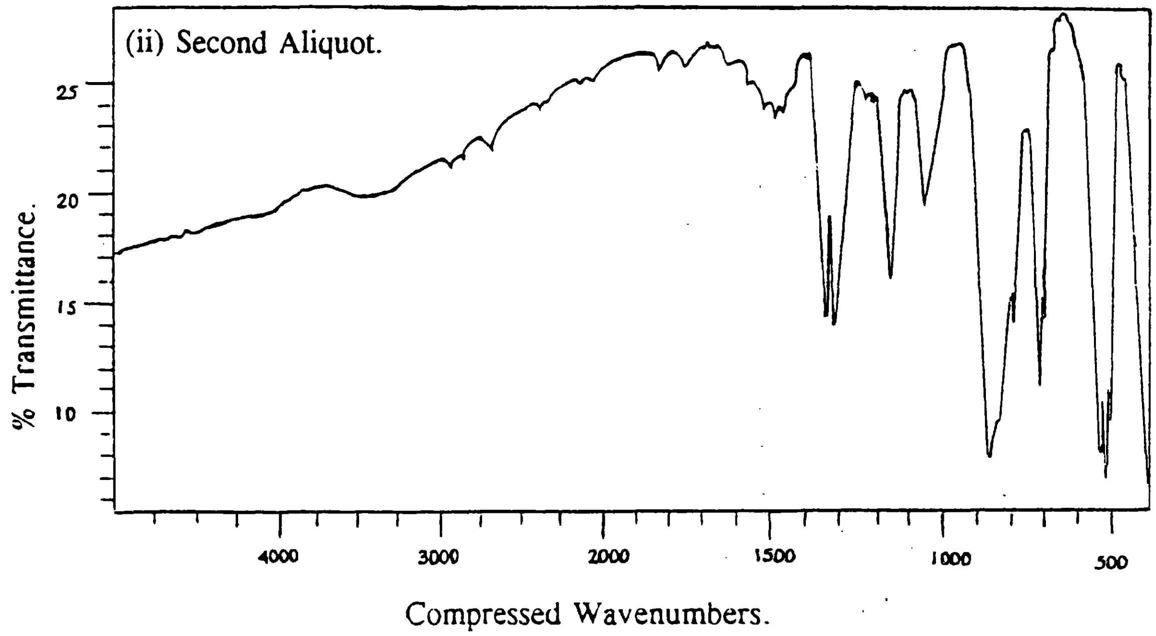
Infra-red analysis of the volatile products after 2h exposure to the first aliquot of 3mmol of sulphur tetrafluoride to calcined materials indicated that thionyl fluoride was a major component in the mixture (Fig.3.2). After the addition of the third aliquot, unchanged sulphur tetrafluoride was a very substantial component, indicating that the fluorination process was complete. The pattern observed was similar in all three cases, indicating that the fluorination mechanism that has been established for γ-alumina also occurred on chromia and volcano chromia.

3.3.2. ANALYSIS OF SULPHUR TETRAFLUORIDE FLUORINATION PROCESS BY PRESSURE CHANGES.

The results of analysis of the stepwise sulphur tetrafluoride fluorination process by pressure change observations are shown in Fig.3.3. The immediate pressure decrease observed on introduction of each aliquot was consistently greater than can be explained purely by expansion. After the initial decrease the pressure increased. The pattern in the pressure changes can be explained in terms of adsorption of sulphur tetrafluoride by the solid and the resultant release of the products from the fluorination reaction, SOF_2 and SO_2. This fluorination process involved the addition of SF_4 (180mmol) to γ-alumina (10.0g), which is a similar ratio as that used for the fluorination of the smaller

Fig.3.2. I.R. Analysis Of Volatile Material From SF_4 Fluorination Process.
(i) γ-Alumina.





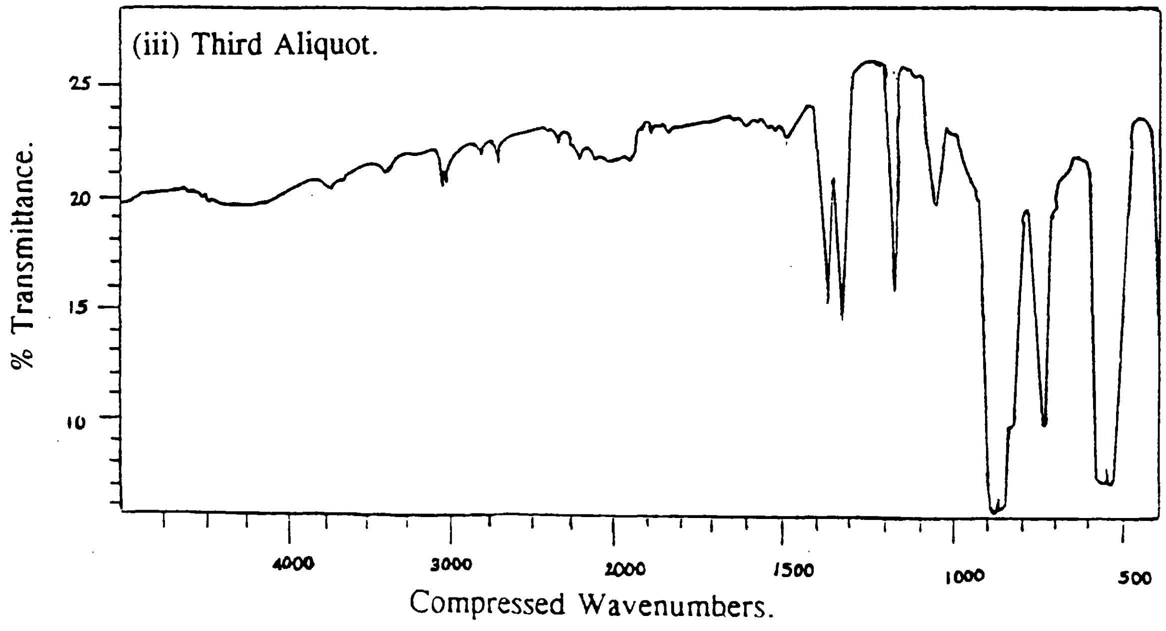


Fig.3.2. I.R. Analysis Of Volatile Material From SF_4 Fluorination Process.
(ii) Chromia.

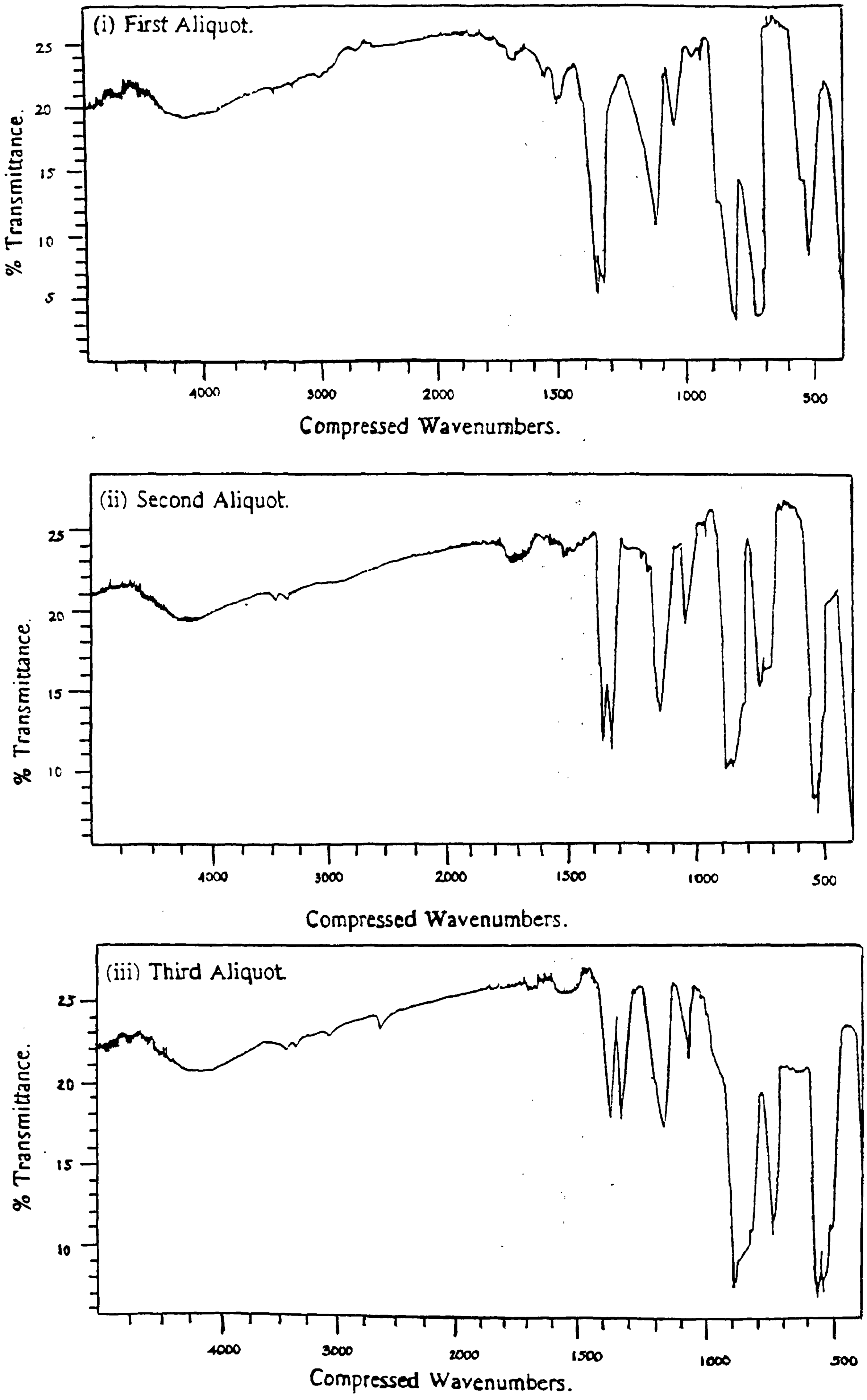


Fig.3.2. I.R. Analysis Of Volatile Material From SF_4 Fluorination Process.

(iii) Volcano Chromia.

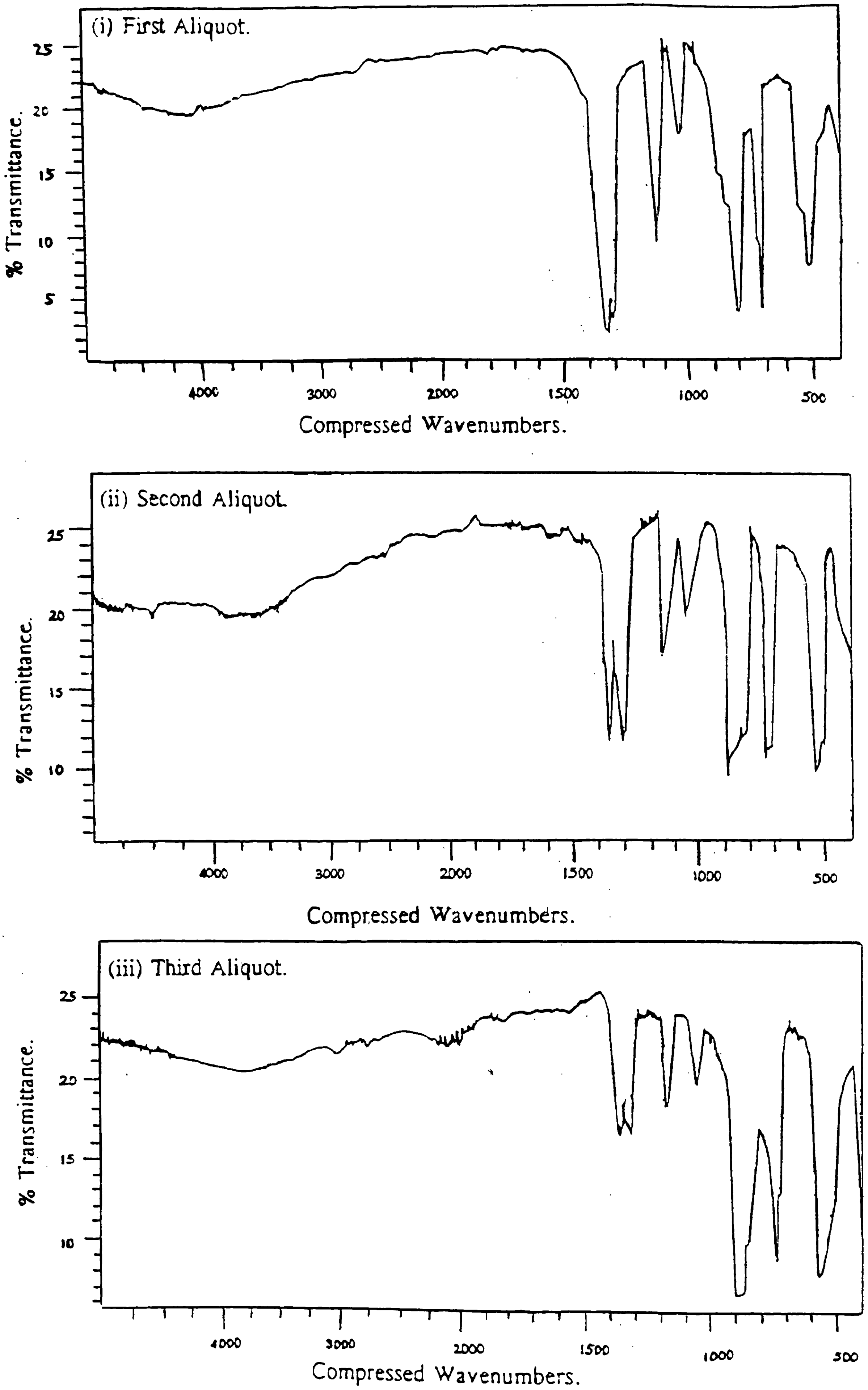
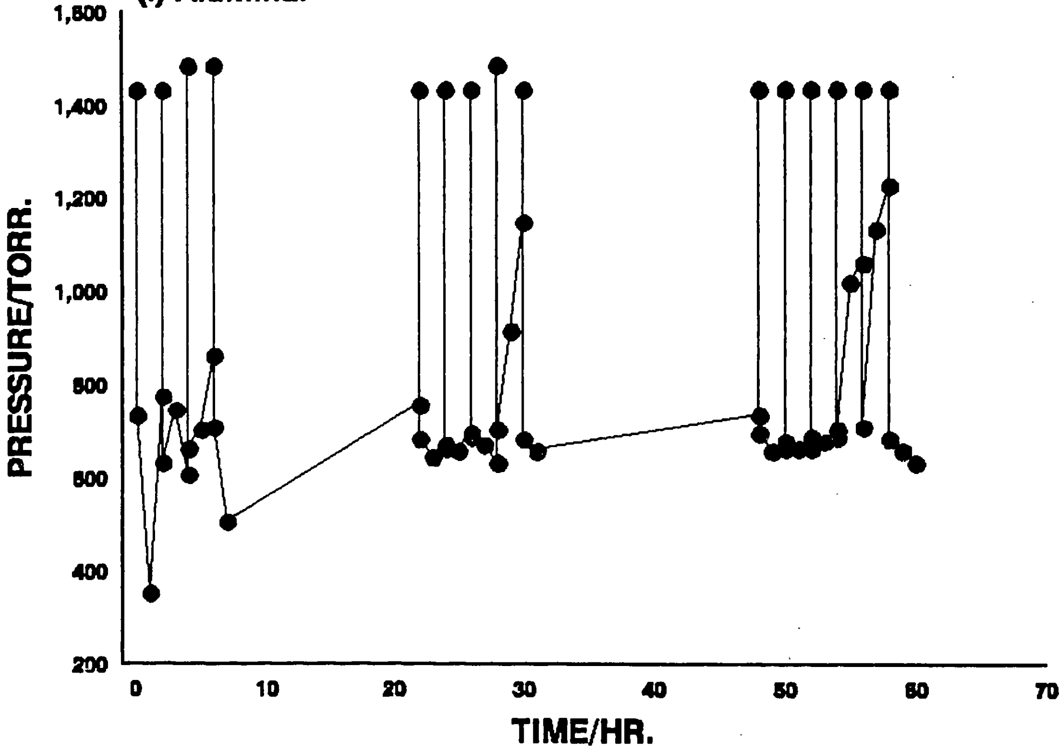
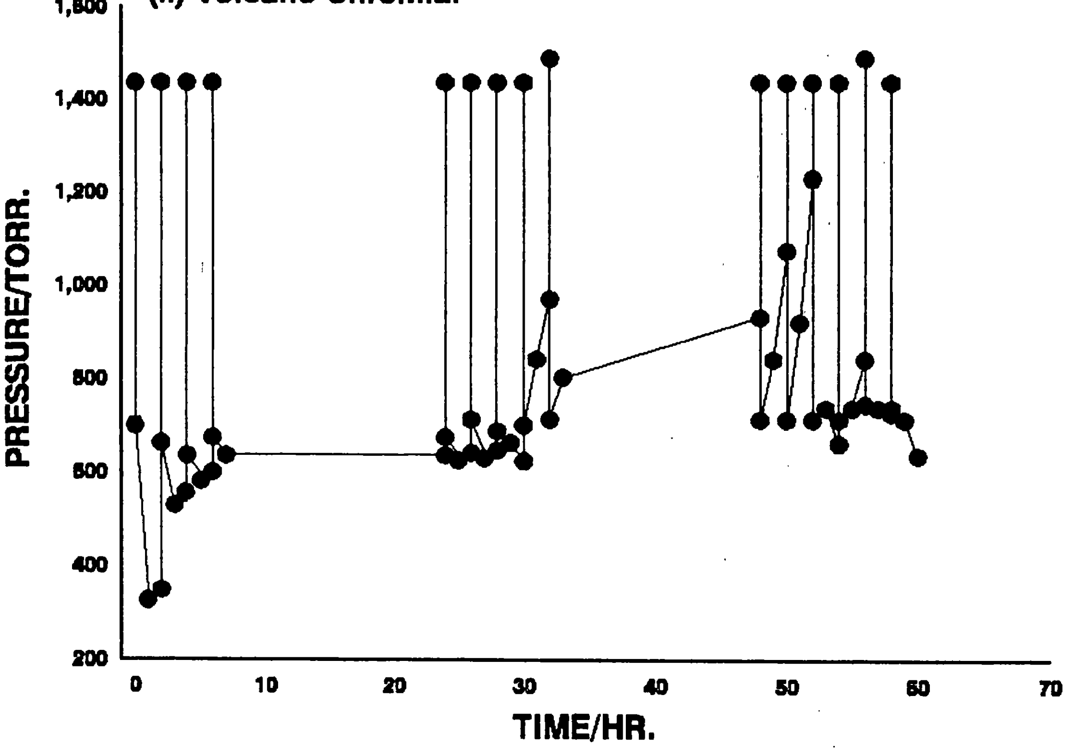


Fig.3.3. Analysis of SF_4 Fluorination Process By Pressure Changes.

(I) Alumina.



(II) Volcano Chromia.



samples studied.

3.3.3. I.R. ANALYSIS OF THE VOLATILE MATERIAL FROM THE 1,1,1-TRICHLOROETHANE CONDITIONING PROCESS.

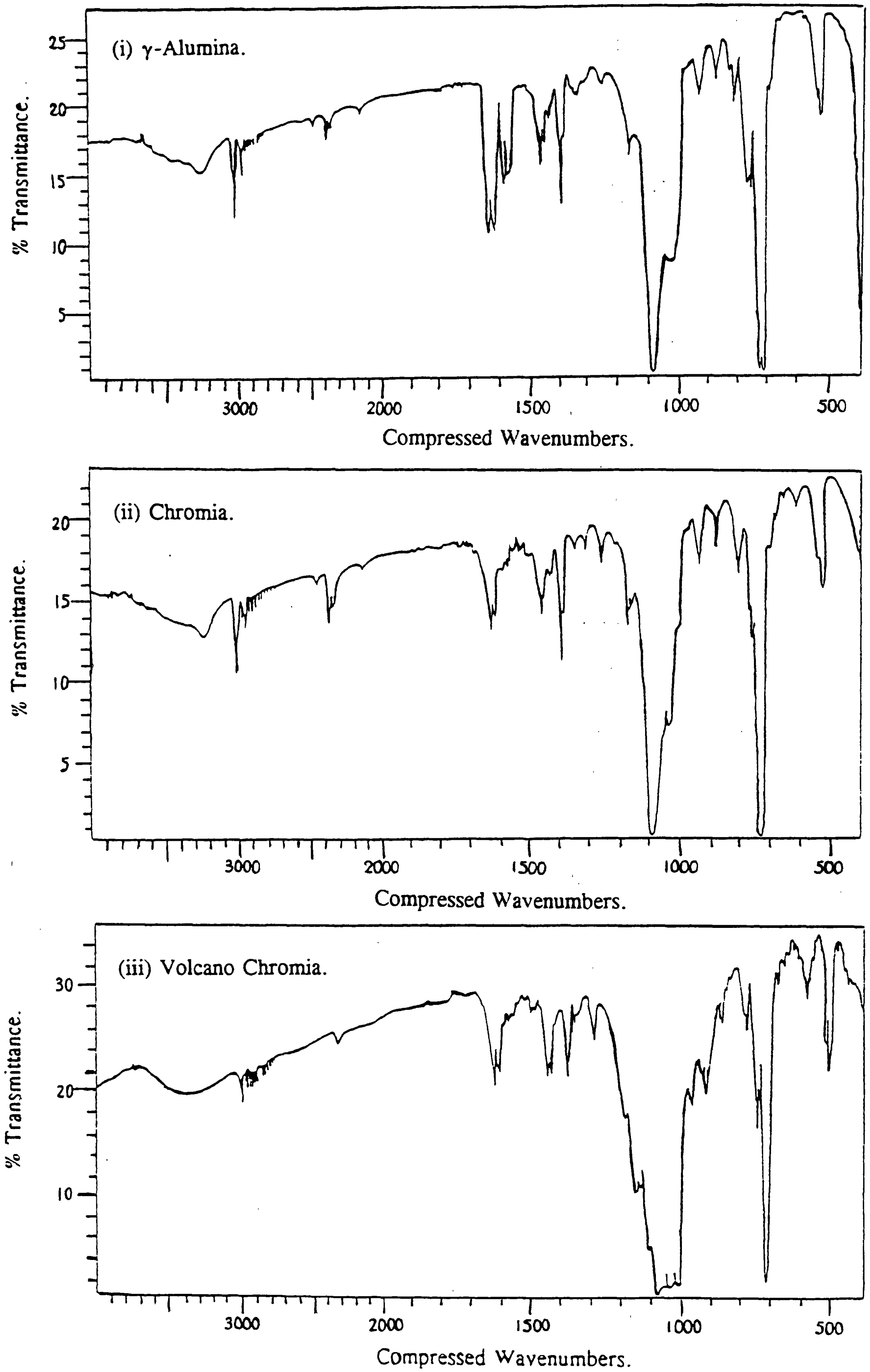
Infra-red analysis of the volatile products after 2h exposure of 1,1,1 trichloroethane (3mmol) to fluorinated materials indicated that the dehydrochlorination reaction had occurred on all three surfaces. The I.R. spectra (Fig.3.4.) showed the presence of unreacted 1,1,1-trichloroethane and the dehydrochlorination products 1,1-dichloroethene and hydrogen chloride. The SF_4 γ-alumina developed the very dark purple colour characteristic of the laydown of the organic layer. There was however, no visible evidence of a colour change on the chromia samples.

The spectra also included several bands in the regions characteristic of C-F stretches particularly at $1030cm^{-1}$ indicating that hydrofluorination reactions had occurred in all three cases.

3.3.4. G.C. ANALYSIS OF THE VOLATILE MATERIAL FROM THE 1,1,1-TRICHLOROETHANE CONDITIONING PROCESS IN MONEL METAL REACTION VESSELS.

Analysis of the volatile material from the conditioning process by gas chromatography indicated similar products from the three solids under examination; unreacted CH_3CCl_3, the dehydrochlorination product $CH_2=CCl_2$, and CH_3CCl_2F (141b), a product of halogen exchange between

Fig.3.4. I.R. Analysis Of Volatile Material From CH_3CCl_3 Conditioning Process.



1,1,1-trichloroethane and the fluorinated surfaces. Other fluorinated products were also detected but only in trace quantities.

From the values in Table 3.3.1, it is obvious that there were substantial differences in the proportions of products from the three surfaces.

Table.3.3.1.G.C. Analysis of Volatile Material from the CH_3CCl_3 Conditioning Process in Monel Metal Reaction Vessels.

	CH_3CCl_3	$CH_2{=}CCl_2$ mol%	CH_3CCl_2F
SF_4 γ-ALUMINA	71.0	5.3	22.9
SF_4 CHROMIA	59.1	21.8	18.8
SF_4 VOLCANO CHROMIA	43.1	18.4	36.5
BF_3 γ-ALUMINA	53.9	42.0	4.1

In all three cases significant quantities of CH_2CCl_2 and CH_3CCl_2F were produced. The chromia sample converts more of the CH_3CCl_3 into products and produces similar quantities of the two products CH_2CCl_2 and CH_3CCl_2F: 21.8 mol% and 18.4 mol% respectively. The reaction over γ-alumina produces a similar quantity of CH_3CCl_2F (22.9 mol%) but substantially less CH_2CCl_2 (5.3 mol%) as the reaction over chromia. Of the three SF_4 fluorinated solids examined, the volcano chromia sample produces the greatest quantity of CH_3CCl_2F. BF_3 fluorinated γ-alumina behaves quite differently from SF_4 fluorinated γ-alumina. It converts more of the starting material into products and produces a more substantial amount of 1,1-dichloroethene than

1,1-dichloro,1-fluoroethane, 42.0 mol% and 4.1 mol% respectively.

3.3.5. G.C. ANALYSIS OF THE VOLATILE MATERIAL FROM THE 1,1,1-TRICHLOROETHANE CONDITIONING PROCESS IN PYREX GLASS REACTION VESSELS.

Analysis by gas chromatography of the volatile materials from two consecutive additions of 3mmol of 1,1,1-trichloroethane to SF_4 fluorinated materials in Pyrex glass vessels indicated the presence of unreacted 1,1,1-trichloroethane and substantial quantities of 1,1-dichloroethene and 1,1-dichloro,1-fluoroethane (Table 3.3.2). These results do not parallel exactly the reaction in the Monel reaction vessel (Section 3.3.4). In the Pyrex reaction vessel, chromia converts more 1,1,1-trichloroethane into products than either γ-alumina or volcano chromia. However, in all three cases, the quantities of CH_2CCl_2 and CH_3CCl_2F are quite similar, with SF_4 chromia producing most CH_3CCl_2F. BF_3 fluorinated γ-alumina produces more CH_2CCl_2 and substantially less CH_3CCl_2F than the reactions over the other solids: for example, 32.7 mol% CH_2CCl_2 and 2.3 mol% CH_3CCl_2F compared to 21.6 mol% CH_2CCl_2 and 22.7 mol% CH_3CCl_2F for SF_4 chromia. The extent of dehydrochlorination and hydrofluorination in the second conditioning reaction appeared to be considerably smaller than in the first reaction. In all four cases the quantity of 1,1,1-trichloroethane converted is considerably less than from the first conditioning step. Also, the quantities of 1,1-dichloroethene and 1,1-dichloro,1-fluoroethane produced were much smaller than from the first addition. The BF_3 fluorinated γ-alumina produced no CH_3CCl_2F in the second conditioning reaction.

Table.3.3.2. G.C. Analysis of Volatile Material from the CH_3CCl_3 Conditioning Process in Pyrex Glass Reaction Vessels.

FIRST ADDITION.	CH_3CCl_3	CH_2CCl_2 mol%	CH_3CCl_2F
SF_4 γ-ALUMINA.	68.8	17.5	13.5
SF_4 CHROMIA.	53.4	21.6	22.7
SF_4 VOLCANO CHROMIA.	60.7	21.6	17.3
BF_3 γ-ALUMINA.	63.7	32.7	2.3

SECOND ADDITION	CH_3CCl_3	CH_2CCl_2 mol%	CH_3CCl_2F
SF_4 γ-ALUMINA.	89.4	8.3	2.2
SF_4 CHROMIA.	81.6	14.1	3.8
SF_4 VOLCANO CHROMIA.	80.6	13.8	5.1
BF_3 γ-ALUMINA.	88.5	13.5	0.0

The purple colour, characteristic of the organic layer, developed on the SF_4 fluorinated γ-alumina as expected, however it was not as dark as the material observed when the conditioning reaction took place in a metal bomb. The addition of the second aliquot of 1,1,1-trichloroethane had little effect on the colouration of the γ-alumina. No colour change was observed during the conditioning process on chromia or volcano chromia: the volcano chromia samples remained green in colour and the chromia samples remained black. It is possible that the initial colouration of the chromia samples masked any colour changes. Conditioning reactions on γ-alumina fluorinated with boron trifluoride instead of sulphur tetrafluoride indicated that this material was also capable of dehydrochlorination and hydrofluorination reactions although the extent of the hydrofluorination reaction was less than that observed on SF_4 fluorinated γ-alumina. For the first conditioning reaction SF_4 γ-alumina produced 17.5 mol% CH_2CCl_2 and 13.5 mol% CH_3CCl_2F in comparison to BF_3 γ-alumina which produced 32.7 mol% CH_2CCl_2 and 2.3 mol% CH_3CCl_2F. The BF_3 fluorinated γ-alumina developed a blue colour indicating the laydown of some organic material but the colouration was not as intense as that developed on the SF_4 fluorinated γ-alumina.

3.3.6. G.C. ANALYSIS OF THE VOLATILE MATERIAL FROM THE 1,1-DICHLOROETHENE CONDITIONING PROCESS IN MONEL METAL REACTION VESSELS.

Analysis by gas chromatography of the volatile material from the 1,1-dichloroethene conditioning reaction on fluorinated materials resulted in similar products as in the 1,1,1-trichloroethane conditioning process.The presence of substantial quantities of 1,1,1-trichloroethane, 50-60 mol%, indicated the occurrence of hydrochlorination reactions in addition to the hydrofluorination reactions that result in the formation of 1,1 -dichloro,1-fluoroethane.The quantity of fluorinated products was greater in the CH_3CCl_3 conditioning reaction than in the $CH_2{=}CCl_2$, for example γ-alumina produced 22.9 mol% CH_3CCl_2F from CH_3CCl_3 and 16.1 mol% CH_3CCl_2F from $CH_2{=}CCl_2$.

Table.3.3.3. G.C. Analysis of Volatile Material from the $CH_2=CCl_2$ Conditioning Process in Monel Metal Reaction Vessels.

	CH_3CCl_3	$CH_2=CCl_2$ mol%	CH_3CCl_2F
SF_4 γ-ALUMINA	60.9	22.6	16.1
SF_4 CHROMIA	50.6	37.3	10.6
SF_4 VOLCANO CHROMIA	53.6	16.2	21.4

Comparison of the values in Table 3.3.3 with those in Table 3.3.1 indicate broad similarities although they are not identical. For example the reaction of CH_3CCl_3 over SF_4 volcano chromia results in 43.1 mol% CH_3CCl_3, 18.4 mol% CH_2CCl_2 and 36.5 mol% CH_3CCl_2F whereas the reaction with CH_2CCl_2 produces 53.6 mol% CH_3CCl_3, 16.2 mol% CH_2CCl_2 and 21.4 mol% CH_3CCl_2F. Therefore it appears that the hydrochlorination of 1,1,-dichloroethene is an important reaction in the conditioning process.

3.3.7. ANALYSIS OF THE MASS CHANGES OF THE SOLIDS FROM THE 1,1,1-TRICHLOROETHANE CONDITIONING PROCESS IN PYREX GLASS REACTION VESSELS.

Exposure of fluorinated materials (*ca.* 0.5g) to two aliquots of 3mmol of 1,1,1-trichloroethane at room temperature resulted in an increase in the mass of the solid indicating that organic material had been laid down on the solids (Table 3.3.4). The mass increases resulting from the conditioning reactions were comparable for SF_4 fluorinated γ-alumina and volcano chromia

(0.5 - 0.6 g(g^{-1}solid)). However the increase determined for SF_4 fluorinated chromia was considerably smaller (0.125 g(g^{-1}solid)).

Table.3.3.4. Mass Changes of Fluorinated Solids in Conditioning Reaction With 1,1,1-trichloroethane in Pyrex Vessels

FIRST ADDITION	MASS OF SOLID (g)	MASS OF CH_3CCl_3 (g)	MASS OF SOLID AFTER REACTION (g)	MASS INCREASE (g)
SF_4 γ-ALUMINA	0.5355	0.3822	0.7756	0.2401
SF_4 CHROMIA	0.5686	0.3235	0.5930	0.0244
SF_4 VOLCANO CHROMIA	0.4490	0.3463	0.7285	0.2795
BF_3 γ-ALUMINA	0.4555	0.370	0.5343	0.0788
SECOND ADDITION				
SF_4 γ-ALUMINA	0.7756	0.3409	0.7885	0.0129
SF_4 CHROMIA	0.5930	0.4093	0.6395	0.0465
SF_4 VOLCANO CHROMIA	0.7285	0.4094	0.7379	0.0094
BF_3 γ-ALUMINA	0.5343	0.3369	0.7025	0.1682

The mass increases observed for the alumina and volcano chromia samples occurred mainly in the first addition, whereas for the chromia sample the mass increase determined was virtually identical for each addition, 0.0244g for the first addition and 0.0465g for the second addition.

It was also established that treatment of BF_3 fluorinated γ-alumina with 1,1,1-trichloroethane resulted in an increase in the mass of the solid (0.0788g for the first addition and 0.1682 g for the second addition). The increase was not as great as for the SF_4 fluorinated γ-alumina, (0.2401g for the first addition) indicating that the laydown of organic material was less extensive.

3.3.8. ANALYSIS OF THE VOLATILE MATERIAL FROM THE 1,1,1-TRICHLOROETHANE CONDITIONING PROCESS BY *IN SITU* GAS INFRARED SPECTROSCOPY.

The results of the *in situ* I.R. analysis of the 1,1,1-trichloroethane conditioning reaction indicate that the dehydrochlorination reaction occurred on all three solids being examined, with 1,1-dichloroethene being detected. In the volatile material from the reaction on volcano chromia there was no evidence for the other product of dehydrochlorination, HCl. In the reaction using 3mmol 1,1,1-trichloroethane (Section 3.3.2) on volcano chromia, HCl was detected suggesting that a portion of the HCl produced in the dehydrochlorination reaction is retained by the volcano chromia and is therefore not detected in the gas phase.

When SF_4 fluorinated γ-alumina was exposed to the 1,1,1-trichloroethane vapour, it was noted that a brick-red colour developed immediately on contact.

Fig.3.5. *In Situ* I.R.Analysis Of Volatile Material From CH_3CCl_3 Conditioning Process:
(i) After 5 Mins.

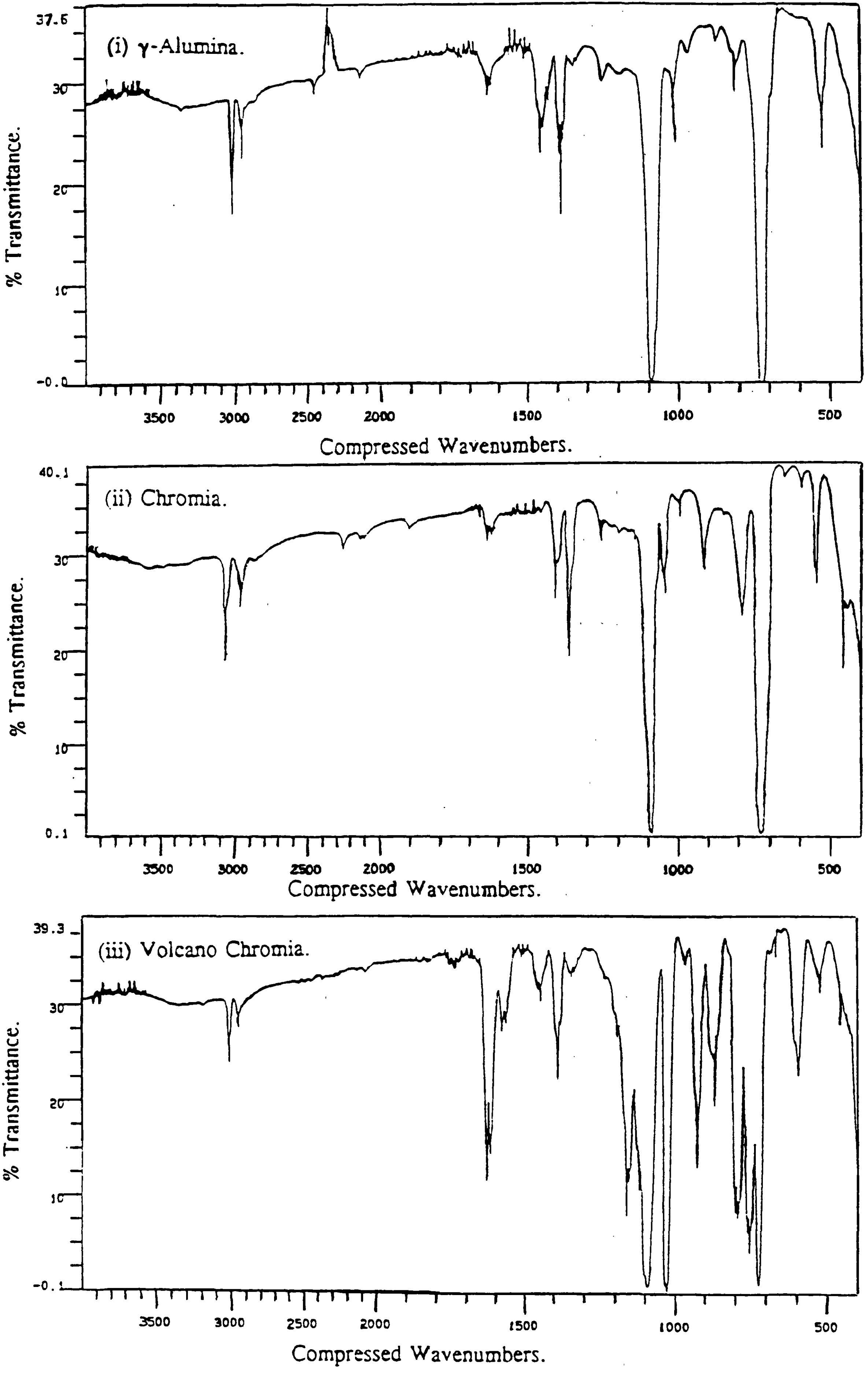
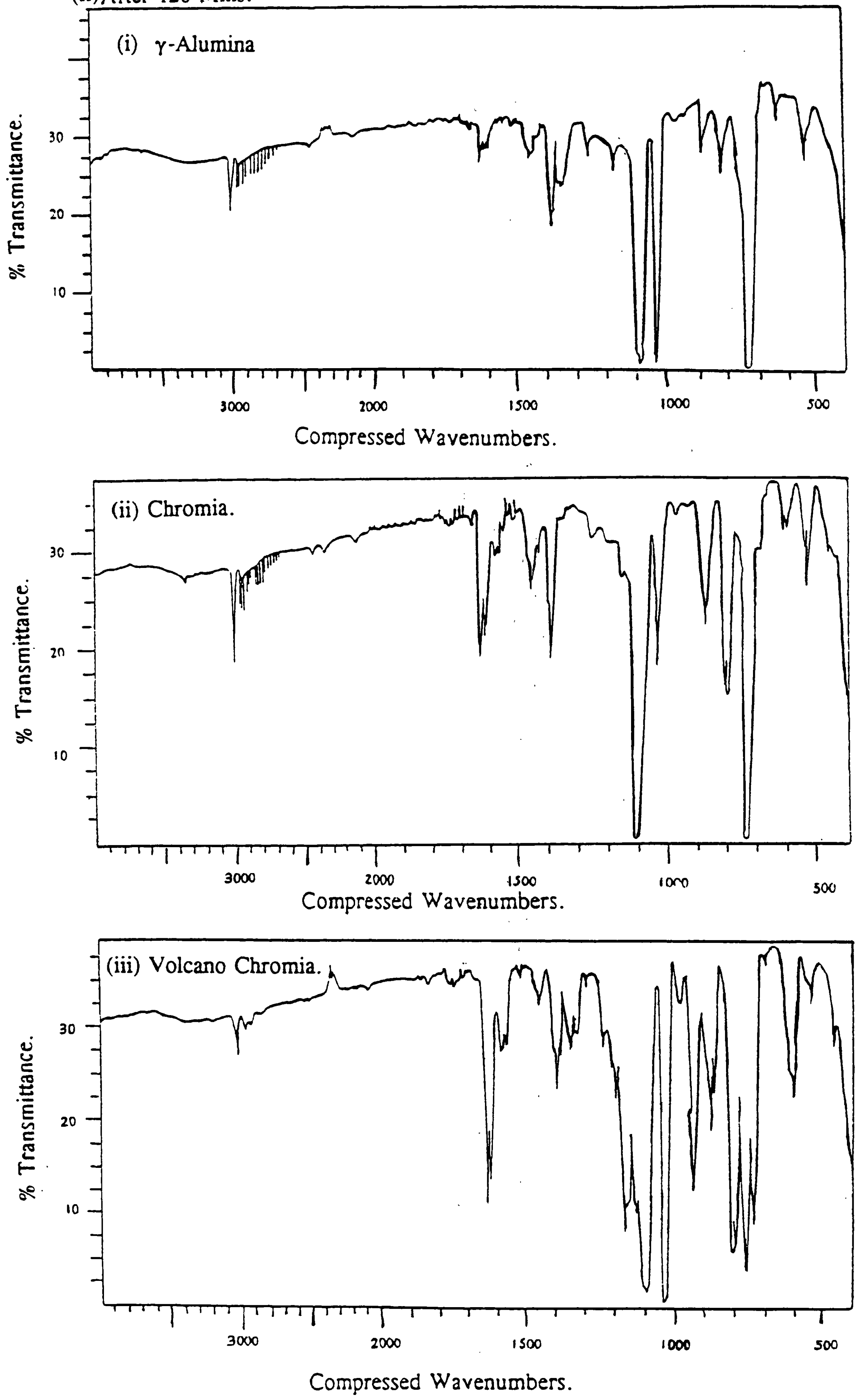


Fig.3.5. *In Situ* I.R.Analysis Of Volatile Material From CH_3CCl_3 Conditioning Process: (ii)After 120 Mins.



Over the course of the reaction this changed through a greenish colour to a more purple colour, although it did not develop the deep purple colouration characteristic of the reaction of 1,1,1-trichloroethane on SF_4 γ-alumina at room temperature. No colour change was observed for either of the chromia samples; volcano chromia remained green and the chromia sample stayed black.

The spectra of the volatiles from reaction over γ-alumina and chromia were broadly similar (Fig.3.5). There are several peaks in the 1400 - 900 cm^{-1} region which are not accounted for by CH_3CCl_3 or $CH_2=CCl_2$. This region is characteristic of C-F bonds, indicating halogen exchange reactions between the solid and the CH_3CCl_3, producing fluorinated species. The spectra from the reaction over volcano chromia also shows the presence of 1,1,1-trichloroethane and 1,1-dichloroethene and several additional peaks in the range 1400 - 900 cm^{-1} which are not present in the spectra of γ-alumina and chromia.

To examine how the concentrations of the reactants and the products changed during the reaction, absorbance bands characteristic of the components of interest were plotted with respect to time. For 1,1,1-trichloroethane the peak at 1385cm^{-1} (CH_3 sym. deformation) and for 1,1-dichloroethene the peak at 1620cm^{-1} (C=C stretch) were plotted. For the fluorinated material a peak at 1030cm^{-1} was plotted. This is in the region for C-F bonds and is identified by comparison with the I.R. of an authentic sample of CH_3CCl_2F. This band could also be due to the formation of SiF_4. However, this peak was common to all three spectra, it was very sharp and was not present in the empty gas

Fig.3.6. I.R. Study Of The Conditioning Of Fluorinated Alumina With 1,1,1-Trichloroethane Under Static Conditions.

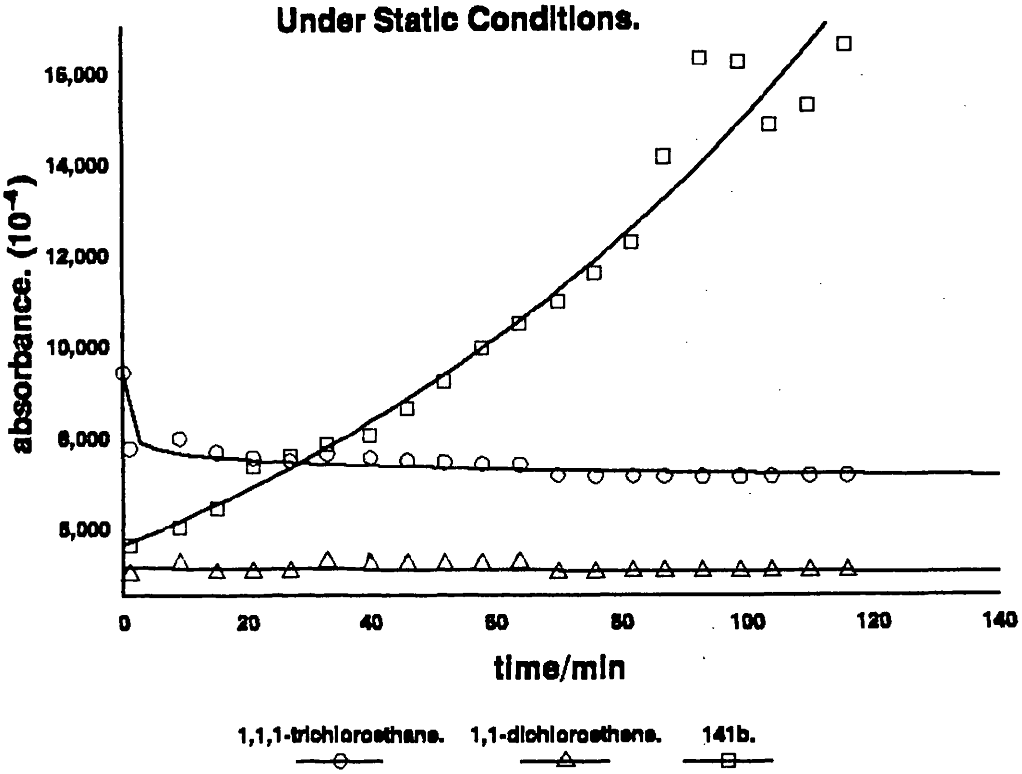


Fig.3.7. Conditioning Of Fluorinated Alumina And Chromias With 1,1,1-Trichloroethane: Disappearance of CH_3CCl_3.

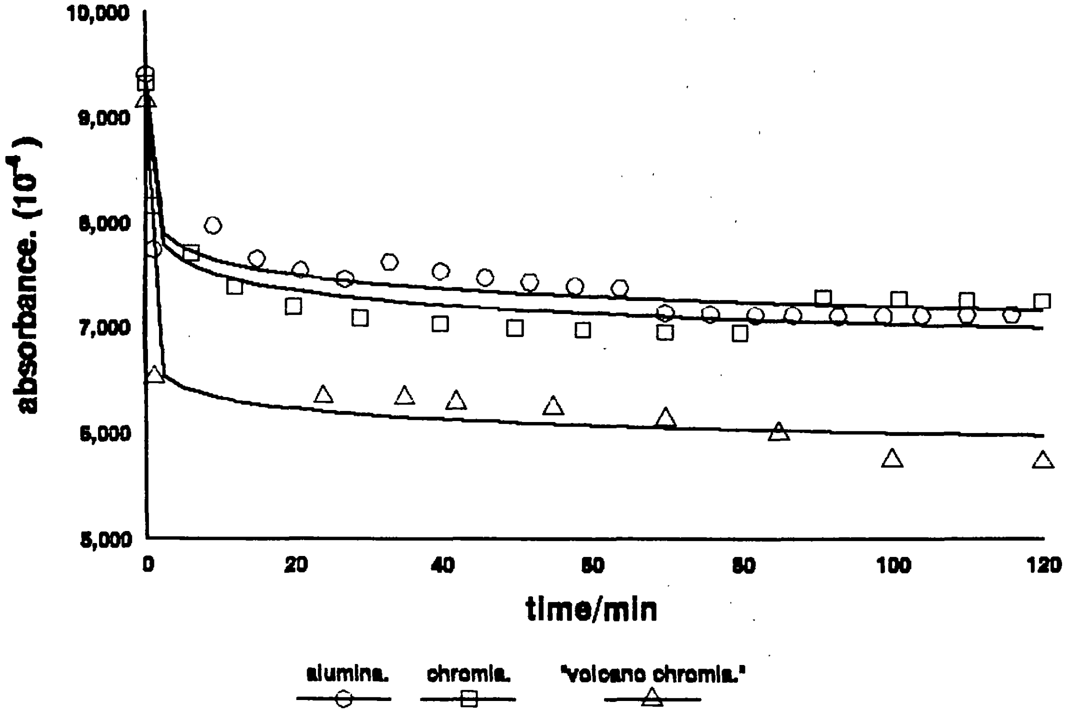


Fig.3.8. Conditioning Of Fluorinated Alumina And Chromias With 1,1,1-Trichloroethane: Production of $CH_2=CCl_2$.

