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## Catalytic Fluorination of Dichloromethane with Hydrofluoric Acid

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CATALYTIC FLUORINATION OF DICHLOROMETHANE  
WITH HYDROFLUORIC ACID

BY

MICHAEL O. MYERS  
B.S., Florida Technological University, 1976

RESEARCH REPORT

Submitted in partial fulfillment of the requirements  
for the degree of Master of Science: Industrial Chemistry  
in the Graduate Studies Program of the College of Natural Sciences  
of Florida Technological University

Orlando, Florida  
1977

## ABSTRACT

The catalytic, vapor-phase fluorination of dichloromethane to chlorofluoromethane with 38% hydrofluoric acid was investigated as a model system for possible direct utilization of hydrofluoric acid in the production of fluorocarbons and chlorofluorocarbons. Catalysts consisting of Cr or Ni supported on alumina and Ni, Cr, Ag, Co, La, Sn, Hg(I), Hg(II), Cu, Fe, Ru, Zn, Na or Ca supported on activated charcoal were utilized at various reaction temperatures and reactor residence times.

Alumina-supported catalysts were found to have low activities for fluorination in comparison to catalysts utilizing anhydrous HF reported in the patent literature. The low activities were attributed to low catalyst surface areas resulting from the fluorination of the catalyst with aqueous HF.

Carbon-supported catalysts were found, in general, to promote thermal cracking of the  $\text{CH}_2\text{Cl}_2$  feed as well as the fluorination reaction. This thermal cracking was usually sufficiently severe to result in drastically lowered yields of the desired product and low catalyst lifetime due to coking.

The greatest selectivities for the desired product,  $\text{CH}_2\text{ClF}$ , relative to the difluorinated product,  $\text{CH}_2\text{F}_2$ , at reasonably high conversions, were obtained with Sn, Cu, or Co fluorides on an activated charcoal support, although overall yields were relatively low due to thermal cracking.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Chris A. Clausen, who directed this research project, for his help and tireless patience.

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## INTRODUCTION

### Historical Perspective

The first report of the production of a fluorocarbon compound was made by Henri Moissan in 1890. Four years earlier, Moissan had succeeded in generating elemental fluorine by electrolysis in a platinum cell. He found that finely divided carbon, and a variety of organic compounds, would burn fiercely in fluorine gas and claimed, in 1890, to have isolated carbon tetrafluoride. Although  $\text{CF}_4$  would be produced in such a reaction, the greater than  $110^\circ\text{C}$  error in the boiling point that was reported for  $\text{CF}_4$  indicates that he had isolated a product other than the one he had claimed. The actual product was probably a fluoroalkane of higher molecular weight than  $\text{CF}_4$ .<sup>1-3</sup>

It was not until 1926 that the French chemists Lebeau and Damiens were able to isolate  $\text{CF}_4$  in a reasonably pure form from the products of the electrolysis of fused beryllium fluoride at a carbon electrode.<sup>1</sup>

Moissan and other chemists attempting to prepare fluorocarbons by direct fluorination of carbon or hydrocarbons attained little success. Solid carbon in contact with fluorine gas tends to form an initial intercalation compound, reported to have the general formula  $(\text{CF})_n$ ,<sup>1</sup> which tends to explode violently with any increase in temperature. Researchers attempting to produce fluorocarbons other than  $\text{CF}_4$  were frustrated by their inability to moderate the violently exothermic free-radical fluorination of hydrocarbons.<sup>1-4</sup>

When the difficulties associated with direct fluorination techniques became obvious, a number of researchers turned toward indirect fluorination methods, including Moissan. The most notable pioneer in the field of indirect fluorination was the Belgian chemist Frederic Swarts. Swarts made his most significant discovery in 1892, when he found that antimony fluorides could be used to exchange fluorine for other halogens on halogenated