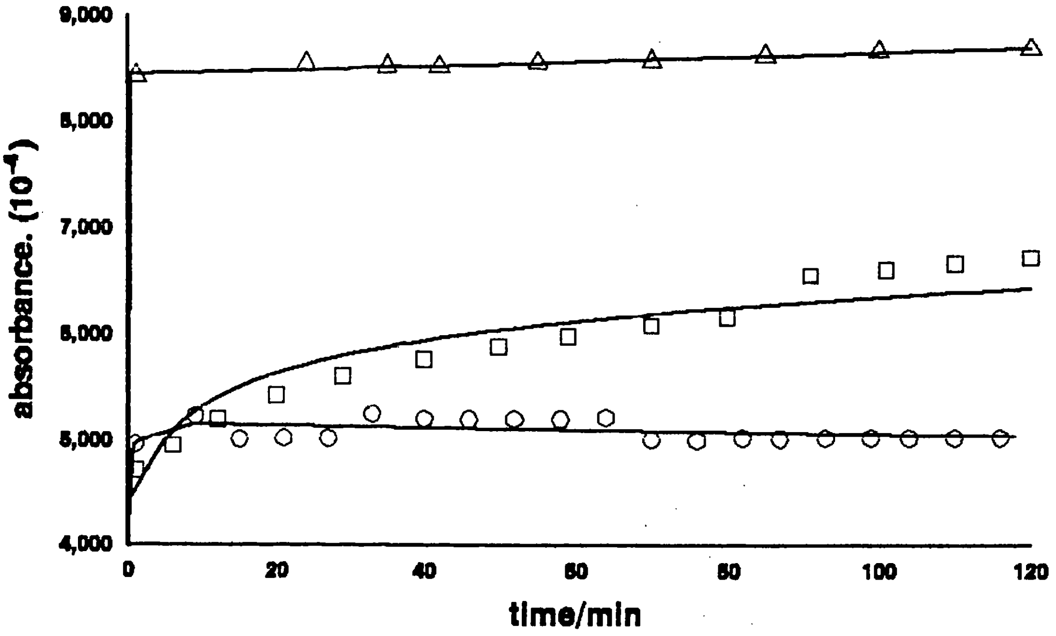
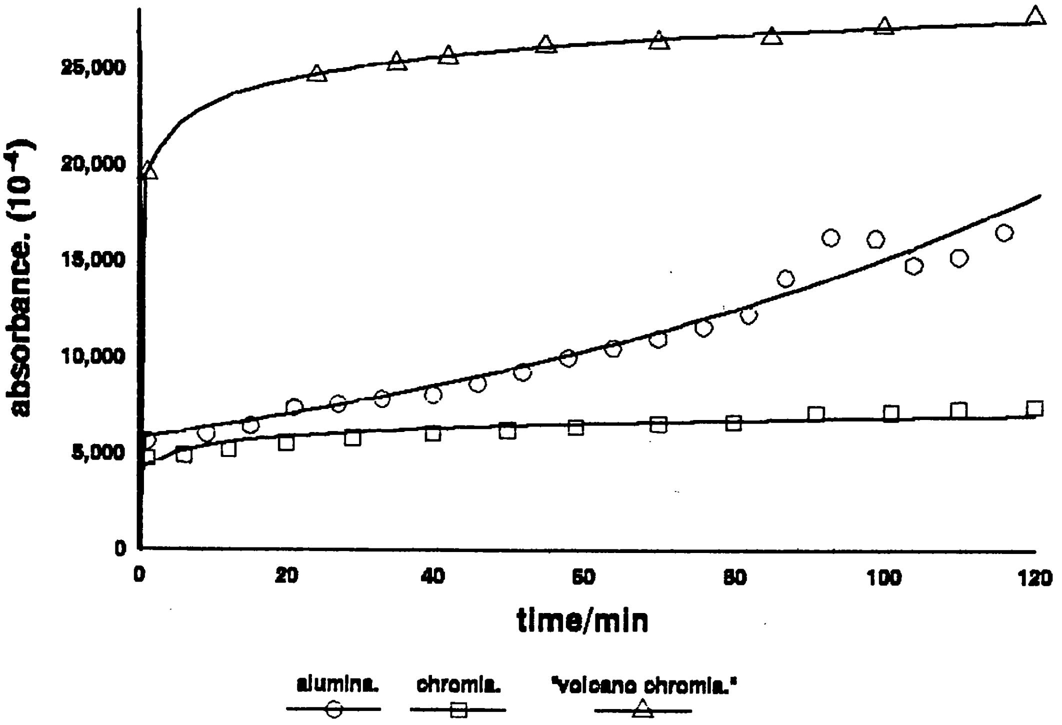


Fig.3.9. Conditioning Of Fluorinated Alumina And Chromias With 1,1,1-Trichloroethane: Production of CH_3CCl_2F.



I.R. cell before or after the reaction therefore indicating that it was due to C-F containing material in the gas phase.

A typical set of data for the decrease in vapour phase 1,1,1-trichloroethane and increase in 1,1-dichloroethene and 1,1-dichloro 1-fluoroethane is given in Fig 3.6. The experiments were performed as far as possible under identical conditions and although absorbance versus concentration calibrations were not determined, comparisons of components in the different reactions are justifiable and are shown in Fig 3.7-3.9. In all three cases the concentration of CH_3CCl_3 decreased with time and that of $CH_2=CCl_2$ and CH_3CCl_2F increased with time. There were some differences in behaviour of the three materials: the $CH_2=CCl_2$ increased in parallel with the CH_3CCl_2F from the chromia, whereas for the γ-alumina and volcano chromia the $CH_2=CCl_2$ increased very slightly in comparison with the CH_3CCl_2F.

The evolution of fluorinated material showed the most obvious differences between the three systems. On both γ-alumina and chromia the concentration climbs slowly, although the increase is greater on the γ-alumina whereas on the volcano chromia the concentration increased rapidly to reach a plateau.

3.3.9. ANALYSIS OF THE VOLATILE MATERIAL FROM THE 1,1-DICHLOROETHENE CONDITIONING PROCESS BY *IN SITU* GAS INFRARED SPECTROSCOPY.

The study of the conditioning reaction using 1,1-dichloroethene as the starting material resulted in a similar overall pattern of results to the analogous

1,1,1-trichloroethane conditioning reaction with a decrease in the concentration of 1,1-dichloroethene and an increase in 1,1,1-trichloroethane and 1,1-dichloro 1-fluoroethane (Fig.3.10).

Exposure of SF_4 fluorinated γ-alumina to 1,1-dichloroethene resulted in the immediate development of a blue/purple colouration which darkened over the period of the experiment. In the spectra of the volatiles from the γ-alumina and chromia samples there were several extra peaks observed in the 1400 - 900 cm^{-1} region, characteristic of C-F, which were not observed in the conditioning with 1,1,1-trichloroethane suggesting that the hydrofluorination reactions occur readily when 1,1-dichloroethene was used as the starting material. These peaks were observed on volcano chromia with both conditioning reagents.

A typical set of data for the changes in vapour pressure composition is given in Fig 3.11 and comparisons of the components for the three solids is made in Figs 3.12-3.14. The γ-alumina and volcano chromia behaved similarly, with the 1,1,1-trichloroethane concentration increasing initially then decreasing gradually over the reaction time. The increase in the concentration of CH_3CCl_2F was greatest on γ-alumina. The reaction on chromia was not as substantial, with 1,1,1-trichloroethane and 1,1-dichloro 1-fluoroethane appearing immediately but the concentration remained virtually constant over the reaction.

Fig.3.10. *In Situ* I.R.Analysis Of Volatile Material From $CH_2=CCl_2$ Conditioning Process:
(i) After 5 Mins.

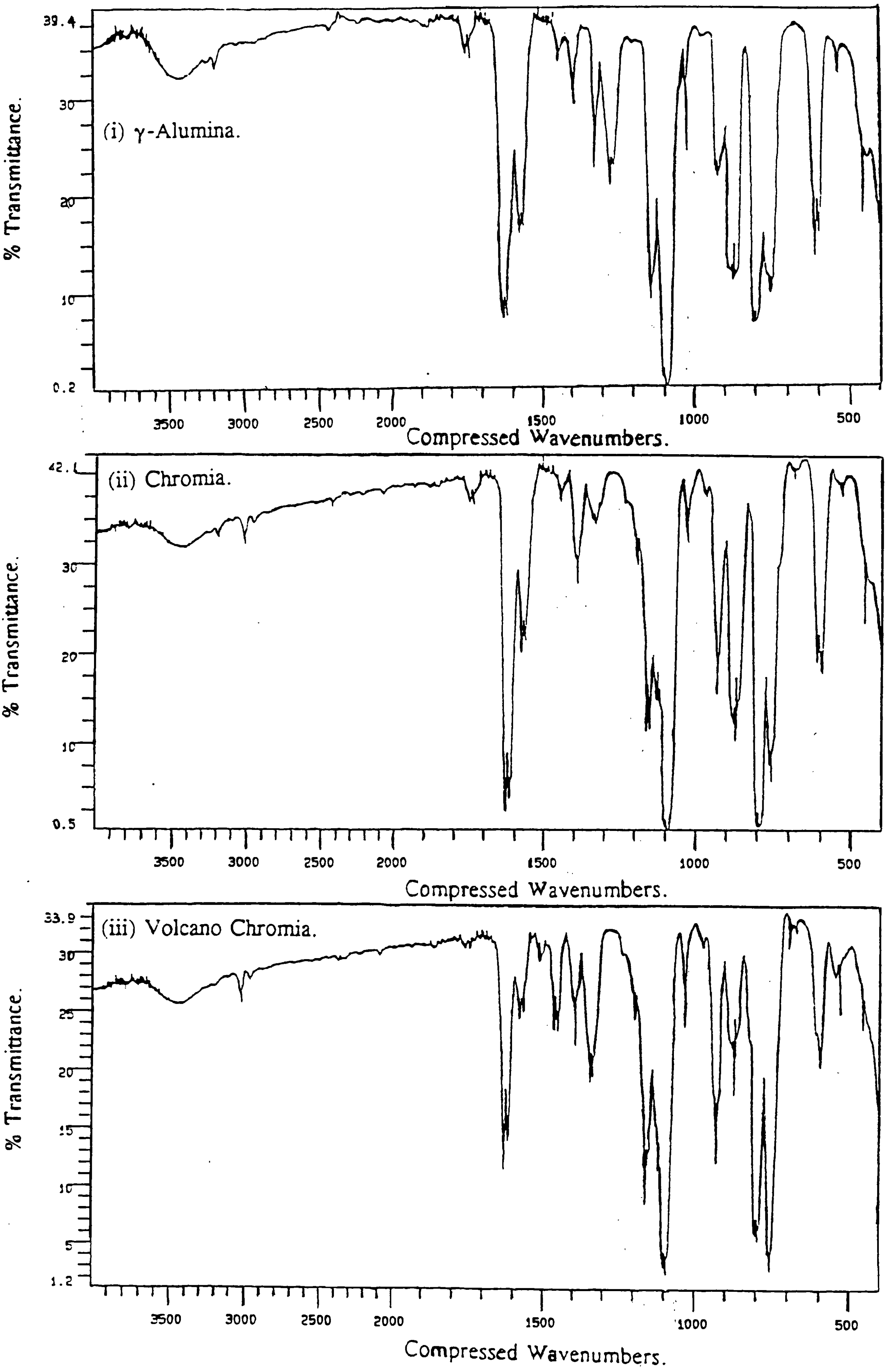


Fig.3.10. *In Situ* I.R. Analysis Of Volatile Material From $CH_2=CCl_2$ Conditioning Process; (ii) After 120 Mins.

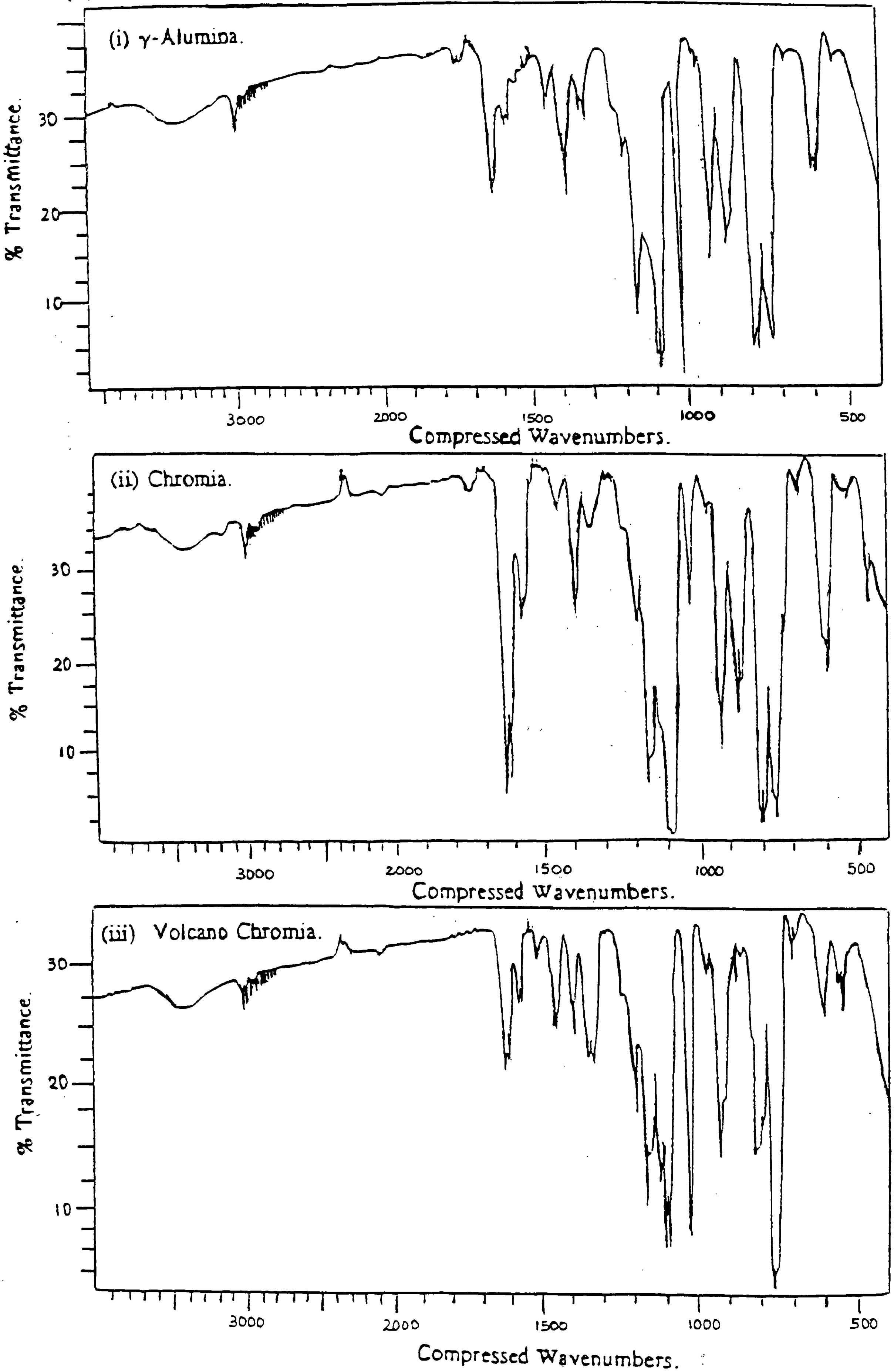


Fig.3.11. I.R.Study Of The Conditioning Of Fluorinated Alumina With 1,1-Dichloroethene Under Static Conditions.

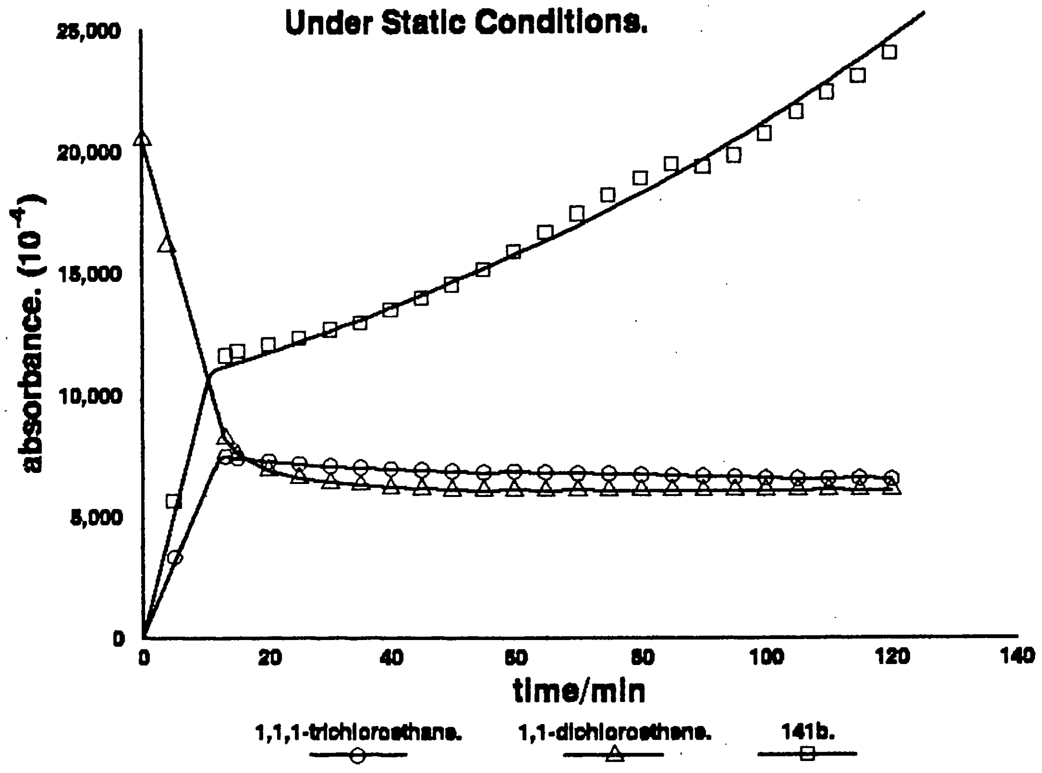


Fig.3.12. Conditioning Of Fluorinated Alumina And Chromias With 1,1-Dichloroethene: Disappearance of $CH_2{=}CCl_2$

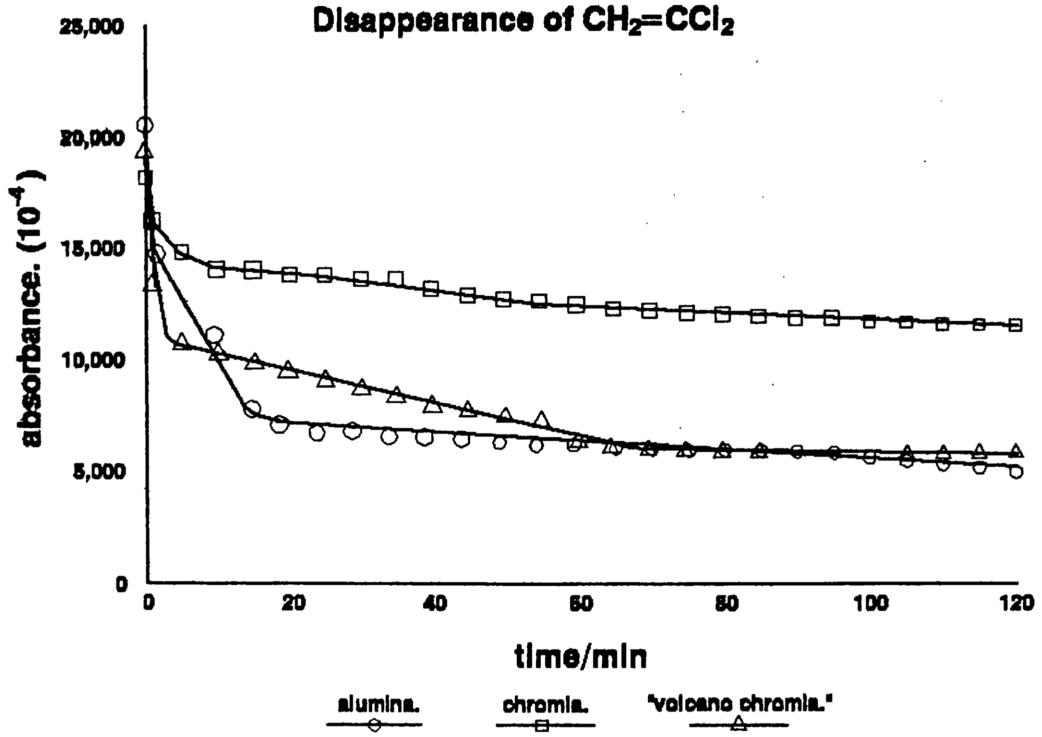


Fig.3.13. Conditioning Of Fluorinated Alumina And Chromias With 1,1-Dichloroethene: Production of CH_3CCl_3.

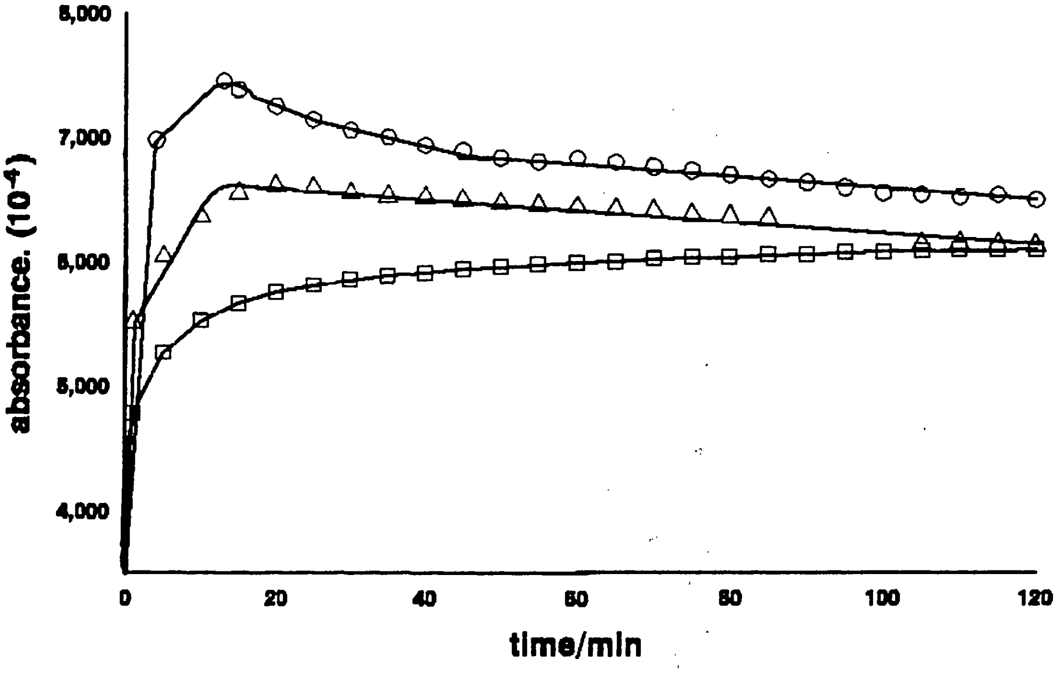
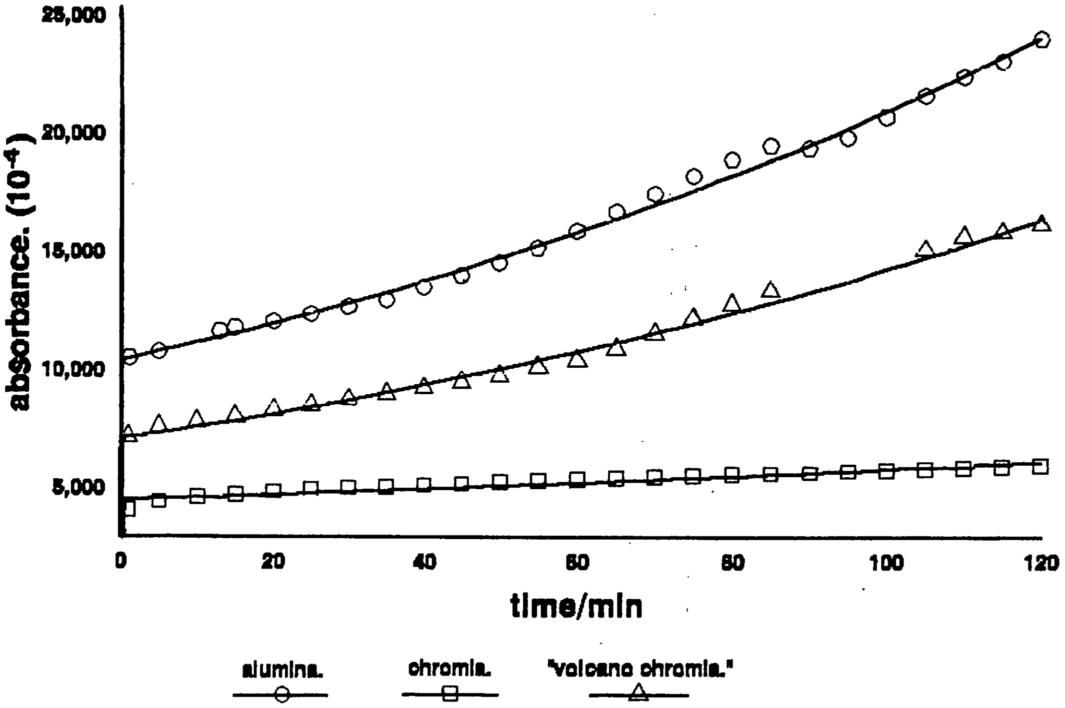


Fig.3.14. Conditioning Of Fluorinated Alumina And Chromias With 1,1-Dichloroethene: Production of CH_3CCl_2F.



3.3.10. ANALYSIS OF THE VOLATILE MATERIAL FROM THE INTERACTION OF ANHYDROUS HYDROGEN CHLORIDE WITH 1,1,1-TRICHLOROETHANE CONDITIONED, SF_4 FLUORINATED MATERIALS.

Analysis by *in situ* I.R. of the volatile materials from the reaction of anhydrous hydrogen chloride with conditioned plus fluorinated materials indicated a reduction in the HCl concentration which was greatest on volcano chromia (Fig.3.15.). In addition to this the spectra showed the development of several peaks in the 1400 - 900 cm^{-1} region, in particular bands at $1385cm^{-1}$, 1030cm-1 and $720cm^{-1}$, suggesting that the hydrogen chloride was reacting with the organic material on the surface producing CH_3CCl_3 and CH_3CCl_2F.

3.3.11. ANALYSIS OF THE 1,1,1-TRICHLOROETHANE CONDITIONING PROCESS ON SF_4 FLUORINATED γ-ALUMINA UNDER FLOW CONDITIONS.

The results of the conditioning reaction of SF_4 fluorinated γ-alumina and volcano chromia indicated that the dehydrochlorination and hydrofluorination reactions occurred on both materials under flow conditions.(Figs 3.16-3.17). There is a delay of 4h. before the dehydrochlorination product, 1,1-dichloroethene is detected from the γ-alumina. This delay was not observed with volcano chromia, where 1,1-dichloroethene is detected in the first sample in quite substantial quantities, but decreased rapidly. There was

Fig.3.15. I.R. Analysis Of Volatile Material From Treatment Of CH_3CCl_3 Conditioned Material with HCl.

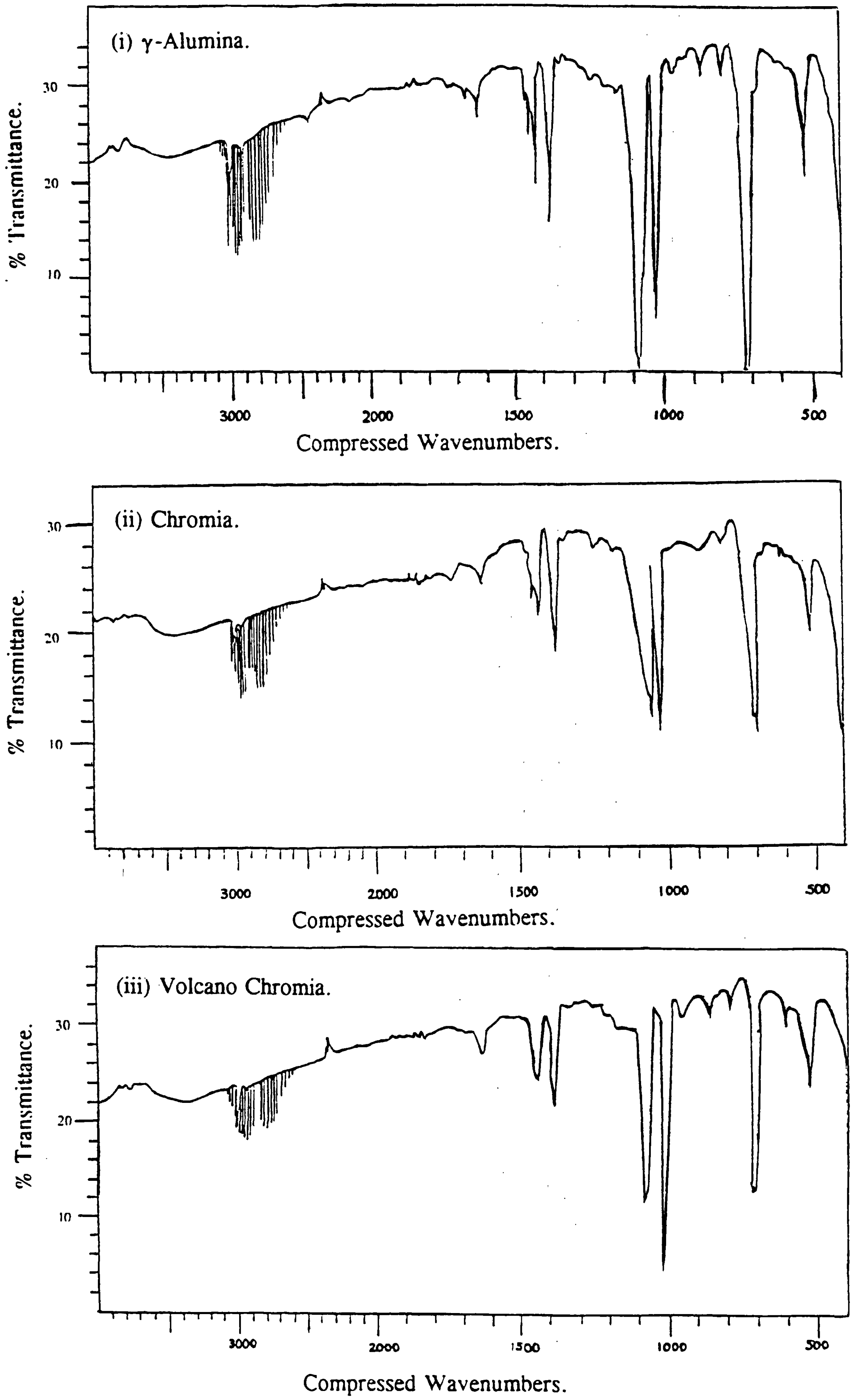


Fig.3.16. Products From CH_3CCl_3 Conditioning Under Flow Conditions. SF_4 Alumina.

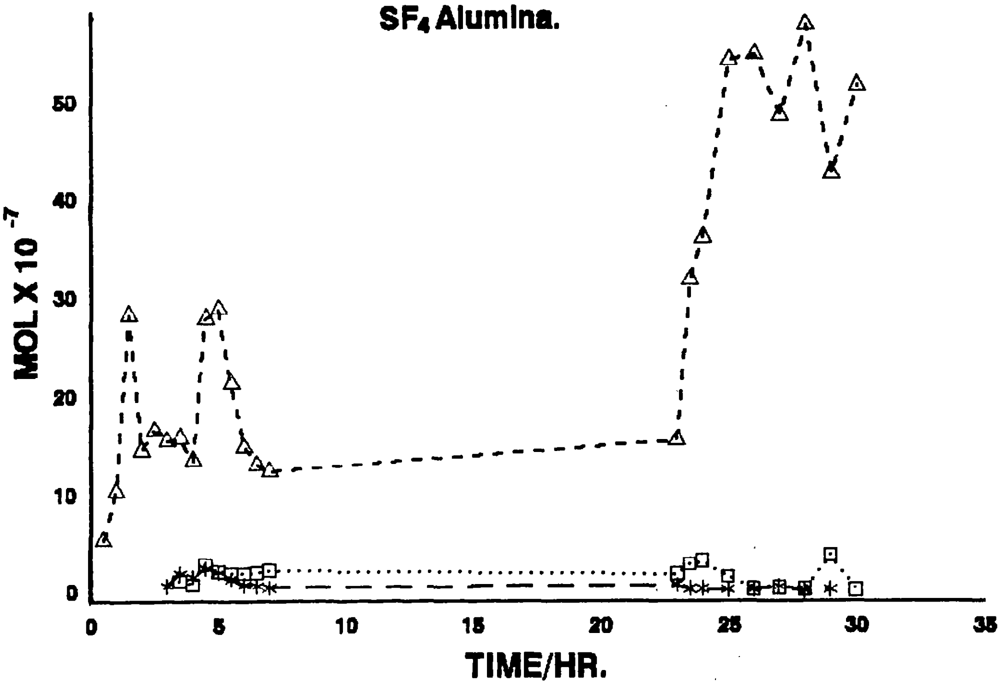
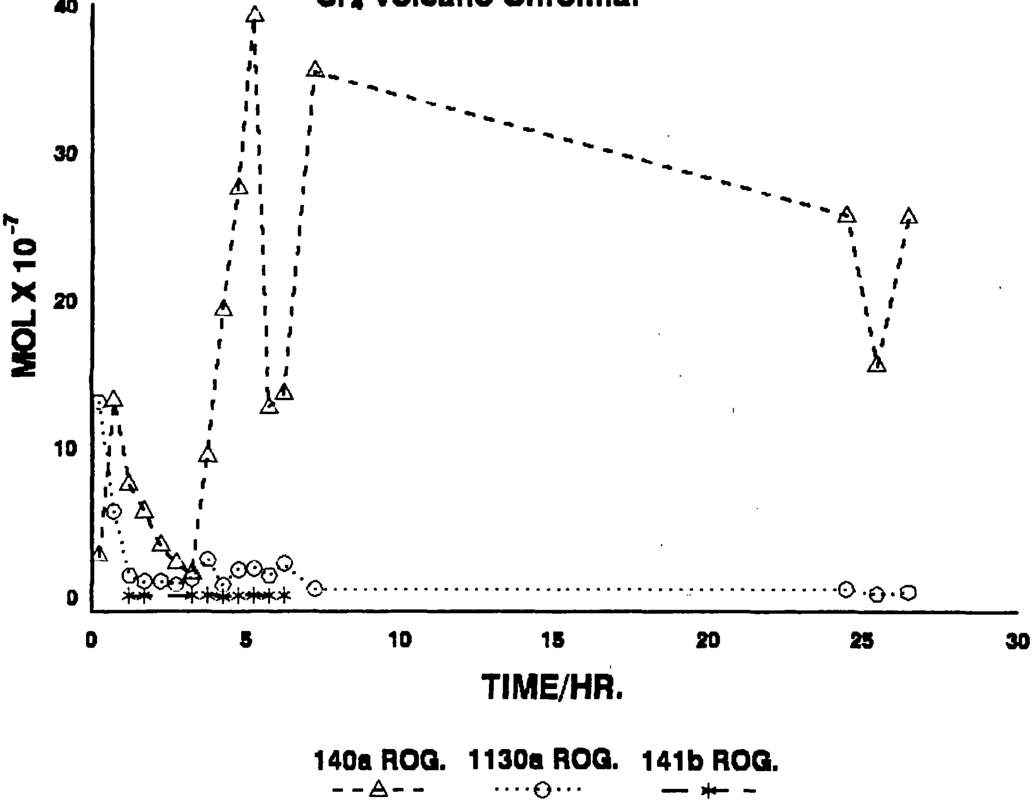


Fig.3.17. Products From CH_3CCl_3 Conditioning Under Flow Conditions. SF_4 Volcano Chromia.



also a time delay on both γ-alumina and volcano chromia before the hydrofluorination product 1,1-dichloro 1-fluoroethane was detected. The delay was greater on the γ-alumina than on the volcano chromia. The fluorinated material appeared with γ-alumina after 3h. and rises to a maximum around 5h. after which time the concentration of this material decreased again whereas on the volcano chromia this remained virtually constant. The quantity of fluorinated material produced was greater for the γ-alumina than for the volcano chromia. Other fluorinated products were detected but only in trace quantities. In the γ-alumina both products appear at approximately the same time where as for the volcano chromia the 1,1-dichloro 1-fluoroethane appears only as the 1,1-dichloroethene concentration decreased.

The volatile materials from the conditioning reaction performed in the Pyrex glass reaction vessel were similar to those in the Monel metal reaction vessel. The SF_4 fluorinated γ-alumina turned from a cream/white colour to a brick-red colour on contact with the 1,1,1-trichloroethane, starting at the CH_3CCl_3 inlet and gradually spreading throughout the whole catalyst. After 2h the material nearest the CH_3CCl_3 inlet became blue in colour and this also spread through the catalyst and after 3.5h. the development of the blue colour appeared to be complete.

The conditioning reaction was allowed to continue overnight. The quantity of $CH_2{=}CCl_2$ and CH_3CCl_2F produced from γ-alumina remained approximately the same as before. The volcano chromia sample continued to produce $CH_2{=}CCl_2$ but no CH_3CCl_2F was detected. This implies that the quantity of fluorine available on volcano chromia for halogen exchange reactions to produce fluorinated products was less than on γ-alumina.

3.3.12. B.E.T. SURFACE AREA ANALYSIS.

From the N_2 adsorption isotherms, all samples were found to contain large mesopores/macropores. The porosity of the γ-alumina was thought to be almost totally mesoporous with cylindrical or spherical pores whereas for the chromia and volcano chromia there were either slit shaped pores or a broad range of pore sizes. The size distribution of pores could not be established.

Table 3.3.5. B.E.T. Surface Area Analysis.

SURFACE	SURFACE AREA m^2/g
CALCINED γ-ALUMINA.	110
SF_4 γ-ALUMINA.	90
CH_3CCl_3, SF_4 γ-ALUMINA.	94
CALCINED CHROMIA.	35
SF_4 CHROMIA.	33
CH_3CCl_3, SF_4 CHROMIA.	29
CALCINED VOLCANO CHROMIA.	52
SF_4 VOLCANO CHROMIA.	44
CH_3CCl_3, SF_4 VOLCANO CHROMIA.	47

The γ-alumina sample has the largest surface area and is also the one which shows the greatest reduction on fluorination. The chromia has a substantially smaller surface area than the volcano chromia and it is not greatly effected by the fluorination process. The conditioning reaction has little effect on the surface areas determined.

3.3.13. D.R.I.F.T.S. STUDY OF ADSORBED PYRIDINE SPECIES ON CALCINED, FLUORINATED AND CONDITIONED γ-ALUMINA.

D.R.I.F.T.S. analysis of calcined, fluorinated and conditioned plus fluorinated materials after interaction with pyridine vapour at room temperature indicated the presence of characteristic pyridine adsorption bands in the 1700-1400cm^{-1} region. Assignments of pyridine adsorption bands in this region are well documented, but there are many discrepancies. The assignments most generally accepted for these absorption bands are given in Table.3.3.6. and were used as guide lines for assignment of adsorption bands observed in this work.

The main peaks determined in this work are listed in Table.3.3.7. Comparisons among the spectra indicate that there is very little difference in the adsorbed pyridine on γ-alumina, chromia and volcano chromia (Fig.3.18). The three samples displayed peaks corresponding to coordinately bonded pyridine, pyridinium and hydrogen bonded pyridine, which therefore indicates the presence of both Brφnsted and Lewis acid sites.

Table.3.3.6. General Assignments Of Pyridine Adsorption Bands.

Coordinately Bonded Pyridine.	1440-1456 (131-135) 1485-1499(131-135) 1545(134) 1577(135) 1620(135)
Pyridinium.	1485-1499(131-135) 1540-1550(131-133,135) 1580(132) 1620(132,135) 1635-1638(132,135)
Hydrogen Bonded Pyridine.	1438(135) 1445(132) 1593(132,135) 1614(135)

(Note: All values in cm^{-1})

Unexpectedly, fluorination had little effect on the adsorbed pyridine. Clearly the enhanced acidity of the resultant fluorinated surface should effect the adsorption of a basic molecule such as pyridine. The most likely cause of this is the conditions used. Exposure of the samples to the atmosphere probably resulted in hydrolysis of the surfaces, removing fluorine and reducing the surface acidity. Conditioning of the samples also had little effect on the observed pyridine adsorption bands.

Table.3.3.7. Assignment Of Observed Pyridine Bands.
(i) γ-Alumina.

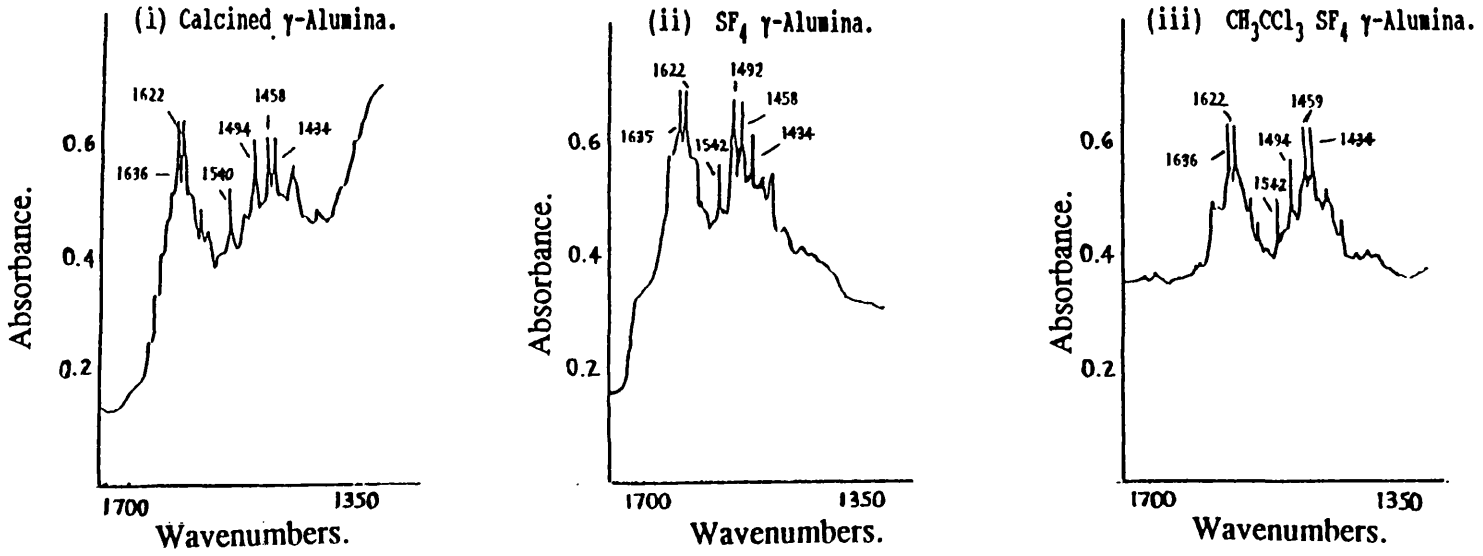
	Alumina	SF_4 Alumina	CH_3CCl_3, SF_4 Alumina	BF_3 Alumina	CH_3CCl_3, BF_3 Alumina
Py (H.B.).	1434	1434	1434	1433	1433
Py (C.B.).	1458	1458	1459	1456	1458
Py(C.B.) /PyH.	1494	1492	1494	1491	1491
Py(C.B.) /PyH.	1540	1542	1542	1541	1541
Py(C.B.) /PyH.	1622	1620	1622	1626	1623
PyH.	1636	1635	1636	1636	1636

Table.3.3.7. Assignment Of Observed Pyridine Bands.
(ii) Chromia And Volcano Chromia.

	Chromia	SF_4 Chromia	CH_3CCl_3, SF_4 Chromia	Volcano Chromia	SF_4 Volcano Chromia	CH_3CCl_3, SF_4 Volcano Chromia
Py (H.B.).	1434	1434	1434	1435	1435	1434
Py (C.B.).	1458	1457	1457	1455	1456	1457
Py(C.B.) /PyH.	1495	1493	1493	1495	1495	1492
Py(C.B.) /PyH.	1540	1540	1542	1540	1539	1540
Py(C.B.) /PyH.	1622	1620	1621	1617	1617	1620
PyH.	1636	1635	1636	1636	1635	1635

Py = Pyridine. PyH = Pyridinium. H.B. = Hydrogen Bonded.
C.B. = Coordinately Bonded. (All Values In cm^{-1}.)

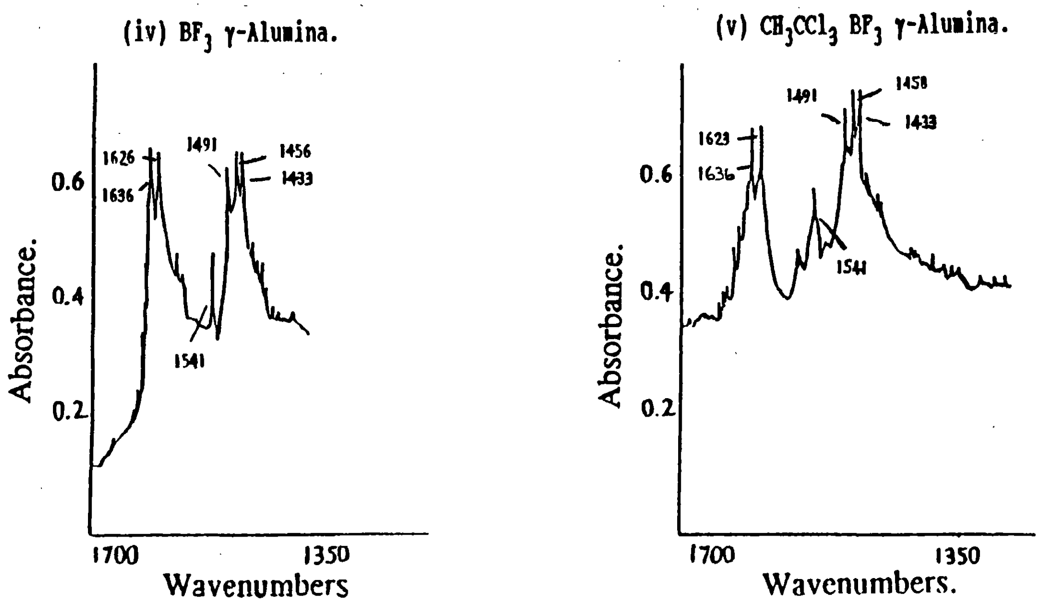
Fig.3.18. DRIFTS Spectrum Of Adsorbed Pyridine.



(i) Calcined γ-Alumina.

(ii) SF$_4$ γ-Alumina.

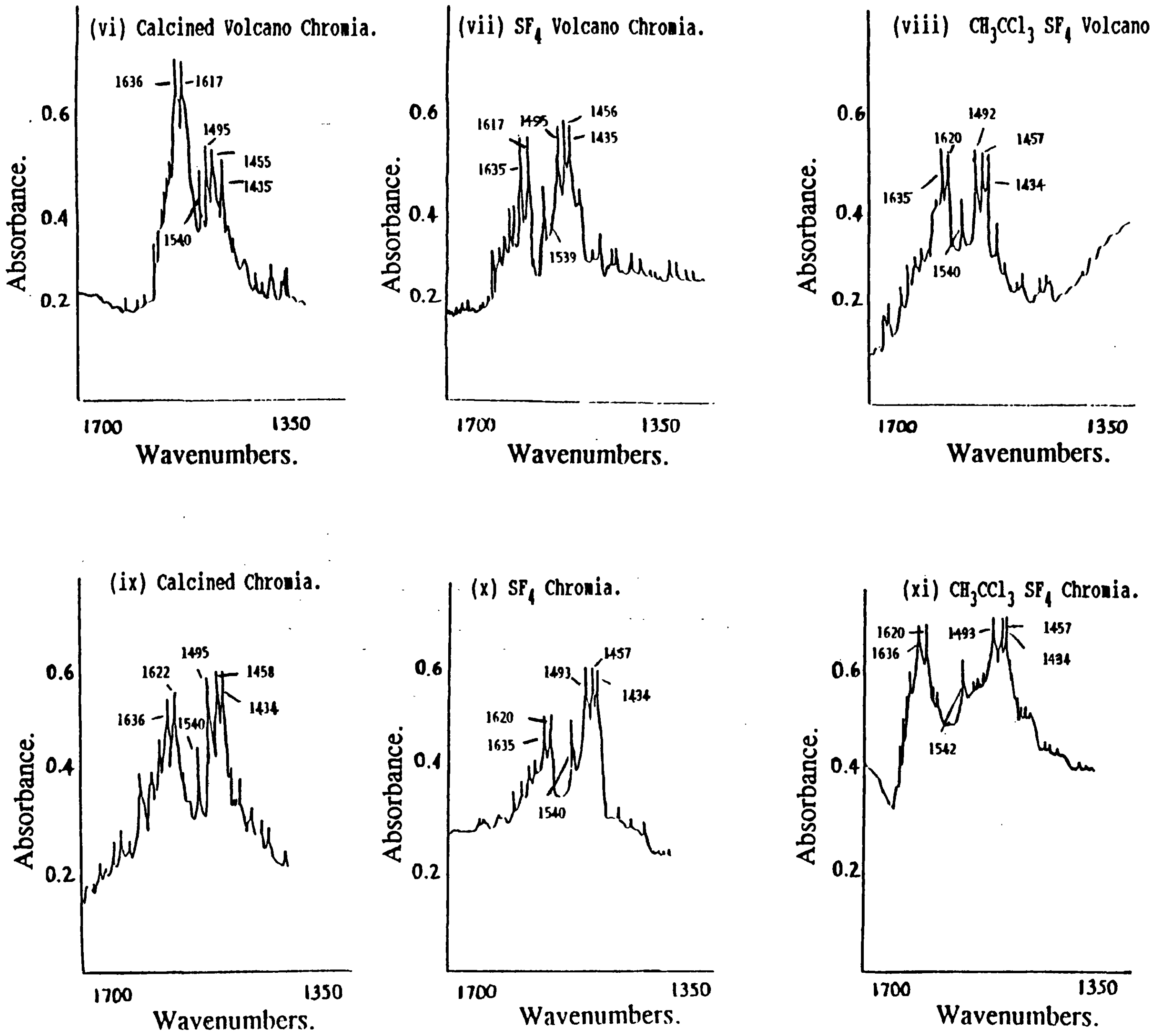
(iii) CH$_3$CCl$_3$ SF$_4$ γ-Alumina.



(iv) BF$_3$ γ-Alumina.

(v) CH$_3$CCl$_3$ BF$_3$ γ-Alumina.

Fig.3.18. DRIFTS Spectrum Of Adsorbed Pyridine.



(vi) Calcined Volcano Chromia.

(vii) SF_4 Volcano Chromia.

(viii) CH_3CCl_3 SF_4 Volcano Chromia.

(ix) Calcined Chromia.

(x) SF_4 Chromia.

(xi) CH_3CCl_3 SF_4 Chromia.

3.4. DISCUSSION.

From the results described in this chapter, it is clear that there are similarities in the reactions on γ-alumina, chromia and volcano chromia but they are by no means identical.

3.4.1. SF_4 FLUORINATION REACTIONS.

From the I.R. spectra of the volatile products, the sulphur tetrafluoride fluorination process appears to occur similarly on the γ-alumina and chromias, producing thionyl fluoride and sulphur dioxide. The course of the fluorination process was postulated by Winfield et al (160) to involve replacement of both terminal and bridging oxygens by fluorine, with SO_2 produced in the reactions:

$$SF_4 + \text{"OH"} \rightarrow SOF_2 + HF$$

$$SOF_2 + \text{"OH"} \rightarrow SO_2 + HF$$

playing a protective role to prevent deactivation by HF in the initial stages of the reaction. It is proposed that a similar fluorination reaction occurs on the chromia samples. The protective role of the SO_2 is probably similar on the chromia samples as for the γ-alumina samples although treatment of chromia with HF itself at elevated temperatures creates surfaces that are active for halogen exchange reactions. Fluorination of chromia with HF has been shown to result in three types of surface fluorine containing species (25) one of which is labile and involved in halogen exchange reactions, but the exact nature of the labile species has not yet been established. There has been a great debate in literature over the active sites on chromia catalysts, but in general the activity is thought to be due to the various oxidation states that can exist. Chromia prepared by pyrolysis of ammonium dichromate is well known to contain significant amounts of high valency chromium species (136,137). Various techniques have been used to study chromia prepared by pyrolysis and from chromium nitrate; E.P.R (36,138,139) and X.P.S.(140,141) studies proposed that oxidation states of III and above existed in the samples. T.P.R.(25) studies of chromia samples revealed that chromium species with oxidation states III, IV and VI were present. X.R.D. (29) and T.E.M. (142) studies indicated the presence of some microcrystalline α-Cr_2O_3. Catalysts that have been extensively fluorinated by continued use for halogen exchange reactions do not contain Cr^{IV} species (25). This has been accounted for by loss of CrF_4 and hydrolysis of the Cr^{IV} species.This therefore points to the active sites involving Cr^{III} and Cr^{VI}, since these are present in the catalytically active material. However, it has also been postulated that Cr^{III} species form CrF_3 (25) which is not active for interaction with HF. Therefore the probability is that Cr^{VI} is the active site in the fluorination reaction.

Studies of fluorination of γ-alumina with SF_4 have indicated that fluorine is incorporated into the bulk of the material without affecting the structure. The fluorine uptake was calculated to be 15 mg atom F (g catalyst)$^{-1}$ which is greater than can be accommodated on the surface due to replacement of surface -OH groups by -F (143). These studies also indicated that HF, the product from the fluorination process, appears to be retained by the solid, although whether the HF diffuses into the bulk material or whether surface $(HF)_n$ oligomers are present is not clear. Fluorination of chromia with HF at elevated temperatures results in an uptake within the range 1.0 - 1.4 mg atom F (g catalyst)$^{-1}$ which is greater than the maximum uptake of monomeric HF (14). The difference was explained as being due to formation of oligomeric HF species. Neutral and charged oligomers of the forms $(HF)_n$ and $(HF)_nF^-$ have been subject to widespread study in literature (144-147). Both charged and neutral oligomeric species are strongly hydrogen bonded. The charged oligomer species is more stable (144,145), which favours charged species as the source of catalytically active halide on chromia. For charged oligomeric species to be created on chromia HF must be dissociatively adsorbed. This is not unexpected as it is known that several other species also dissociatively adsorb onto chromia, for example dichlorine (148), dioxygen (149) and water (150). The adsorption is thought to occur at coordinatively unsaturated chromium sites (39,148-150). If the fluorination of chromia samples with SF_4 results in the formation of HF oligomers either instead of or in addition to incorporation of fluorine into the bulk of the solid may account for the differences in the quantities of fluorinated products formed. For fluorine from the bulk of the material to be involved in hydrofluorination reactions, there must be a complex reaction involving diffusion of fluorine through the material to the surface which indicates that any fluorine present as surface oligomers may be more easily accessible for the reaction. It is also possible that the fact Al^{3+} is a harder acid than Cr^{3+} produces a stronger bond between

Al-F than Cr-F (151), which results in more readily available fluorine species from the chromia samples. The differences observed between the two chromia samples with respect to the quantity of fluorinated product may be a reflection of the difference in the surface areas of the samples which is due to the preparation procedures involved. One of the features that makes γ-alumina a widely used catalyst and catalyst support is its high surface area. Calcination enhances surface area by removal of water and hydroxyl groups from the surface of the material. The reduction in the surface area due to fluorination is greater for γ-alumina than for the chromia samples. This suggests that the fluorination process is more extensive on the γ-alumina. This may be an indication of the presence of HF oligomers on the chromia samples rather than the surface fluorination procedures that are thought to occur on γ-alumina. However, despite the reduction due to fluorination, γ-alumina has the greatest surface area of the three materials. The conditioning reaction does not have a great effect on the surface area of any of the materials, suggesting that there may not a "blanket" coverage of the surface but rather there may be "islands" of organic material on the surface.

3.4.2.BF_3 FLUORINATION REACTIONS

Fluorination of γ-alumina with BF_3 also creates a surface that is capable of supporting dehydrochlorination and hydrofluorination reactions although neither is as substantial as on SF_4 fluorinated γ-alumina. A pale blue colouration develops on the BF_3 γ-alumina rather than the dark purple colour on the SF_4 γ-alumina. This suggests that the laydown of organic material on BF_3 γ-alumina is less extensive than on SF_4 γ-alumina. It is postulated therefore, that BF_3 does not create Lewis acid sites that are as strong or as abundant as SF_4, which may be due to the protective role proposed for the SO_2. This is not thought to occur to the same extent with BF_3 although BOF_2^- species created in the reaction:

$$BF_3 + \text{"OH"} \longrightarrow BOF_2^- + HF$$

may protect the surface to some extent allowing some degree of fluorination to occur. This will be discussed at greater length in Chapter 4.

3.4.3. 1,1,1-TRICHLOROETHANE CONDITIONING REACTION.

The fluorination process clearly creates strong Lewis acid sites on the chromia samples in a similar way as on the γ-alumina samples, as shown by the subsequent activity for dehydrochlorination reactions. Comparisons of the conditioning reaction performed in Monel metal and Pyrex glass vessels indicated that Monel is favoured. This may be a simple reflection of the fact that there are fewer manipulations involved or it may be an effect of light on the reaction in the glass vessels. It is known that 1,1,1-trichloroethane and 1,1-dichloroethene tend to photopolymerize quite readily. Normally these compounds are stabilized to prevent this occurring. However, the effect of the stabilizer on the reaction is unclear and therefore unstabilized materials were used throughout this work.

(i) ANALYSIS OF THE MASS CHANGES OF FLUORINATED MATERIALS IN THE 1,1,1-TRICHLOROETHANE CONDITIONING REACTION.

The study of the weight changes of fluorinated materials on conditioning indicates that organic material is laid down on the solids as demonstrated by the mass increases observed. γ-Alumina behaves in a similar manner to volcano chromia, with mass increases of 0.5-0.6g(g solid)$^{-1}$ determined. Less material is incorporated into the chromia (0.125g(g solid)$^{-1}$) and BF_3 γ-alumina (0.1687g(g solid)$^{-1}$). The difference observed between the chromia and the volcano chromia samples may be a reflection of the differences in surface area. Introduction of a further aliquot of CH_3CCl_3 to the conditioned material resulted in little difference in the mass of γ-alumina and volcano chromia, suggesting therefore that little additional organic material is laid down. (For γ-alumina the mass increase was 0.0129g and for volcano chromia 0.0094g). It would therefore appear that SF_4 fluorinated γ-alumina is more effective for dehydrochlorination than BF_3 γ-alumina since more organic material is laid down. It is also clear that organic material is laid down on SF_4 fluorinated volcano chromia in similar proportions to SF_4 γ-alumina although there is no visible evidence of the purple organic layer on volcano chromia.

(ii) G.C.ANALYSIS OF 1,1,1-TRICHLOROETHANE CONDITIONING REACTION.

Examination of the conditioning process by gas chromatography provides information regarding the relative quantities of products from the solids under examination and allows comparisons to be made. As can be seen in Table 3.3.2, conditioning γ-alumina with 1,1,1-trichloroethane produced a much greater quantity of CH_3CCl_2F than $CH_2{=}CCl_2$ (22.9 mol% and 5.3 mol% respectively), indicating that the hydrofluorination process occurs readily. The chromia sample produces similar proportions of 1,1-dichloroethene (21.8 mol%) and 1,1-dichloro 1-fluoroethane (18.8 mol%), apparently converting more 1,1,1-trichloroethane to the products. Of the three solids under examination, volcano chromia appears to convert the 1,1,1-trichloroethane to the fluorinated product most readily. This may indicate that there are some differences in the behaviour of fluorine species present on the γ-alumina and the chromia samples.

G.C. analysis of the conditioning reaction with 1,1-dichloroethene confirms the occurrence of dehydrochlorination/hydrochlorination reactions on the surface:

$$\text{1,1,1-trichloroethane} \rightleftharpoons \text{1,1-dichloroethene.}$$

This was studied by Winfield et al using deuterium labelled substrates and surfaces (160), however it was not possible to determine the route absolutely. Clearly the hydrochlorination of 1,1-dichloroethene requires chlorine containing species on the surface of the catalyst which must come from the dehydrochlorination of 1,1-dichloroethene which will be accompanied by laydown of organic material on the surface. The 1,1,1-trichloroethane produced in this reaction is then available for further dehydrochlorination reactions to produce the organic layer catalyst. The hydrofluorination reaction is thought to occur after the dehydrochlorination of 1,1,1-trichloroethane although it is not known if this step is concerted or whether additions of H^+ and F^- occur separately. From this section it is not clear if the hydrofluorination occurs directly with the 1,1-dichloroethene or if it is necessary to build up the organic layer on the surface before this reaction can occur. This was studied fully using *in situ* I.R. analysis and will be discussed later. The study of the CH_3CCl_3 conditioning process under flow conditions also indicated similarities in the behaviour of γ-alumina and volcano chromia, with both dehydrochlorination and hydrofluorination reactions occurring. The volcano chromia reacts more quickly than γ-alumina but the reaction is longer lasting and more substantial on the γ-alumina.

The exact nature of the sites and reactions involved in the halogen exchange reactions are not known but the mechanism which was postulated from work at Glasgow (27) on HF fluorinated chromia involves a substitution reaction occurring at adsorbed chlorofluoroethane molecules and the $(HF)_n$ oligomeric chain. The nature of the Lewis sites involved or the structure of the adsorbed chlorofluoroethane is not known. However, D.R.I.F.T.S. (14) has shown that CCl_2FCClF_2 is physically adsorbed onto fluorinated chromia and also physical adsorption of CCl_2FCClF_2 on uranium (IV) oxide (12) and of chlorofluoromethanes on CrF_3 (10) has been quantified. The adsorption of chlorofluoroethanes was explained by Winfield et al as involving a C-Cl bond for fluorination or a C-F bond for fluorination reactions with the entering halogen species the terminal atom of an oligomeric chain. As discussed previously, the Lewis acid site required on chromia for such reactions is thought to involve chromium in oxidation states of III and above, possibly Cr^{VI}, since this oxidation state is known to be present in fluorinated chromia (25) and other chromia-based catalysts (140,141). The nature of the site has not been established on γ-alumina, but it will also involve strong Lewis acid sites. These are required to polarize strongly the adsorbed chlorofluorocarbon compound prior to the reaction. It has been suggested by Kemnitz et al (88,89) that Lewis acid sites are not required and that chlorofluorocarbon compounds are only weakly adsorbed on the surface of certain metal halides and oxides known to catalyse these reactions. However from the reactions observed on $AlCl_3$ and on fluorinated γ-alumina and chromia, Lewis acid sites are thought to be necessary. The mechanisms involved in halogen exchange reactions involving oxide supported organic layer catalysts at room temperature are possibly different to those postulated on HF fluorinated chromia, due to the presence of the organic layer.

(iii) *IN SITU* I.R. ANALYSIS OF 1,1,1-TRICHLOROETHANE CONDITIONING REACTION.

To obtain a more detailed understanding of the dehydrochlorination and halogen exchange reactions involved in the 1,1,1-trichloroethane conditioning process, the vapour phase above the solid during the reaction was analysed by *in situ* I.R. spectroscopy. Addition of SF_4 γ-alumina , chromia and volcano chromia to 1,1,1-trichloroethane lead to a decrease in the 1,1,1-trichloroethane concentration, as expected. The SF_4 γ-alumina and chromia samples behave similarly with the decrease from volcano chromia somewhat greater. The dehydrochlorination product, $CH_2=CCl_2$, was detected immediately in the vapour phase in all three cases, but the amount then appears to remain virtually constant over the reaction period. The reaction appears to be a little slower on the chromia. The proportion of 1,1-dichloroethene in the vapour phase at the end of the reaction is in the order

volcano chromia > chromia > γ-alumina.

The hydrofluorination product CH_3CCl_2F was also observed in the vapour phase immediately. The level was effectively constant over the reaction period for chromia sample, but for volcano chromia and γ-alumina the level increased gradually. The fluorinated volcano chromia produced the greatest quantity of CH_3CCl_2F and the chromia the least. This suggests that the fluorine present on the volcano chromia is most readily available for halogen exchange reactions.

In the analogous reaction using the dehydrochlorination product $CH_2=CCl_2$ as starting material, a similar overall pattern of reaction was observed. The presence of 1,1,1-trichloroethane in the products supports the model of a reversible surface reaction involving hydrochlorination of 1,1-dichloroethene/ dehydrochlorination of 1,1,1-trichloroethane. The concentration increased immediately, then gradually decreased over the reaction. The hydrofluorination product also appears immediately. There is not a delay as the organic material builds up on the surface before the hydrofluorination products are detected,therefore these reactions take place in conjunction with the laydown of the organic material. Data for the disappearance of 1,1-dichloroethene compared to disappearance of 1,1,1-trichloroethane are broadly similar, although the fluorinated chromia appears to be less effective at reacting with 1,1-dichloroethene. Production of 1,1,1-trichloroethane, by hydrochlorination of 1,1-dichloroethene, appears to occur similarly on all three solids with γ-alumina performing slightly better than the others. Formation of CH_3CCl_2F from 1,1-dichloroethene is favoured on fluorinated γ-alumina, whereas from 1,1,1-trichloroethane it was favoured on fluorinated volcano chromia. The reaction in the presence of γ-alumina is not identical to that in the presence of volcano chromia.

(iv) *IN SITU* I.R. ANALYSIS OF THE INTERACTION OF HCl WITH 1,1,1-TRICHLOROETHANE CONDITIONED MATERIALS.

The *in situ* I.R. study of the volatile materials from the reaction of HCl with conditioned plus fluorinated materials indicated that the concentration of HCl in the gas phase decreased over the reaction. This was accompanied by the development of several bands in the region of 1400-900cm^{-1} which correspond to CH_3CCl_3 and CH_3CCl_2F. This indicates that halo-organic material is displaced from the organic layer material by the action of the HCl and that hydrochlorination and hydrofluorination reactions occur. The results in this section can be linked with previous studies (160) of conditioned γ-alumina, which indicated a "turn-over" of organic material on the surface. This work should also be considered in conjunction with the [^{36}Cl]-chlorine labelled HCl and CH_3CCl_3 studies in Chapter 5, which indicate that HCl is adsorbed onto the surface of the materials studied regardless of the presence of the organic layer and that surface chlorine-containing species can be displaced by and/or react with incoming HCl. This is very significant for the subsequent catalytic action of the organic layer, where HF and CH_3CCl_3 are flowed over the catalyst producing fluorinated products.

3.4.4. D.R.I.F.T.S. STUDY OF ADSORBED PYRIDINE SPECIES.

The use of bases e.g. pyridine, as a probe molecule to study the acidic nature of catalytic surfaces is a well established and documented process. (118-135). Introduction of pyridine vapour to acidic surfaces at room temperature results in a surface coverage of 17-20% (121). In this work the surface coverage is analysed using DRIFTS technique to determine the different pyridine-pyridinium species present on the surface. The spectroscopic region which is most useful is the "ring frequency" region, 1700-1400cm^{-1}.

Coordinately bonded pyridine is associated with Lewis acid sites, hydrogen bonded pyridine is associated with terminal hydroxyl groups and pyridinium species are associated with bridging hydroxyl groups.

Comparisons among the spectra indicate that there is very little difference in the adsorbed pyridine on γ-alumina, chromia and volcano chromia. Unexpectedly the fluorination makes very little difference to the adsorbed species. The fact that fluorination does not greatly alter the pyridine adsorption was unexpected, as it is well established that fluorination enhances the surface acidity. The most likely cause of this result is the conditions used for the analysis. Attempts to use an inert atmosphere shroud to prevent the exposure of the moisture sensitive samples to the atmosphere failed due to the unacceptably high background noise levels this created. Scanning times were kept as short as possible to minimise hydrolysis of the samples however, the results obtained indicate that the samples were probably hydrolysed resulting in removal of fluorine and reduction of the surface acidity.

The conditioned materials also showed similar adsorption bands to those observed on the calcined materials, again probably an effect of hydrolysis of the surfaces. However, the colour of the conditioned γ-alumina did not fade from the dark purple to the grey colour characteristic of the hydrolysed organic layer.

Therefore, due to the problems encountered, a detailed analysis of the pyridine adsorption on fluorinated and conditioned surfaces was not possible. However, what can be established is that γ-alumina, chromia and volcano chromia all have Lewis and Brϕnsted acid sites as demonstrated by the coordinately bonded and hydrogen bonded pyridine and the pyridinium species. From the work already discussed in this section it has been established that SF_4 fluorination enhances Lewis acidity and that γ-alumina, chromia and volcano chromia behave similarly. Therefore the study of pyridine adsorption confirms the similarities observed between the samples studied.

In conclusion, the work in this Chapter has established that fluorination of chromias with SF_4 results in the formation of strong Lewis acid sites, capable of dehydrochlorinating CH_3CCl_3. During the conditioning process hydrofluorination reactions, producing CH_3CCl_2F, also occur. The reactions are very similar to those observed on γ-alumina treated in an identical way. However there is no visible evidence of laydown of organic material on the chromia samples. Mass changes observed when the material is conditioned, Section 3.3.7, indicate that organic material is incorporated onto the fluorinated materials. The reaction of HCl with conditioned materials also demonstrates the presence of organic material on the surfaces and that this material can undergo hydrochlorination and hydrofluorination reactions and be displaced from the surfaces.

INTERACTION OF [^{18}F]-FLUORINE LABELLED GASES WITH OXIDE SURFACES:UPTAKE AND EXCHANGE REACTIONS.

4.1 INTRODUCTION.

Halogenation of an oxide surface results in the promotion of acidity on the surface due to the formation of new Brϕnsted and/or Lewis acid sites by replacing surface hydroxyl groups and some in-plane bridging oxygen atoms by the halogen (Figs.1.5 and 1.6). This model was based on γ-alumina chlorinated with carbon tetrachloride, carbonyl chloride or hydrogen chloride: Chlorination with hydrogen chloride at room temperature enhances only Brϕnsted acidity whereas chlorination with carbon tetrachloride or carbonyl chloride enhances Brϕnsted plus Lewis acidity (69,70).

Radiotracer studies using [^{36}Cl]-chlorine labelled species, showed that the type of acidity promoted could be differentiated: chlorine associated with Brϕnsted acid sites is labile with respect to [^{36}Cl]-chlorine exchange at room temperature, whereas chlorine associated with Lewis acid sites is inert to chlorine exchange (69,70).

The formation of Lewis acid sites was described by A.G. Goble and P.A. Lawrance (72) as an exchange of two chlorine atoms for each surface oxygen atom. Chlorination of γ-alumina with reagents containing an even number of chlorine atoms has been shown to enhance Lewis acidity, so it has been proposed that a concerted reaction is required to replace an in-plane oxygen atom (Fig 4.1)

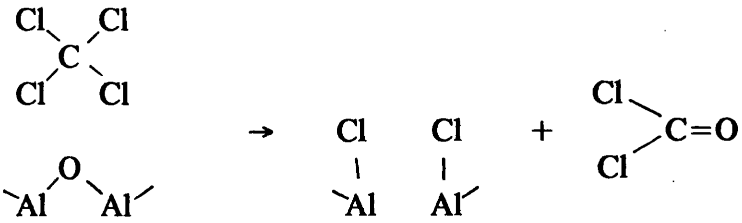


Fig.4.1. Replacement Of An In-plane Oxygen Atom Of γ-Alumina With Chlorine

Formation of Brφnsted sites involves reactions with reagents with an odd number of chlorine atoms resulting in the replacement of terminal Al-OH groups and dissociative addition of HCl (Fig 4.2).

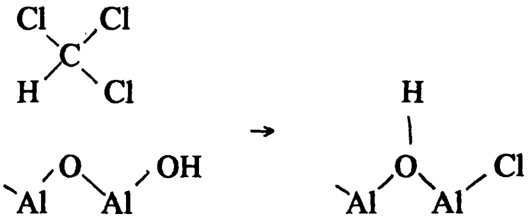


Fig.4.2.Replacement Of Terminal Hydroxyl Group Of γ-Alumina with Chlorine.

Fluorination of γ-alumina, using several fluorinating agents, has been studied quite extensively. Although there is significant uptake of fluorine by γ-alumina using thionyl fluoride, carbonyl fluoride and liquid hydrogen fluoride (92,160), materials treated in this way do not dehydrochlorinate 1,1,1-trichloroethane, which is a specific probe reaction for Lewis acidity (Section 1.5): although fluorination with F_2SO, F_2CO or HF at room temperature promotes Brφnsted acidity of γ-alumina, sulphur tetrafluoride is the only reagent so far investigated in detail that is capable of promoting both

Brϕnsted plus Lewis acidity.

The behaviour of sulphur tetrafluoride was studied using [^{35}S]-sulphur labelled sulphur tetrafluoride (160) and by monitoring the vapour phase above the surface using I.R. spectroscopy (160). These indicated that in the early part of the reaction the partial pressure of SF_4 decreased rapidly and F_2SO was formed but no SO_2 is detected initially. There was immediate [^{35}S] adsorption followed by a decrease in surface count rate. These results can be explained as rapid surface reactions leading to formation of adsorbed SO_2 and -OH/F exchange reactions. The sulphur dioxide adsorbed on to the surface protects the surface to an extent from fluorination. As SO_2 desorbs, the exposure of a fresh surface allows in-plane bridging oxygen atoms to be fluorinated with generation of Lewis sites.

Halogen exchange reactions used in industry for production of CFCs generally involve flowing hydrogen fluoride and the appropriate haloalkane over a chromia catalyst at elevated temperatures. Work using [^{18}F]-fluorine labelled hydrogen fluoride (25) on chromia catalysts presented evidence for three types of surface species:

(i) Weakly adsorbed hydrogen fluoride molecules or oligomers. This is a minor fraction of the total fluorine.

(ii) Inert fluorine containing species that do not undergo exchange with or displacement by HF at 623K. This type of fluorine is thought to be directly bonded to chromium (III). The proportion of fluorine in this category increases as the catalyst is used.

(iii) Labile fluorine containing species that do undergo exchange with and displacement by HF and are the source of fluorine incorporated into haloalkanes (24). The exact nature of this active fluorine has not been determined but the sites involved are believed to be Cr(IV) and Cr(VI).

The uptake of fluorine on amorphous chromia in the reaction with HF was determined to be in the range 1.0 - 1.4 (mg atom F) g^{-1} (14). Studies into the reaction of hydrogen fluoride on γ-alumina indicate that the extent of interaction is smaller than that of SF_4 with γ-alumina: Uptakes were determined as 2.5 (mg atom F) g^{-1} for HF on γ-alumina (160) and 15 (mg atom F) g^{-1} for SF_4 on γ-alumina (143). This substantial difference was postulated to be due to fluorine containing species diffusing into the bulk of the material. If more fluorine is incorporated into chromia by treatment with SF_4 rather than HF, this may create a catalyst that is even more effective for catalytic fluorination reactions

The SF_4 fluorinated γ-alumina surface has been the basis of a great deal of research into catalysts for halogen exchange reactions at room temperature as an alternative to chromia treated with HF at elevated temperatures. Central to the understanding of the oxide supported organic layer catalysts is the behaviour of the fluorine containing species on the surface. In particular how much of the surface fluorine is labile? What effect does the organic layer have on the lability? In the present work, $[^{18}F]$-fluorine labelled species have been used to examine uptake and exchange reactions on calcined, fluorinated and fluorinated plus conditioned materials to allow a detailed study of the behaviour of the fluorine species on these materials and so to attempt to determine mechanisms for the reactions.

Comparisons have been made among γ-alumina, chromia and volcano chromia samples, treated in an identical manner to examine the nature of the fluorine containing species on the surfaces of these oxides when fluorinated with SF_4. Further work has examined the effect of 1,1,1-trichloroethane conditioning on the lability of the fluorine species to establish the role of the organic layer.

4.2 EXPERIMENTAL.

4.2.1. EXCHANGE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED SULPHUR TETRAFLUORIDE WITH SF_4 FLUORINATED γ-ALUMINA AND CH_3CCl_3 CONDITIONED, SF_4 FLUORINATED γ-ALUMINA.

[^{18}F]-Fluorine labelled SF_4 was prepared as previously described (Section 2.2.3). The specific count rate was determined before the reaction by condensing a known quantity of [^{18}F]-SF_4 into a single limbed counting vessel (Fig 2.14) containing dry pyridine.

A sample of [^{18}F]-SF_4 was condensed at 77K into a Monel metal bomb containing SF_4 fluorinated γ-alumina (0.5g) and allowed to react for one hour. After this time, a sample of the volatile material was removed from the reaction bomb and condensed into a single limb counting vessel containing dry pyridine. Thus, the specific activity of [^{18}F]-SF_4 before the reaction with SF_4

fluorinated γ-alumina and after the reaction could be determined and from these measurements the exchange factor, the amount of activity exchanged between gas and solid could be determined (Section 4.2.5).

The procedure to investigate room temperature exchange reactions of [^{18}F]-fluorine labelled sulphur tetrafluoride with CH_3CCl_3 conditioned, SF_4 fluorinated γ-alumina was the same as described above. This method was also used for room temperature exchange reactions of [^{18}F]-fluorine labelled boron trifluoride with SF_4 fluorinated γ-alumina, chromia and volcano chromia and CH_3CCl_3 conditioned, SF_4 fluorinated γ-alumina, chromia and volcano chromia.

4.2.2. FLUORINE UPTAKE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED BORON TRIFLUORIDE WITH CALCINED γ-ALUMINA.

A sample of calcined γ-alumina (0.5g) was loaded into one limb of a double limb counting vessel (Fig 2.15) in the dry box. The counting vessel was degassed and a 1.0mmol aliquot of [^{18}F]-fluorine labelled boron trifluoride was condensed at 77K into the empty limb. The [^{18}F]-BF_3 was allowed to warm to room temperature and the count rate determined. The stopcock connecting the two limbs was opened and the [^{18}F]-BF_3 vapour allowed to interact with the solid, which was counted immediately. The counts from both limbs were determined at regular intervals. After one hour the two components were separated by condensing the vapour back into the limb without the solid. The counts were determined for both the vapour and the solid.

The [^{18}F]-fluorine labelled vapour was removed and a second aliquot (1.0mmol) was condensed into the empty limb, allowed to warm to room temperature and then introduced to the solid. The counts from both limbs were determined at regular intervals. This process was repeated, with in total four aliquots of 1.0mmol interacting consecutively with the calcined γ-alumina.

The procedure to investigate room temperature fluorine uptake reactions of [^{18}F]-fluorine labelled boron trifluoride with calcined volcano chromia was the same as described above.

4.2.3. FLUORINE UPTAKE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED BORON TRIFLUORIDE WITH SF_4 FLUORINATED γ-ALUMINA AND CH_3CCl_3 CONDITIONED, SF_4 FLUORINATED γ-ALUMINA.

A sample (0.5g) of SF_4 fluorinated γ-alumina was loaded into one limb of a double-limbed counting vessel (Fig 2.15). This was undertaken in the dry box. After degassing the counting vessel, a known quantity of [^{18}F]-fluorine labelled BF_3 was condensed at 77K into the second,empty limb. The [^{18}F]-BF_3 was allowed to warm to room temperature and the counts determined. The stopcock connecting the two limbs was opened and the [^{18}F]-BF_3 vapour allowed to interact with the solid, which was counted immediately. The counts from both limbs were determined at regular intervals.

After one hour the two components were separated by condensing the vapour back into the limb without the solid. The counts were determined for both the vapour and the solid. A sample of the vapour was removed and condensed into dry pyridine to determine the specific count rate after the reaction. The solid was degassed by pumping and the count rate determined.

The [^{18}F]-fluorine labelled vapour was removed and a sample of unlabelled BF_3 condensed into the empty limb. The solid was exposed to unlabelled BF_3 under identical conditions and the counts from both limbs determined at regular intervals. The components were then separated by condensing the vapour back into the empty limb without the solid and the count rate determined for both vapour and solid. The solid was degassed by pumping and the count rate determined.

The procedure to investigate room temperature exchange reactions of [^{18}F]-fluorine labelled boron trifluoride with CH_3CCl_3 conditioned, SF_4 fluorinated alumina was the same as described above. This method was also used for the fluorine uptake reactions of [^{18}F]-fluorine labelled BF_3 with SF_4 fluorinated chromia and volcano chromia, CH_3CCl_3 conditioned, SF_4 fluorinated chromia and volcano chromia and BF_3 fluorinated γ-alumina, chromia and volcano chromia.

4.2.4. DETERMINATION OF SPECIFIC COUNT RATE OF [^{18}F]-FLUORINE LABELLED SULPHUR TETRAFLUORIDE AND BORON TRIFLUORIDE.

A measured pressure of [^{18}F]-SF_4 or [^{18}F]-BF_3 in a known volume was condensed onto a sample (0.5ml) of dried pyridine in a Pyrex glass counting vessel.(Fig 2.14). The adduct formed was counted for a period long enough to give sufficient counts to minimize the radiochemical errors. Normally a minimum of 10,000 counts were accumulated which results in a radiochemical error of < 1%. The results were expressed as specific count rate i.e. counts min^{-1} (mg atom F^{-1}).

4.2.5. EXCHANGE FACTORS.

Isotope exchange reactions can be described in terms of the fraction exchanged,f,defined as:

$$f = \frac{\text{Fraction of isotope in initially unlabelled compound after reaction.}}{\text{Fraction of exchangeable atoms in the initially unlabelled compound.}} \qquad \text{Eqn.4.1.}$$

Consider the exchange reaction:

$$AX + B^*X = A^*X + BX \qquad \text{Eqn.4.2.}$$

in which AX and BX contain m_1 and m_2 mg atom X respectively. Compound BX is labelled initially, count rate A_o $cmin^{-1}$; after separation of the components, the count rates of A*X and B*X are A_1 and A_2 $cmin^{-1}$ respectively.

The fraction exchanged ,

$$f = \frac{\dfrac{A_1}{A_1 + A_2}}{\dfrac{m_1n_1}{m_1n_1 + m_2n_2}} \qquad \text{Eqn.4.3.}$$

where,

m = no of mmol, n = no of exchangeable atoms i.e. 4 for SF_4.

m_1n_1 is the available pool of fluorine on the γ-alumina, assumed to be 15 mg atom g^{-1}.

Complete exchange, f = 1 corresponds to the random distribution of the *X label throughout m_1 and m_2 mg atom X.

The initial specific count rate, $S_o = A_o/m_2n_2$ c.min^{-1}(mg atom X)$^{-1}$.

The final specific count rate, $S_t = A_2/m_2n_2$ c.min^{-1}(mg atom X)$^{-1}$.

For f = 1, $S_\infty = A_o/(m_1n_1 + m_2n_2)$.

Hence, substituting in equation 4.3,

$$f = \frac{S_o - S_t}{S_o - S_\infty} \qquad \text{Eqn.4.4.}$$

Therefore, if

$S_o = S_t$ then f=0, corresponding to no observable exchange.

$S_t = S_\infty$ then f=1, corresponding to complete exchange, i.e. random distribution of the radiolabel throughout the two components.

4.3. RESULTS.

4.3.1. EXCHANGE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED SULPHUR TETRAFLUORIDE WITH SF_4 FLUORINATED γ-ALUMINA AND CH_3CCl_3 CONDITIONED,SF_4 FLUORINATED γ-ALUMINA.

The results of the exchange reactions of [^{18}F]-fluorine labelled SF_4 with SF_4 fluorinated γ-alumina showed that there was a large proportion of fluorine on the solid which was labile with respect to [^{18}F]-SF_4.

A series of five separate experiments, involving different γ-alumina samples was carried out. The results, given in Table 4.1 show that there is a wide range of exchange values, f, obtained, 0.29 - 0.90. This indicates that there is not a clear-cut distinction between fluorine which is labile to exchange reactions and that which is inert. The range of f values suggests the occurrence of a complex exchange system involving more than one step, or that there is a degree of irreproducibility in the fluorination process adopted for the catalyst preparation.

Attempts to determine whether any correlation exists between the quantity of [^{18}F]-SF_4 used and the f values obtained were unsuccessful. It was a common feature throughout the experiments described in this chapter that there did not appear to be a simple relationship. The generally high values obtained were consistent with the existence of a "pool" of labile fluorine on the solid.

Table 4.1. [^{18}F]-SF_4 Exchange Reactions With SF_4 γ-Alumina

[^{18}F]-SF_4 (mmol)	Exchange Factor. f
0.97	0.53 ± 0.04
1.03	0.90 ± 0.05
2.76	0.67 ± 0.05
3.00	0.85 ± 0.04
3.00	0.29 ± 0.06

The results of a comparable series of five experiments on γ-alumina fluorinated with SF_4 then conditioned with CH_3CCl_3 are given in Table 4.2.

Table 4.2. [^{18}F]-SF_4 Exchange Reactions With CH_3CCl_3, SF_4 γ-Alumina

[^{18}F]-SF_4 (mmol)	Exchange Factor. f
1.03	0.42 ± 0.05
1.59	0.43 ± 0.05
2.15	0.54 ± 0.05
2.90	0.48 ± 0.05
3.00	0.60 ± 0.04

The data obtained were similar to those for the fluorinated samples (Table 4.1), with f values ranging from 0.42 - 0.60. Although this range of values was smaller than that for the fluorinated material, it was evident that the organic layer deposited on the SF_4 γ-alumina did not affect greatly the lability of the fluorine. This suggests that either the organic layer does not completely cover the surface or that fluorine is able to diffuse through the organic material. The formation of fluorinated products, a mixture of $CH_3CCl_{3-n}F_n$ (n = 1 - 3) during the conditioning process (Section 3.3.3) results in a pool of available labile fluorine which would be expected to be smaller in the conditioned plus fluorinated samples than the fluorinated samples. This may account for the slightly smaller exchange values determined for the conditioned materials compared to the fluorinated materials.

4.3.2. EXCHANGE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED BORON TRIFLUORIDE WITH SF_4 FLUORINATED γ-ALUMINA AND CH_3CCl_3 CONDITIONED, SF_4 FLUORINATED γ-ALUMINA.

From the results of exchange reactions of [^{18}F]-fluorine labelled BF_3 with SF_4 fluorinated γ-alumina it is clear that there is a considerable quantity of fluorine, that has been deposited on the solid during the SF_4 fluorination process, which is labile with respect to room temperature exchange with [^{18}F]-BF_3.

Five separate experiments involving different SF_4 γ-alumina samples were performed. Table 4.3. shows the results obtained expressed as exchange values. The wide range of exchange values determined, 0.26 - 0.88, was comparable to that for [^{18}F]-SF_4 on SF_4 γ-alumina (Table 4.2), indicating that the source of the labelled fluorine species does not affect the lability of the surface fluorine.

Table 4.3.[^{18}F]-BF_3 Exchange Reactions With SF_4 γ-Alumina

[^{18}F]-BF_3 (mmol)	Exchange Factor. f
1.03	0.75 ± 0.04
1.03	0.35 ± 0.04
1.55	0.88 ± 0.05
1.55	0.44 ± 0.06
3.00	0.26 ± 0.05

Examination of the comparable experiments on CH_3CCl_3, SF_4 γ-alumina resulted in a similar outcome. The data for a series of five separate experiments, given in Table 4.4, were similar to those obtained for the fluorinated material (Table 4.3.), with f values ranging from 0.25 - 0.77. Again, it is clear that the organic material laid down in the conditioning process does not affect the lability of the surface fluorine, and this fluorine is equally labile with respect to SF_4 and BF_3.

Table 4.4. [^{18}F]-BF_3 Exchange Reactions With CH_3CCl_3, SF_4 γ-Alumina.

[^{18}F]-BF_3 (mmol)	Exchange Factor. f
1.03	0.77 ± 0.04
1.55	0.25 ± 0.05
2.50	0.46 ± 0.05
3.00	0.62 ± 0.06
3.00	0.72 ± 0.04

4.3.3. EXCHANGE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED BORON TRIFLUORIDE WITH SF_4 FLUORINATED CHROMIA AND VOLCANO CHROMIA AND CH_3CCl_3 CONDITIONED, SF_4 FLUORINATED CHROMIA AND VOLCANO CHROMIA.

The results of room temperature exchange reactions of [^{18}F]-fluorine labelled BF_3 with SF_4 fluorinated chromia and volcano chromia were very similar to those for SF_4 fluorinated γ-alumina indicating that the materials all undergo similar exchange reactions.

Five experiments involving [^{18}F]-BF_3 with different samples of SF_4 fluorinated chromia and volcano chromia were performed. The results obtained expressed as exchange factors,f, are given in Tables 4.5 and 4.6. The wide ranges of the f values obtained, 0.23 - 0.53 for SF_4 chromia and 0.38 - 0.54 for SF_4 volcano chromia, indicate that the SF_4 fluorination of chromia and volcano chromia provides a quantity of fluorine that is labile to exchange reactions with BF_3, but that there is no clear cut distinction between labile and inert fluorine species. Comparisons of the exchange values for [^{18}F]-BF_3 with SF_4 chromia and SF_4 volcano chromia with those for [^{18}F]-BF_3 with SF_4 γ-alumina suggest that the quantity of labile fluorine present on the chromia samples is less than on SF_4 γ-alumina. However, the range of values determined for both sets of chromia samples indicates that as in the case of the γ-alumina there is a complex exchange system involved.

Table 4.5. [^{18}F]-BF$_3$ Exchange Reactions With SF$_4$ Chromia.

[^{18}F]-BF$_3$ (mmol)	Exchange Factor. f
0.35	0.23 ± 0.06
1.00	0.42 ± 0.04
1.00	0.35 ± 0.05
2.00	0.53 ± 0.05
3.00	0.53 ± 0.05

Table 4.6. [^{18}F]-BF$_3$ Exchange Reactions With SF$_4$ Volcano Chromia.

[^{18}F]-BF$_3$ (mmol)	Exchange Factor. f
0.35	0.38 ± 0.06
1.00	0.41 ± 0.05
1.00	0.52 ± 0.05
2.00	0.51 ± 0.04
3.00	0.54 ± 0.04

A comparable series of experiments was carried out on five samples of both CH_3CCl_3, SF$_4$ chromia and volcano chromia. The values given in Tables 4.7. and 4.8. indicate that there is a substantial amount of labile fluorine present. The data obtained were very similar to those from the fluorinated chromia samples (Tables 4.5 and 4.6). Thus, it is clear that the conditioning process does not affect the lability of the fluorine species present. These results again indicate similarities between γ-alumina and the chromias, when treated in identical manners. However,the exchange values determined on the chromia samples are smaller than those for the γ-alumina samples indicating that there is less labile fluorine available on the chromia samples.

Table 4.7.[^{18}F]-BF_3 Exchange Reactions With CH_3CCl_3, SF_4 Chromia.

[^{18}F]-BF_3 (mmol)	Exchange Factor. f
0.35	0.23 ± 0.04
1.00	0.47 ± 0.04
1.00	0.29 ± 0.04
2.00	0.39 ± 0.05
3.00	0.53 ± 0.05

Table 4.8. [^{18}F]-BF_3 Exchange Reactions With CH_3CCl_3, SF_4
Volcano Chromia.

[^{18}F]-BF_3 (mmol)	Exchange Factor.
0.35	0.38 ± 0.06
1.00	0.55 ± 0.06
1.00	0.26 ± 0.06
2.00	0.39 ± 0.05
3.00	0.54 ± 0.05

4.3.4. EXCHANGE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED BORON TRIFLUORIDE WITH BF_3 FLUORINATED γ-ALUMINA AND VOLCANO CHROMIA.

A preliminary study of [^{18}F]-fluorine labelled BF_3 with BF_3 fluorinated γ-alumina and volcano chromia indicated that there was labile fluorine present on these materials also. The quantity appears to be less than in the SF_4 fluorinated material but it is a significant amount (Table 4.9). This indicates that BF_3 can fluorinate γ-alumina and volcano chromia, but that it is not as effective as SF_4.

Table 4.9. [^{18}F]-BF_3 Exchange Reactions With BF_3 γ-Alumina and Volcano Chromia

	[^{18}F]-BF_3 (mmol)	Exchange Factor. f
γ-Alumina.	1.00	0.35 ± 0.05
	1.50	0.27 ± 0.05
Volcano Chromia.	1.00	0.29 ± 0.05
	1.50	0.31 ± 0.05

4.3.5. FLUORINE UPTAKE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED BF_3 WITH CALCINED γ-ALUMINA AND VOLCANO CHROMIA.

The results of the room temperature fluorine uptake reactions of [^{18}F]-fluorine labelled BF_3 with calcined γ-alumina (0.505g) showed an immediate interaction, on introduction of the first aliquot (1mmol). There was an initial rapid increase in the counts from the solid followed by a stage where the counts increased only very slightly (Fig.4.3) over a period of 60min. On removal of the vapour, by condensing it back into the limb without γ-alumina, the gas counts increased and the solid counts decreased (Table 4.10),

Fig.4.3. Reaction Of [^{18}F]-BF_3 With Calcined Alumina.

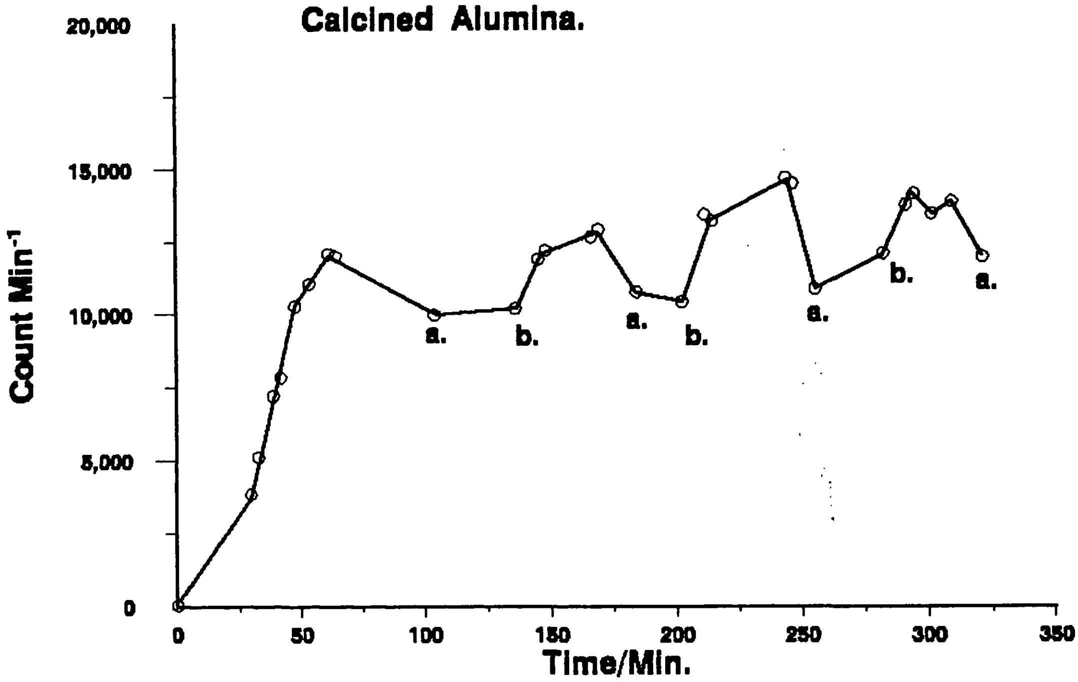
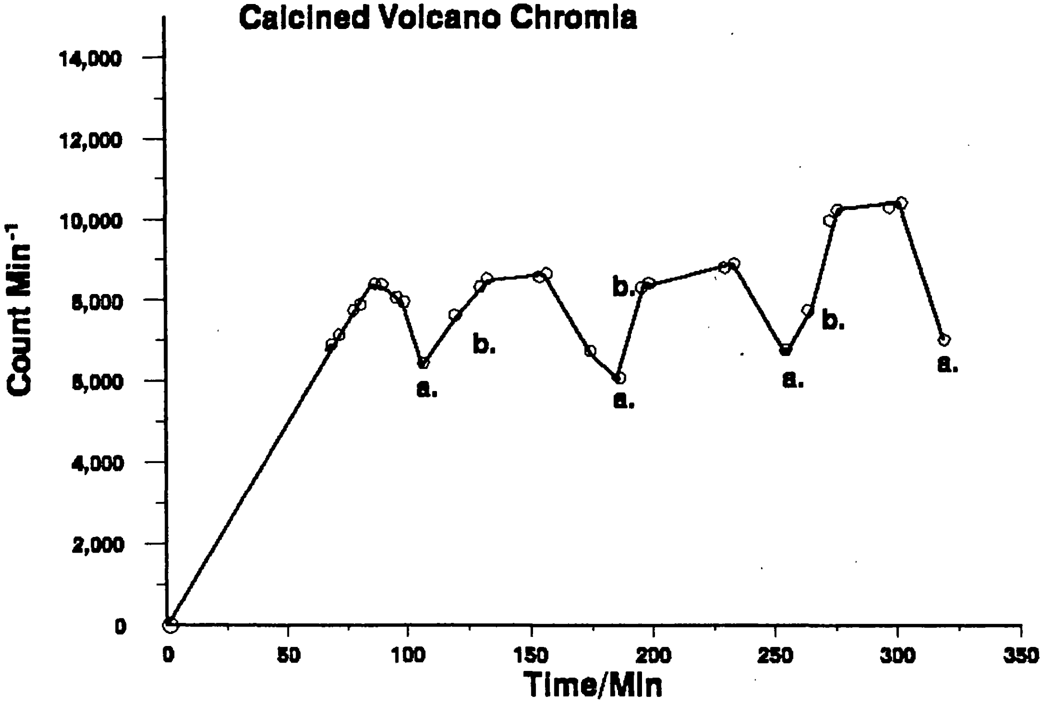


Fig.4.4. Reaction Of [^{18}F]-BF_3 With Calcined Volcano Chromia



a. = Solid Count Rate After Removal Of Aliquot Of BF_3.

b. = Solid Count Rate After Introduction Of Next Aliquot Of BF_3.

indicating the presence of some weakly attached fluorine species on the surface which were easily removed.

Table 4.10 Fluorine Uptake with BF_3 On Calcined γ-Alumina.

BF_3 Aliquot No. (mmol)	Initial Gas Count Rate. (c.min^{-1})	Initial Solid Count Rate. (c.min^{-1})	Final Gas Count Rate. (c.min^{-1})	Final Solid Count Rate. (c.min^{-1})
1. (1.00)	5614±75	3836±62	2254±47	9992±90
2. (1.00)	5848±76	10210±101	3892±62	10872±104
3. (1.00)	5202±72	10431±102	4309±66	10872±104
4. (1.00)	6931±83	11080±131	6404±80	11305±106

A second aliquot of [^{18}F]-BF_3 was introduced to the solid (1mmol) and again there was an increase in the solid counts, but it was less marked than in the case of the first aliquot. On removal of the gas phase, there was a decrease in the surface counts.

This procedure was repeated twice, giving a total of four aliquots each of 1mmol. The increase in solid count rate became less substantial with each aliquot. The fluorine uptake was calculated to be 2.05 mg atom F.g^{-1} catalyst. This is not as great as that obtained from SF_4 fluorine uptake reactions (15 mg atom F. g^{-1} catalyst).

An analogous experiment with calcined volcano chromia (0.535g) displayed a similar pattern of fluorine uptake (Fig 4.4). The increase in the solid count rates on addition of the first aliquot to volcano chromia (1mmol) was less substantial than for γ-alumina.

Removal of the vapour resulted in a large decrease in the solid count rate indicating a considerable quantity of weakly adsorbed fluorine species on the solid (Table 4.11). This procedure was repeated three times, giving a total of four aliquots of 1mmol.

Table 4.11. Fluorine Uptake With BF_3 On Calcined Volcano Chromia.

BF_3 Aliquot No. (mmol)	Initial Gas Count Rate. ($c.min^{-1}$)	Initial Solid Count Rate. ($c.min^{-1}$)	Final Gas Count Rate. ($c.min^{-1}$)	Final Solid Count Rate. ($c.min^{-1}$)
1. (1.00)	5829±76	6920±83	4176±65	6448±80
2. (1.00)	4958±70	7628±87	5281±73	6232±82
3. (1.00)	5310±73	6083±78	5099±71	6762±82
4. (1.00)	5465±74	7731±88	5317±73	7017±89

It appears that the majority of the fluorine is taken up by the volcano chromia on the first addition, with subsequent additions adding mainly weakly adsorbed fluorine species that are readily removed

The fluorine uptake was calculated to be 1.45 mg atom $F.g^{-1}$ catalyst. This is not as great as the value calculated for the γ-alumina (2.05mg atom F.) and much less than that obtained from SF_4 fluorine uptake reactions on γ-alumina.

4.3.6. FLUORINE UPTAKE REACTIONS AT ROOM TEMPERATURE OF [^{18}F]-FLUORINE LABELLED BF_3 WITH SF_4 FLUORINATED γ-ALUMINA AND CH_3CCl_3 CONDITIONED, SF_4 FLUORINATED γ-ALUMINA.

The results of room temperature fluorine uptake reactions of [^{18}F]-fluorine labelled BF_3 with SF_4 fluorinated γ-alumina indicated that fluorine was incorporated into the solid from the vapour.(Table 4.12).

Table 4.12. Fluorine Uptake Of [^{18}F]-BF_3 On SF_4 γ-Alumina.

	[^{18}F]-BF_3 Initial (c.min^{-1})	[^{18}F]-BF_3 Final (c.min^{-1})	[^{18}F]-BF_3 Removed (c.min^{-1})	BF_3 Initial (c.min^{-1})	BF_3 Final (c.min^{-1})
Gas Phase	4753±68	1410±44	1529±39	635±25	1186± 34
Solid Phase	9043± 113	16320± 131	16907± 135	15195± 123	11845± 114

The [^{18}F]-fluorine growth curve (Fig 4.6) was determined by subtracting the counts from the vapour alone from the counts from solid plus vapour (Fig 4.5). The relationship represents the growth of [^{18}F]-fluorine activity on the solid with time. It is clear that there was an immediate interaction with a rapid increase in the count rate of the solid which slowed to a more gradual increase almost levelling to a plateau.

On separation of the two components of the reaction, the gas count rate increased slightly (Table 4.12), indicating that some of the [^{18}F]-fluorine was

Fig.4.5. SF_4 Fluorinated Alumina. $[^{18}F]$-BF_3 Uptake and Exchange.

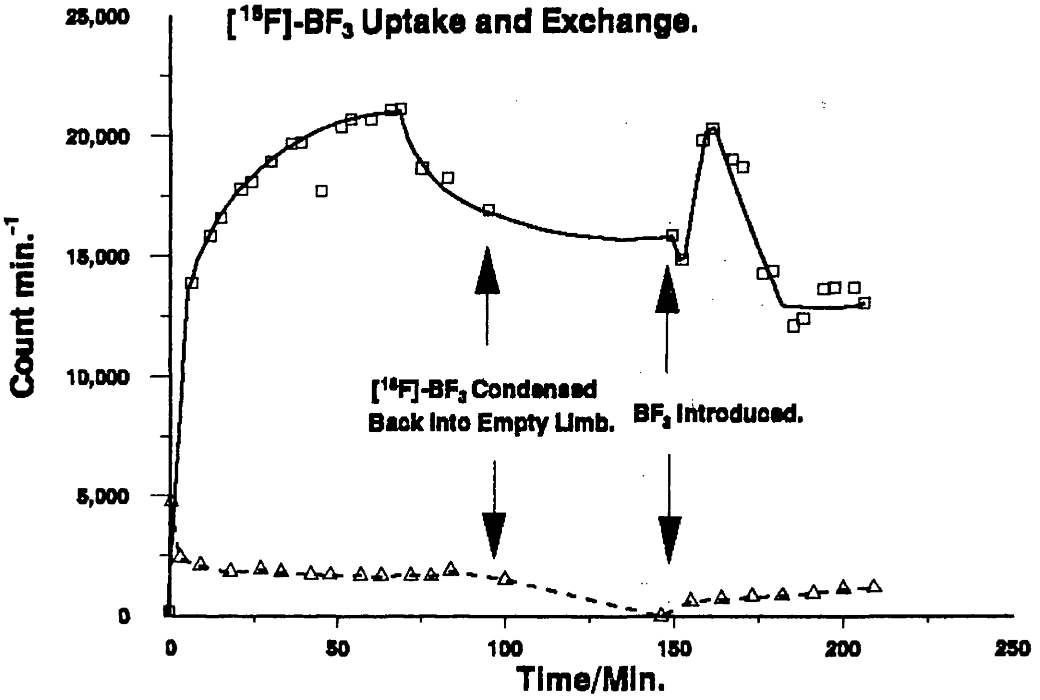
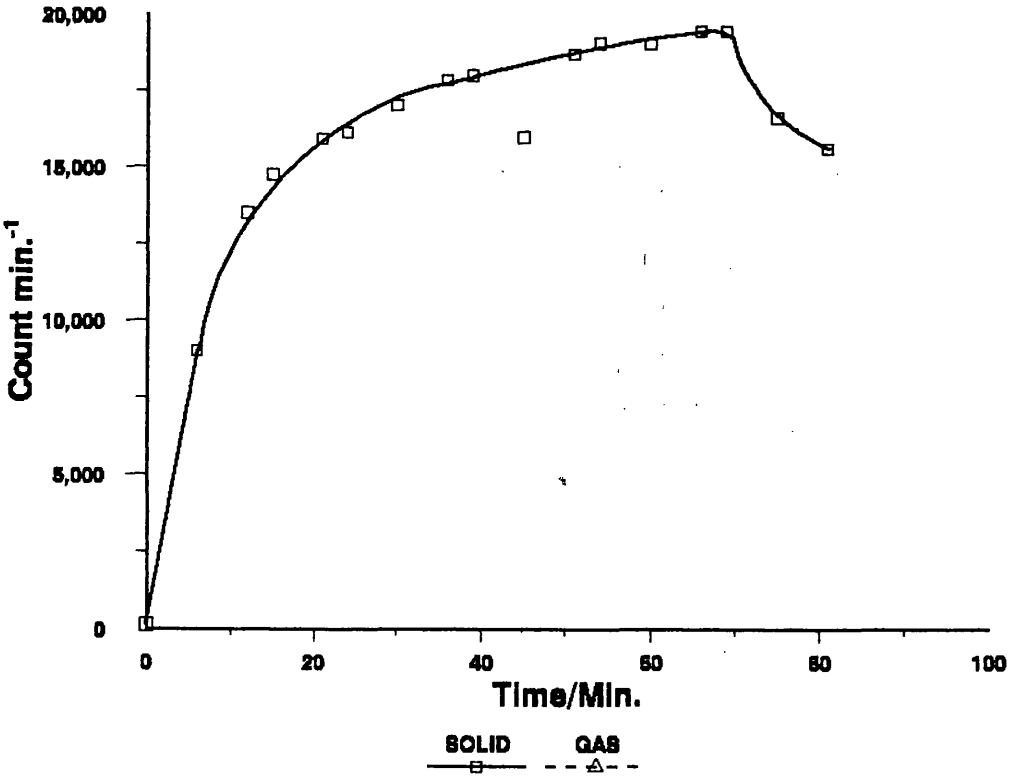


Fig.4.6. SF_4 Fluorinated Alumina. $[^{18}F]$-Fluorine Growth Curve.



only weakly attached to the solid. Unexpectedly, the solid count rate also increased slightly. No explanation has been established for this although this phenomenon was also observed on γ-alumina and volcano chromia treated with [^{18}F]-HF (152,160).

From Table 4.12 [^{18}F]-BF$_3$ (0.35 mmol) interacted with fluorinated γ-alumina (0.528g) resulting in a count rate for the solid alone of 16907 cmin^{-1}. Thus the fluorine uptake plus exchange for SF$_4$ fluorinated γ-alumina was calculated as 1.55mg atom F, compared with 2.05 mg atom F for calcined γ-alumina. In order to determine fluorine uptake alone, equation 4.3. was used to establish the quantity of the final solid counts due to exchange alone.

$$f = \frac{\dfrac{A_1}{A_1 + A_2}}{\dfrac{m_1n_1}{m_1n_1 + m_2n_2}} \qquad \text{Eqn.4.3.}$$

where,

m_2 = no of mmol of BF$_3$, n_2 = no of exchangeable atoms i.e. 3 for BF$_3$. m_1n_1 is the available pool of fluorine on the γ-alumina, assumed to be 15 (mg atom F) g^{-1}. A_1 is the solid count rate due to exchange and A_2 is the activity of BF$_3$ after the reaction. For example, for this reaction with SF$_4$ fluorinated γ-alumina, $f = 0.62$ and the A_1 value was determined, using the equation, to be 13353 count min^{-1}. The difference between the solid count rate and the A_1 value is due to fluorine uptake i.e.

16907 - 13353 = 3554 count min^{-1}, which equals 0.33 mg atom F.

On the introduction of unlabelled BF_3 (0.35mmol) to the [^{18}F]-BF_3 treated solid, there was a decrease in the solid count rate and an increase in the gas count rate (Fig 4.5), indicating that there was [^{18}F]-fluorine exchange between the solid and the vapour, with [^{18}F]-fluorine being incorporated into the gas phase. The exchange factor determined for the reaction between unlabelled BF_3 and [^{18}F]-fluorine treated SF_4 fluorinated alumina was 0.31.

The results from reactions at room temperature of [^{18}F]-BF_3 with conditioned plus fluorinated γ-alumina displayed a similar pattern, with immediate interaction and a rapid increase in the counts from the solid, although it was not as rapid as for the fluorinated material (Figs.4.7 and 4.8).

The increase in the gas counts on separation of the components was more substantial than for the fluorinated material, indicating more weakly bound fluorine on the conditioned plus fluorinated material than on the fluorinated material. This was accompanied by an decrease in the solid count rate.

From Table 4.13, [^{18}F]-BF_3 (0.35 mmol) interacted with conditioned plus fluorinated γ-alumina (0.539g) resulting in a solid count rate of 10206 c.min^{-1} Thus, the fluorine uptake plus exchange was determined to be 0.93 mg atom F. Using equation 4.3 as described above, fluorine uptake alone was determined as 0.65 mg atom F.

Introduction of unlabelled BF_3 (0.35mmol) to the [^{18}F]-fluorine treated solid resulted in an increase in the gas counts and an unexpected, though slight, increase in the solid phase counts (Table 4.13). The exchange factor between

Fig.4.7. Conditioned SF_4 Alumina.
$[^{18}F]$-BF_3 Uptake And Exchange.

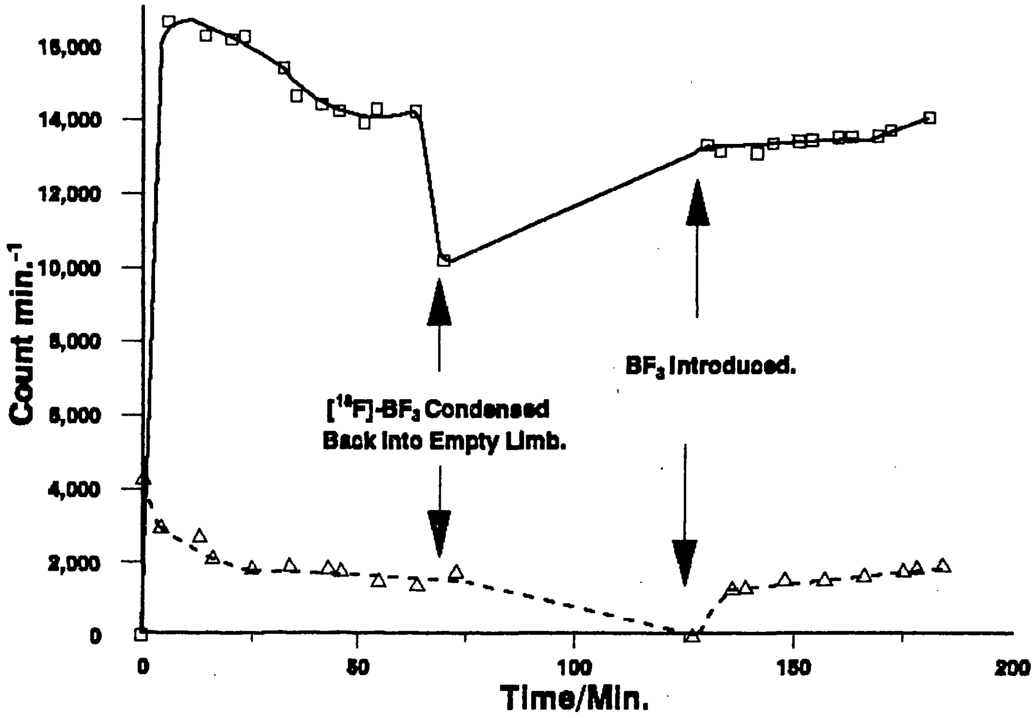
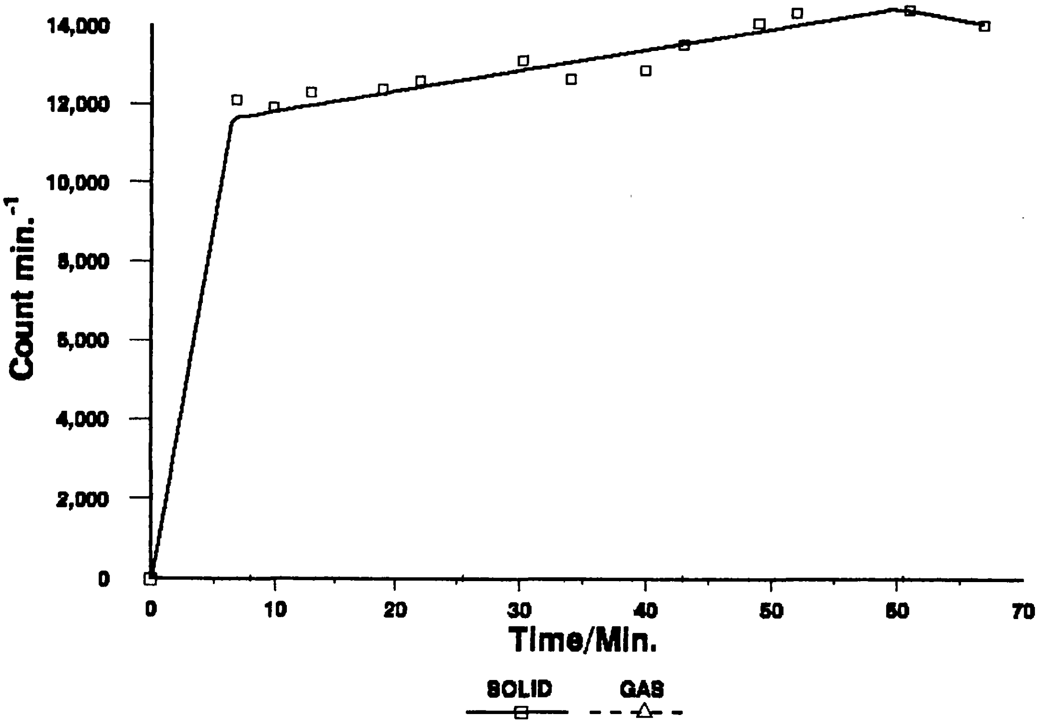


Fig.4.8. Conditioned SF_4 Alumina.
$[^{18}F]$-Fluorine Growth Curve.



unlabelled BF_3 and the $[^{18}F]$-fluorine treated conditioned plus fluorinated γ-alumina was 0.15.

Table 4.13. Fluorine Uptake Of $[^{18}F]$-BF_3 On CH_3CCl_3, SF_4 γ-Alumina.

	$[^{18}F]$-BF_3 Initial ($c.min^{-1}$)	$[^{18}F]$-BF_3 Final ($c.min^{-1}$)	$[^{18}F]$-BF_3 Removed ($c.min^{-1}$)	BF_3 Initial ($c.min^{-1}$)	BF_3 Final ($c.min^{-1}$)
Gas Phase	4260±65	1362±37	1725±42	1257±35	1888±43
Solid Phase	12128± 128	13102± 120	10206± 127	12059± 115	12458± 120

4.3.7. FLUORINE UPTAKE REACTIONS AT ROOM TEMPERATURE OF $[^{18}F]$-FLUORINE LABELLED BF_3 WITH SF_4-FLUORINATED CHROMIA AND VOLCANO CHROMIA AND CH_3CCl_3 CONDITIONED, SF_4 FLUORINATED CHROMIA AND VOLCANO CHROMIA.

Room temperature fluorine uptake reactions of $[^{18}F]$-fluorine labelled boron trifluoride with SF_4 fluorinated chromia and volcano chromia were similar to those on SF_4 γ-alumina.

Table 4.14. Fluorine Uptake Of [^{18}F]-BF_3 On SF_4 Chromia.

	[^{18}F]-BF_3 Initial (c.min^{-1})	[^{18}F]-BF_3 Final (c.min^{-1})	[^{18}F]-BF_3 Removed (c.min^{-1})	BF_3 Initial (c.min^{-1})	BF_3 Final (c.min^{-1})
Gas Phase	4776±69	1770±42	3573±60	630±25	1980± 45
Solid Phase	9616± 114	16363± 134	14561± 121	13020± 117	12494± 122

Table 4.15. Fluorine Uptake Of [^{18}F]-BF_3 On SF_4 Volcano Chromia.

	[^{18}F]-BF_3 Initial (c.min^{-1})	[^{18}F]-BF_3 Final (c.min^{-1})	[^{18}F]-BF_3 Removed (c.min^{-1})	BF_3 Initial (c.min^{-1})	BF_3 Final (c.min^{-1})
Gas Phase	4073±64	2254±48	3691±61	966±31	1467±38
Solid Phase	9370± 115	14760± 130	12941± 114	14076± 122	12843± 119

The [^{18}F]-fluorine growth curves (Figs 4.10 and 4.12) show that there is a build up of activity on the solid although the rate of the reaction appears to be much slower on the chromia samples compared to the γ-alumina.(Fig 4.6). The quantity of fluorine incorporated into the chromias also appears to be much less than in the case of the γ-alumina.(Tables 4.14, 4.15 compared with Table 4.12).

For both chromia samples, on separation of the two components of the reaction the gas counts increased and the solid counts decreased, (Tables 4.14

Fig.4.9. SF_4 Fluorinated Chromia.

$[^{18}F]$-BF_3 Uptake And Exchange.

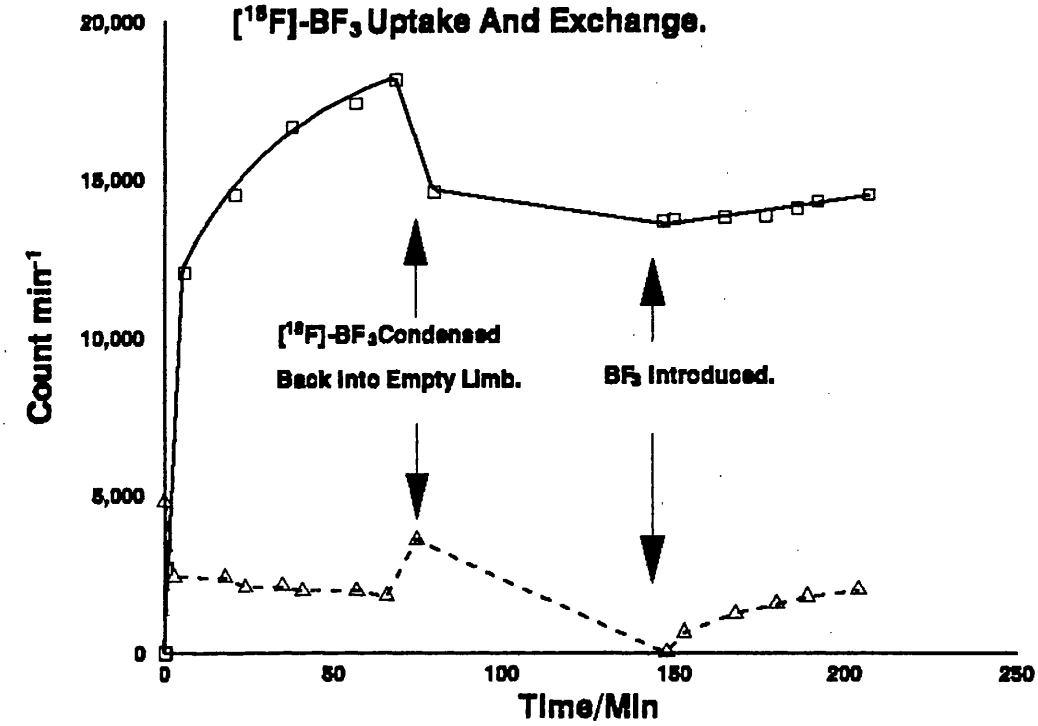


Fig.4.10. SF_4 Fluorinatd Chromia.

$[^{18}F]$-Fluorine Growth Curve.

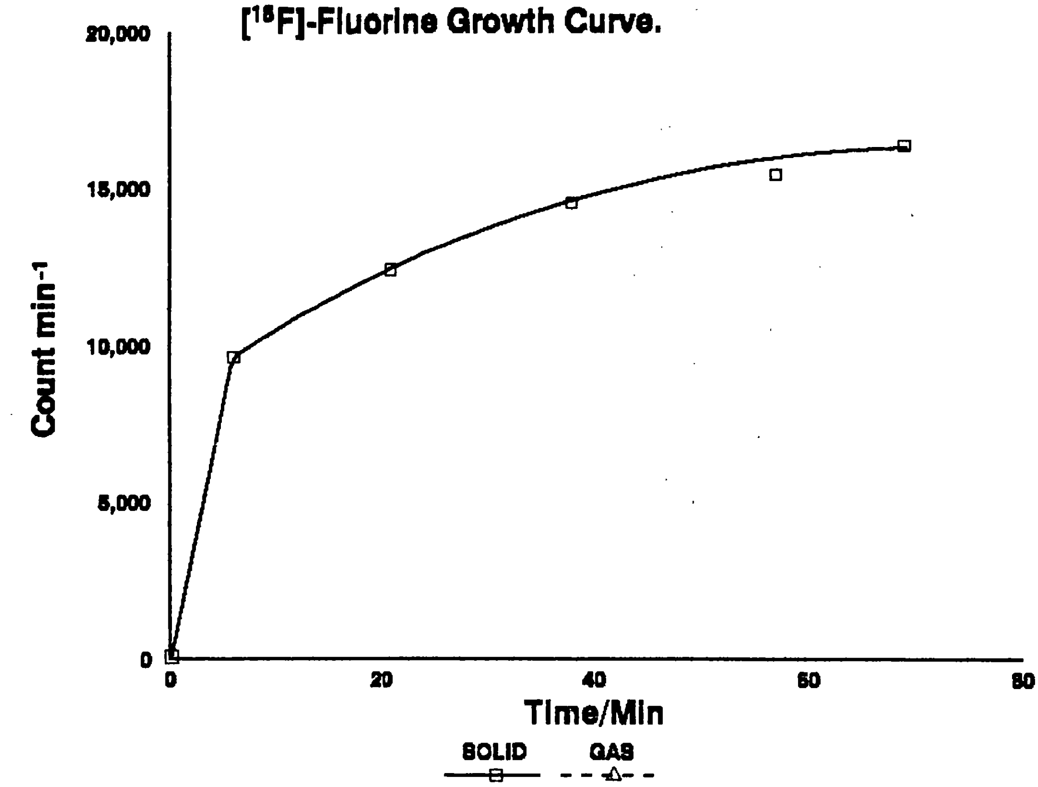


Fig.4.11. SF_4 Volcano Chromia.
$[^{18}F]$-BF_3 Uptake And Exchange.

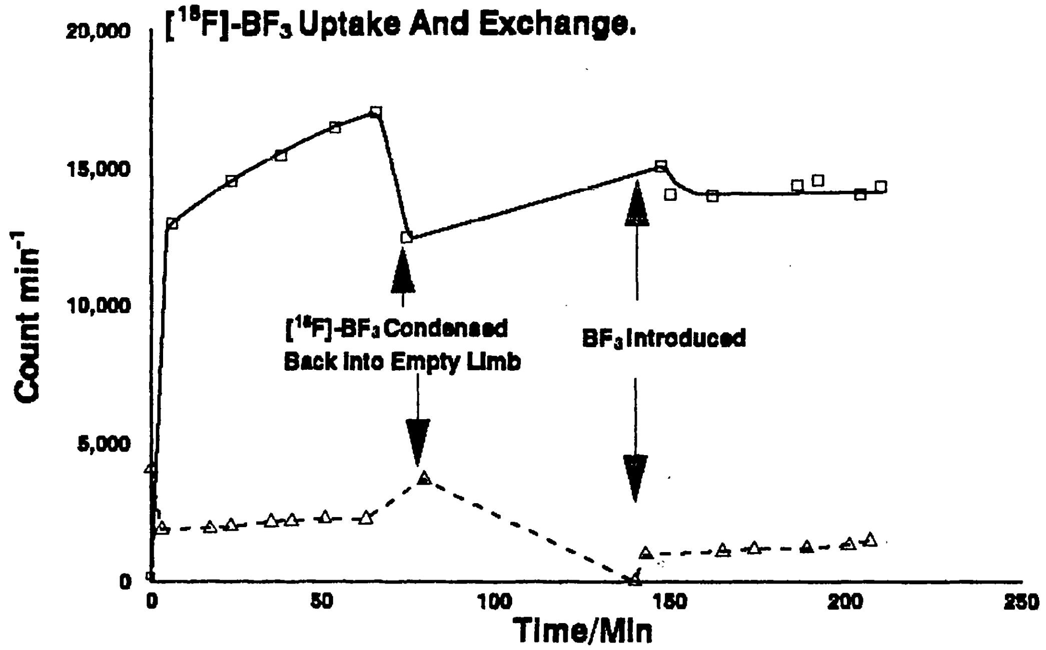
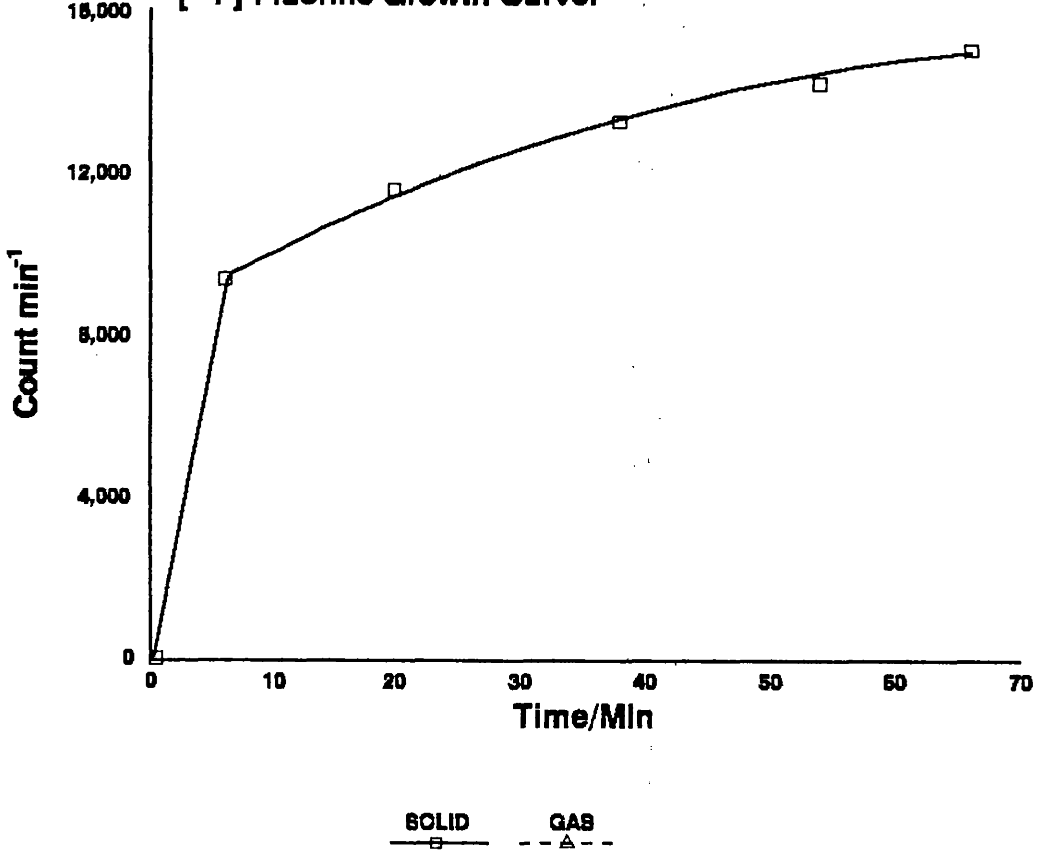


Fig.4.12. SF_4 Volcano Chromia.
$[^{18}F]$-Fluorine Growth Curve.



and 4.15), indicating that a portion of the [^{18}F]-fluorine taken up by the solid was only weakly bound. From Table 4.14 [^{18}F]-BF_3 (0.35mmol) interacted with fluorinated chromia (0.541 g) resulting in a count rate for the solid of 14561 c.min^{-1}. Thus, the fluorine uptake plus exchange was 2.09 mg atom F. Using the method described above, the fluorine uptake was determined to be 1.74mg atom F. Similarly, [^{18}F]-BF_3 (0.35 mmol) interacted with fluorinated volcano chromia (0.537 g) resulting in a count rate for the solid of 12941 c.min^{-1}. Thus, the fluorine uptake plus exchange was 1.86 mg atom F. The fluorine uptake was determined to be 1.34mg atom F.

On introduction of unlabelled BF_3 (0.35 mmol) to the [^{18}F]-fluorine treated solids, both systems reacted in a similar manner. There was a decrease in the solid counts and an increase in the gas counts indicating [^{18}F]-fluorine exchange between the solid and the vapour (Figs 4.9 and 4.11). The exchange factor determined for the reaction between unlabelled BF_3 and SF_4 fluorinated chromia was 0.52 and for SF_4 fluorinated volcano chromia it was 0.46.

Results of comparable reactions of [^{18}F]-fluorine labelled BF_3 with conditioned plus fluorinated chromia and volcano chromia indicated similar but less substantial interactions than on the fluorinated samples (Tables 4.16 and 4.17, Figs.4.14 and 4.16). The quantity of fluorine taken up by the conditioned plus fluorinated chromias is much smaller than that taken up by conditioned plus fluorinated γ-alumina (Table 4.13).

Separation of the two components resulted in an increase in the gas counts and a decrease in the solid counts indicating the presence of weakly adsorbed

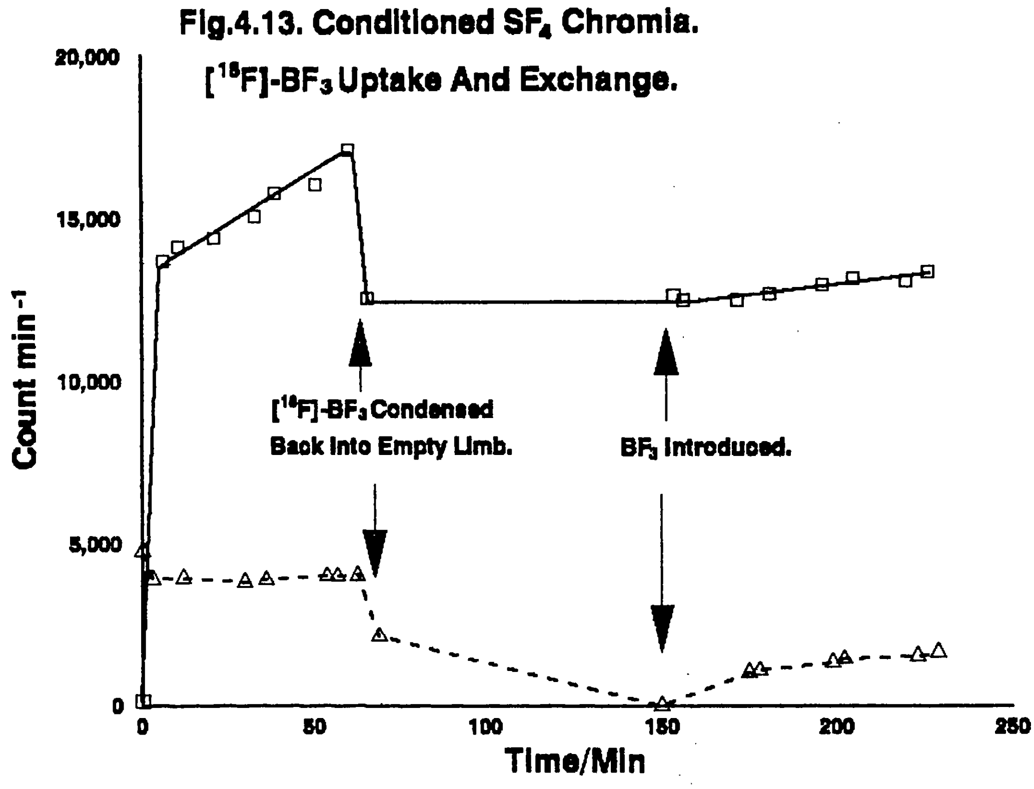


Fig.4.13. Conditioned SF_4 Chromia. $[^{18}F]$-BF_3 Uptake And Exchange.

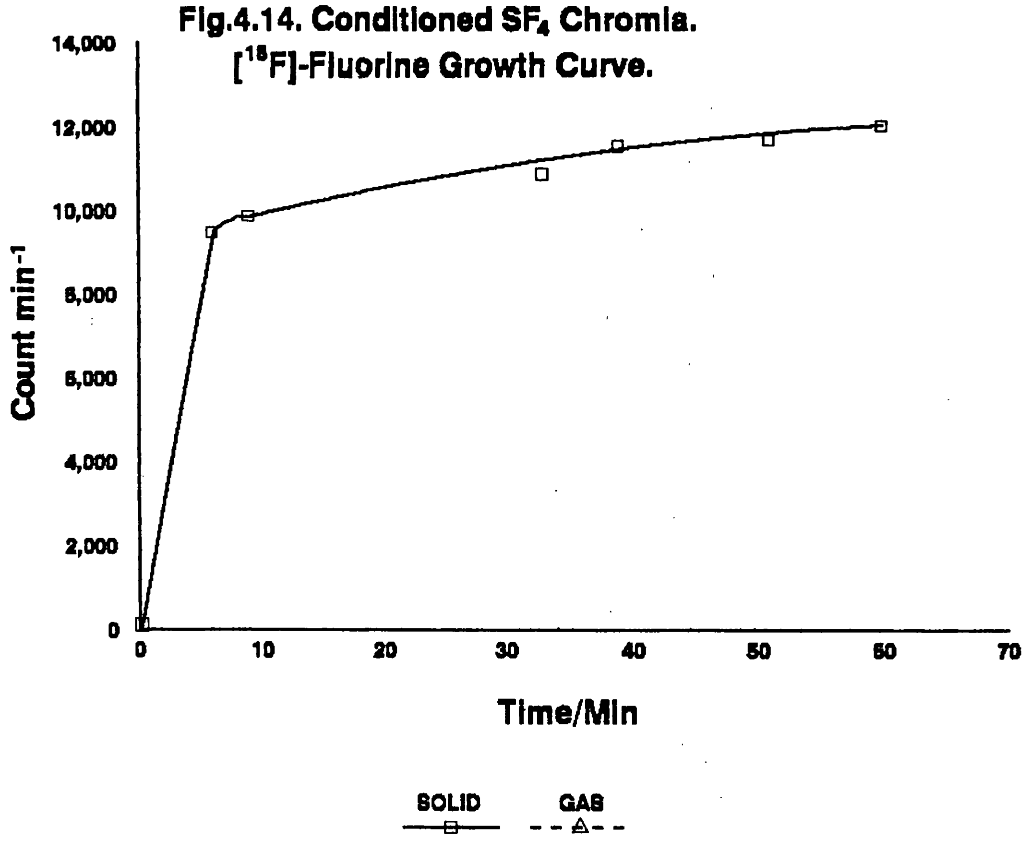


Fig.4.14. Conditioned SF_4 Chromia. $[^{18}F]$-Fluorine Growth Curve.

Fig.4.15. Conditioned SF_4 Volcano Chromia. [^{18}F]-BF_3 Uptake and Exchange.

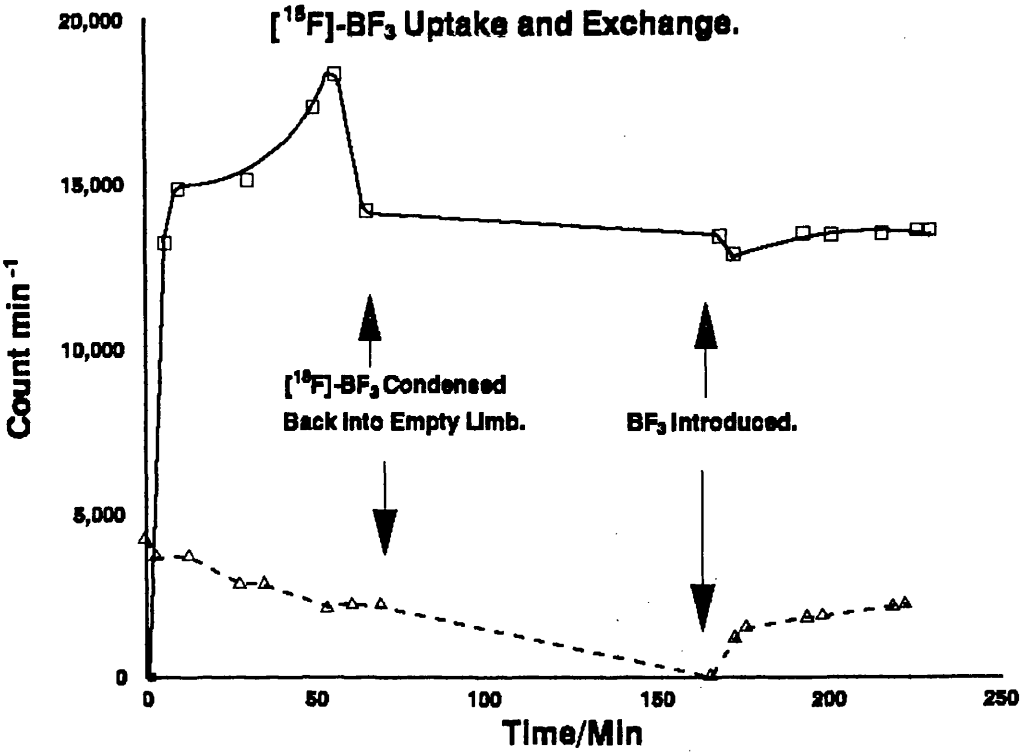
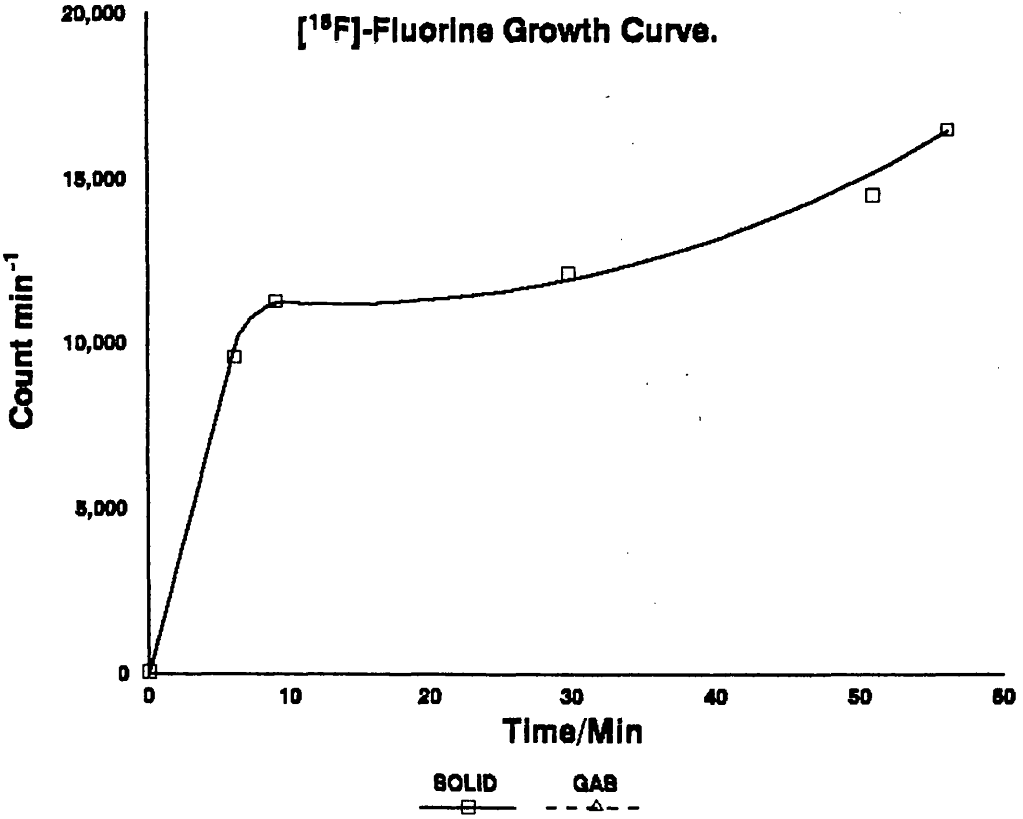


Fig.4.16. Conditioned SF_4 Volcano Chromia. [^{18}F]-Fluorine Growth Curve.



fluorine containing species.

From Table 4.16, [^{18}F]-BF$_3$ (0.35mmol) interacted with conditioned plus fluorinated chromia (0.508g) resulting in a solid count rate of 12703 cmin^{-1}. Thus the fluorine uptake plus exchange was determined to be 1.3 mg atom F. The fluorine uptake was determined to be 0.95 mg atom F. Similarly, [^{18}F]-BF$_3$ (0.35mmol) interacted with conditioned plus fluorinated volcano chromia (0.505g) resulting in a solid count rate of 14561 cmin^{-1}. (Table 4.17.) Thus, fluorine uptake plus exchange was determined to be 1.48 mg atom F and the fluorine uptake was 1.19 mg atom F.

Table 4.16. Fluorine Uptake Of [^{18}F]-BF$_3$ On CH$_3$CCl$_3$, SF$_4$ Chromia.

	[^{18}F]-BF$_3$ Initial (c.min^{-1})	[^{18}F]-BF$_3$ Final (c.min^{-1})	[^{18}F]-BF$_3$ Removed (c.min^{-1})	BF$_3$ Initial (c.min^{-1})	BF$_3$ Final (c.min^{-1})
Gas Phase	4751±69	4021±63	4318±46	1012±32	1653±41
Solid Phase	9470± 119	13098± 126	12703± 113	11802± 109	11888± 107

Table 4.17.Fluorine Uptake Of [^{18}F]-BF$_3$ On CH$_3$CCl$_3$ SF$_4$ Volcano Chromia.

	[^{18}F]-BF$_3$ Initial (c.min^{-1})	[^{18}F]-BF$_3$ Final (c.min^{-1})	[^{18}F]-BF$_3$ Removed (c.min^{-1})	BF$_3$ Initial (c.min^{-1})	BF$_3$ Final (c.min^{-1})
Gas Phase	4176±64	2262±47	2935±54	1485±39	2229±47
Solid Phase	9616± 114	16363± 134	14561± 121	12069± 116	11424± 117

Introduction of unlabelled BF_3 (0.345 mmol) to the [^{18}F]-fluorine treated solids resulted in an increase in the gas count rates and a decrease in the solid count rate (Figs 4.13 and 4.15), indicating [^{18}F]-fluorine exchange between the solid and the gas phase. The exchange factor determined between unlabelled BF_3 and the [^{18}F]-fluorine treated conditioned plus fluorinated chromia was 0.06 and for conditioned plus fluorinated volcano chromia was 0.37.

4.4 DISCUSSION.

The results of the experimental work in this section, using [^{18}F]-fluorine labelled sulphur tetrafluoride and boron trifluoride have yielded a great deal of information regarding the behaviour of fluorine containing species in both uptake and exchange reactions, providing details of the proportion of labile fluorine available and the effect of the conditioning process on the lability of the surface fluorine. It has also allowed comparisons to be made among the γ-alumina, chromia and volcano chromia systems.

4.4.1.[^{18}F]-SF_4 And [^{18}F]-BF_3 Fluorine Exchange Reactions.

In this work the initial aim was to use [^{18}F]-SF_4 throughout. However, due to technical problems with the reactor, the activity of the [^{18}F]-fluorine labelled CsF produced was lower than desired. Clearly the subsequent activity of the [^{18}F]-SF_4 is dependent on the initial activity of the [^{18}F]-CsF, which must be high as the preparation of [^{18}F]-SF_4 from [^{18}F]-CsF is a long, time consuming process. Initial work comparing the exchange reactions between [^{18}F]-SF_4 and

[^{18}F]-BF_3 with SF_4 fluorinated γ-alumina indicated that these reagents acted similarly and therefore BF_3 would be a suitable alternative reagent to examine the lability of surface fluorine species. BF_3 is an intermediate in the preparation of SF_4 from CsF (Section 2.2.2) and is therefore prepared more quickly and will subsequently have a higher specific activity than SF_4. The similarity in the behaviour of [^{18}F]-sulphur tetrafluoride and [^{18}F]-boron trifluoride was a little unexpected. Previous work has shown that [^{18}F]-SF_4 undergoes complete exchange at room temperature with $(NbF_5)_4$ and $(TaF_5)_4$, strong Lewis acids, undergoes substantial [^{18}F]-fluorine exchange with solid AlF_3 and CrF_3 (153) and undergoes no exchange with CsF, a Lewis base (154). This behaviour was explained as being consistent with the behaviour expected of SF_4 functioning as a Lewis base at surfaces containing strong Lewis acid sites associated with Al(III) species. On this basis the [^{18}F]-fluorine exchange behaviour of BF_3 is unexpected since it is a strong Lewis acid. Thus, it is suggested that the reaction of BF_3 involves fluorine exchange reactions, where BF_3 acts as the Lewis acid and the fluoride ions on the surface act as the Lewis base. Theoretically, SF_4 could also act in a similar way however, this is not consistent with the evidence presented above; the SF_4 is thought to react as a Lewis base. These results raise questions as to the nature of the surface fluorine species involved in the exchange reactions: are the fluorine species that are labile with respect to [^{18}F]-SF_4 the same as those that are labile with respect to [^{18}F]-BF_3? Is there a Lewis acid/Lewis base mechanism occurring in both case with the differences due to differences in the relative Lewis acid strengths of the reagents? Or are there several fluorine species, some which are labile with only $[^{18}F]$-SF_4, some labile with only $[^{18}F]$-BF_3 and some labile with both?

Room temperature exchange reactions of $[^{18}F]$-SF_4 and $[^{18}F]$-BF_3 appear to be very similar with comparable ranges of exchange factor values (Tables 4.1 and 4.3). Clearly there is a substantial "pool" of fluorine which is labile with respect to both reagents. Work by Winfield et al (160) using $[^{18}F]$-HF on SF_4 γ-alumina also gave similar results with exchange factors in the range 0.79 - 0.85 and for conditioned plus fluorinated γ-alumina exchange factors were in the range 0.42 - 0.88. The fact that there is a range of exchange factors determined indicates that there is no clear cut distinction between labile and inert fluorine in this material. This is very different from the situation for chlorinated γ-alumina, where radiotracer studies (69,70) showed that chlorine associated with Brφnsted acid sites is labile and easily exchangeable, whereas that associated with Lewis sites is inert and do not readily undergo exchange.

Previous work has assumed that the descriptions given for Brφnsted and Lewis surface sites on chlorinated γ-alumina are also applicable to fluorinated γ-alumina. A major difference is that in the case of chlorinated materials, there is no evidence of incorporation of additional halogen into the bulk of the solid, whereas for the fluorinated materials it has been indicated that fluorine must be incorporated into the bulk. Fluorine content, determined by sequential additions of aliquots of SF_4 (143), has been shown to be 15mg atom $F.g^{-1}$, which is much greater than can be accommodated on the surface alone by replacement of surface -OH groups by -F, determined to be 3.5 mg atom F.g^{-1} (160). This, along with the observation that there is little or no hydrogen fluoride evolved from the surface during the fluorination reaction, indicates that fluorine is probably incorporated into the bulk. There is, however, no detectable structural change, in particular no AlF_3 is observed (160). A recent report on the reaction of cerium dioxide with F_2 below 270°C describes fluorine incorporation into the material without change in the structure (154). This may be analogous with observations in this work. Treatment of chromia with anhydrous HF at 700K results in the slow conversion to CrF_3 (25) which is inactive. There is no evidence for this reaction when chromia is treated with SF_4 at room temperature (156).

In the SF_4 fluorination process, SF_4 is converted to OSF_2 and SO_2 by reaction with surface Al-OH groups, which are converted to Al-F groups, and bridging oxygen atoms, which are also replaced to some extent by fluorine. As mentioned above, the HF produced by these reactions is not detected in the gas phase (Section 3.3.1) and appears to be retained by the solid. It has been concluded therefore that SF_4 fluorinated γ-alumina has at least three types of fluorine: Al-F (terminal), Al-F-Al (bridging) and sorbed HF, the exact nature of which is not yet clear. The nature of the bulk fluorine has not been established. The types of fluorine observed to be present on chromia treated with HF (25), as explained in the introduction (Section 4.1), were described as weakly adsorbed HF oligomers, inert fluorine which does not exchange and labile fluorine that readily undergoes exchange reactions. It does not appear that these descriptions correspond to fluorine present on SF_4 γ-alumina, as there is no clear cut distinction between labile and inert fluorine. The SF_4 fluorinated alumina and SF_4 fluorinated chromia appear to have similar fluorine containing species. This is substantiated by the fact that both SF_4 fluorinated chromia and volcano chromia readily undergo fluorine exchange with $[^{18}F]$-BF_3 giving a range of exchange factors similar to those obtained for the same reaction on SF_4 fluorinated γ-alumina. In the case of the chromias, as in that of alumina, there is a wide range of exchange factors obtained, but unlike the case of HF fluorinated chromia, there is no definite separation of labile and inert fluorine. This suggests the possibility that fluorine present both on γ-alumina and the chromias from the SF_4 fluorination process can exchange between being labile and inert. It is possible that there is a complex system, where exchange involves both bulk and surface fluorine species, in operation on the SF_4 fluorinated γ-alumina and chromias, where the diffusion of fluorine into and out of the bulk of the material may account for the irreproducibility of the exchange factors. The range of f values determined for chromia and volcano chromia was slightly smaller than that for γ-alumina. This indicates that there is a smaller pool of labile fluorine on chromia and volcano chromia which may be due at least in part to the smaller surface areas of the chromia samples compared to the γ-alumina.

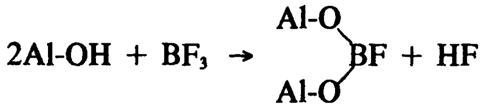
The CH_3CCl_3 conditioning process does not affect the lability of the fluorine on the γ-alumina, chromia or volcano chromia samples and the range of exchange factors obtained for all the samples were similar to those obtained for the fluorinated materials. This indicates that fluorine must also be capable of diffusing through the organic layer or that the organic layer does not completely cover the surface. Previous work (160) has shown that the organic layer on SF_4 fluorinated γ-alumina contains both fluorine and chlorine.The incorporation of fluorine into the organic layer plays an important role in the conditioning and the catalytic reactions, which will be discussed later.

4.4.2.[^{18}F]-BF_3 Fluorine Uptake Experiments.

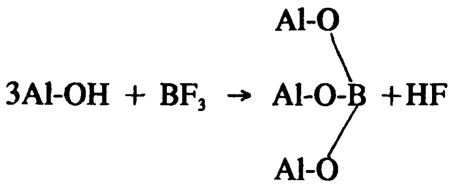
As described previously, fluorine uptake experiments using [^{18}F]-SF_4 gave a fluorine content on calcined γ-alumina of 15mg atom F.g^{-1} (143). It has been assumed that this value would also extended to chromia and was a function of the fluorination process. The exact value for the chromia samples is likely to be lower than this due to the smaller surface areas. In this work fluorine uptake reactions using [^{18}F]-BF_3 on γ-alumina, chromia and volcano chromia have been examined to allow comparisons between γ-alumina and the chromias and also between SF_4 and BF_3. It can be seen from the results of the [^{18}F]-BF_3 uptake experiments on calcined alumina and calcined chromias that fluorine from [^{18}F]-BF_3 is taken up by the solids in a similar way to fluorine from SF_4. The calculated fluorine content for BF_3 fluorinated γ-alumina is less than for SF_4 fluorinated γ-alumina (2.05mg atom F compared to 15mg atom F) and the value for BF_3 fluorinated chromia is less than for BF_3 fluorinated γ-alumina.The differences in the uptake of fluorine on γ-alumina and chromias may be at least partially due to differences in the surface areas.

Unlike SF_4, BF_3 produces no volatile oxides or oxofluorides in the fluorination reaction. There has been a great deal of debate concerning the nature of acid sites created by BF_3 and the manner of fluorination of alumina. Previous studies of the modification of oxide catalysts by boron trifluoride (157) using I.R. spectroscopy show that when BF_3 is deposited, bands corresponding to B-O and B-F vibrations are observed in the spectrum. Kozorezov et al (158) suggested that modification of γ-alumina with BF_3 was associated with the formation of electron pair acceptor surface groups:

$$\text{Al-OH} + BF_3 \rightarrow \text{Al-O-}BF_2 + HF$$

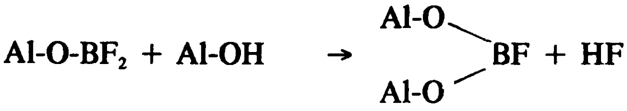


$$2\text{Al-OH} + BF_3 \rightarrow \begin{matrix}\text{Al-O}\\ \text{Al-O}\end{matrix}\!\!>\!BF + HF$$

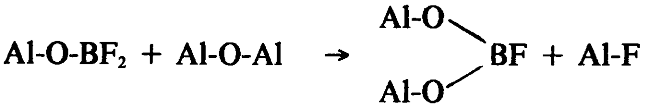


$$3\text{Al-OH} + BF_3 \rightarrow \begin{matrix}\text{Al-O}\\ \text{Al-O}\\ \text{Al-O}\end{matrix}\!\!>\!B + HF$$

Secondary surface reactions which decrease electron acceptor properties may also occur:



$$\text{Al-O-}BF_2 + \text{Al-OH} \rightarrow \begin{matrix}\text{Al-O}\\ \text{Al-O}\end{matrix}\!\!>\!BF + HF$$



$$\text{Al-O-}BF_2 + \text{Al-O-Al} \rightarrow \begin{matrix}\text{Al-O}\\ \text{Al-O}\end{matrix}\!\!>\!BF + \text{Al-F}$$

etc.

So, it appears that boron is incorporated onto the surface of the material and fluorination may occur through the incorporation of the HF produced in the reaction. This reaction therefore appears to be similar to that occurring in the SF_4 fluorination process. It is possible that the fact that less fluorine appears to be incorporated from BF_3 than from SF_4 is due to the BOF_2^- groups being less effective at protecting the surface in the initial stages or that these groups do not desorb from the surface as the SOF_2^- groups do, thus reducing the amount of fluorine taken up by the solid.

However, what is clear from the results of BF_3 uptake reactions on SF_4 fluorinated alumina, chromia and volcano chromia and also on the conditioned plus fluorinated materials, is that as in the case of SF_4, fluorine is taken up by the solid in quite substantial quantities and that the laydown of the organic layer has little effect on the uptake of fluorine by the solid. It has also been shown that a large quantity of the fluorine incorporated into the solid from BF_3 is labile and readily undergoes exchange reactions and again the organic layer does not affect the lability.

4.4.3. [^{18}F]-BF_3 Fluorine Exchange With BF_3 Fluorinated Materials.

Preliminary experiments with BF_3 fluorinated γ-alumina and volcano chromia indicate that there is also a substantial quantity of labile fluorine present on these materials. This confirms the results from [^{18}F]-BF_3 uptake reactions on calcined materials that indicated substantial fluorine uptakes occurred when the fluorination process used BF_3 rather than SF_4. Previous studies on BF_3 fluorinated γ-alumina (81,82) suggested that the centres responsible for acid catalysed reactions were a considerable number of

Brφnsted acid sites and a small number of Lewis acid sites. This agrees with the results presented here, in that the necessary Lewis acid sites are present, but not in the abundance or with the strength as when the material is fluorinated with SF_4.

So, from the work in this section, it has been determined that there is a substantial pool of fluorine on SF_4 fluorinated γ-alumina that is labile with respect to $[^{18}F]$-SF_4 and BF_3 and that the lability of this material is not affected by the laydown of an organic layer by treatment with CH_3CCl_3. This description can also be extended to SF_4 fluorinated chromia and volcano chromia and the conditioned plus fluorinated chromias. This suggests that the catalyst pretreatment steps, i.e. fluorination and conditioning, occur similarly on γ-alumina, chromia and volcano chromia and therefore that the strong Lewis sites formed on γ-alumina by the fluorination process are also produced on chromias. It has also been shown that BF_3 can be used to fluorinate materials in a similar manner to SF_4, although it does not appear to be as effective.

INTERACTION OF [^{36}Cl]-CHLORINE LABELLED HYDROGEN CHLORIDE AND 1,1,1-TRICHLOROETHANE WITH γ-ALUMINA, CHROMIA AND VOLCANO CHROMIA.

5.1 INTRODUCTION.

Halogenation of oxide surfaces enhances Brφnsted and Lewis acidity. Dehydrochlorination of 1,1,1,-trichloroethane at room temperature is a specific probe reaction for strong Lewis acids. The behaviour of CCl_4 or $COCl_2$ chlorinated γ-alumina towards 1,1,1-trichloroethane at room temperature is analogous to that observed using the strong solid Lewis acid, anhydrous aluminium (III) chloride (91), with dehydrochlorination occurring more slowly at room temperature on the chlorinated γ-alumina than the rapid reaction on aluminium (III) chloride. In both cases, however, the $CH_2=CCl_2$ produced in the dehydrochlorination reaction undergoes further reaction at the solid surface to give a purple organic layer (Fig 5.1). Fluorination of γ-alumina with SF_4 also results in the production of Lewis acid sites that are sufficiently strong to dehydrochlorinate CH_3CCl_3. However, the formation of the purple organic layer is accompanied by the formation of chlorofluorohydrocarbons: CH_3CCl_2F, CH_3CClF_2 and CH_3CF_3, by halogen exchange reactions with the fluorinated surface (Fig 5.2). The same behaviour is observed from SF_4 fluorinated γ-alumina conditioned with $CH_2=CCl_2$, with the formation of chlorofluorohydrocarbons and also CH_3CCl_3, demonstrating that as well as dehydrochlorination, hydrochlorination also occurs on the surface.

Fig.5.1. Dehydrochlorination Of CH_3CCl_3 Over CCl_4 Chlorinated γ-Alumina.

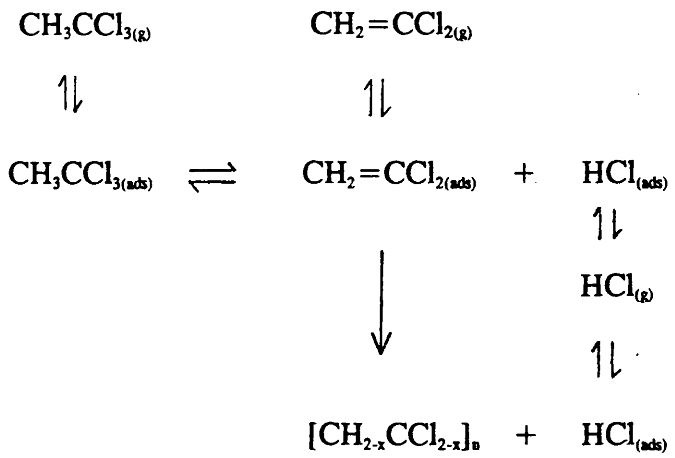
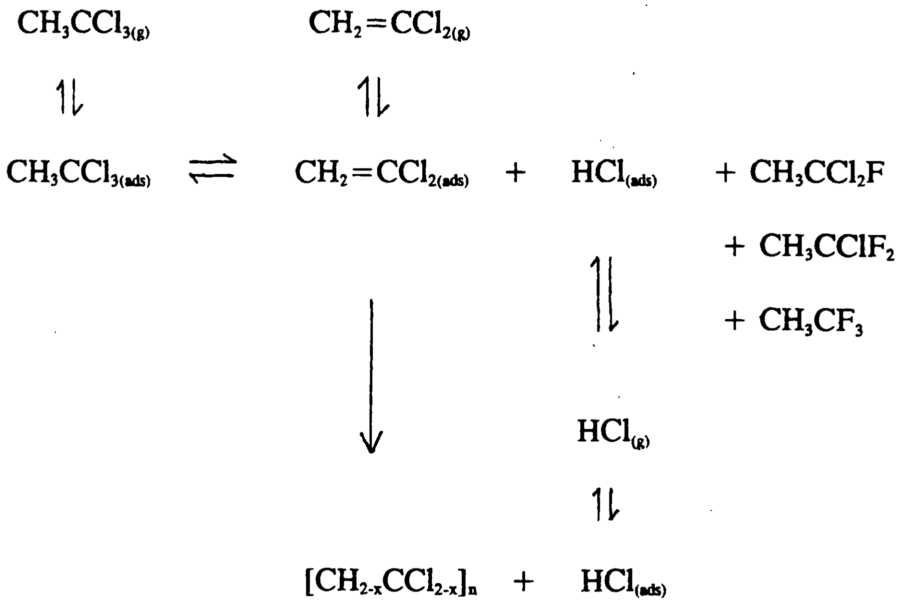


Fig.5.2. Dehydrochlorination Of CH_3CCl_3 Over SF_4 Fluorinated γ-Alumina.



The organic layer appears to co-exist with the halogenated metal oxide, and its deposition modifies the catalytic activity of the solid, but does not appear to cause deactivation. The exact nature of the organic layer is still under debate and will be discussed more fully later (Section 6.3), however, it is though to involve the formation of partially dehydrochlorinated -CH_2-CCl_2- oligomers (160). There is spectroscopic evidence of CH_3 and -CH_2- groups and also -CH_2X, -$CH=CX$- and CH_3X groups ($X=$ F or Cl). There is some evidence for "dissolution" of CH_3CCl_3 and $CH_2=CCl_2$ in the organic layer, suggesting a "quasi-liquid" structure.

Previous studies of the interaction of [^{36}Cl]-chlorine labelled HCl and CH_3CCl_3 on SF_4 fluorinated γ-alumina provided information on the surface chlorine containing species, the reactivity of these species and the organic layer laydown. Exchange reactions between [^{36}Cl]-HCl and CH_3CCl_3 conditioned, SF_4 fluorinated γ-alumina indicated that a very large proportion of the chlorine adsorbed onto the surface of the catalyst was labile (69). Using [^{36}Cl]-chlorine labelled CH_3CCl_3 in the conditioning reaction showed that after an initial rapid reaction,the [^{36}Cl]-chlorine containing material continued to be deposited on the solid gradually over time, all of which was retained by the solid after degassing (160). Flowing [^{36}Cl]-CH_3CCl_3 over conditioned plus fluorinated γ-alumina indicated a turnover of organic material occurring, with inactive CH_3CCl_3 present in the organic layer from the conditioning process being displaced by the incoming CH_3CCl_3.

It is known that treatment of chromia with HF and CH_3CCl_3 at >600K results in formation of a mixture of chlorofluorohydrocarbons (24,25). There have been no reports of a catalytically active organic layer like the one produced on SF_4 fluorinated γ-alumina at room temperature, although it has been shown that there are both chlorine and fluorine containing species present on the chromia after such reactions (25,26).

The objective of this section of work was to make direct comparisons among γ-alumina, chromia and volcano chromia, all fluorinated with SF_4, then conditioned with CH_3CCl_3. [^{36}Cl]-Chlorine labelled HCl has been used to examine the uptake of chlorine containing species on the materials and to examine the differences, if any, made by the fluorination process and the fluorination plus conditioning process. [^{36}Cl]-Chlorine labelled CH_3CCl_3 was used to make a detailed examination of the conditioning process under static conditions on the fluorinated materials and to obtain information relating to the displacement reactions occurring between [^{36}Cl]-CH_3CCl_3 and the organic material on the surface of the conditioned plus fluorinated solids. Comparisons of the reactions of γ-alumina, chromia and volcano chromia will determine if there is laydown of chlorine containing species on the fluorinated materials. If the behaviour of the chromias and γ-alumina are similar, this implies the presence of organic material, since it is known that the CH_3CCl_3 treatment of SF_4 fluorinated γ-alumina results in the formation of a chlorine containing organic layer. The lability of the chlorine containing species deposited on the materials was also examined by treating the [^{36}Cl]-CH_3CCl_3 conditioned material with unlabelled HCl.

5.2. EXPERIMENTAL.

5.2.1. INTERACTION AT ROOM TEMPERATURE OF [^{36}Cl]-CHLORINE LABELLED ANHYDROUS HYDROGEN CHLORIDE WITH CALCINED γ-ALUMINA.

This work made use of the direct monitoring Geiger Müller counting technique described previously (Section 2.8).

A sample (0.520g) of calcined γ-alumina was loaded into a dry, flamed-out dropping vessel in the dry box, degassed and attached to the counting vessel. The solid was dropped from the ampoule into the boat and positioned under G.M.tube 2. Increasing pressures of [^{36}Cl]-HCl were expanded into the manifold and the counting cell. The counting cell was isolated and the count rate determined from both G.M. tubes. The counts from gas alone were recorded by G.M.1. and G.M.2. recorded counts from gas plus solid. This sequence was continued until further additions of [^{36}Cl]-HCl did not appear to have any marked effect on the surface count rate. In each case the surface [^{36}Cl]-count rate (the difference between the count rates from the gas plus solid and the gas only) was plotted against the gas count rate. The latter is a measure of the gas pressure above the solid. Throughout these experiments the specific count rate of the H^{36}Cl was identical, 1000 count.min^{-1} $\equiv$ *ca.*20 - 25 Torr. In order to examine the lability of the chlorine containing species retained on the surface after removal of all volatile material, increasing pressures of unlabelled anhydrous HCl were then introduced and counts determined from both G.M. tubes.

This procedure was also used for fluorinated, fluorinated plus conditioned γ-alumina and CH_3CCl_3 treated, unfluorinated γ-alumina. Examination of the room temperature interactions of [^{36}Cl]-HCl with calcined, fluorinated and fluorinated plus conditioned chromia samples was carried out using an identical method.

5.2.2. INTERACTION AT ROOM TEMPERATURE OF [^{36}Cl]-CHLORINE LABELLED 1,1,1-TRICHLOROETHANE WITH SF_4 FLUORINATED γ-ALUMINA.

A sample (0.531g) of SF_4 fluorinated γ-alumina was loaded into a dry flamed-out dropping vessel. It was degassed and attached to the counting cell. A known quantity (1.00mmol) of [^{36}Cl]-chlorine labelled 1,1,1-trichloroethane was expanded into the manifold and the counting cell. Throughout these experiments the specific count rate of the [^{36}Cl]-CH_3CCl_3 was identical with 1000 count.min^{-1} ≡ *ca.* 10 - 15 Torr. The counting cell was then isolated from the rest of the line and the count rates determined from both G.M. tubes. The solid was dropped from the ampoule into the glass boat which was then positioned under G.M.2. The count rates from both G.M. tubes were determined over time with G.M.1. recording counts from gas only and G.M.2 recording counts from gas plus solid.

The reaction was allowed to continue for 120mins, after which the vapour was condensed out of the counting cell and the counts from the solid determined. A sample of unlabelled HCl (1.00mmol) was then introduced and the reaction followed by determining the count rates from both G.M. tubes. This reaction was studied also using 3mmol of both [^{36}Cl]-CH_3CCl_3 and HCl. The method described was also used for CH_3CCl_3 conditioned, SF_4 fluorinated γ-alumina. The procedure to investigate the room temperature interactions of [^{36}Cl]-chlorine labelled CH_3CCl_3 with fluorinated and conditioned plus fluorinated chromia was identical.

In all cases a minimum of 10,000 counts were accumulated which results in a radiochemical error of $<1\%$. The isotope [^{36}Cl]-chlorine is a ß-emitter. A proportion of the emissions interact with surrounding matter and are absorbed. This effect is termed self absorption. Generally a correction is made unless the same weight of material is used throughout. This correction is achieved by measuring apparent β^- activity from different thicknesses of samples of identical specific activity. The absorption correction necessary to relate observations at one weight to observations at any other weight is the quotient of the values at the two weights.

5.3 RESULTS.

5.3.1. INTERACTION AT ROOM TEMPERATURE OF [^{36}Cl]-CHLORINE LABELLED HYDROGEN CHLORIDE WITH CALCINED, SF_4 FLUORINATED AND CH_3CCl_3 CONDITIONED, SF_4 FLUORINATED γ-ALUMINA AND CHROMIA SAMPLES.

The results from the examination of a series of samples of γ-alumina and chromia with respect to the room temperature interaction of [^{36}Cl]-chlorine labelled hydrogen chloride indicated the occurrence of similar reactions and substantial uptake of chlorine containing species on the surfaces in all of the reactions.

On introduction of the [^{36}Cl]-chlorine labelled HCl to the calcined material, the surface count recorded increased very rapidly initially, after which introduction of increasing pressures of [^{36}Cl]-HCl had little effect on the surface counts (Table.5.1.).

The final surface count rate was higher for calcined γ-alumina than for calcined chromia (3000 count.min^{-1} compared with 1740 count.min^{-1}), indicating that less [^{36}Cl]-chlorine labelled material was adsorbed onto the chromia. On removal of the gas, the solid counts decreased, indicating the presence of some weakly bonded [^{36}Cl]-chlorine containing species, with more apparently present on the γ-alumina (Fig 5.3 and 5.4).

Fig.5.3. H^{35}Cl On Calcined Alumina.

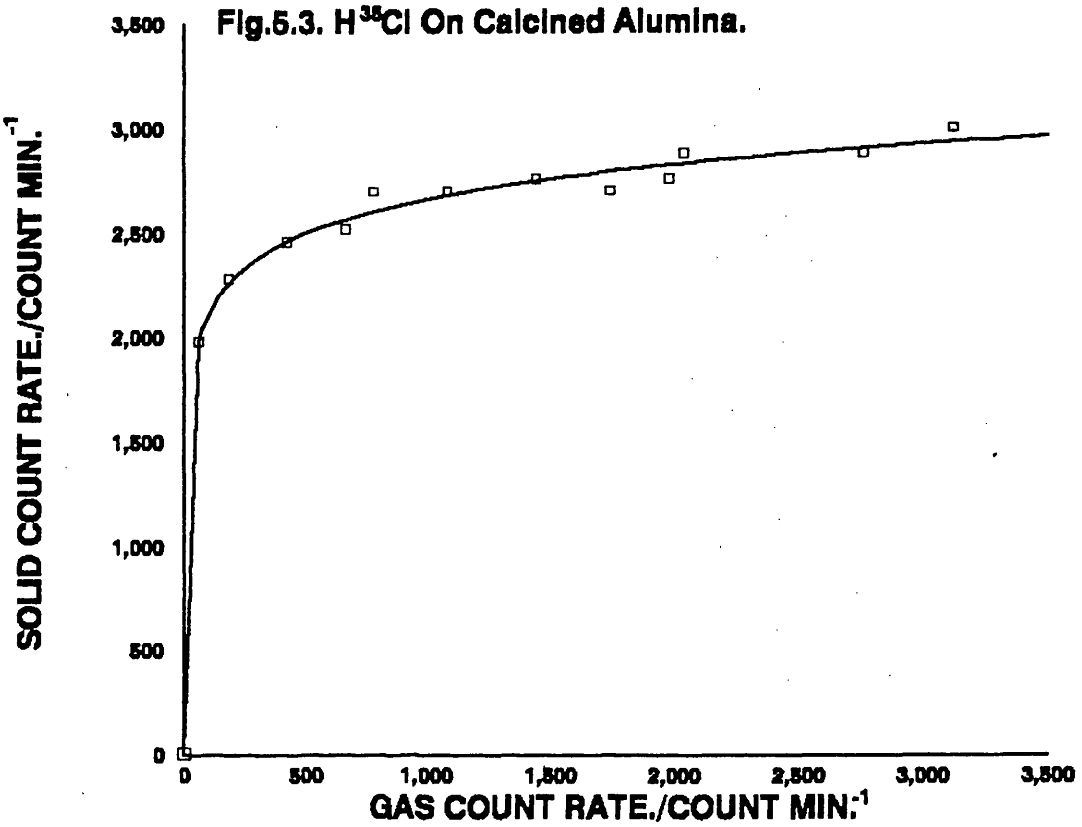


Fig.5.4. H^{35}Cl On Calcined Chromia.

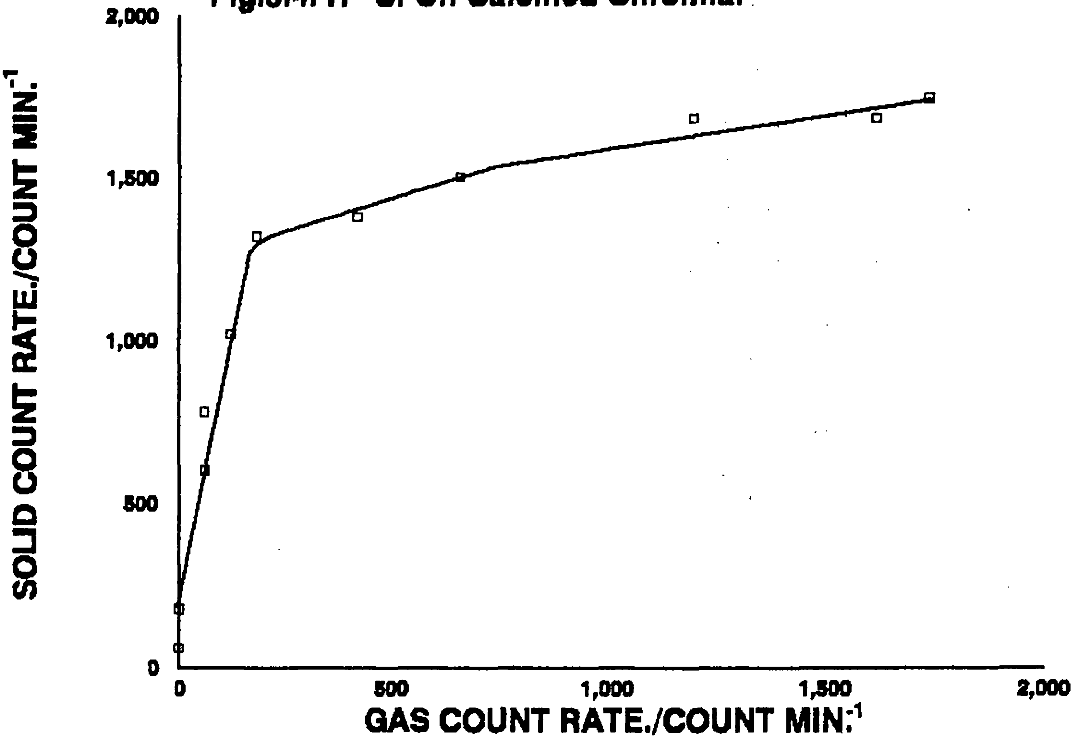


Table.5.1. Interaction of $H^{36}Cl$ with Calcined γ-Alumina and Chromia, Followed by Interaction With Unlabelled HCl.

	Saturation Count Rate. (count.min^{-1})	Retained By Solid After Vapour Removed. (count.min^{-1})	Retained By Solid After HCl Treatment. (count.min^{-1})
γ-Alumina	3000±29	2340±25	480±5
Chromia	1740±15	1620±14	1140±10

Despite this, the surface count rate of γ-alumina was still much greater than that of the chromia (2,340 count.min^{-1} compared with 1,620 count.min^{-1}). In order to examine the lability of the [^{36}Cl]-chlorine containing species on the solids, aliquots of unlabelled HCl were introduced to the solid and the gas and solid phases monitored. There was a substantial decrease in the count rate of the γ-alumina. In the case of the chromia, there was also a decrease in the surface count rate, although it was not as substantial as for the γ-alumina. (480 count.min^{-1} compared with 1860 count.min^{-1}), which indicates that there was a much greater quantity of labile chlorine on γ-alumina than on chromia.

A similar pattern of interactions was observed with [^{36}Cl]-chlorine labelled hydrogen chloride with both fluorinated and fluorinated plus conditioned γ-alumina and chromia (Fig.5.5 -5.8). The increase in the surface counts on γ-alumina was much more rapid than on chromia, for both the fluorinated and the fluorinated plus conditioned samples, although the final surface count rates were virtually identical (Table.5.2). The final surface count rates determined for all the fluorinated and the conditioned plus fluorinated samples were similar, *ca.*300count.min^{-1}, although they were substantially lower than those

Fig.5.5. $H^{36}Cl$ On SF_4 Fluorinated Alumina.

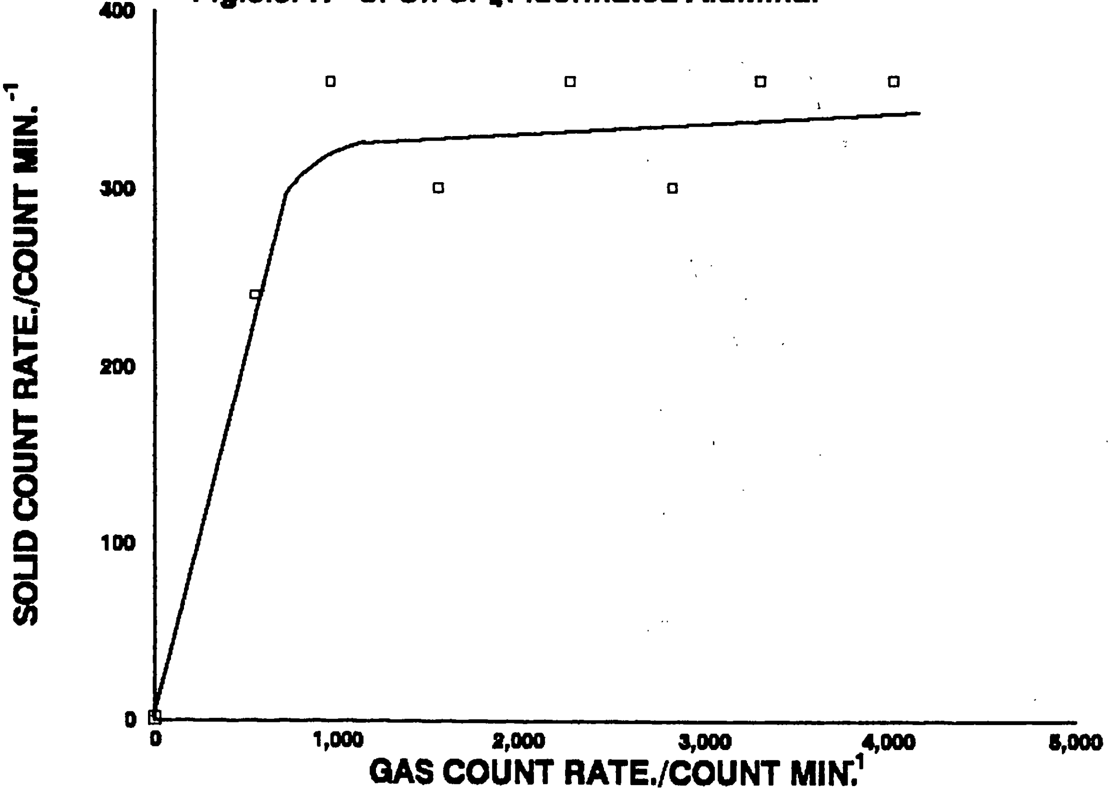


Fig.5.6. $H^{36}Cl$ On SF_4 Fluorinated Chromia.

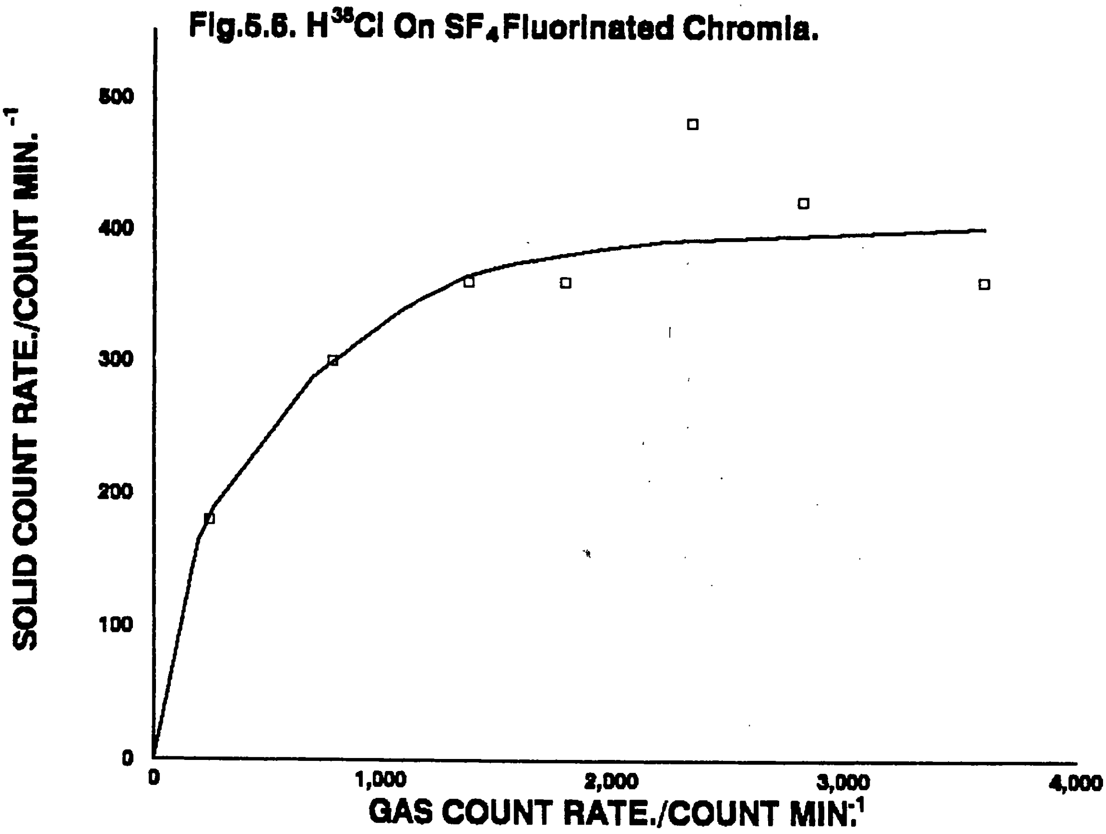


Fig.5.7. $H^{36}Cl$ On CH_3CCl_3 Treated SF_4 Fluorinated Alumina.

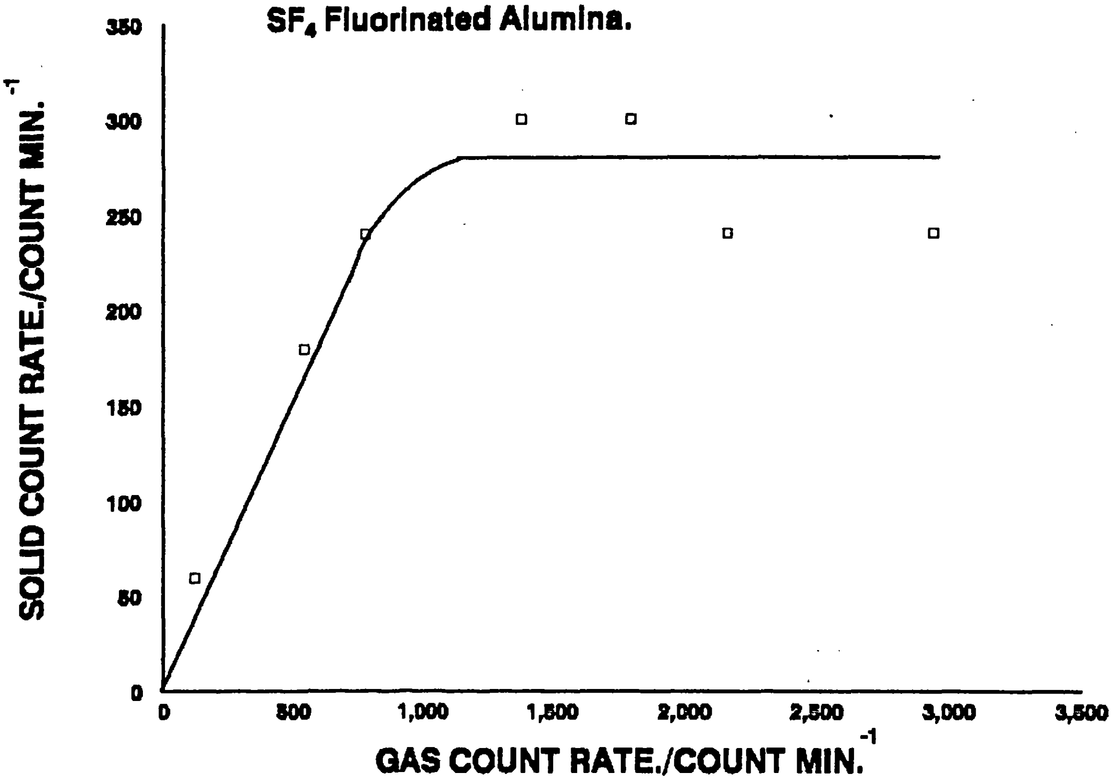
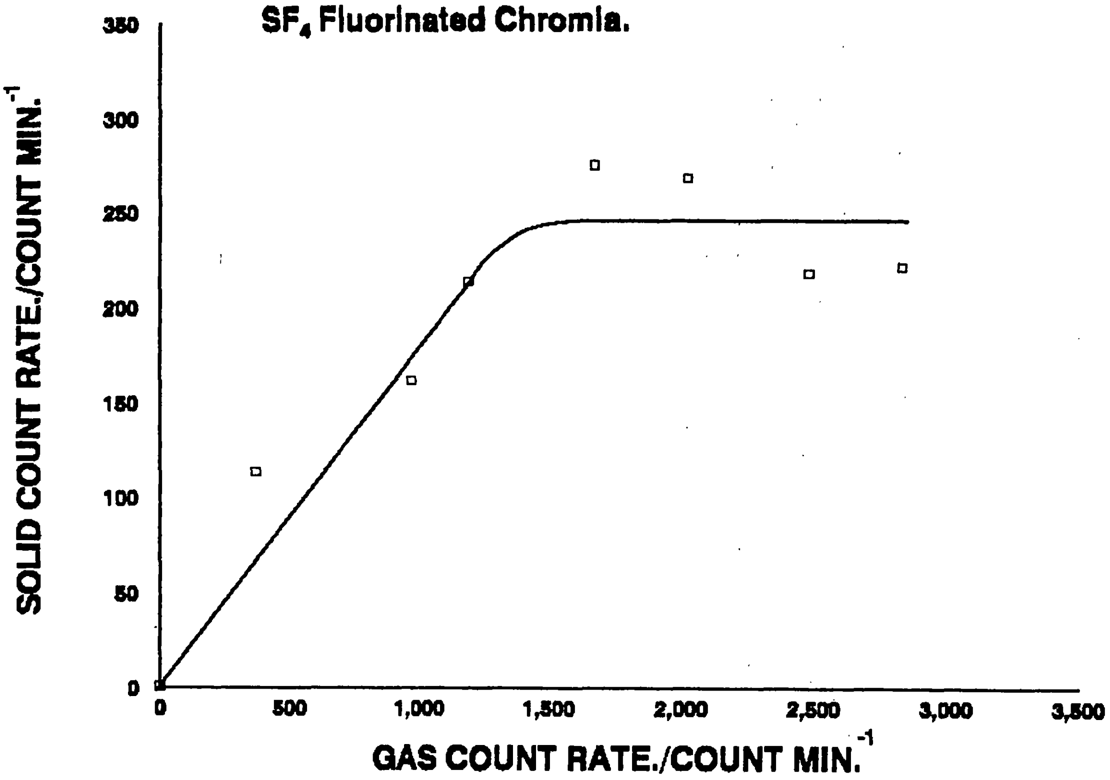


Fig.5.8. $H^{36}Cl$ On CH_3CCl_3 Treated SF_4 Fluorinated Chromia.



on the calcined materials. For calcined γ-alumina the final surface count rate was 3000 count.min^{-1} and for calcined chromia it was 1620 count.min^{-1}. The reduction due to the fluorination is expected due to the enhanced acidity of the surfaces and the reduction in the surface area (Section 3.3.12). The fact that the conditioning process had very little effect on the surface count rate is unexpected and indicates that the laydown of the organic layer has a negligible effect on the adsorption of [^{36}Cl]-HCl.

Removal of the [^{36}Cl]-HCl from the gas phase did not have a great effect on the surface count rate, although there was a very small increase in the surface count rates of the fluorinated and the fluorinated plus conditioned γ-alumina samples. This may be due to self absorption of [^{36}Cl]-chlorine containing species. The fact that this was observed only on the fluorinated and fluorinated plus conditioned γ-alumina samples and not on the chromia samples suggests that there may be less substantial laydown of [^{36}Cl]-chlorine containing species present on these materials. From the reaction with unlabelled HCl, it appears that there is a quantity of labile chlorine on all the surfaces, with γ-alumina samples having a greater quantity than chromia samples.

Table 5.2. Interaction Of $H^{36}Cl$ With Fluorinated And Conditioned Plus Fluorinated γ-Alumina And Chromia, Followed By Interaction With Unlabelled HCl.

	Saturation Count Rate. (count.min^{-1})	Retained By Solid After Vapour Removed. (count.min^{-1})	Retained By Solid After HCl Treatment. (count.min^{-1})
SF_4 γ-Alumina	330±3	360±4	60±1
SF_4 Chromia	270±3	180±2	120±2
CH_3CCl_3, SF_4 γ-Alumina	270±3	420±4	120±2
CH_3CCl_3, SF_4 Chromia	270±3	240±3	60±1

A less detailed study of the interaction of [^{36}Cl]-HCl with CH_3CCl_3 treated, unfluorinated γ-alumina and chromia also indicated a similar pattern of reaction. The final surface count rate was greater for the CH_3CCl_3 γ-alumina than for the chromia (Table 5.3).

Table.5.3. Interaction Of $H^{36}Cl$ With CH_3CCl_3 Treated γ-Alumina And Chromia, Followed By Interaction With Unlabelled HCl.

	Saturation Count Rate.(c.min^{-1})	Retained By Solid After Vapour Removed.(c.min^{-1})
CH_3CCl_3 γ-Alumina	1680±17	1200±11
CH_3CCl_3 Chromia	960±10	840±7

Comparisons between the results shown in Figs 5.9 and 5.10 and among the other results in this section demonstrate that the uptake of [^{36}Cl]-chlorine

Fig.5.9. $H^{36}Cl$ On CH_3CCl_3 Treated Alumina.

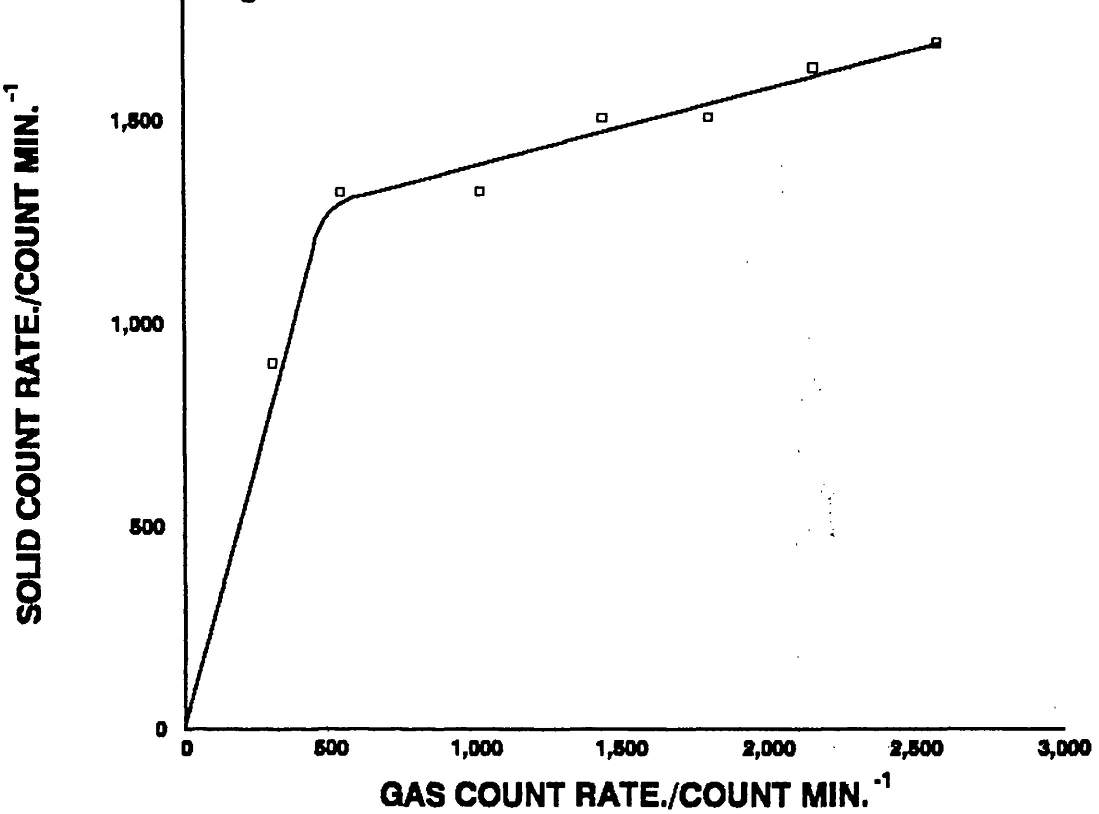
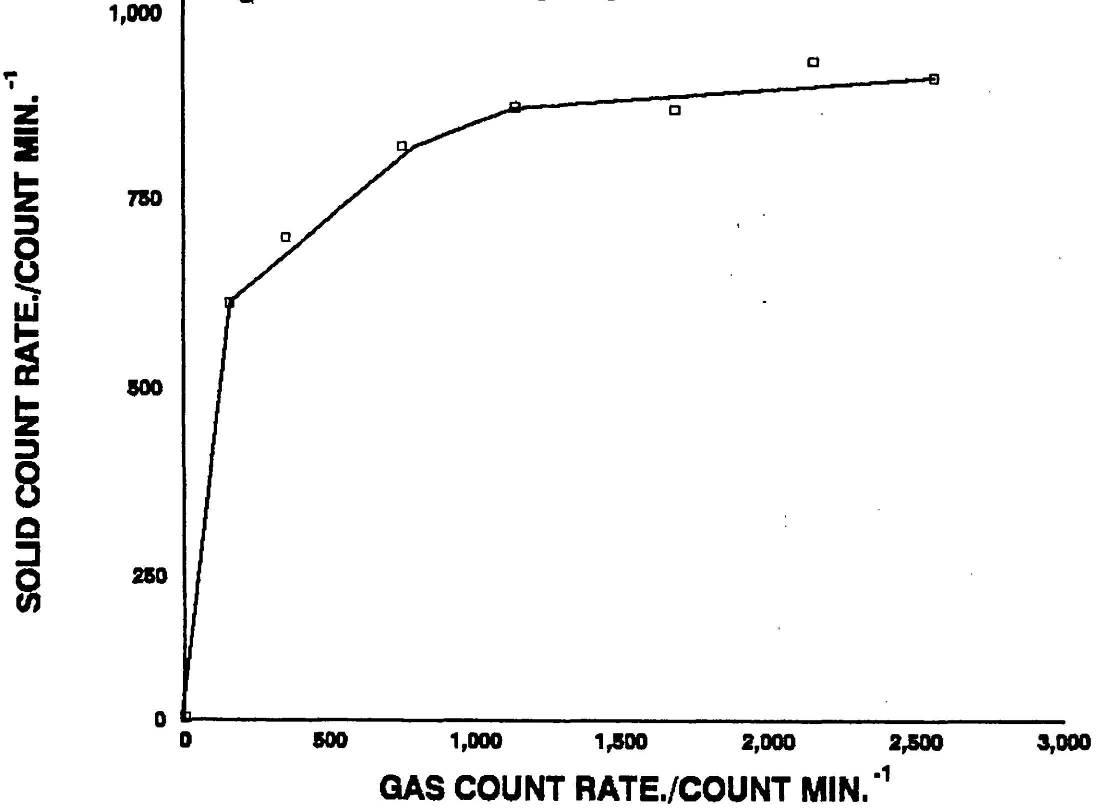


Fig.5.10. $H^{36}Cl$ On CH_3CCl_3 Treated Chromia.



containing species is reduced by the pretreatment of calcined materials with CH_3CCl_3, by 1320 count.min^{-1} for γ-alumina and 780 count.min^{-1} for chromia. However, the reduction is not as substantial as that observed by pretreatment of calcined materials with SF_4, where the count rate for γ-alumina was reduced by 2640 count.min^{-1} and for chromia by 1440 count.min^{-1}. The reduction in the [^{36}Cl]-chlorine uptake by the surfaces due to treatment with CH_3CCl_3 is probably due to reduction in the surface area and also blocking of reactive sites on the surfaces by a simple interaction between the surface and the CH_3CCl_3.

5.3.2. INTERACTION AT ROOM TEMPERATURE OF [^{36}Cl]-CHLORINE LABELLED CH_3CCl_3 WITH SF_4 FLUORINATED AND CH_3CCl_3 CONDITIONED, SF_4 FLUORINATED γ-ALUMINA, CHROMIA AND VOLCANO CHROMIA SAMPLES.

Two sets of studies of the room temperature interaction of [^{36}Cl]-chlorine labelled 1,1,1-trichloroethane with SF_4 fluorinated and CH_3CCl_3 conditioned, SF_4 fluorinated γ-alumina chromia and volcano chromia were performed. One used 1mmol [^{36}Cl]-CH_3CCl_3 and the other used 3mmol [^{36}Cl]-CH_3CCl_3. The results were similar and indicated that there was an immediate interaction with incorporation of [^{36}Cl]-chlorine containing species onto the surface of the materials.

Introduction of [^{36}Cl]-CH_3CCl_3 resulted in an immediate decrease in the gas phase count rate with a corresponding increase in the solid count rate.

Table.5.4. Interaction Of 1mmol [^{36}Cl]-CH_3CCl_3 With Fluorinated Surfaces, Followed By Interaction with Unlabelled HCl.

	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) Start.	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) End.	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) Removed.	Unlabelled HCl (Count Min^{-1}) Start.	Unlabelled HCl (Count Min^{-1}) End.	Unlabelled HCl (Count Min^{-1}) Removed.
Elapsed Time.	0	120	130	140	300	310
SF_4 Alumina. GAS	2,250 $\pm$ 24	1,079 $\pm$ 12	0	180 $\pm$ 3	360 $\pm$ 4	0
SF_4 Alumina. SURFACE	800 $\pm$ 10	600 $\pm$ 8	420 $\pm$ 4	780 $\pm$ 9	804 $\pm$ 9	360 $\pm$ 4
SF_4 Chromia. GAS	2,560 $\pm$ 26	1,290 $\pm$ 14	0	300 $\pm$ 3	360 $\pm$ 4	0
SF_4 Chromia. SURFACE	900 $\pm$ 11	660 $\pm$ 8	660 $\pm$ 8	1,080 $\pm$ 12	1,200 $\pm$ 13	660 $\pm$ 9
SF_4 V.C. GAS	2,560 $\pm$ 26	986 $\pm$ 11	0	300 $\pm$ 3	480 $\pm$ 6	0
SF_4 V.C. SURFACE	1,320 $\pm$ 14	1,140 $\pm$ 13	720 $\pm$ 9	1,200 $\pm$ 13	1,260 $\pm$ 13	660 $\pm$ 9

Note: V.C.= "Volcano Chromia."

Table.5.5. Interaction Of 1mmol [^{36}Cl]-CH_3CCl_3 With Conditioned Surfaces, Followed By Interaction with Unlabelled HCl.

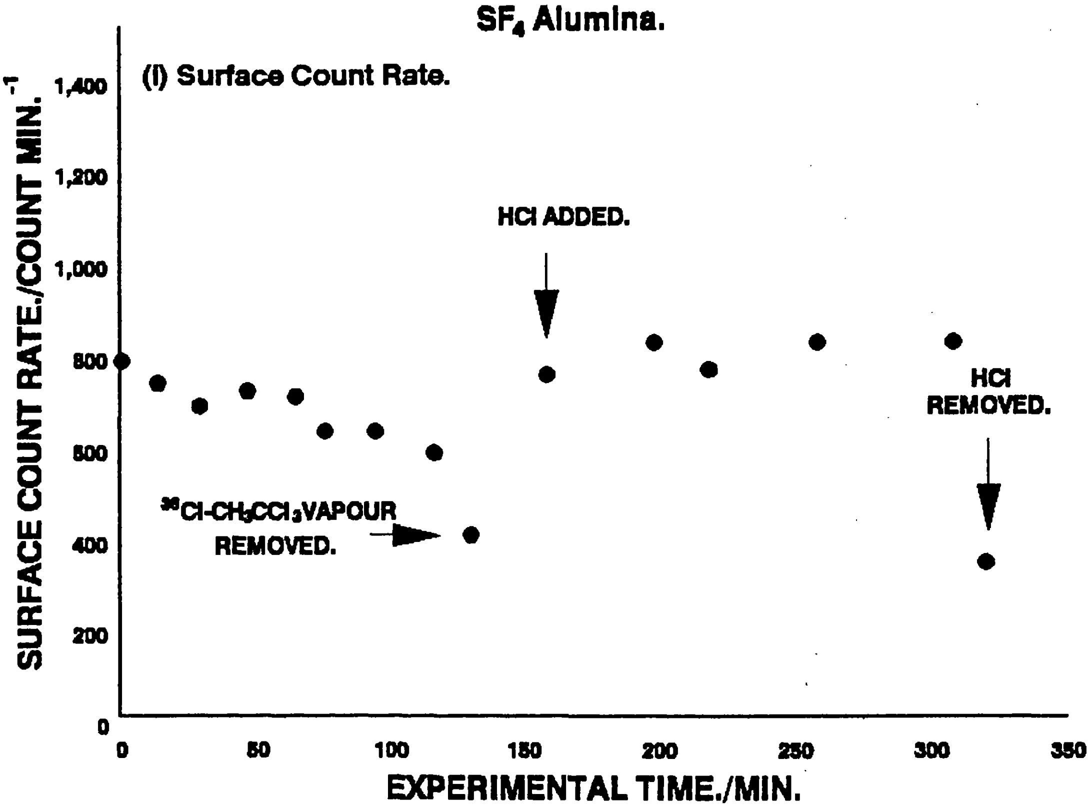
	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) Start.	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) End.	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) Removed.	Unlabelled HCl (Count Min^{-1}) Start.	Unlabelled HCl (Count Min^{-1}) End.	Unlabelled HCl (Count Min^{-1}) Removed.
Elapsed Time.	0	120	130	140	300	310
SF_4 Alumina. GAS	2,500 ± 25	1,002 ± 12	0	150 ± 2	200 ± 4	0
SF_4 Alumina. SURFACE	750 ± 9	1,250 ± 14	200 ± 3	300 ± 4	400 ± 5	200 ± 3
SF_4 Chromia. GAS	2,480 ± 25	1,308 ± 14	0	140 ± 2	260 ± 4	0
SF_4 Chromia. SURFACE	680 ± 8	1,050 ± 12	180 ± 3	240 ± 4	360 ± 4	220 ± 3
SF_4 V.C. GAS	2,530 ± 25	990 ± 11	0	300 ± 4	480 ± 6	0
SF_4 V.C. SURFACE	750 ± 9	1,300 ± 14	200 ± 3	350 ± 4	400 ± 5	200 ± 3

Note: V.C. = "Volcano Chromia."

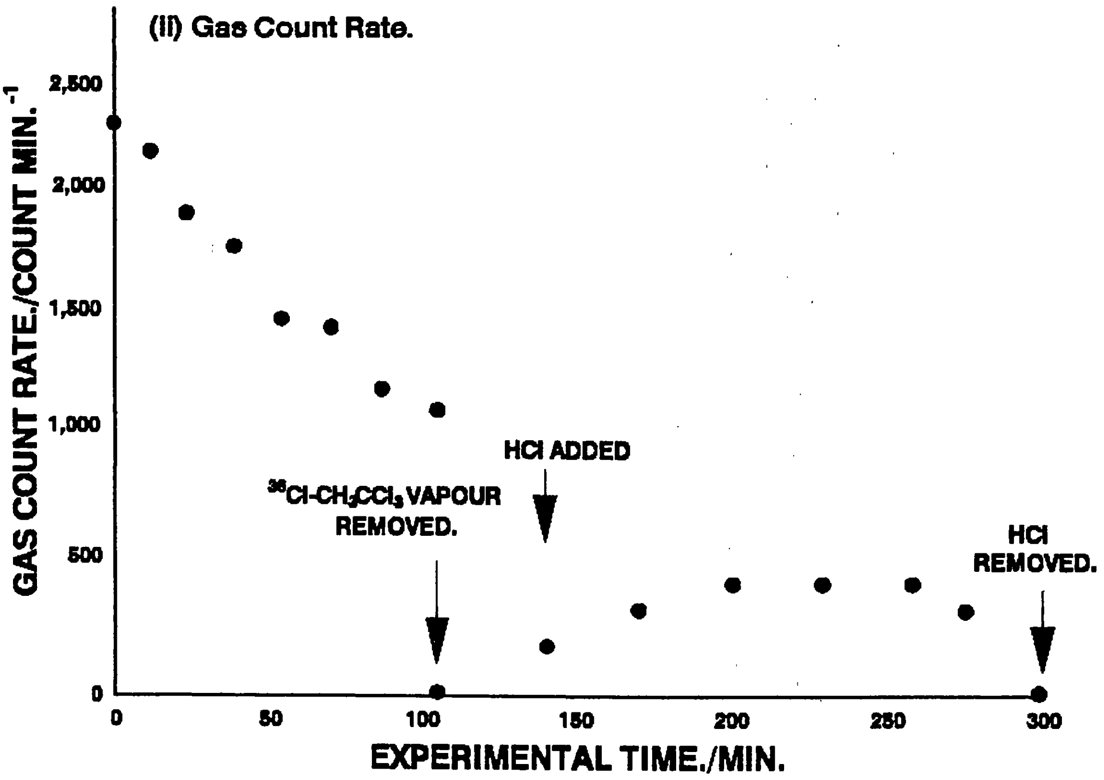
The chromia and the γ-alumina samples behaved similarly and the prior conditioning with inactive CH_3CCl_3 did not greatly effect the [^{36}Cl]-chlorine count rate on the surface. After the initial increase in the surface count rates there was a slow decrease in the surface count rate for most of the samples. It is suggested that this is due to [^{36}Cl]-chlorine containing species diffusing into the organic layer and/or a build up of organic material on the surface masking the true [^{36}Cl]-chlorine count rate. There is also the possibility that dehydrochlorination/ hydrofluorination reactions release [^{36}Cl]-chlorine back into the vapour phase (Figs.5.11-5.22).

In the series of reactions that used 1mmol [^{36}Cl]-CH_3CCl_3, removal of the [^{36}Cl]-CH_3CCl_3 vapour from SF_4 γ-alumina, chromia and volcano chromia samples resulted in a decrease in the surface counts, *ca.*30%, indicating that the majority of the [^{36}Cl]-chlorine containing material laid down on the surface was retained (Table 5.4). In the case of the conditioned plus fluorinated, γ-alumina, chromia and volcano chromia, removal of the [^{36}Cl]-CH_3CCl_3 vapour resulted in a larger decrease in the surface counts, *ca.*80% (Figs.5.11-5.16). This suggests that most of the [^{36}Cl]-chlorine containing species laid down on the surface of fluorinated material that had been pretreated with CH_3CCl_3 were not as strongly bonded to this surface as they were to the fluorinated materials. This is consistent with the formation of a permanently retained [^{36}Cl]-chlorine containing organic layer on SF_4 fluorinated surfaces and has been demonstrated previously on γ-alumina (96-98). Further treatments of conditioned materials with CH_3CCl_3 resulted in laydown of additional organic

Fig.5.11. ^{36}Cl-CH_3CCl_3 (1mmol) On Fluorinated Surfaces.
SF_4 Alumina.

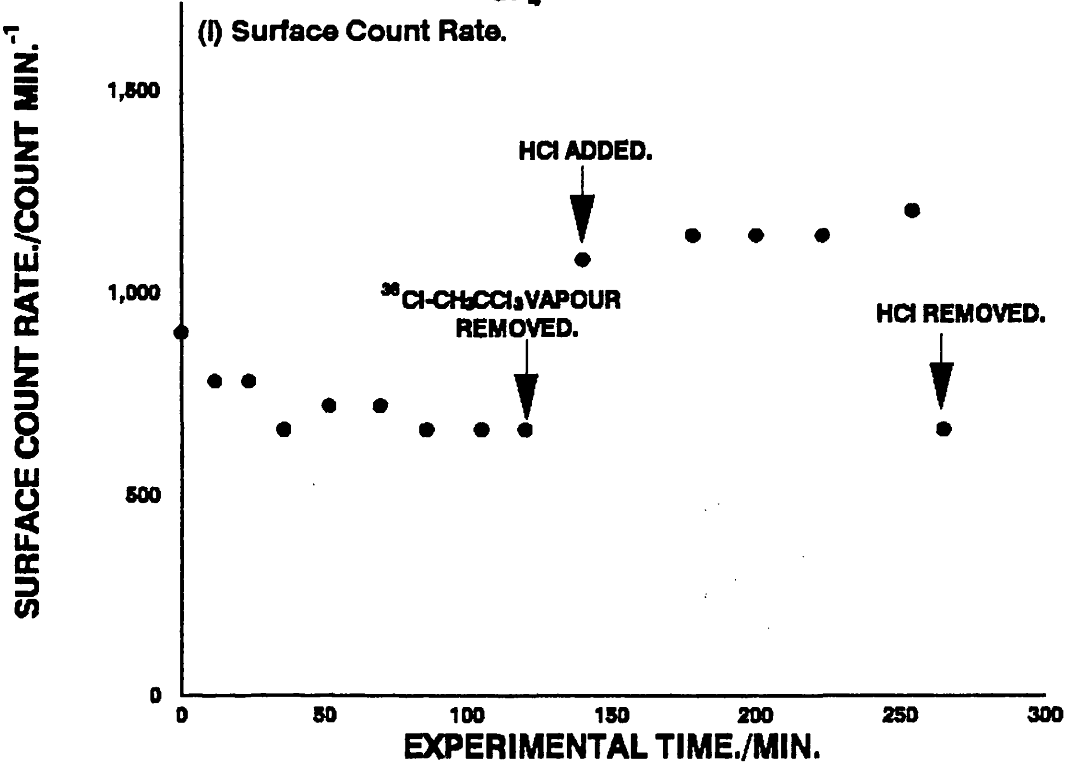


(i) Surface Count Rate.



(ii) Gas Count Rate.

Fig.5.12. ^{36}Cl-CH$_3$CCl$_3$ (1mmol) On Fluorinated Surfaces.
SF$_4$ Chromia.


(I) Surface Count Rate.

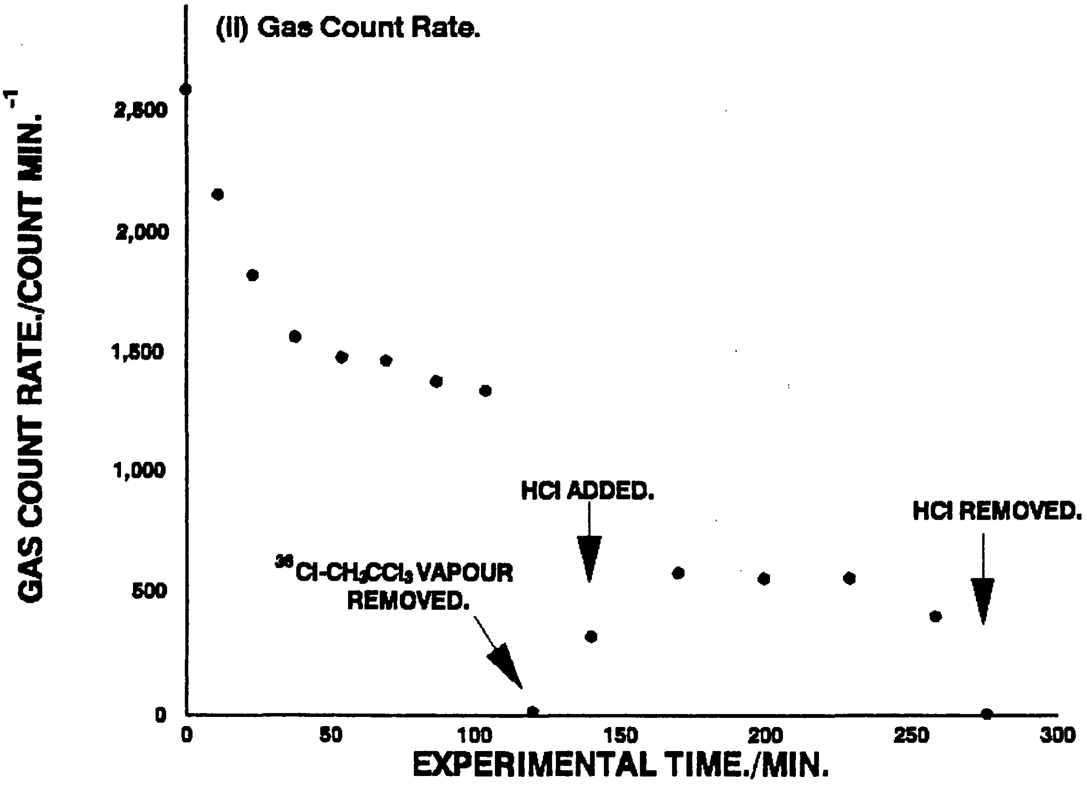
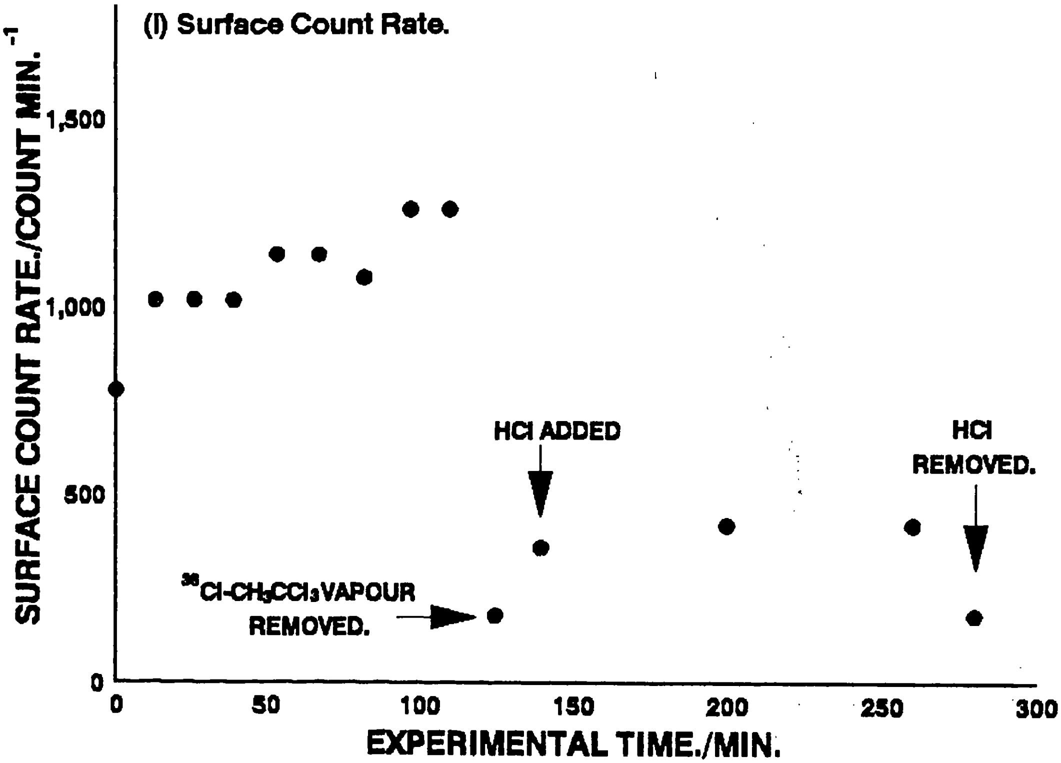
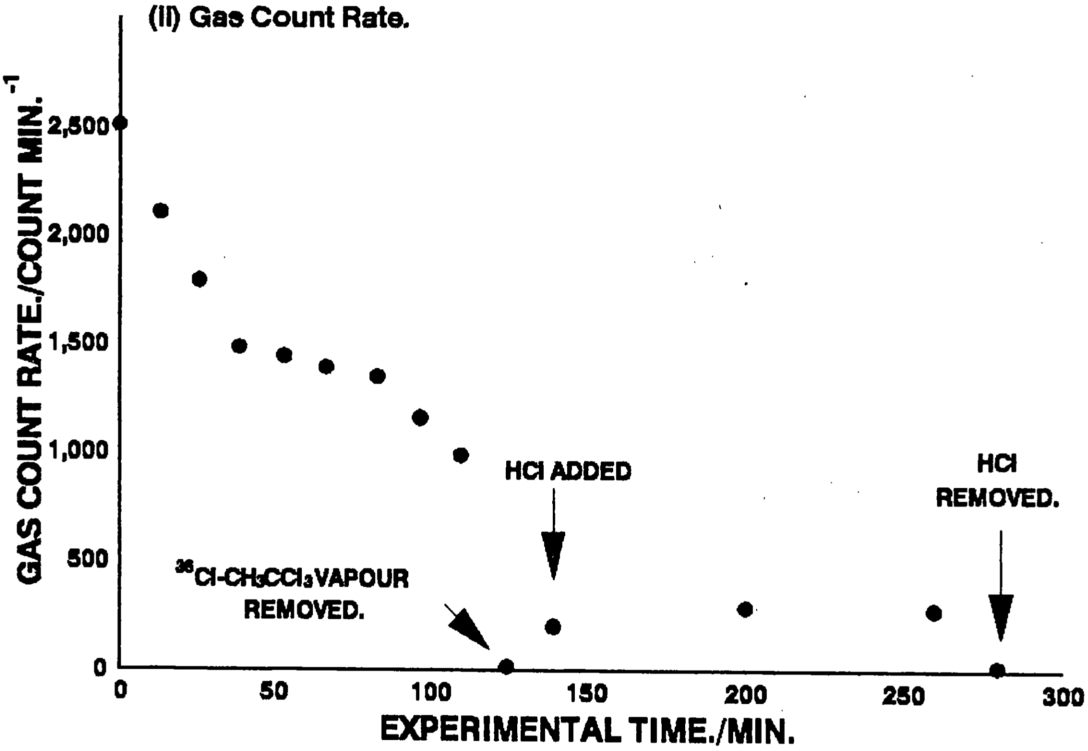

(II) Gas Count Rate.

Fig.5.14. $^{36}Cl-CH_3CCl_3$ (1mmol) On Conditioned Surfaces.

Conditioned Alumina.



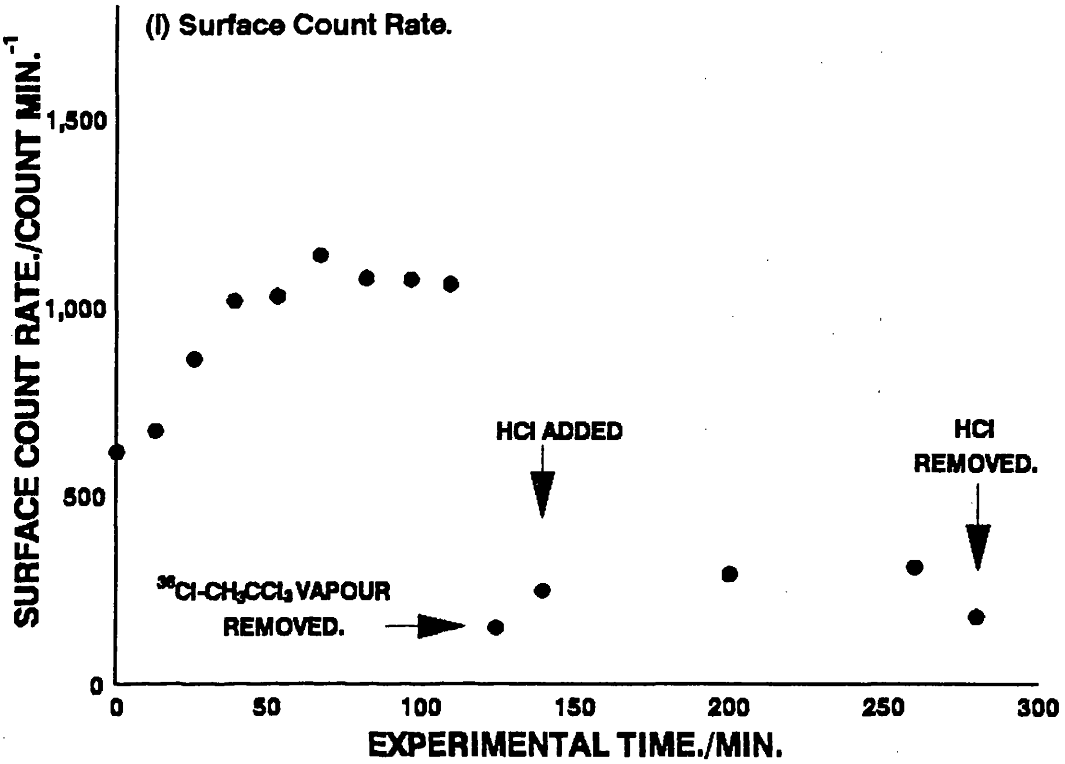
(I) Surface Count Rate.



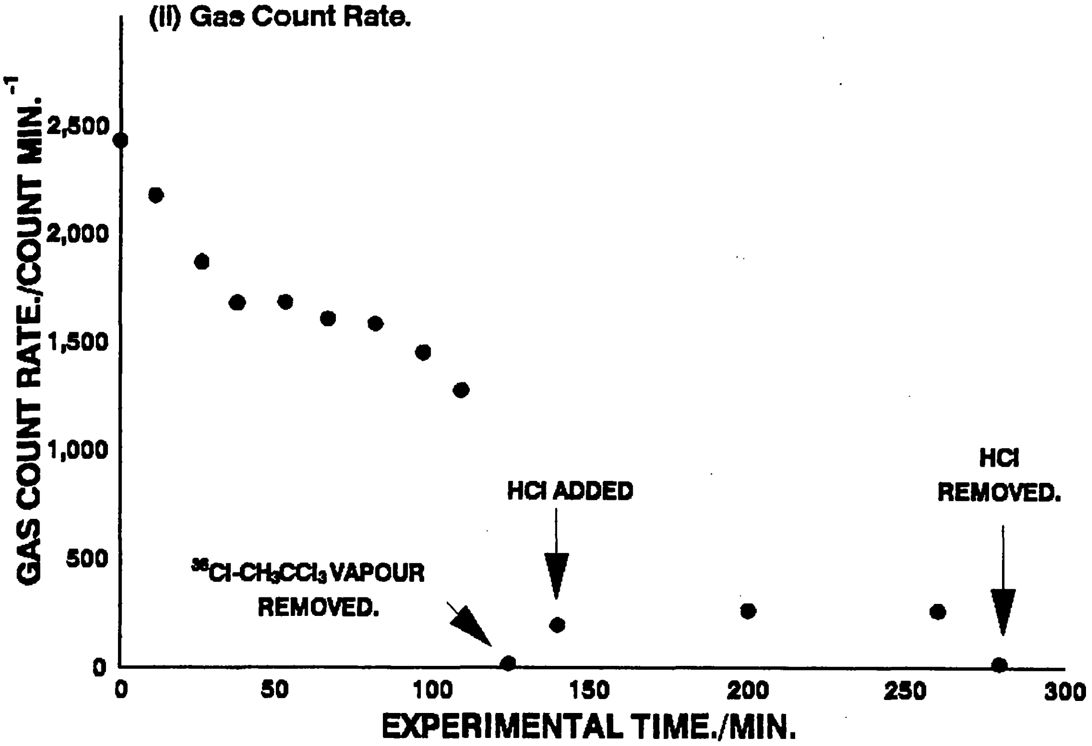
(II) Gas Count Rate.

Fig.5.15. $^{36}Cl-CH_3CCl_3$ (1mmol) On Conditioned Surfaces.

Conditioned Chromia.



(ii) Gas Count Rate.



material but the quantity of material permanently retained is less substantial. This was demonstrated also in Section 3.3.5. where the second conditioning process resulted in a less substantial conversion of 1,1,1-trichloroethane to 1,1-dichloroethene and 1,1-dichloro,1-fluoroethane.

In order to examine the lability of the [^{36}Cl]-chlorine containing species on the surface, exchange reactions with unlabelled anhydrous hydrogen chloride were studied. For all samples, the gas count rate increased immediately on introduction of the unlabelled HCl but then remained virtually constant over the rest of the reaction, indicating that there was some exchange between the gas phase and the surface. Unexpectedly however, the surface count rate also increased. This surprising result can be rationalised as being due to self absorption of the [^{36}Cl]-chlorine containing species within the organic layer. [^{36}Cl]-Chlorine is only detected from the surface of the sample since it is a β^- emitter. Therefore if there is a substantial layer of material laid down the true count rate may be masked. The introduction of unlabelled HCl may draw [^{36}Cl]-chlorine containing species to the surface and/or the exchange of surface [^{36}Cl]-chlorine may expose more labelled material. Removal of the vapour phase resulted in the surface count rate decreasing to approximately the same as before the unlabelled HCl was introduced.

Comparison between reactions that used 1mmol CH_3CCl_3 or 3mmol CH_3CCl_3 (Tables 5.4 and 5.6) with the various materials indicated that there was very little difference in the pattern of the results (Figs.5.11-5.22). Unexpectedly, the final [^{36}Cl]-surface count rate in the reaction employing

Table.5.6. Interaction Of 3mmol [^{36}Cl]-CH_3CCl_3 With Fluorinated Surfaces, Followed By Interaction with Unlabelled HCl.

	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) Start.	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) End.	^{36}Cl-CH_3CCl_3 (Count Min^{-1}) Removed.	Unlabelled HCl (Count Min^{-1}) Start.	Unlabelled HCl (Count Min^{-1}) End.	Unlabelled HCl (Count Min^{-1}) Removed.
Elapsed Time.	0	120	130	140	300	310
SF_4 Alumina. GAS	7,900 ± 82	3,960 ± 41	0	300 ± 4	240 ± 4	0
SF_4 Alumina. SURFACE	3,420 ± 35	5,160 ± 52	2,160 ± 22	2,040 ± 22	2,160 ± 22	2,100 ± 22
SF_4 Chromia. GAS	7,800 ± 81	4,500 ± 46	0	140 ± 3	260 ± 4	0
SF_4 Chromia. SURFACE	3,000 ± 31	2,100 ± 22	1,360 ± 15	1,380 ± 15	1,420 ± 15	1,340 ± 15
SF_4 V.C. GAS	8,050 ± 82	4,380 ± 44	0	170 ± 3	480 ± 6	0
SF_4 V.C. SURFACE	3,300 ± 35	2,700 ± 27	1,420 ± 15	1,420 ± 15	1,560 ± 16	1,420 ± 15

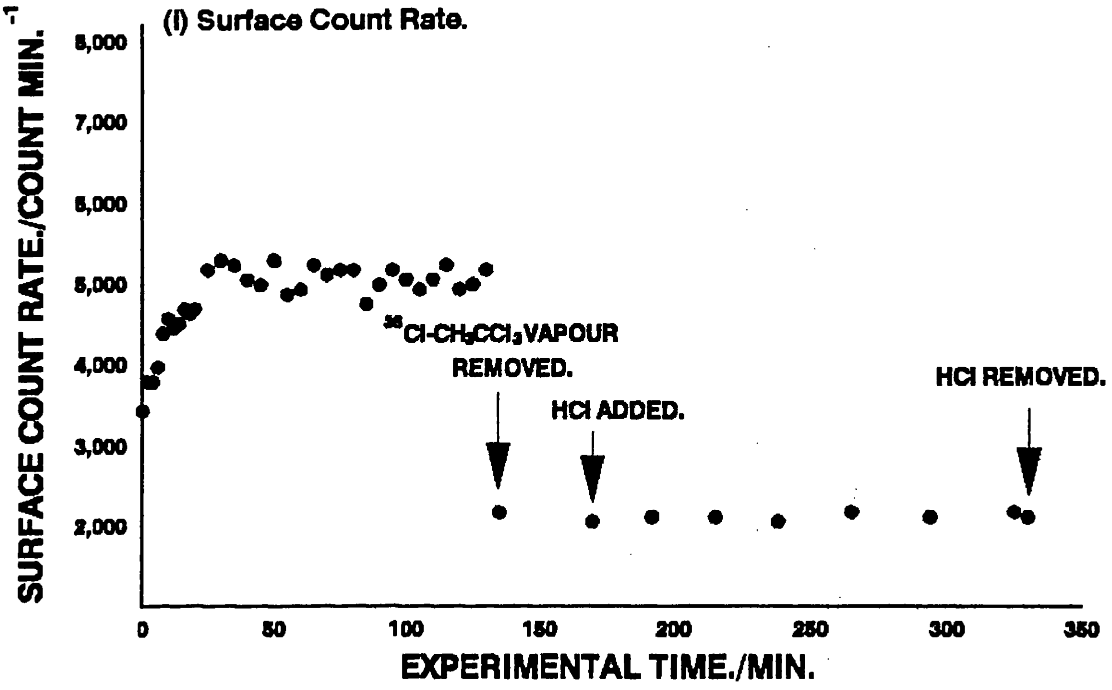
Note: V.C.= "Volcano Chromia."

Table.5.7. Interaction Of 3mmol [^{36}Cl]-CH$_3$CCl$_3$ With Conditioned Surfaces,Followed By Interaction with Unlabelled HCl.

	^{36}Cl-CH$_3$CCl$_3$ (Count Min^{-1}) Start.	^{36}Cl-CH$_3$CCl$_3$ (Count Min^{-1}) End.	^{36}Cl-CH$_3$CCl$_3$ (Count Min^{-1}) Removed.	Unlabelled HCl (Count Min^{-1}) Start.	Unlabelled HCl (Count Min^{-1}) End.	Unlabelled HCl (Count Min^{-1}) Removed.
Elapsed Time.	0	120	130	140	300	310
SF$_4$ Alumina. GAS	7,900 ± 82	3,500 ± 36	0	500 ± 6	650 ± 7	0
SF$_4$ Alumina. SURFACE	2,300 ± 24	1,500 ± 16	250 ± 3	260 ± 3	400 ± 5	300 ± 3
SF$_4$ Chromia. GAS	7,850 ± 81	5,320 ± 54	0	400 ± 5	600 ± 6	0
SF$_4$ Chromia. SURFACE	2,100 ± 22	1,850 ± 19	200 ± 2	300 ± 4	350 ± 5	200 ± 3
SF$_4$ V.C. GAS	8,100 ± 82	4,000 ± 41	0	800 ± 9	1,000 ± 6	0
SF$_4$ V.C. SURFACE	3,300 ± 35	2,700 ± 27	200 ± 3	520 ± 6	800 ± 9	300 ± 4

Note: V.C.= "Volcano Chromia."

Fig.5.17. ^{36}Cl-CH_3CCl_3 (3mmol) On Fluorinated Surfaces.
SF_4 Alumina.



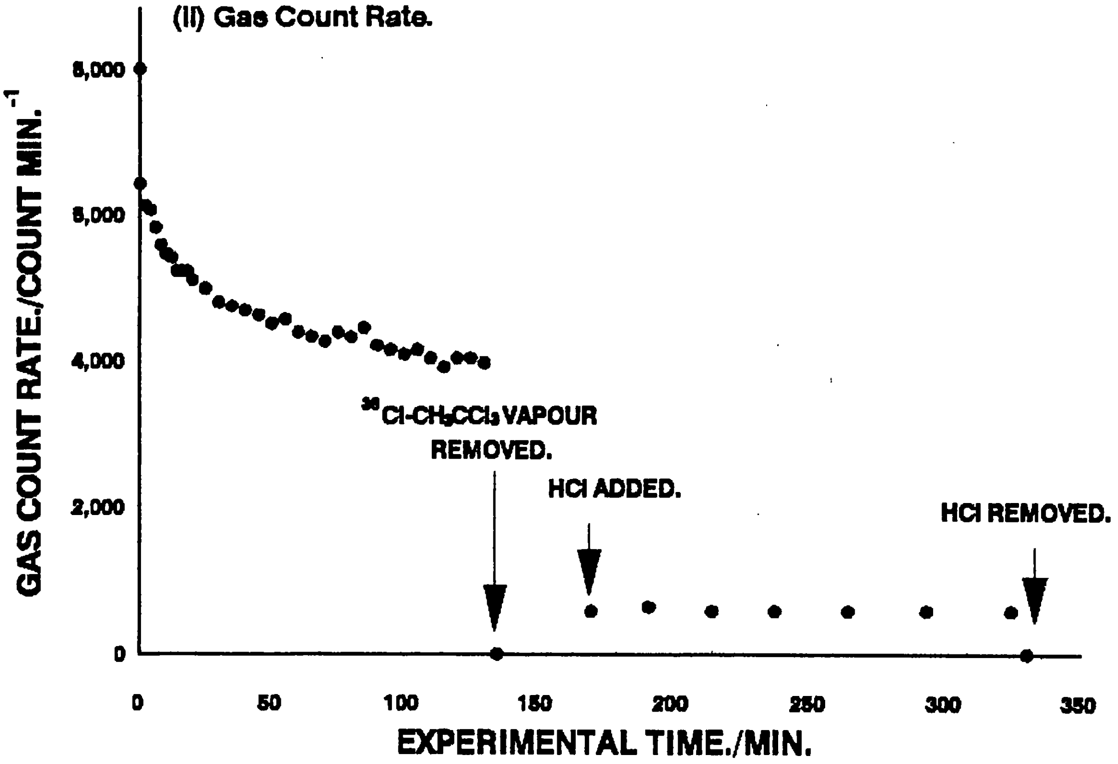


Fig.5.18. ^{36}Cl-CH$_3$CCl$_3$ (3mmol) On Fluorinated Surfaces.
SF$_4$ Chromia.

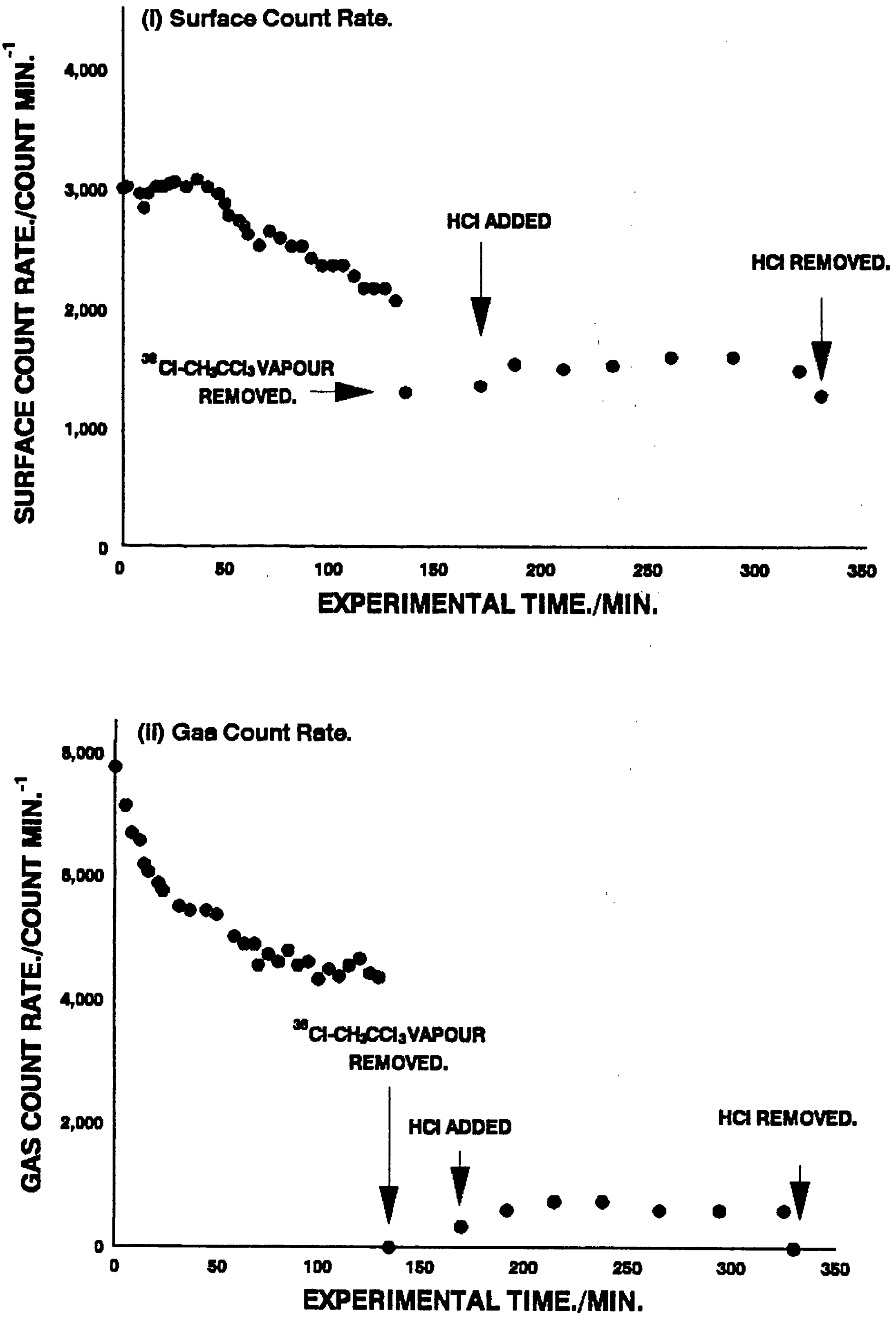


Fig.5.19. ^{36}Cl-CH$_3$CCl$_3$ (3mmol) On Fluorinated Surfaces.
SF$_4$ Volcano Chromia

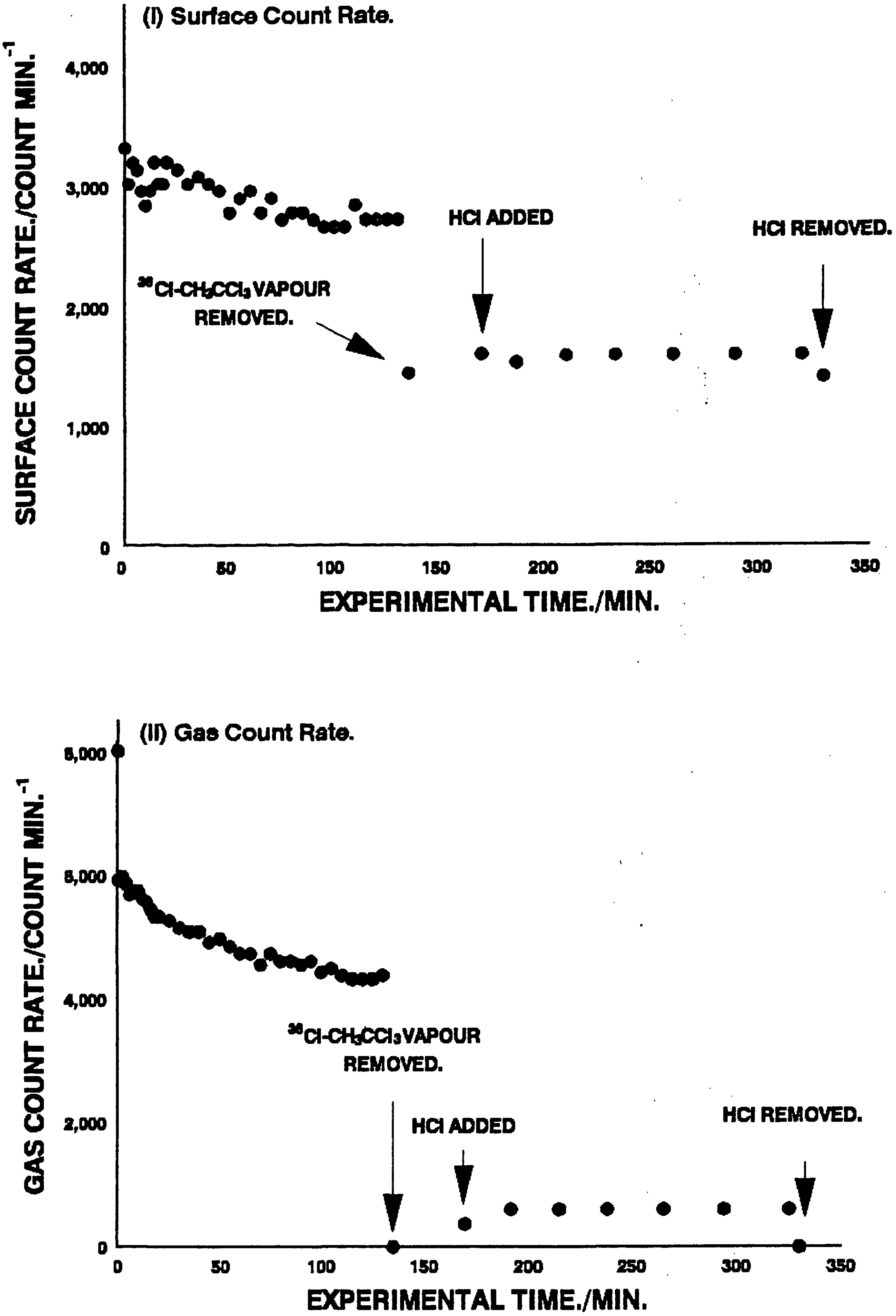


Fig.5.20. ^{36}Cl-CH$_3$CCl$_3$ (3mmol) On Conditioned Surfaces.
Conditioned Alumina.

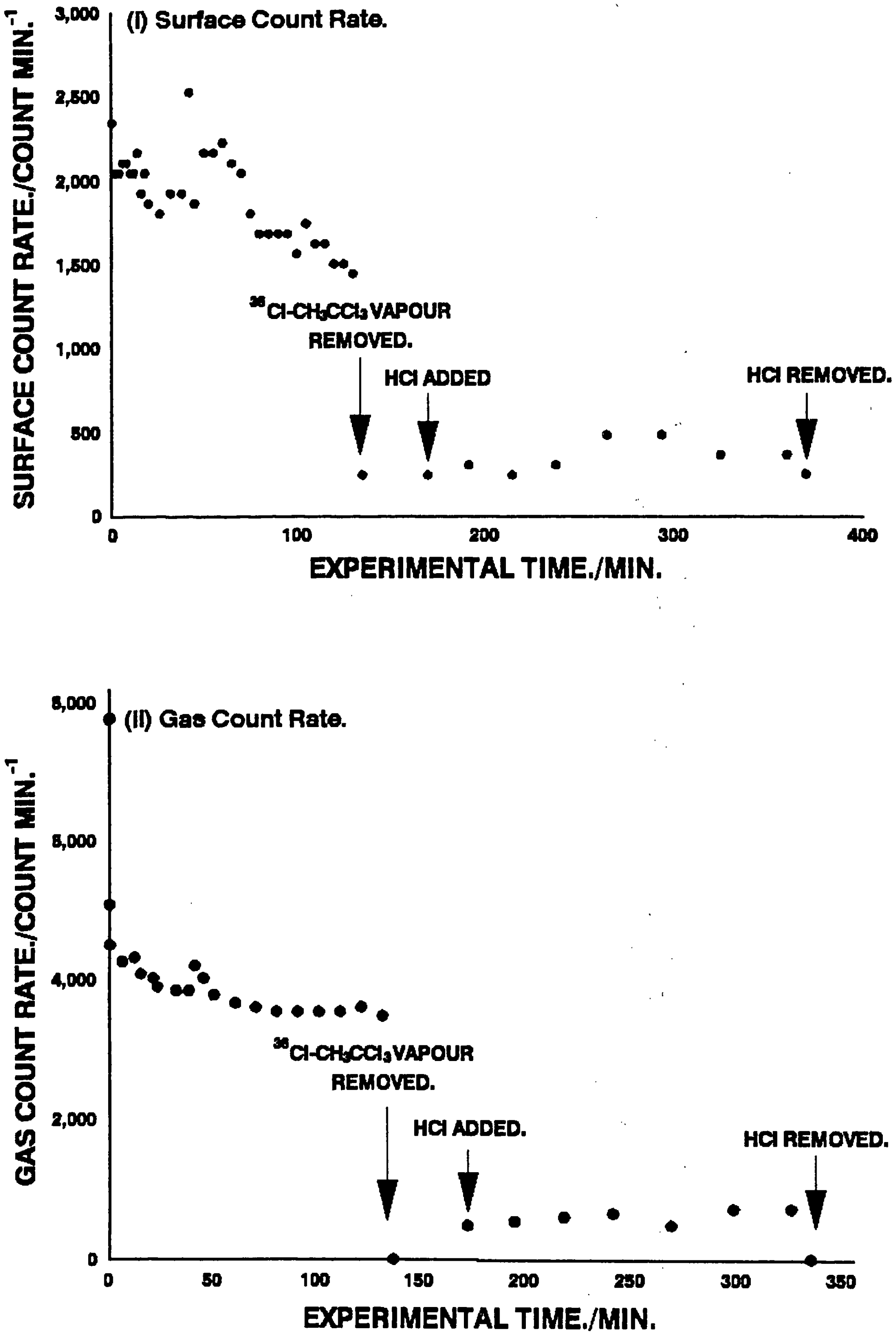


Fig.5.21. ^{36}Cl-CH_3CCl_3 (3mmol) On Conditioned Surfaces.
Conditioned Chromia.

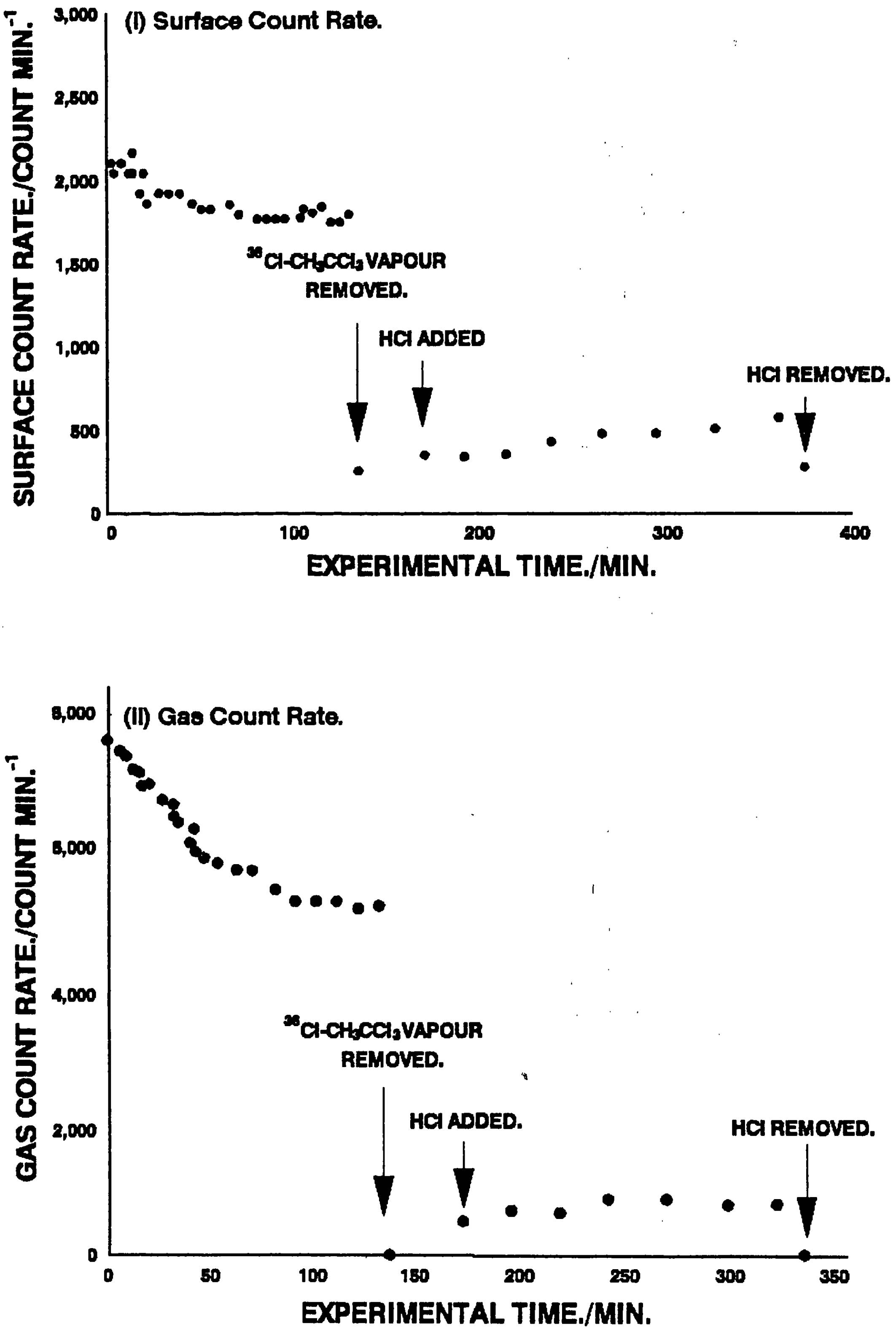
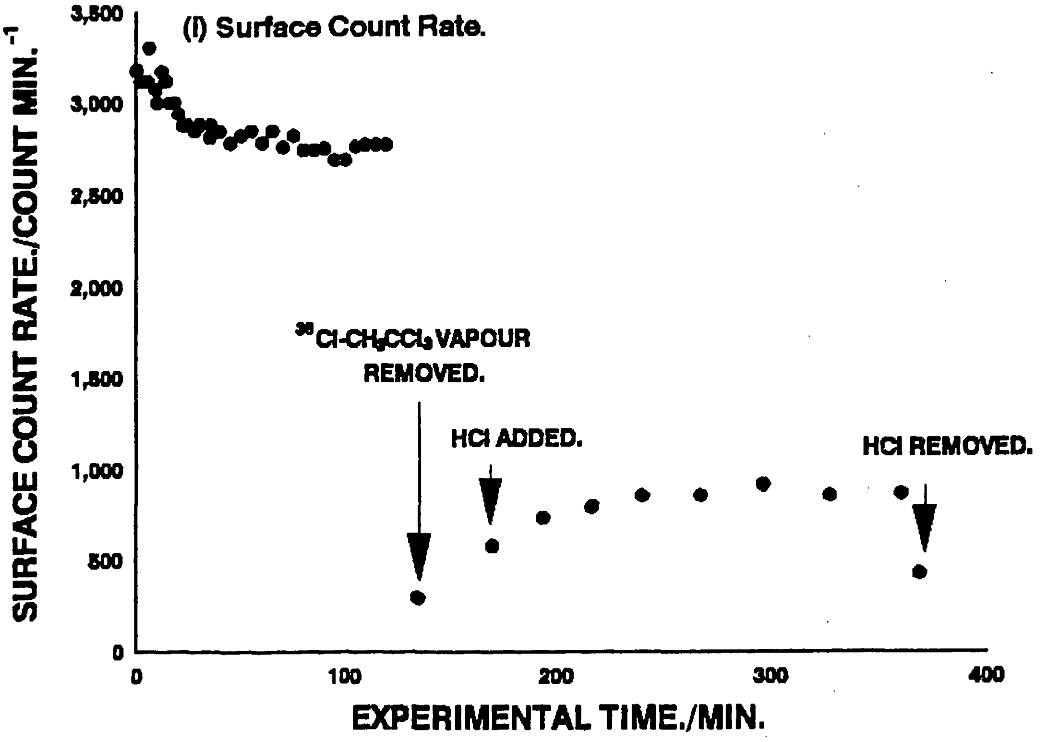
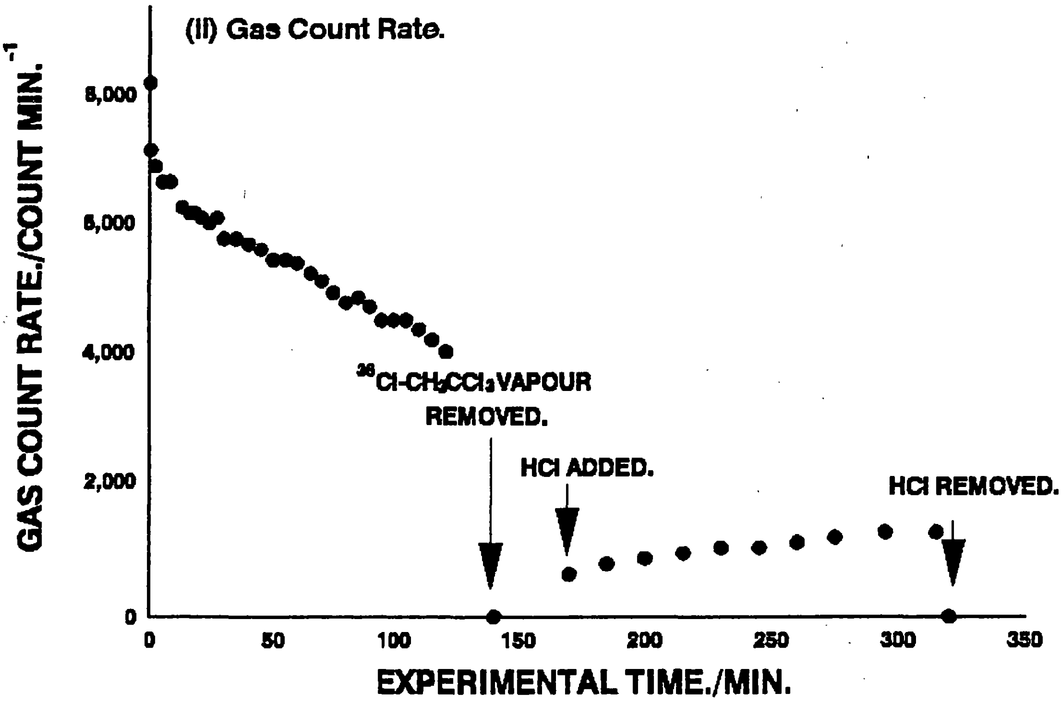


Fig.5.22. ^{36}Cl-CH_3CCl_3 (3mmol) On Conditioned Surfaces.
Conditioned Volcano Chromia.





3mmol was very similar to that for the reaction with 1mmol. This is may be due to self absorption disguising the true value of [^{36}Cl]-chlorine in the solid or that the layer formation does not depend directly on the initial pressure of CH_3CCl_3.

The relative proportions of [^{36}Cl]-chlorine activity on the surfaces were determined from the changes in the gas count rate, as the surface count rates were unreliable for this purpose due to self absorption. From the values presented in Table 5.8. it can be deduced that in the series using 1mmol [^{36}Cl]-CH_3CCl_3, *ca.*50 - 60% of the available [^{36}Cl]-chlorine is present on each of the three solids. Conditioning of the materials with unlabelled CH_3CCl_3, prior to the introduction of the [^{36}Cl]-CH_3CCl_3 has little effect on the quantity of [^{36}Cl]-chlorine retained on the solids.

Table.5.8. Percentage Available [^{36}Cl]-Chlorine Label Present In Gas And Solid Phases At the End Of The Reaction With 1mmol [^{36}Cl]-CH_3CCl_3.

	Percentage Available ^{36}Cl Present In Gas Phase.	Percentage Available ^{36}Cl Present In Solid.
SF_4 γ-Alumina.	42.8%	57.2%
SF_4 Chromia.	50.0%	50.0%
SF_4 Volcano Chromia.	38.5%	61.5%
CH_3CCl_3, SF_4 γ-Alumina.	40.1%	59.9%
CH_3CCl_3, SF_4 Chromia.	52.7%	47.3%
CH_3CCl_3, SF_4 Volcano Chromia.	39.1%	60.9%

The reactions with 3mmol [^{36}Cl]-CH_3CCl_3 resulted in a very similar pattern of percentage of [^{36}Cl]-chlorine distributed between the gas and the solid phases. In these cases also, the conditioning process had very little effect on the values determined for each solid.

Table 5.9. Percentage Available [^{36}Cl]-Chlorine Label Present In Gas And Solid Phases At The End Of The Reaction With 3mmol [^{36}Cl]-CH_3CCl_3.

	Percentage Available ^{36}Cl Present In Gas Phase.	Percentage Available ^{36}Cl Present In Solid.
SF_4 γ-Alumina.	49.6%	50.4%
SF_4 Chromia.	57.7%	42.3%
SF_4 Volcano Chromia.	54.4%	45.6%
CH_3CCl_3, SF_4 γ-Alumina.	43.8%	56.2%
CH_3CCl_3, SF_4 Chromia.	67.7%	32.3%
CH_3CCl_3, SF_4 Volcano Chromia.	49.4%	50.6%

5.4. DISCUSSION.

The objective of this section of the work was to examine how chlorine was taken up by γ-alumina and chromia, how the organic material is laid down and the effects pre-fluorination and conditioning have on these reactions.

5.4.1.[^{36}Cl]-Chlorine Labelled Hydrogen Chloride Adsorption Studies.

Adsorption studies of [^{36}Cl]-chlorine labelled HCl were performed to examine chlorine uptake on calcined, SF_4 fluorinated and fluorinated plus conditioned γ-alumina and chromia samples. Since this was essentially a sighting experiment for the later [^{36}Cl]-CH_3CCl_3 work, it was not thought necessary to perform these experiments on all three solids. It should be noted that the counts determined were rather lower than the optimum and this limits the information that can be obtained. Since the adsorption studies were performed using $H^{36}Cl$ of identical specific count rates, in principle, the data are directly comparable. However, care should be taken in making too detailed interpretations of the figures, since γ-alumina and chromia have different surface areas, 110 m^2/g for calcined γ-alumina and 35 m^2/g for calcined chromia,and the pretreatments do not necessarily alter the surface areas by the same amount.

All of the adsorption isotherms (Figs 5.3 - 5.8) were similar in shape with an initial rapid increase in surface count rate with increasing pressure of gas, after which increasing the amount of [^{36}Cl]-HCl had little or no effect on the surface count rate. The similarities suggest that the adsorption processes occurring on γ-alumina and chromia were similar. It should be noted that the amount of [^{36}Cl]-chlorine adsorbed on the surface of γ-alumina was much greater than on chromia (2,340 count min^{-1} compared with 1,620 count min^{-1}). This may be a reflection of the differences in surface area (Section 3.3.12) of the samples. However, it is important that chlorine is adsorbed onto the surfaces of both γ-alumina and chromia at room temperature in quite substantial quantities.

Fluorination of both γ-alumina and chromia resulted in a substantial reduction in the surface count rates observed. This is expected due to the reduction in surface area (Section 3.3.12) and the enhanced acidity of the surfaces caused by the fluorination process. Previous work (26) on chromia at elevated temperatures indicated that catalytically active chlorine and fluorine species occupy the same sites with adsorbed fluorine species being difficult to displace by incoming chlorine species. Therefore HCl molecules are thought to adsorb by hydrogen bonding to fluorine species already adsorbed at the surface. This gives rise to the HCl-HF- oligomers discussed previously on HF fluorinated chromia (Section 3.4.1). It is not clear if such oligomers are formed on the SF_4 fluorinated materials or if the HCl is dissociatively adsorbed on the surface, although comparisons with chlorinated γ-alumina (69) suggest that dissociative adsorption is most likely in this case.

The conditioning of fluorinated material prior to the introduction of $H^{36}Cl$ had little effect on the surface counts which indicates that the laydown of the organic layer has a negligible effect on the adsorption of [^{36}Cl]-chlorine containing material. It is suggested that in addition to HCl adsorbed at the organic layer surface, it can also diffuse into the organic layer material. Since [^{36}Cl]-chlorine is detectable from the surface alone, this [^{36}Cl]-chlorine is not observed.

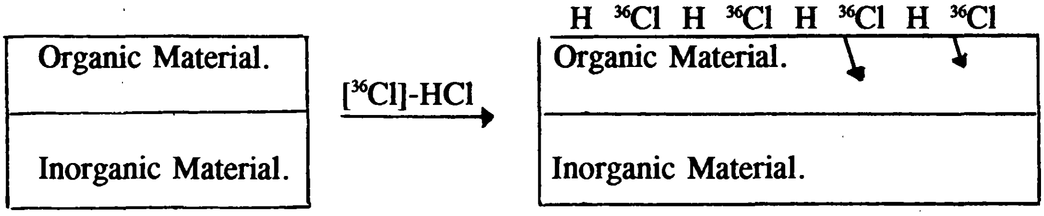


Fig.5.23.Adsorption Of [^{36}Cl]-HCl On CH_3CCl_3 Conditioned, SF_4 Fluorinated Surfaces.

The reaction of HCl with conditioned material was examined in Section 3.3.10, by the *in situ* I.R. study which demonstrated that CH_3CCl_3 and CH_3CCl_2F were displaced from the organic layer following the interaction of HCl. This is important in understanding catalytic activity of the organic layer, in the reaction between 1,1,1-trichloroethane and HF. Displacement of the organic layer material, CH_3CCl_3 and CH_3CCl_2F by incoming reactants points to the important role of the organic layer in catalysis with the incoming halocarbon and/or hydrogen halide able to replace the surface species thus gaining access to active sites. It is this process which demonstrates why the lay down of the organic material does not deactivate the catalyst. The organic layer is a dynamic part of the catalytic process.

Treatment of calcined material, that had not been fluorinated with SF_4, with 1,1,1-trichloroethane also resulted in surface count rates that were considerably lower than those observed for the calcined materials. There is no evidence for dehydrochlorination of 1,1,1-trichloroethane on unfluorinated surfaces, which in conjunction with the fact that there was no colour change observed on γ-alumina, implies that there is no polymeric layer formed. This has also been shown in literature (11), where it was demonstrated that temperatures of >400K were required for the dehydrochlorination of CH_3CCl_3 on unfluorinated γ-alumina and the reaction did not occur at room temperature. So it is suggested that the reduction in the interaction of $H^{36}Cl$ is due to the reduction in surface area and/or blocking of reactive sites by interactions between the surface and 1,1,1-trichloroethane, the former being the most significant, since as discussed previously, adsorption of hydrogen halide and halocarbon compounds occur at different sites.

The [^{36}Cl]-chlorine count rate for the material retained on the surface at room temperature was determined by removing the vapour from the counting vessel by condensing under static vacuum and then pumping the sample to remove any weakly adsorbed species. From the data in Table 5.1. it appears that calcined γ-alumina and CH_3CCl_3 treated γ-alumina show the most significant reduction in surface count rates after this treatment. In all the other cases the count rates do not decrease by such a great extent, indicating that most of the [^{36}Cl]-chlorine containing species laid down on the surface were retained.

Having determined the surface count rate for the [^{36}Cl]-chlorine containing species retained by the solid, the lability of this chlorine was studied by introducing unlabelled HCl and examining exchange reactions. In all the solids examined, there was some increase in the gas count rate and decrease in the surface count rate indicating the occurrence of exchange reactions. Previous studies with [^{36}Cl]-chlorine labelled HCl (69,160) confirm the findings that there is a substantial quantity of labile chlorine present on conditioned plus fluorinated γ-alumina.

Thus, from the results in this section, it is clear that H^{36}Cl is adsorbed on calcined materials, with only a small quantity of weakly adsorbed [^{36}Cl]-chlorine species removed by pumping. HCl is also adsorbed on both fluorinated and conditioned plus fluorinated solids materials. The quantity of material adsorbed on these solids is apparently less than for calcined solids. It should be noted that [^{36}Cl]-chlorine is detected only from the surface and therefore it is possible that some of the adsorbed [^{36}Cl]-chlorine diffuses into the organic layer on the conditioned materials and is not detected.

5.4.2. Treatment Of Fluorinated Materials With [^{36}Cl]-Chlorine Labelled 1,1,1,-Trichloroethane.

From the results of the work in this section, it appears that the interaction of [^{36}Cl]-chlorine labelled 1,1,1-trichloroethane occurs similarly on fluorinated γ-alumina, chromia and volcano chromia which indicates that the conditioning process is comparable for the three solids. In each case there was a substantial uptake of chlorine containing species. It is known from previous work (70) that the interaction of CH_3CCl_3 with fluorinated γ-alumina results in the laydown of a permanently retained chlorine containing organic layer. As discussed previously (Section 3.3.3), fluorinated chromia and volcano chromia can dehydrochlorinate CH_3CCl_3, producing fluorinated chlorohydrocarbons in a similar way to fluorinated γ-alumina. Thus, SF_4 fluorination of chromia and volcano chromia creates Lewis acid sites that are strong enough to dehydrochlorinate CH_3CCl_3 and the fluorine on the surface is labile enough to be involved in halogen exchange reactions to produce the HCFCs. The results in this section, where [^{36}Cl]-chlorine containing material is laid down on the surfaces, can be examined in conjunction with the results in Section 3.3.7. where the conditioning process resulted in mass increases for the three solids. This leads to the suggestion that, since γ-alumina and chromias have displayed such similarities in the reaction with CH_3CCl_3, a chlorine containing organic layer is also being formed on the surface of the chromia samples, although there is no visible purple layer formed.

The initial [^{36}Cl]-chlorine labelled 1,1,1-trichloroethane work involved the reaction of 1mmol of labelled gas in order to get a clear picture of the interactions occurring, without building up a complete organic layer. Although these experiments showed that there was incorporation of [^{36}Cl]-chlorine containing material on the surface of the fluorinated and fluorinated plus conditioned γ-alumina and chromia, the counts were rather low and the problem of self-absorption was indicated by the apparent increase in the solid count rate observed on introduction of unlabelled HCl to [^{36}Cl]-CH_3CCl_3 treated materials. In order to overcome the low counts, the process was repeated using 3mmol CH_3CCl_3, the standard quantity used in the conditioning process. The counts recorded were much greater but the pattern of behaviour was not greatly altered.

Introduction of [^{36}Cl]-CH_3CCl_3 resulted in a decrease in the gas phase count rate and an increase in the surface count rate, so clearly, [^{36}Cl]-chlorine containing material is being incorporated into the solid, with 50-60% of the available [^{36}Cl]-chlorine label incorporated into the solid. It is known that the reaction between CH_3CCl_3 and SF_4 fluorinated material results in the formation of $CH_2{=}CCl_2$, CH_3CCl_2F and HCl. All of these, in addition to CH_3CCl_3 will be present in the gas phase and will contain the [^{36}Cl]-chlorine radiolabel. The G.C. data presented in Section 3.3.5 indicated that CH_2CCl_2 accounts for *ca.*20 mol% and CH_3CCl_2F *ca.*15 mol% of the products from the CH_3CCl_3 conditioning reaction of SF_4 fluorinated material.

The introduction of unlabelled HCl, to examine the lability of the surface chlorine species, produced some unexpected results. The increase in the gas count rate in each case indicated that there was a quantity of labile chlorine on the solids. The *in situ* I.R. study of the reaction of HCl with CH_3CCl_3 treated SF_4 fluorinated materials (Section 3.3.10) demonstrated that CH_3CCl_3 and CH_3CCl_2F could be displaced from the solid, probably by hydrochlorination and hydrofluorination reactions. The increase in the gas phase count rate is probably due to exchange/displacement reactions between gas phase and surface chlorine species and also due to the reactions between the [^{36}Cl]-chlorine labelled organic layer material and the HCl. However, the accompanying increase in the surface count rate was rather unexpected. Obviously, if there is exchange between the gas and the solid, the count rate of the surface would be expected to decrease. The observed increase in the surface count rate is explained by self-absorption of the β^- radiation from the [^{36}Cl]-chlorine containing species. Since β^- radiation from [^{36}Cl]-chlorine can only be detected from the surface of the material, development of a substantial layer of [^{36}Cl]-chlorine containing species will mean that not all the radiation will be detected. It is suggested that introduction of unlabelled HCl to the [^{36}Cl]-CH_3CCl_3 treated fluorinated materials results in displacement of and hydrochlorination/hydrofluorination reactions with [^{36}Cl]-chlorine containing organic layer material. The products from such reactions may then be weakly adsorbed on the surface of the materials, resulting in the apparent increase in surface count rate.

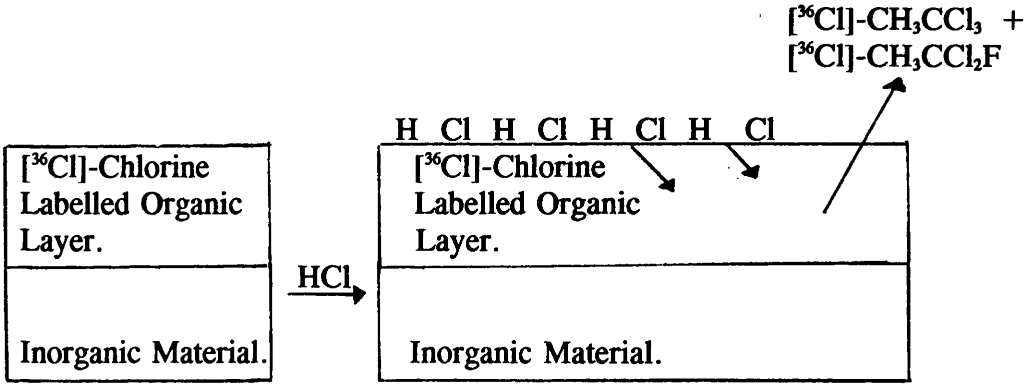


Fig.5.24.Interaction Of HCl With [^{36}Cl]-CH_3CCl_3 Conditioned, SF_4 Fluorinated Surfaces.

It is also probable that exchange reactions between HCl and surface [^{36}Cl]-species exposes more [^{36}Cl]-chlorine on the surfaces, possibly at the inorganic interface, resulting in an apparent increase in the surface count rate i.e. the organic layer is being "thinned" by removal of organic layer material. Since this phenomenon is observed with γ-alumina, chromia and volcano chromia, it appears that there is substantial laydown of [^{36}Cl]-chlorine containing species on all the surfaces. The increase in the surface count rates on introduction of HCl appears to be similar in the 1mmol and 3mmol [^{36}Cl]-chlorine labelled 1,1,1-trichloroethane treated solids and conditioning of the fluorinated materials does not appear to effect the lability of the surface [^{36}Cl]-chlorine containing species.

5.4.3. Treatment Of Conditioned Materials With [^{36}Cl]-Chlorine Labelled 1,1,1-Trichloroethane.

From the results in this section it appears that the process follows a similar pattern to that observed on fluorinated materials. In each case there is substantial uptake of chlorine containing species. The final surface count rates determined for the conditioned materials are lower than for the fluorinated materials. This suggests that either, less organic material is laid down on the conditioned surfaces or that the presence of the organic material on the surfaces allows in-coming [^{36}Cl]-CH_3CCl_3 to be incorporated within the organic layer already present, in addition to adsorption on the surface of the layer, therefore masking the true [^{36}Cl]-chlorine count rate. The latter explanation is favoured, in view of the fact that the percentage of the available [^{36}Cl]-chlorine present on the conditioned solid is calculated to be similar to that on the fluorinated material, *ca.*50%. The results of the reaction of [^{36}Cl]-chlorine

CH_3CCl_3 with conditioned materials corresponds to the previous proposal of a "turnover" of surface organic material, with in-coming CH_3CCl_3 displacing that already present on the surface. If the percentage of [^{36}Cl]-chlorine present in the gas phase had been very high, this would have implied a direct conversion of [^{36}Cl]-CH_3CCl_3 to various [^{36}Cl]-chlorine containing species. Comparisons of these results with the G.C. data in Section 3.3.5 which indicated that treatment of conditioned material with a further aliquot of CH_3CCl_3 results in some dehydrochlorination and hydrofluorination, although the extent is much less than for the initial conditioning of SF_4 γ-alumina. This may be due to less extensive reaction or it may be due to "turnover" of surface material, producing CH_3CCl_3. The later process is favoured, but studies of the reaction of [^{36}Cl]-CH_3CCl_3 under flow conditions over conditioned materials are required to establish the source of the gas phase CH_3CCl_3 and therefore the reaction routes involved.

Comparisons can be made between this work and CCl_4 chlorinated γ-alumina treated with [^{36}Cl]-chlorine labelled CH_3CCl_3 at room temperature. This reaction leads to a build-up of [^{36}Cl]-chlorine activity on the surface. Admission of HCl led to a 24% reduction in the surface count rate, as a result of chlorine exchange (166). There was no evidence of increasing surface count rate. Previous studies of the reaction of $H^{36}Cl$ with CH_3CCl_3 conditioned γ-alumina indicated that 92% of the chlorine adsorbed on the catalyst surface is labile (160). From the results reported in this section, it appears that the quantity of labile chlorine on CH_3CCl_3, SF_4 γ-alumina and chromias is similar.

The most important findings of this section of work are that chlorine containing species are adsorbed at room temperature onto γ-alumina and chromia surfaces and as expected fluorination reduces the quantity of chlorine adsorbed with both chromia and γ-alumina being affected similarly. Conditioning of the fluorinated materials with CH_3CCl_3 does not appear to affect the adsorption process. This confirms that the conditioning process does not deactivate the surface and indicates the important role played by the organic layer in the catalytic reaction.

The second area under investigation was the treatment of fluorinated and conditioned materials with [^{36}Cl]-chlorine labelled CH_3CCl_3. This demonstrates that the behaviour of γ-alumina and chromia are very similar, with a substantial quantity of chlorine containing material laid down on the surfaces of both fluorinated and conditioned plus fluorinated materials. A substantial portion of the chlorine laid down on the surface is labile with respect to HCl, which is an important consideration for the further catalytic activity of the organic layer. It is very significant that γ-alumina and the chromia samples behave similarly and this work, with [^{36}Cl]-CH_3CCl_3, in conjunction with the studies in Chapter 3 indicate that halogen containing organic material is incorporated into chromia and γ-alumina in a similar way.

REACTION OF ANHYDROUS HF AND 1,1,1-TRICHLOROETHANE OVER OXIDE SUPPORTED ORGANIC LAYER CATALYSTS.

6.1. INTRODUCTION.

The catalytic fluorination procedure used most widely in industry for the production of fluorinated materials involves flowing anhydrous hydrogen fluoride and the appropriate haloalkane over a chromia catalyst at temperatures of >600K. This reaction involves a series of F-for-Cl and Cl-for-F halogen exchange reactions and isomerization reactions as discussed in Chapter 1. The sequence of halogen exchange and isomerization reactions, starting with CCl_2F-$CClF_2$ (CFC-113) and determined using [^{18}F]-fluorine and [^{36}Cl]-chlorine radiotracer techniques (25,26,27) is shown in Fig.6.1.

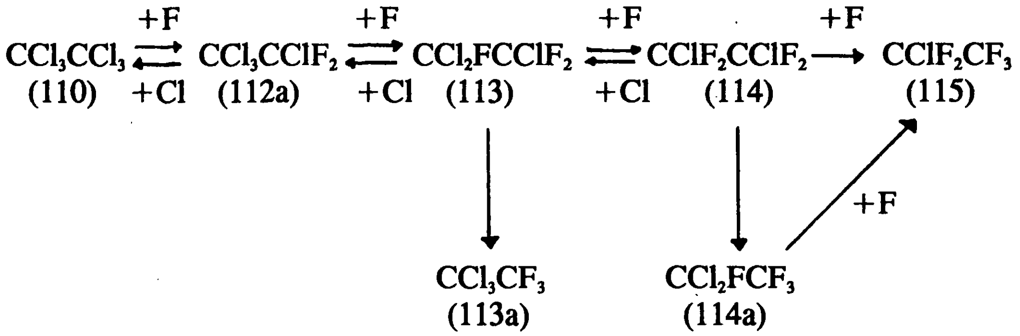


Fig.6.1. Halogen Exchange and Isomerization Reactions of Chlorofluoroethanes Over Chromia Catalyst at 700K.

The compound CCl_3CCl_2F (CFC-111) was not detected, but may have been present as an intermediate species. Clearly from the reactions observed, both fluorination and chlorination processes are occurring. It was from such work that the models for the fluorination, chlorination and isomerization reactions, discussed in Chapter 1, were determined.

Previous studies have demonstrated that 1,1,1-trichloroethane undergoes dehydrochlorination at room temperature on solid anhydrous aluminium (III) chloride (91). This is accompanied by the formation of a purple organic layer on the surface of the solid, as the dehydrochlorination product $CH_2=CCl_2$ undergoes further dehydrochlorination and oligomerization. Studies to investigate the production of strong Lewis acid sites on γ-alumina led to the discovery that a similar reaction occurs on γ-alumina when it has been pretreated with carbon tetrachloride or carbonyl chloride (69,70). Treatment of γ-alumina with sulphur tetrafluoride also created a surface that was capable of dehydrochlorinating 1,1,1-trichloroethane. However, this was accompanied by formation of fluorinated products, by halogen exchange reactions between the surface and the CH_3CCl_3. At room temperature these organic layers are capable of catalysing the reaction of 1,1,1-trichloroethane with anhydrous HF (mole ratio 3:1) producing a mixture of HCFCs , $CH_3CCl_{3-n}F_n$ (n=0-3). This organic layer catalyst can also be used for the fluorine for chlorine exchange reactions of other C_2 and C_3 chlorohydrocarbons, e.g.$CHCl_2CHCl_2$, $CH_3CCl_2CH_3$, $CClH_2CCl_3$ and $CClH=CCl_2$ with HF (98). The mechanisms of the catalytic reactions that occur on the CH_3CCl_3 treated SF_4 γ-alumina are not thought to be identical to those on HF fluorinated chromia. The most obvious difference is that the reaction over the γ-alumina supported organic layer takes place at room temperature whereas temperatures of > 600K are required for the reaction on fluorinated chromia. The organic layer material clearly plays an important role in the catalytic reaction, since there is no observable reaction between HF and CH_3CCl_3 at room temperature in the absence of the organic layer. It has been indicated, from radiotracer experiments, that the reaction between the organic substrate and HF at room temperature involves a turnover of organic material, with incoming halocarbon displacing that which is present on the solid, and incorporation of fluorine into the organic layer (160). The reaction mechanisms on HF treated chromia were described in Chapter 1 and involve substitutions occurring at adsorbed chlorofluoroethane molecules, in which the incoming halogen species is the terminal atom of a $Cr-F(HF)_nHX$ (X=F or Cl) oligomer (26).

The objective of this section of work was to establish if volcano chromia, pretreated with SF_4 and CH_3CCl_3 in an identical way to γ-alumina is also catalytically active for the fluorination of 1,1,1-trichloroethane with HF at room temperature. Comparisons have been made between the products from the catalytic reactions on volcano chromia and γ-alumina under identical conditions.

The second stage of this section of work was to extract and characterize the organic material from SF_4 γ-alumina and chromia treated with 1,1,1-trichloroethane. The presence of organic layer material on volcano chromia has been implied, for example by mass changes observed on conditioning (Section 3.3.7.), however there is no visible evidence of its presence. Previous attempts to characterize the organic layer material from CH_3CCl_3, SF_4 γ-alumina have indicated the presence of CH_3-, $-CH_2$- and $-CH_2X$ and also unsaturated species although the exact nature of the organic layer has not been characterised (160). In the present work, comparisons have been made between the material extracted from the γ-alumina and volcano chromia catalysts and spectroscopic methods were used to identify the constituents of the material. This should prove useful in substantiating the model of the catalytic fluorination reactions of the organic layer catalysts developed from previous work (98) and work presented in this thesis.

6.2. EXPERIMENTAL.

6.2.1. CATALYTIC FLUORINATION OF 1,1,1-TRICHLOROETHANE WITH ANHYDROUS HF OVER OXIDE SUPPORTED ORGANIC LAYER CATALYSTS UNDER STATIC CONDITIONS.

A sample of γ-alumina (0.520g) was fluorinated with SF_4 as described in section 2.4.2. This sample was then conditioned with 1,1,1-trichloroethane as described in section 2.4.3. The catalytic fluorination reaction was carried out using 1,1,1-trichloroethane and anhydrous hydrogen fluoride in a molar ratio of 3:1. This ratio of reactants was developed in previous studies (98), and although not optimised, the proportions of HCFC products were greater than in experiments where the mole ratio was 1:2 or 1:3. Under the conditions used, complete consumption of HF corresponds to a volatile organic product mixture in which the total fluorine component was 33.3g atom%. The CH_3CCl_3 (3mmol) was condensed into the Monel metal reaction vessel followed by the HF (1mmol). The order ensures that the HF does not deactivate the surface (160). The reaction mixture was allowed to react for 2h.

at room temperature, before the volatile products were removed for analysis by G.C. An identical method was used to study the CH_3CCl_3/HF catalytic reaction on volcano chromia.

6.2.2. EXTRACTION AND ANALYSIS OF ORGANIC LAYER MATERIAL FROM THE 1,1,1-TRICHLOROETHANE CONDITIONING OF SF_4 FLUORINATED γ-ALUMINA AND VOLCANO CHROMIA SAMPLES.

(i) Soxhlet Extraction.

γ-Alumina was fluorinated and conditioned as described previously (Section 3.2.2. and 3.2.4.) (Sample prepared by R.Spence.). Soxhlet extraction was performed on a sample of this material (22.04g) with 150cm^3 CH_3CCl_3 (Extraction performed by R.Marshall (159)). After the extraction process the solid was grey in colour. The extracted material was dark brown. Samples of this extracted material were prepared for analysis by GCMS and NMR.

(ii) Extraction Under Vacuum.

γ-Alumina was fluorinated and conditioned as described previously (Section 3.2.2. and 3.2.4.). A sample of this material (3.05g) was transferred, in the dry box, to one limb of a double limbed reaction vessel (Fig.6.2) which was then attached to the manifold of the Pyrex glass vacuum line. A volume of 1,1,1-trichloroethane was condensed into the limb containing the catalyst and allowed to react at room temperature for 2h. After this time the liquid was tipped into the empty limb of the double limbed reaction vessel. The CH_3CCl_3

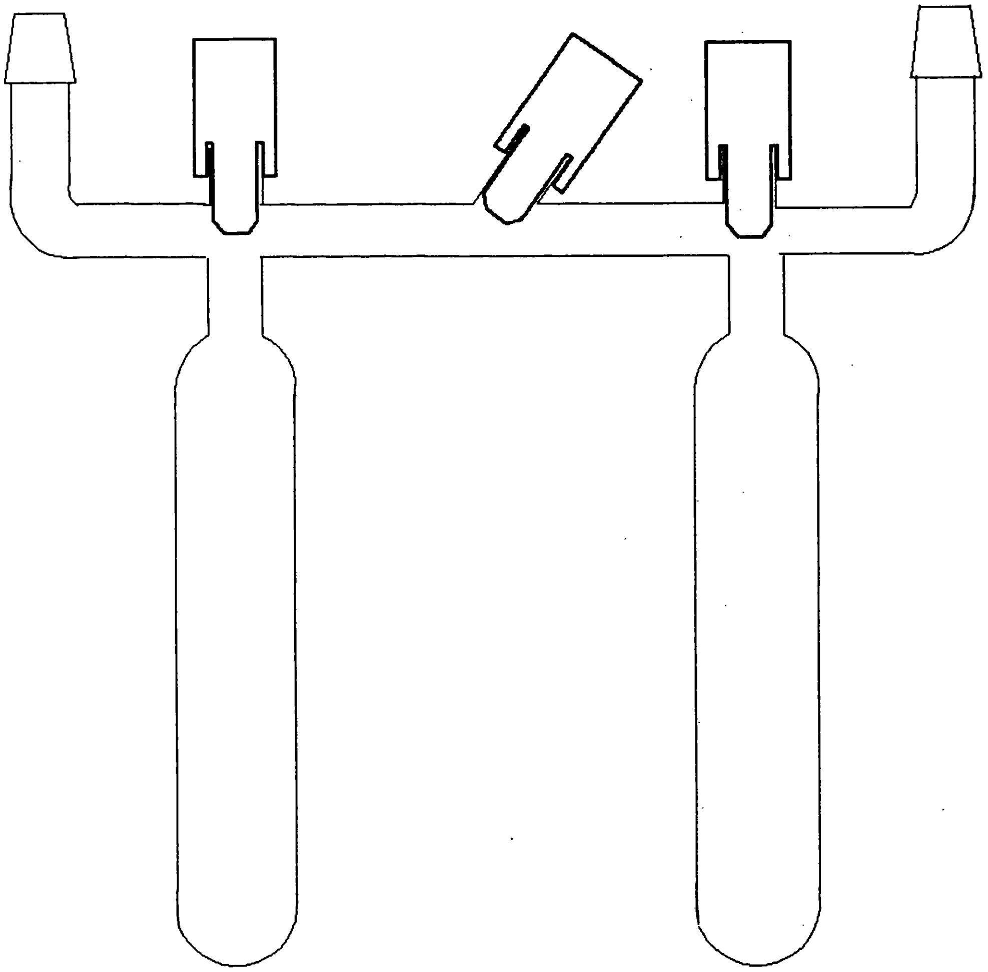


Fig.6.2. Double Limbed Reaction Vessel.

solvent was then back-distilled into the limb containing the solid, leaving behind a yellow/brown involatile liquid, the extracted organic material. It was not possible to remove completely all of the CH_3CCl_3 solvent and consequently traces of the solvent were present in the samples prepared for analysis by GCMS and NMR. (Extraction performed by R.Marshall (159)).

This method was also used to extract the organic material from volcano chromia.

6.3. RESULTS.

6.3.1. CATALYTIC FLUORINATION OF 1,1,1-TRICHLOROETHANE WITH ANHYDROUS HF OVER OXIDE SUPPORTED ORGANIC LAYER CATALYSTS UNDER STATIC CONDITIONS.

The result of a series of catalytic fluorination reactions of 1,1,1-trichloroethane with anhydrous hydrogen fluoride over organic layer catalysts supported on γ-alumina and volcano chromia catalysts indicate that the reactions on both surfaces is similar.

Table 6.1 shows the G.C. analysis of the volatile material after the reaction. It is clear that the products from reaction on γ-alumina and volcano chromia catalysts are similar. In all samples the main constituent present is unchanged CH_3CCl_3 (80-90 mol%). The product from the dehydrochlorination of CH_3CCl_3, 1,1-dichloroethene is also present, although the quantities are rather small *ca* 0.5 mol%. This, however, is consistent with further build-up of organic oligomeric material on the surface and with the idea of a "turnover" of organic layer material, where incoming halocarbons displace organic material already present on the surface. It is also consistent with the postulated role of the $CH_2=CCl_2$ in the hydrofluorination reactions,where $CH_2=CCl_2$ is fluorinated by surface fluorine species.

Table.6.1. G.C. Analysis of Volatile Material From HF/CH_3CCl_3 (1mmol:3mmol) Catalytic Fluorination Reaction.

Run No.	CH_3CCl_3	CH_2CCl_2	CH_3CCl_2F mol%	CH_3CClF_2	CH_3CF_3
SF_4 Alumina. 1.	88.8	0.1	7.5		2.0
2.	92.0	0.4	6.2	0.4	
3.	78.8	0.2	19.6		0.5
4.	84.2		4.4	11.4	
5.	95.0		4.8		0.1
BF_3 Alumina.	98.6	0.9	0.4		0.4
V.C. 1.	93.4	0.5	5.3	0.3	0.2
2.	81.9	2.7	14.3	0.6	
3.	97.5	0.4	2.1		
4.	95.0	1.5	3.5		
5.	97.3	0.8	1.7	0.1	

Probably the most important product is CH_3CCl_2F, which is present in substantial quantities on both γ-alumina (up to 19.6 mol%) and volcano chromia (up to 14.3 mol%). This is significant as it demonstrates that the catalytic hydrofluorination reactions, which are known to occur on conditioned γ-alumina also occur on conditioned volcano chromia. It also appears that volcano chromia is an effective catalyst, although not quite as good as γ-alumina for this reaction. Both catalysts display a wide range of values for the quantity of CH_3CCl_2F produced: γ-alumina 4.4 - 19.6 mol% and volcano chromia 1.7 - 14.3 mol%. In addition to the production of CH_3CCl_2F, other fluorinated products were detected although generally in trace amounts. This indicates that further fluorination reactions can also occur on both catalysts.

A single catalytic fluorination reaction of CH_3CCl_3 with HF at room temperature with a conditioned BF_3 fluorinated γ-alumina indicated that very little hydrofluorination took place. This is consistent with the work in Section 3.3.7 which indicated that very little organic material was laid down on this surface in the conditioning reaction and that the halogen exchange reactions occurring in the conditioning step were less substantial than for SF_4 fluorinated γ-alumina (Section 3.3.4).

6.3.2. EXTRACTION AND ANALYSIS OF ORGANIC LAYER MATERIAL FROM THE 1,1,1-TRICHLOROETHANE CONDITIONING OF SF_4 FLUORINATED γ-ALUMINA AND VOLCANO CHROMIA SAMPLES.

Most emphasis in this work was directed to the extraction and characterisation of organic material from conditioned SF_4 γ-alumina (159). Initially a Soxhlet extraction technique was used. Using this method, however, the catalyst was exposed to the atmosphere before extraction proceeded to any extent. It is known that these materials are hygroscopic and so exposure to the atmosphere probably resulted in a rapid hydrolysis of the organic layer material. This method was used to extract the organic layer material from a γ-alumina catalyst (Sample A), fluorinated with SF_4 and conditioned under flow conditions with CH_3CCl_3 and then used in the CH_3CCl_3/HF catalytic fluorination reaction under flow conditions for *ca.*50h. ^{1}H,^{13}C and ^{19}F N.M.R. spectra of the extracted material revealed various aspects of the nature of the organic layer (Table.6.2). Most importantly, ^{19}F N.M.R. spectroscopy indicated the presence of fluorine in the organic layer but suggested that the amount was fairly low. This may have come from SF_4, in the preparation of the organic layer, or it may have been incorporated from HF, in the catalytic reaction. A peak at -227.5ppm has been assigned to a $-CFH_2$ group and one at -187.5ppm, tentatively assigned to trans CHF=CHF by analogy with literature (161). The signal at -150ppm is in agreement with the reported value for the HF_2^- anion (162). $^{13}C\{^1H\}$ N.M.R. spectra indicated the presence of primary, secondary and tertiary carbons, with a collection of peaks in the region -71.5 to -82.5ppm attributed to -CH-O- and $-CH_2-O-$ groups. The presence of $-CH_2$ groups is indicated by peaks between -23.7 and -29.7ppm. (163). An attempt to assign ^1H N.M.R. chemical shifts by analogy with literature (164) is made in Table 6.2.

Table.6.2(i). Assignment Of ^1H NMR Chemical Shifts For Organic Layer Extracts.

Shift (ppm).	Assignment.
0.96	CH_3-R
1.26	CH_3-C-OR
1.47	$R-CH_2-R$
3.49	$R-CH_2-OR$
3.63	$R-CH_2-OH$
4.44	$R-CH_2-OH$ (or F)

The most revealing information came from GCMS, which revealed the presence of at least thirteen constituents in the organic layer material. Two series of constituents have been established from M.S. data, one indicating that the "building blocks" are acyclic aliphatic hydrocarbons, starting with $C_2H_5^+$ (m/z 29) and the second series being typical of primary alcohols and ethers with the base peak m/z 31 corresponding to the oxonium ion $[CH_2=OH]^+$ Both series were found to increase by increments of 14, corresponding to a CH_2 group. An important feature of this analysis was the absence of chlorine, which would have been indicated by the characteristic isotopic abundance pattern, 2 peaks separated by two units (corresponding to ^{35}Cl and ^{37}Cl) with a ratio of 3:1. Due to the complexity of the spectra obtained it has not been possible to characterise completely the constituents of the organic layer.

The results from Sample A, which was a working catalyst, was compared to those from organic material prepared under identical conditions but which had not been used for the catalytic fluorination reaction, Sample B. This material was extracted under vacuum, without exposing it to atmospheric moisture.

The most important outcome from ^{19}F N.M.R. spectroscopy was that this sample contained fluorine, as in Sample A. Therefore, one source of fluorine in the organic layer must be from SF_4 in the catalyst preparation procedure. The ^{19}F N.M.R. data from Samples A and B are similar although the spectra from Sample B have several additional peaks at *ca* -60ppm which have been tentatively attributed to either $-CClF_2$ or $-CCl_2F$ groups (161), indicating the presence of chlorine in this material which was apparently absent from Sample A. This could be a direct reflection of the fact that this sample had not been exposed to atmosphere and had therefore not lost chlorine by hydrolysis. The ^1H and ^{13}C N.M.R. data for organic material extracted from Sample A and B were very similar.

Table.6.2(ii). ^{19}F NMR Chemical Shift Data For Organic Layer Extracts.

Sample A.	Sample B.
-227.5	-228.5
-187.5	
-175.7	
-151.1	
-150.0	-150.8
-145.5	
-129.7	-60.2
-129.0	-60.1
-127.8	-59.6
-109.5	-55.9
-108.2	-55.4
-107.4	-55.2
-106.7	-34.8

Analysis of the extracted material by GCMS indicated a very complex material, therefore it was not possible to identify all of the constituents present. However, some of the species identified include the C_2 species, $CH_2=CCl_2$, $CHCl=CCl_2$ and $CHCl_2CH_2Cl$, the C_4 species, $C_4H_2Cl_4$ and $C_4H_3Cl_5$, cyclo-$C_6H_7Cl_5$ and cyclo-$C_8H_8Cl_6$. Although it was not possible to characterize fully the organic material, it seems clear that the building blocks are C_2 units, as expected from CH_3CCl_3 starting material.

Extraction of organic material from conditioned volcano chromia which had not been used for the CH_3CCl_3/HF catalytic fluorination reaction was also performed under vacuum. Analysis of the extracted material by G.C. indicated the presence of CH_2CCl_2, CH_3CCl_2F and also trace quantities of other fluorinated products. M.S. facilities were not available when this extraction was performed. Comparisons between the N.M.R. results from the organic layer extract from γ-alumina and volcano chromia revealed great similarities. ^{19}F N.M.R. revealed several peaks around -60ppm, assigned as in Sample B, above, to $-CClF_2$ or $-CCl_2F$ groups and -227.5ppm assigned to $-CH_2F$ group. The ^1H and ^{13}C N.M.R. data for both γ-alumina and volcano chromia were very similar. Although the examination of organic material extracted from volcano chromia was not as extensive as for γ-alumina, it was established that organic material could be extracted and that the material on volcano chromia appeared to be similar to that for γ-alumina, with both fluorine and chlorine present. This indicated that there is an organic layer present on volcano chromia which is probably analogous to that on γ-alumina.

6.4. DISCUSSION.

The objective of this section of work was to establish further the similarities between γ-alumina and volcano chromia: to determine whether the organic material which is laid down on the volcano chromia is analogous to that on γ-alumina and is catalytically active in the room temperature CH_3CCl_3/HF fluorination reaction.

6.4.1. Catalytic Activity of the SUPPORTED Organic Layer Material.

The room temperature catalytic fluorination reaction of CH_3CCl_3 with HF in the presence of organic layer material supported on halogenated γ-alumina has been studied quite extensively. As described previously, pretreatment of calcined γ-alumina with CCl_4, CCl_2O or SF_4 results in surfaces capable of dehydrochlorinating CH_3CCl_3, producing CH_2CCl_2 and HCl, followed by formation of a purple oligomeric organic layer (70). At room temperature this layer is capable of catalysing the reaction of CH_3CCl_3 with HF, giving a mixture of fluorinated products. These supported organic layer catalysts can be used for F-for -Cl exchange reactions of other C_2 and C_3 compounds. The objective of this section of work was to establish if the room temperature catalytic reaction is unique to γ-alumina or if it is a more general feature, characteristic of the halocarbon conditioning, SF_4 fluorination pretreatment process and can be extended to chromia.

Clearly the G.C. data in Table 6.1., the products of the HF/CH_3CCl_3 catalytic fluorination reactions, indicate that γ-alumina and volcano chromia behave similarly. In all of the samples, the main constituent is unchanged

CH_3CCl_3 (80-90 mol%). The dehydrochlorination product, CH_2CCl_2, is detected, but only in small quantities (*ca* 0.5 mol%). The most abundant fluorinated product is, as expected, CH_3CCl_2F although others, CH_3CClF_2 and CH_3CF_3 are detected, generally in trace amounts. This information is consistent with previous studies into the catalytic fluorination reaction on organic layer catalysts. Radiotracer studies (160) have indicated that in these reactions the organic substrate is incorporated into the organic layer, where it is thought to undergo dehydrochlorination and fluorination by surface fluorine species. The G.C. data presented here are consistent with this reaction route. The fact that CH_2CCl_2 is detected only in rather small quantities is consistent with it being incorporated into the organic layer and undergoing hydrofluorination. The catalyst based on γ-alumina appears to produce more CH_3CCl_2F and the other fluorinated products than the one based on volcano chromia although the differences are small. This may be a reflection of the fact that volcano chromia has a smaller surface area than γ-alumina. It also concurs with the slightly lower quantity of labile fluorine available on volcano chromia than γ-alumina as indicated by the [^{18}F]-fluorine exchange reactions in Chapter 4. From the similarities in the products from the two solids it is clear that both are good supports for the organic layer material. It is known (11) that γ-alumina alone is not capable of catalysing halogen exchange reactions at room temperature and from this work, it is clear that the character of the support does not greatly affect the catalytic activity of the surface Therefore, the role of the organic layer material in catalysing the halogen exchange reactions is highlighted.

Clearly therefore, from the results in this section of work, both γ-alumina and volcano chromia are capable of supporting organic layers that are catalytically active for the room temperature hydrofluorination reaction of HF and CH_3CCl_3. This is despite the fact that there is no visible purple organic layer laid-down on the volcano chromia. The catalytic activity of the material coupled with other evidence discussed previously, for example the weight changes determined on conditioning the fluorinated material with CH_3CCl_3 (Section 3.3.7) and the [^{36}Cl]-CH_3CCl_3 treatment leading to a build up of [^{36}Cl]-chlorine activity on the surface (Section 5.3.2), indicate that there is an organic layer present on volcano chromia, similar to that on γ-alumina. However, further more extensive work on the catalytic reaction is required to determine if chromia is as effective as γ-alumina for the catalytic reaction under flow conditions and over longer time scales similar to the conditions required for industrial use.

6.4.2. Extraction Of Organic Layer Material.

An important factor in determining reaction routes and mechanisms for catalytic halogen exchange reactions is the nature of the organic layer material. Most of the information about organic layer material supported on γ-alumina comes from GCMS data, although NMR data also provides some useful information. It is clear that the organic layer material is very complex. It seems improbable that the exact nature can be determined, due to the complexity of spectra obtained. However several important features have been established. The "building blocks" of the organic layer material are -[CH_2-CCl_2]- units, which is expected as the starting material is CH_3CCl_3. The CH_3CCl_3 undergoes dehydrochlorination producing $CH_2=CCl_2$, which undergoes further reaction to give an organic layer based on C_2 units. The probable route for the build up of the organic layer is

$CH_2=CCl_2 \rightarrow$ C_4 Species $\rightarrow$ C_6 Species $\rightarrow$ C_8 Species $\rightarrow$ etc.

Comparisons can be made with the organic material derived from the liquid-phase fluorination of 1,1,1-trichloroethane with $SbCl_5.4HF$ (18-20). The 1,1-dichloroethene formed in the reaction oligomerises according to the reaction:

$$nCH_2=CCl_2 \overset{H^+}{\rightarrow} CH_3CCl_2(CH_2CCl_2)_{n-2}CH_2CCl_2$$

Hydrolysis of the purple organic residue revealed chloro-aromatic compounds, derived from the trimer and the pentamer of CH_2CCl_2. As in the present work, the building-blocks for the organic layer material are C_2 units from the CH_3CCl_3 starting material.

It has been established that the organic layer contains fluorine, although the quantity is rather small. This is present both in freshly prepared material and also in material that had been used extensively for the HF/CH_3CCl_3 catalytic fluorination process. The fact that fluorine is present in the organic material which had not been used in the catalytic reaction determines that the fluorine probably comes from the SF_4 prefluorination step. This is consistent with the idea that CH_3CCl_3 is adsorbed onto the surface undergoes dehydrochlorination and reacts with surface fluorine species. The other important conclusion is that, since fluorine is still detected in the organic material after extensive use in catalytic fluorination reactions, the fluorine in the organic layer must be replenished by the HF, presumably via the sequence

HF → Fluorinated γ-alumina → Organic Layer Material.

From the GCMS data, the presence of chlorine in the organic layer is also indicated, but only when the material had not been exposed to the atmosphere. Previous work (160) to investigate the effect of trace water, including $^1H/^2H$ isotopic labelling, indicated a degree of hydrolytic instability. The loss of chlorine, on exposure to the atmosphere is explained as due to rapid hydrolysis of the organic layer which also results in the hydroxylated constituents indicated in the N.M.R. data presented in Table 6.2.

Previous investigations of the supported organic layer catalysts (160) have made use of solid state MAS NMR. This provided good evidence for the presence of CH_3- or CH_2- groups indicating aliphatic saturated components and also $-CH_2X$, CH_3X ($X=F$ or Cl) conjugated components. The spectra of layers derived from CH_3CCl_3, CH_2CCl_2 and $CH_3CCl_2CH_3$ are broadly similar.

The most important result of the brief study of the organic material supported on volcano chromia is the fact that there is organic material present. This indicates the presence of a supported organic layer which, in conjunction with other information in this section, is catalytically active for fluorine exchange reactions. The organic layer material on volcano chromia, like that on γ-alumina, contains fluorine and chlorine. As this material had not been used in the HF/CH_3CCl_3 catalytic reaction, the fluorine in the organic layer must come from the SF_4 pretreatment step.

Thus, the conclusion that can be drawn from the study of the catalytic fluorination reactions and the extraction of the organic layer material is that SF_4 fluorination followed by conditioning with CH_3CCl_3 of both γ-alumina and volcano chromia results in a supported organic layer catalyst which is active for room temperature halogen exchange reactions. This organic layer material contains both chlorine, which is easily lost by hydrolysis on exposure to atmosphere, and fluorine and is based on C_2 units, although the exact nature of the material is too complex to be fully determined.

DISCUSSION AND CONCLUSIONS.

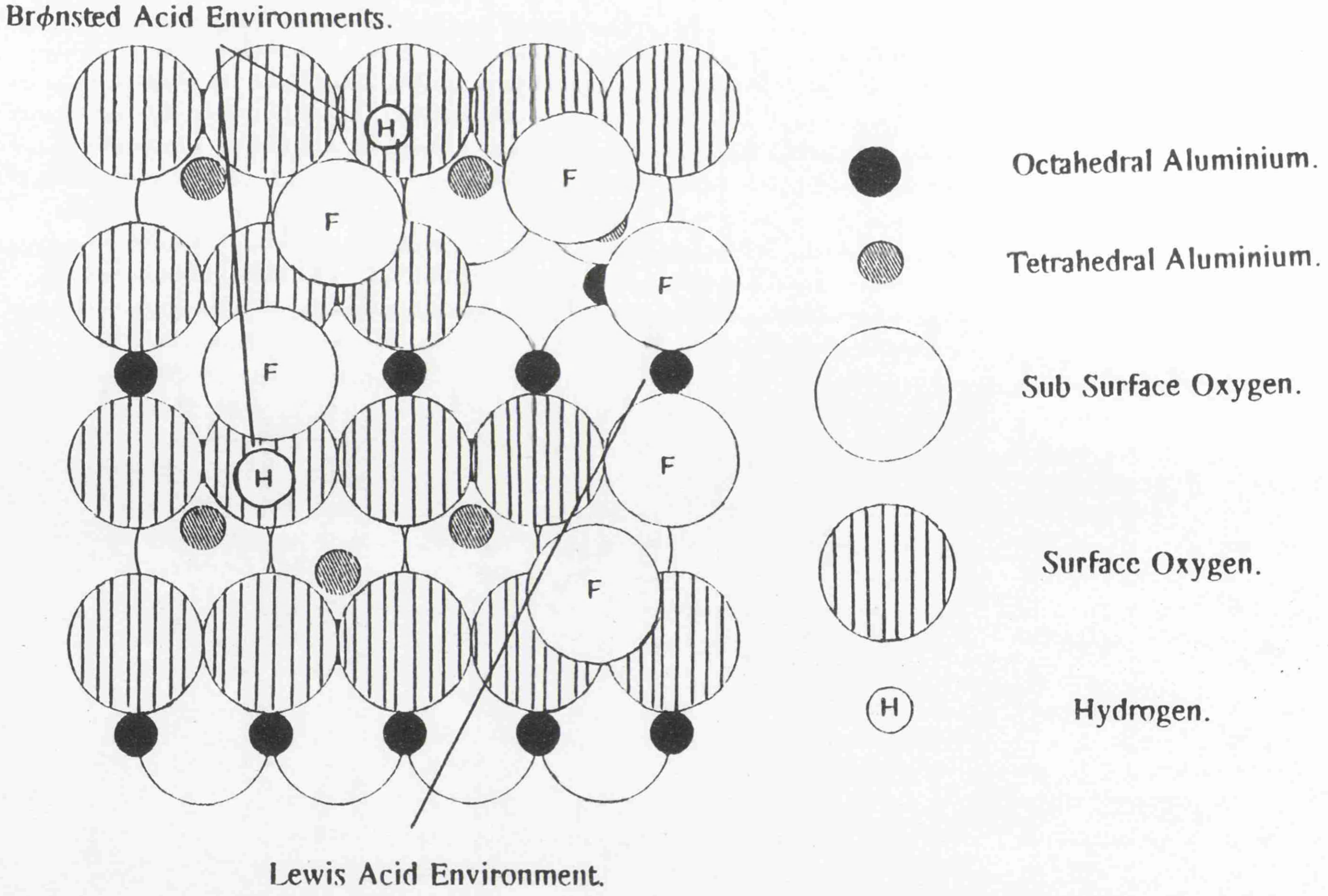
7.1.DISCUSSION.

There were several aspects of oxide supported organic layer catalysts under investigation in this work. Previous work (98) has established that CH_3CCl_3 treatment of SF_4 γ-alumina results in a surface capable of catalysing the fluorination of CH_3CCl_3 with HF at room temperature. To understand fully the catalytic reactions occurring, it is essential to examine the catalyst preparation process, the SF_4 fluorination step and the conditioning reaction with CH_3CCl_3.

7.1.1.FLUORINATION PROCESS.

Fluorination of γ-alumina with SF_4 has been demonstrated to enhance the Lewis acidity of the surface. This has been shown by its ability to dehydrochlorinate 1,1,1-trichloroethane. Models (Figs.1.5 and 1.6) have been developed to explain the structure of the Lewis and Brϕnsted acid sites on γ-alumina chlorinated with CCl_4 or $OCCl_2$. It had been assumed that the acid sites on SF_4 fluorinated γ-alumina would be analogous to those on chlorinated γ-alumina (Fig.7.1). If the models proposed for chlorinated γ-alumina are extended to fluorinated γ-alumina, there will be Al-F-Al triply bridging fluorine, associated with Lewis acid sites and Al-F terminal fluorine species associated with Brϕnsted acid sites. Exchange and uptake experiments with [^{18}F]-fluorine (Chapter 4.) have established that, like chlorinated γ-alumina, a portion of the surface halogen species is labile to exchange with incoming halogen containing species. By analogy with chlorinated γ-alumina it could be

Fig.7.1. Possible Brϕnsted And Lewis Acid Sites On SF_4 Fluorinated γ-Alumina.



argued that the fluorine that does not undergo exchange will be associated with Lewis acid sites. However, from the results of the [^{18}F]-fluorine exchange reactions, the amount of labile fluorine present on the surface does not appear to be uniform. There is a wide range of exchange values (0.3 - 0.9). Therefore, it appears that, unlike the situation in chlorinated γ-alumina, there is no well defined quantity of labile fluorine. Fluorination with SF_4 has been demonstrated to result in the uptake of more fluorine than can be accommodated on the surface alone, therefore there must be fluorine incorporated into the bulk, although the nature of this fluorine has not been established. However there is no evidence of structural change, for example there is no evidence for AlF_3. This reaction can be compared with the situation with HF treated chromia, where the catalyst is slowly deactivated by reaction with HF leading to the formation of CrF_3. The relatively large exchange factors observed in the present work indicate that exchange is unlikely to be limited to the surface. Thus, in addition to labile surface fluorine associated with Brφnsted sites, the "bulk" fluorine must also be labile. In order to speculate about the nature of this "bulk" fluorine, the fluorination process must be examined. As discussed in Chapters 3 and 4, fluorination of γ-alumina and chromias with SF_4 should produce HF, although this is not detected in the vapour phase. Therefore this appears to be a likely source of the "bulk" fluorine. The HF may be present as oligomers or associatively or dissociatively incorporated into the oxides. The presence of surface oligomers seems unlikely in view of the fact that conditioning does not affect the lability.

Dissociatively incorporated HF, although favoured from comparisons with previous studies (24-26,160), where HF dissociatively adsorbs at the surface, appears unlikely as this would result in the presence of H^+ in addition to F^- species. Therefore it seems possible that the "pool" of labile fluorine consists of HF, associatively incorporated in the bulk of the oxide. The lability of the fluorine species is not affected by the conditioning process, with the laydown of organic material. Thus, the organic layer does not block the fluorine exchange process, but instead fluorine is apparently able to diffuse through the organic material from the inorganic surface and/or is part of the layer. The complex nature of this diffusion process may also account in part for the range of exchange factors determined.

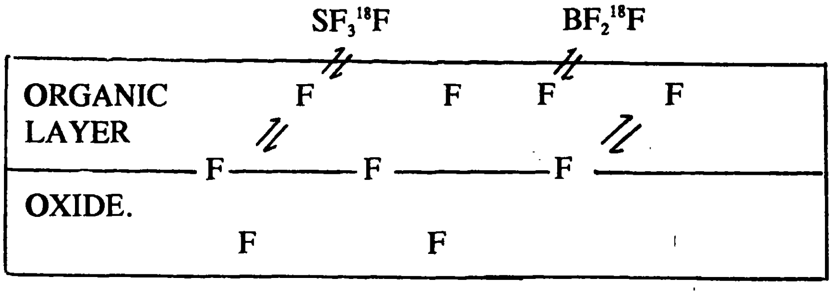


Fig.7.2. Model For Uptake And Exchange Of [^{18}F]-Fluorine On CH_3CCl_3 Conditioned,SF_4 Fluorinated γ-Alumina.

The fact that the conditioning process does not affect the lability of fluorine, emphasises the important role of the organic layer in the further catalytic activity of the material. The lability of the fluorine within the layer suggests that this is probably the site for the catalytic reaction, a "holding area" for organic material in conjunction with available fluorine to undergo halogenation reactions.

Chlorination of γ-alumina results only in surface coverage (69). Due to the greater size of chlorine compared with fluorine, it could not be incorporated into the bulk without disruption to the γ-alumina structure. There is some recent evidence that this is also true for bromination of γ-alumina (165). The fact that in chlorinated γ-alumina there are only surface chlorine species present is significant in determining the catalytic activity of the organic layer, i.e. less halogen is available for exchange. In contrast, the "pool" of fluorine on SF_4 γ-alumina can be replenished by the reagent HF during the catalytic reaction. This aspect will be discussed more fully later. In summary, the hypothesis is that the surface acid sites on SF_4 fluorinated γ-alumina are similar to those on CCl_4 or $OCCl_2$ chlorinated γ-alumina, but there is addition "bulk" fluorine, possibly associatively incorporated HF, creating a "pool" of labile fluorine, enabling the catalytic activity to be rationalised.

It has been established in this work that fluorine on the solid is labile with respect to $[^{18}F]$-fluorine exchange with $SF_3{}^{18}F$ and $BF_2{}^{18}F$. Previous work (160) indicated that this fluorine is also labile with respect to $H^{18}F$. As discussed in Chapter 4, SF_4 is able to behave as a Lewis acid or base. This is in contrast with the behaviour of BF_3 which acts as a Lewis acid. HF is able to act as a Brφnsted acid and also as a Lewis acid or base. Based on models developed for HCl exchange with chlorinated γ-alumina, it is considered that these reactions involve Brφnsted sites, since the fluorine associated with such sites should be labile. It is not possible to establish definitive mechanisms for

[^{18}F]-fluorine exchange reactions, however from the experimental evidence presented it is possible to speculate on the mechanisms involved. It is probable that the mechanism will involve two steps: adsorption of the reagent on the surface followed by exchange with surface fluorine species. The surface fluorine species are believed to undergo exchange with bulk fluorine species. SF_4 and HF could adsorb at a Lewis acid or a Lewis base site on the surface. However, BF_3 will adsorb only at Lewis base sites. The similarities in the exchange data determined indicate that the reactions occurring between the fluorinated surface and SF_4 are the same as those occurring with BF_3 and HF. Therefore, it seems probable that the adsorption site will be common to all three reagents, i.e. a site associated with Lewis basicity. Such a reaction would result in SF_4- - ·F or BF_3- - ·F species which could then undergo exchange with labile surface fluorine. Further work is required to establish a definitive mechanism.

7.1.2.CONDITIONING PROCESS.

In the present work, studies of the conditioning reaction indicate that CH_3CCl_3 and $CH_2=CCl_2$ behave similarly. The model developed for the dehydrochlorination process on CCl_4 chlorinated γ-alumina (166), involving reactions at Lewis acid sites, may be extended to SF_4 fluorinated γ-alumina (Fig.7.3).

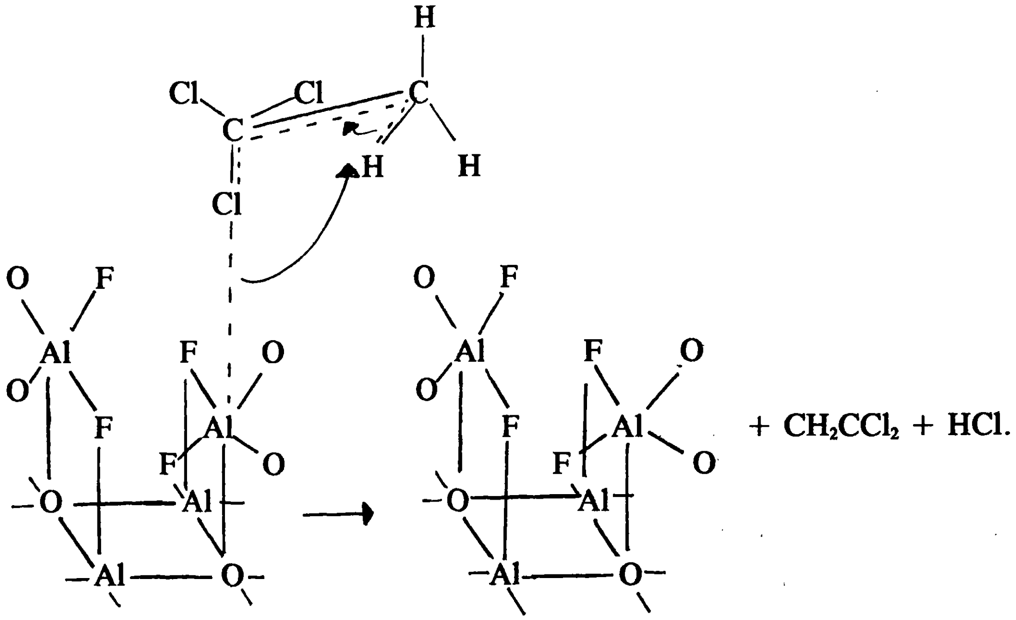


Fig.7.3. Dehydrochlorination Of 1,1,1-Trichloroethane On SF_4 γ-Alumina.

The product of dehydrochlorination, $CH_2{=}CCl_2$, is then able to undergo several possible reactions for example it may be retained by the surface and incorporated into the oligomeric organic material, it may be fluorinated by surface fluorine species forming species such as CH_3CCl_2F or it may undergo hydrochlorination, forming CH_3CCl_3. These reactions have been demonstrated by following the conditioning reaction of SF_4 fluorinated materials, starting with both CH_3CCl_3 and $CH_2{=}CCl_2$, by *in situ* I.R.analysis (Sections 3.3.8 and 3.3.9). These studies indicated that there was no delay as the organic layer was built up before hydrochlorinated and hydrofluorinated products appeared in the vapour phase. Thus, these reactions probably take place at the inorganic interface.

The role of the organic layer material can also be considered with respect to the behaviour of $H^{36}Cl$ as described in Section 5.3.1. $H^{36}Cl$ is adsorbed on fluorinated surfaces and the conditioning process had little effect on this procedure. This suggests that $H^{36}Cl$ is present probably both on the surface of the organic layer and at the interface between the organic and inorganic materials, emphasising the important role of the organic layer in the catalytic halogen exchange reactions.

The *in situ* I.R. study of the interaction of HCl with conditioned γ-alumina demonstrates that CH_3CCl_3 and CH_3CCl_2F are removed from the conditioned surfaces, therefore showing not only the occurrence of displacement reactions, with adsorption of HCl displacing organic material from the bulk, but also hydrochlorination and hydrofluorination reactions. It is suggested that hydrofluorination reactions involve both Lewis and Brφnsted acid sites, with the latter associated with labile fluorine species.

Examination of the conditioning of SF_4 fluorinated materials with [^{36}Cl]-CH_3CCl_3 indicates a build-up of [^{36}Cl]-chlorine activity on the surface of SF_4 fluorinated γ-alumina, consistent with a laydown of chlorine containing organic layer material. Similar treatment of CH_3CCl_3 conditioned, SF_4 fluorinated materials with [^{36}Cl]-CH_3CCl_3 also resulted in the laydown of [^{36}Cl]-chlorine containing material on the surface. The results in Section 5.3.2 indicate that the percentage of [^{36}Cl]-chlorine present in the gas phase at the end of the reaction on conditioned material is similar to that on fluorinated surfaces. In view of the rather small surface count rates observed, [^{36}Cl]-chlorine containing material is not only adsorbed on the surface of the conditioned layer, but is also incorporated into the "bulk" of the organic material.

Previous studies flowing [^{36}Cl]-CH_3CCl_3 over CH_3CCl_3, SF_4 γ-alumina indicated that there is a "turnover" of surface organic layer material, with surface material being displaced with incoming CH_3CCl_3. Analysis by G.C. (Section 3.3.5) of the volatile material from CH_3CCl_3 treatment of CH_3CCl_3 conditioned, SF_4 fluorinated solids indicate that some 1,1-dichloroethene and 1,1-dichloro,1-fluoroethane are produced in this reaction. The majority of the volatile material after this reaction is 1,1,1-trichloroethane. This may be unreacted starting material or material that had been displaced from the organic layer.

Extraction of the organic layer material provides substantial evidence of the character of the material. As expected, the organic material is built up from C_2 units derived from CH_3CCl_3. The organic layer material contains both fluorine and chlorine. It has been established that the fluorine present in the organic material comes initially from the SF_4 fluorination process. It is suggested that, as fluorine is removed from the solid by halogen exchange in the catalytic reaction, it is replenished by the HF.

Considering the evidence presented in this work in conjunction with that from previous studies, a model has been developed to demonstrate the reactions occurring in the catalytic halogenation process. This model is presented in Fig.7.4:

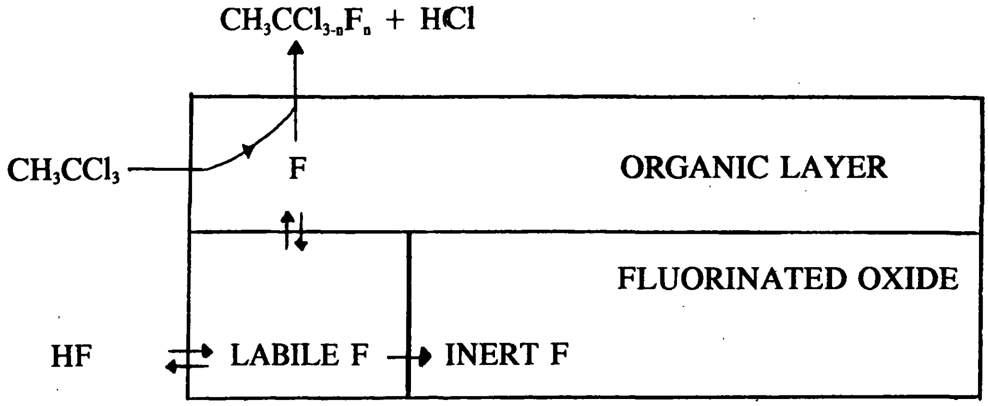


Fig.7.4. Model For Catalytic Halogenation Over CH_3CCl_3 Conditioned, SF_4 Fluorinated γ-Alumina.

From the [^{18}F]-fluorine exchange reactions studied in Chapter 4 it is clear that this involves both bulk and surface fluorine species, with incoming HF replenishing the "pool" of fluorine available for the hydrofluorination reactions. The organic layer acts as a "sink", incorporating the incoming CH_3CCl_3, as demonstrated in Section 5.3.2 where treatment of conditioned γ-alumina with [^{36}Cl]-CH_3CCl_3 resulted in incorporation of [^{36}Cl]-chlorine on the surface and also bulk of organic layer. The CH_3CCl_3 substrate undergoes dehydrochlorination on the halogenated surface of γ-alumina. The dehydrochlorinated product is fluorinated by surface fluorine, producing a mixture of chlorofluorohydrocarbons, $CH_3CCl_{3-n}F_n$.

A brief examination of the fluorination of γ-alumina with BF_3 indicated that although this process was not as effective as fluorination with SF_4, it did create Lewis acid sites. This was demonstrated by the ability of BF_3 γ-alumina to dehydrochlorinate CH_3CCl_3. Previous studies have suggested that only

Brϕnsted acid sites are present on BF_3 γ-alumina (81). However, the results presented here indicate Lewis acidity, although it is suggested that the strength and quantity of such sites are not as great as on SF_4 γ-alumina. In the fluorination reaction using SF_4, it has been suggested that the SO_2 produced initially protects the surface from the interaction of HF, which deactivates the surface. The SO_2 finally desorbs from the surface. In the BF_3 fluorination process it appears that the BOF_2^- formed remain on the surface, thereby limiting the fluorine available to take part in halogenation reactions.

7.1.3.COMPARISONS BETWEEN THE REACTIONS OF γ-ALUMINA, CHROMIA AND VOLCANO CHROMIA.

One of the main objectives of this work involved comparison between γ-alumina, chromia and volcano chromia samples treated under identical conditions. Comparisons were made between the materials in the SF_4 fluorination process, the CH_3CCl_3 conditioning of the fluorinated material and also in the activity of fluorinated plus conditioned material in the catalytic fluorination reactions of CH_3CCl_3 with HF.

Comparisons of the SF_4 fluorination of γ-alumina and chromias indicated that this process occurs on both solids. [^{18}F]-Fluorine exchange studies demonstrated that there is a quantity of labile fluorine on both surfaces. In both cases there is a wide range of exchange factors determined. It is therefore suggested that, as discussed previously for SF_4 γ-alumina, there is a "pool" of available fluorine on the chromia samples that can be involved in halogen exchange reactions.

Studies of the CH_3CCl_3 conditioning of SF_4 γ-alumina and chromias also indicate similar reactions. Conditioning SF_4 chromia and volcano chromia results in the production of the dehydrochlorination product, $CH_2=CCl_2$ and the hydrofluorination product, CH_3CCl_2F and also traces of other fluorinated products. Although there is no visible evidence of the laydown of organic material on the surface of the chromia samples, the increase in the mass observed (Section 3.3.7.), the volatile materials produced on conditioning the fluorinated materials (Section 3.3.4) and the extraction of organic material from the conditioned volcano chromia (Section 6.3.2), indicates that there is organic material laid down. The *in situ* I.R. analysis of the volatile material from the conditioning reaction indicate that the quantities of the various products formed is dependent on the support material used. From these studies it appears that the hydrofluorination occurs most readily with volcano chromia support. This is also suggested by the G.C. analysis of the volatiles from the conditioning process (Section 3.3.4). Studies of the conditioning reaction under flow conditions indicated that volcano chromia reacts faster than γ-alumina initially, however the hydrofluorination reaction on γ-alumina continued over a much longer period of time than that on volcano chromia. Therefore it appears that although the volcano chromia reacts faster initially, γ-alumina is more capable of sustaining the hydrofluorination reaction over longer time scales. This may be a reflection on the fact that the fluorine uptake on calcined volcano chromia is smaller than on γ-alumina possibly due to differences in surface areas.

Examination of the room temperature catalytic fluorination reactions over conditioned γ-alumina and volcano chromia indicates similarities in the behaviour of the two catalysts. In both cases substantial quantities of the fluorinated product, CH_3CCl_2F, is produced. Therefore it is clear that, despite the fact that there is no visible organic material laid down on the surface of volcano chromia, the SF_4 fluorination, CH_3CCl_3 conditioning process creates a surface that is capable of catalysing room temperature hydrofluorination. This reaction is not unique to γ-alumina but is a feature of the pretreatment process. It is suggested therefore, that the preparation of oxide supported organic layers, capable of catalysing the room temperature hydrofluorination of chlorocarbons with HF, may be extended to other oxides, providing that fluorination of the surface with SF_4 creates strong Lewis acid sites that can dehydrochlorinate CH_3CCl_3 resulting in the laydown of the organic layer material. The activity of such oxide supported organic layers in the catalytic halogen exchange reactions appears to be dependent to some degree on the surface area of the oxide support: γ-alumina, which has a greater surface area than volcano chromia, takes up more fluorine and is able to sustain the catalytic reaction over a longer time.

7.2.CONCLUSIONS.

This work has established that fluorination of γ-alumina with SF_4 results in the formation of both surface and bulk fluorine species. A very large proportion of this fluorine is labile and readily undergoes exchange with various reagents. The character of the surface fluorine species is believed to be analogous to the surface species on chlorinated γ-alumina: Al-F terminal fluorine species, associated with Brφnsted acid sites and readily exchangeable and Al-F-Al bridging fluorine species, associated with Lewis acid sites and inert to exchange reactions. In addition to these surface species, bulk fluorine species, possibly associatively incorporated HF, are also present and labile to exchange. The conditioning of SF_4 fluorinated material with CH_3CCl_3 results in an oligomeric organic layer and production of fluorinated derivatives of CH_3CCl_3. The presence of this layer does not affect the lability of the fluorine. The layer material can interact with HCl and also with CH_3CCl_3. It is suggested that this occurs both at the organic layer surface and at the organic/inorganic interface. The supported organic layer is catalytically active at room temperature for fluorination reactions of CH_3CCl_3 with HF. This reaction is thought to occur within the organic layer, with incoming CH_3CCl_3 incorporated into the organic layer and the HF replenishing the "pool" of fluorine available for reaction.

Comparisons between the behaviour of γ-alumina and chromia in these reactions indicate that both solid behave similarly with respect to the fluorination and conditioning processes and are effective supports for the organic layer catalysts. The character of the support does appear to effect the distribution of products, but it suggested that this is an effect of differences in surface area rather than fundamental differences in the reactions occurring.

REFERENCES.

1. T.Midgely and A.L.Henne, U.S.Patent 1,930,129.

   A.L.Henne and E.C.Ladd, J.Am.Chem.Soc. 58 (1936) 402.
2. R.P.Wayne. Chemistry of the Atmospheres. Oxford Press. London. 1985. p154.
3. J.Lovelock, R.J.Maggs and R.J. Webb, Nature 214 (1973) 194.
4. M.J.Molina and F.S. Rowlands, Nature 249 (1974) 810.
5. R.P.Wayne. Chemistry of the Atmospheres. Oxford Press. London. 1985. p10.
6. L.C.Manzer, Catal.Today 13 (1992) 13.
7. R.E.Banks, J.Fluorine Chem. 33 (1986) 3.
8. M.Hudlicky. Chemistry of Organofluorine Compounds. 2nd Edn. Prentice Hall Organic Chemistry Series. New York. 1992.
9. K.C.Waugh, J.Chromatog. 155 (1978) 83.
10. E.Kemnitz,D.Hass, W.Metzgen, A.Kohne, M.Noak and J.Janchen, Z.Phys.Chem. 271 (1990) 515.
11. T.H.Ballinger and J.T.Yates Jr., J.Phys.Chem. 96 (1992) 1417.
12. J.C. Stakebake, J.Colloid Interface Sci. 113 (1986) 308.
13. M.D. Taylor and T.T.Cheung, J.Inorg.Nucl. Chem. 35 (1973) 3499.
14. L.Rowley, PhD Thesis, Glasgow University. 1987.
15. J.Kvicaka, O.Paleta and V.Dedek, J.Fluorine Chem. 43 (1989) 155.
16. L.Kolditz and S.Schultz, J.Fluorine Chem. 5 (1975) 141.

17. E.Santacesaria, M.DiSerio, G.Basile and S.Carra, J.Fluorine Chem. 44 (1989) 87.

18. M.Blanchard and S.Brunet, J.Mol.Catal. 62 (1990) L33.

19. S.Brunet, C.Batiot, J.Barrault and M.Blanchard, J.Fluorine Chem. 59 (1992) 33

20. S.Brunet, C.Batiot, J.Barrault, M.Blanchard and J.M.Coustard, J.Fluorine Chem. 63 (1993) 227.

21. M.Vecchio, G.Gropelli and J.Tatlow, J.Fluorine Chem. 4 (1974) 117.

22. L.Marangoli, C.Gervasutti and L.Conte, J.Fluorine Chem. 19 (1981/82) 21.

23. L.Marangoni, G.Rasia, C.Gervasutti and L.Colombo, Chim Ind. 64 (1982) 135.

    L.Marangoni, D.Carnello and R.Passerini, Chim Ind. 67 (1985) 467.

24. J.Kijowski, G.Webb and J.M.Winfield, J.Fluorine Chem. 27 (1985) 213.

25. J.Kijowski, G.Webb and J.M.Winfield, Appl. Catal. 27 (1986) 181.

26. L.Rowley, G.Webb and J.M.Winfield, Appl.Catal. 52 (1989) 69.

27. L.Rowley, J.Thomson, G.Webb, J.M.Winfield and A.McCulloch. Appl.Catal. 79 (1991) 89.

28. R.Burwell Jnr, G.L.Haller, K.C.Taylor and J.F.Read, Adv.Catal. 20 (1969) 1.

29. D.R.Coulson, P.W.J.G.Wijnen, J.J.Lerou and L.E.Manzer, J.Catal. 140 (1993) 103.

30. J.Kalman and L.Guczi, J.Catal. 47 (1977) 371.

31. S.R.Dyne, J.B.Butt and G.Haller, J.Catal. 25 (1972) 391.

32. L.Nondek, O.Mihajlova, A.Andreev A.Palazov, M.Krauss and D.Shopov, J.Catal. 40 (1975) 46.

33. I.Mochida and Y.Yoneda, J.Org.Chem 33 (1968) 2163.

34. S.R.Morrison, J.Catal. 47 (1977) 69.

35. N.E.Cross and H.F.Leach, J.Catal. 21 (1971) 239.

36. L.Kolditz, V.Nitzsche, G.Heller and R.Stosser, Z.Anorg.Allg.Chem. 476 (1981) 23.

37. A.Andreev, N.Neshev, D.Mihajlova, L.Prahov and D.Shopov, J.Catal. 27 (1972) 266.

38. J.Barrault, S.Brunet, B.Requieme and M.Blanchard, J.Chem.Soc.,Chem. Comm. (1993) 374.

39. A.Zecchina, F.Coluccia, E.Guglielminotti and G.Ghiotti, J.Phys.Chem. 75 (1971) 2774.

40. L.Kolditz, G.Kauschka and W.Schmidt, Z.Anorg.Allg.Chem. 434 (1977) 41.

41. H.Knozinger and P.Rotnasamy, Cat.Rev.Sci.Eng. 17 (1978) 31.

42. G.Weatherbee and C.H.Bartholomew, J.Catal. 87 (1984) 55.

43. B.C.Gates, J.R.Katzer and G.A.Schuit, "Chemistry of Catalytic Processes" McGraw-Hill Chem Eng.Series. New York. 1979.

44. C.S.John and M.S.Scurrell, Catalysis 1 (1977) 136.

45. U.Steinke, Z.Anorg.Allg.Chem.338 (1965) 78.

46. J.H.deBoer, J.M.H.Fortuin, B.C.Lippens and W.H.May, J.Catal 2 (1963) 1.
47. J.B.Peri, J.Phys.Chem.69 (1965) 231.
48. G.M.Schwab and H.Kral, Proc.3rd.Int.Congr.Catal.Amsterdam (1964) 433.
49. B.D.Flockhart, C.Naccacke, J.A.N.Scott and R.Pink, J.Chem.Soc., Chem.Comm (1965) 238.
50. N.D.Parkyns and B.C.Patterson, J.Chem.Soc.,Chem. Comm. (1965) 30.
51. F.A.Cotton and G.Wilkinson, "Adv Inorg Chem" J.Wiley and Sons. New York. 5th Edn. 1985. 211.
52. J.J.Kipling and D.B.Peakall, J.Chem.Soc. (1957) 834.
53. K.B.Day and V.J.Hill, J.Phys.Chem. 57 (1953) 946.
54. J.F.Brown, D.Clark and W.Elliot, J.Chem Soc. (1953) 84.
55. B.C.Lippens, PhD Thesis, Delft University of Technology. 1961.
56. L.L.Van Reijen, PhD Thesis, Technical University of Eindhoven. 1964.
57. S.Soled, J.Catal, 81 (1983) 252.
58. A.F.Wells, "Structural Inorganic Chemistry", 5th Edn.Oxford Press. London. 1984. 553.
59. H.Jagodszinski and H.Saalfield, Z.Kristallogr. 110 (1958) 197.
60. J.B.Peri, J.Phys.Chem. 69 (1965) 220.
61. D.S.McIver, H.H.Tobin and R.T.Barth, J.Catal. 2 (1963) 485.
62. J.C.Lavelley and M.Benaissa, "Adsorption And Catalysis On Oxide Surfaces" (M.Che and G.C.Bond Eds.) Elseiver, Amsterdam. 1985. 251.

63. J.N.Brφnsted, Rec.Trov.Chim.42 (1923) 718.

64. T.M.Lowry, Chem. Ind. 42 (1923) 43.

65. J.N.Brφnsted, Z.Phys.Chem. 108 (1924) 185.

66. J.N.Brφnsted and R.P.Bell, Proc.Roy.Soc.143A (1934) 377.

67. G.N.Lewis, Franklin Inst. 226 (1938) 293.

68. B.C.Gates, J.V.Boegel and G.A.Fuentes, J.Catal. 78 (1982) 436.

69. J.Thomson, G.Webb and J.M.Winfield, J.Mol.Catal. 67 (1991) 117.

70. J.Thomson, G.Webb and J.M.Winfield, J.Mol. Catal. 68 (1991) 347.

71. M.Tanaka and S.Ogasawara, J.Catal. 16 (1970) 157.

72. A.G.Goble and P.A.Lawrance, Proc.3rd Int.Congr.Amsterdam. (1964) 320.

73. J.Basset, F.Figueras, M.V.Mathieu and M.Prettre, J.Catal. 16 (1970) 53.

74. J.B.Perri, J.Phys.Chem. 69 (1965) 211.

75. K.Tanabe, M.Misono, Y.Ono and H.Hatton, "New Solid Acids and Bases and Their Catalytic Properties". Elsevier, Amsterdam. 1989.

76. H.Pines, J.Catal. 78 (1982) 1.

77. Y.F.Shen, S.L.Suib, M.Deeba and G.S.Koermer, J.Catal. 146 (1994) 483.

78. Y.Amenomiya, J.Catal. 46 (1977) 326.

79. J.N.Finch and A.Clark, J.Catal. 19 (1970) 292.

80. K.Matsuura, A.Suzuki and M.Itoh, J.Catal. 23 (1971) 395.

81. K.Matsuura, A.Suzuki and M.Itoh, J.Catal. 26 (1972) 127.

82. L.Gonzalez Tejuca, C.H.Rochester, A.Lopez Agudo and J.L.Gargia Fierro, J.Chem. Soc. Faraday Trans.I 79 (1983) 2543.

83. A.Corma, V.Fornes and E.Ortega, J.Catal. 92 (1985) 284.

84. J.Schlup and R.W.Vaughan, J.Catal 99 (1986) 304.

85. E.Kemnitz, D.Hass and B.Grimm, Z.Anorg.Allg.Chem. 589 (1990) 228.

86. A.Hess and E.Kemnitz, Appl.Catal. 82 (1992) 247.

87. A.Heß, E.Kemnitz, A Lippitz, W.E.S.Unger and D.H.Menz, J.Catal. 149 (1994) 449.

88. V.M.Allenger,C.Fairbridge, D.D.McLean and M.Ternan, J.Catal. 105 (1987) 71.

89. A.Corma, V.Fornes and F.Melo, Appl.Catal. 61 (1990) 175.

90. V.M.Allenger, D.D.McLean and M.Ternan, J.Catal. 131 (1991) 305.

91. D.G.McBeth, J.M.Winfield, B.Cooke and N.Winterton, J.Chem.Soc. Dalton Trans. (1990) 671.

92. J.P.Damon, B.Delmon and J.M.Bonnier, J.Chem.Soc.Faraday Trans. I. 73 (1977) 372.

93. M.Blanchard,D.Bechadergue and P.Canesson, Heterogeneous Catalysis and Fine Chemicals. 41 (1988) 257.

94. D.M.C.Kavanagh, T.A.Ryan and B.Mile, J.Fluorine Chem. 64 (1993) 167.

95. J.Kijowski,J.M.Winfield and G.Webb, J.Fluorine.Chem. 24 (1984) 133.

96. J.Thomson, G.Webb and J.M.Winfield, Eur. Pat. 0439338A1 1991.

97. J.Thomson, G.Webb and J.M.Winfield, J.Chem.Soc.Chem.Comm. (1991) 323.

98. J.Thomson, G.Webb, J.M.Winfield, D.Boniface, C.Shortman and N.Winterton, Appl.Catal A:General (1993) 97 67.

99. F.Fairbrother and J.F.Nixon, J.Chem. Soc. (1958) 3224.

100. C.R.C.Handbook Of Chemistry And Physics, 75th Edn. 11-37.

101. C.R.C.Handbook Of Chemistry And Physics, 75th Edn. 11-40.

102. K.W.Dixon, PhD Thesis, Glasgow University 1986

103. A.J.Vogel, "Textbook of Practical Inorg.Chem" Longmans, London. (1962) 179.

104. R.N.Maxson, Inorg. Synth. 1 (1939) 147.

105. G.Webb, Catal. Today 7 (1990) 139.

106. R.L.Burwell Jnr, A.B.Littlewood, M.Cardew, G.Pass and C.T.H.Stoddart, J.Amer.Chem.Soc. 82 (1960) 6273.

107. D.Klissurski, K.Hadjiivanov and A.Davydov, J.Catal. 111 (1988) 421.

108. D.J.Malcome-Lawes, "Introduction to Radiochemistry." Macmillan Press Ltd. London. (1979).

109. A.S.Al-Ammar, G.Webb, J.Chem.Soc. Faraday Trans.I. 74 (1978) 195.

110. G.A.Kolta, G.Webb and J.M.Winfield, Appl.Catal. 2 (1982) 257.

111. G.Friedlander, J.W.Kennedy, E.S.Macias and J.M.Miller, "Nuclear and Radiochemistry", J.Wiley, New York. (1981).

112. K.A.Brownlee, "Statistical Theory and Methodology in Science and Enginering" J.Wiley, New York. (1960).

113. C.A.Bennet and N.L.Franklin, "Statistical Analysis in Chemistry." J.Wiley, New York. (1954).

114. E.Breitnberger, "Scintillation Spectrometer Statistics. Progress in Nuclear Physics." Pergammon Press, London. (1955).

115. L.Kolditz, U.Calov, G.Kauschka and W.Schmidt, Z.Anorg.Allg.Chem. 434 (1977) 55.

116. M.Blanchard, L.Wendlinger and P.Canesson, Appl.Catal. 59 (1990) 123.

117. D.Bechadergue, M.Blanchard and P.Canesson, Appl.Catal. 20 (1986) 179.

118. T.R.Hughes, H.M.White and R.J.White, J.Catal. 13 (1969) 58.

119. M.R.Basila and T.R.Kanter, J.Phys.Chem. 70 (1966) 1681.

120. J.B.Perri and R.B.Hannah, J.Phys.Chem. 64 (1960) 1526.

121. S.M.Riseman, F.E.Massoth, G.Murazi-Dhar and E.M.Eyring, J.Phys. Chem. 86 (1982) 1760.

122. P.Hirva and T.A.Pakkan, Surf.Science. 277 (1992) 389.

123. D.Michel, A.Germanus and H.Pfeifer, J.Chem.Soc.Faraday Trans.I. 78 (1982) 237.

124. J.Ripmeester, J.Am.Chem.Soc. 105 (1983) 2925.

125. R.M.Pearson, J.Catal. 46 (1977) 279.

126. J.Dewing, G.T.Monks and B.Youll, J.Catal. 44 (1976) 226.

127. A.Corma, C.Rodellas and V.Fornes, J.Catal. 88 (1984) 374.

128. H.Knozinger, H.Krietenbrink and P.Ratnasamy, J.Catal. 48 (1977) 436.

129. H.Benesi, J.Catal. 28 (1973) 176.

130. J.Mederna, J.J.G.M.Van Bokhoven and A.E.T. Kuiper, J.Catal. 25 (1972) 238.

131. E.P.Parry, J.Catal. 2 (1963) 341.

132. N.S.Gill, R.H.Nuttal, D.E.Scaife and D.W.A.Sharp, J.Inorg.Chem. 18 (1961) 79.

133. F.R.Canning, J.Phys.Chem. 77 (1968) 4691.

134. E.E.Getty and R.S.Drago, Inorg.Chem. 26 (1990) 1186.

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

136. M.Shelef, K.Otto and H.Gandhi, J.Catal. 12 (1968) 361.

137. M.McDaniel and R.Burwell, J.Catal. 36 (1975) 404.

138. A.Comino, D.Cordischi, S.Febbraro, D.Gazzoli, V.Indovina, M.Occhiuzzzi, M.Valigi, F.Boccuzzi, A.Chiorino and G.Ghiotti, J.Mol.Catal.55 (1989) 23.

139. F.M.Ashmawy, J.Chem Soc. Faraday Trans.I. 76 (1980) 2096.

140. A.Cimino, D.Cordischi, S.DeRossi, G.Ferraris, D.Gazzoli, V.Indovina, G.Minelli, M.Occhiuzzi and M.Valigi, J.Catal. 127 (1991) 744

141. K.Jagannathan, A.Srinivasan and C.N.R.Rao, J.Catal. 69 (1981) 418.

142. Y.F.Yu Yao, J.Phys.Chem. 69 (1965) 3930.

143. A.Bendada, PhD Thesis, Glasgow University. 1990.

144. R.L.Redington, J.Phys.Chem. 86 (1982) 552.

145. J.W.Larson and T.B.McMahon, J.Amer.Chem.Soc. 105 (1983) 2944.

146. J.G.Powles and M.Wojcik, J.Chem.Phys. 78 (1983) 5277.

147. P.Kollman, J.Amer.Chem.Soc. 99 (1977) 4875.

148. J.S.Frood and R.M.Lambert, Langmuir 2 (1986) 677.

149. J.S.Frood and R.M.Lambert, Surf.Sci. 169 (1986) 327.

150. A.Zecchina, S.Coluccia, E.Guglieminotti and G.Ghiotti, J. Phys. Chem. 75 (1971) 2790.

151. R.G.Pearson, J.Amer.Chem.Soc. 85 (1963) 3533.

152. S.Bowers, Undergraduate Project, Glasgow University. 1992.

153. K.W.Dixon, M.F.Ghorab and J.M.Winfield, J.Fluorine Chem. 37 (1987) 357.

154. K.W.Dixon and J.M.Winfield, J.Fluorine Chem. 29 (1985) 355.

155. M.Takashima, S.Fukami, Y.Nosaka and T.Unishi, J.Fluorine Chem. 57 (1992) 131.

156. S.Gardiner, Undergraduate Project, Glasgow University. 1993.

157. K.H.Rhee and M.R.Basila, J.Catal. 10 (1968) 243.

158. Yu.I.Kozorezov and I.P.Erofeeva, Zh.Fiz.Khim. 49 (1975) 666.

159. R.Marshall, Undergraduate Project, Glasgow University. 1994.

160. J.Thomson, G.Webb and J.M.Winfield, Unpublished work.

161. F.J.Weigert, J.Fluorine Chem. 46 (1990) 375.

162. K.O.Christie and W.W.Wilson, J.Fluorine Chem. 46 (1990) 339.

163. J.B.Stothers, "Carbon-13 N.M.R. Spectroscopy." Academic Press, New York. 1972. 56.

164. D.H.Williams and I.Fleming, "Spectroscopic Methods In Organic Chemistry." McGraw-Hill, London. 1989. 135.

165. P.R.Stevenson, PhD Thesis, Glasgow University. 1992.

166. J.Thomson, PhD Thesis, Glasgow University. 1989.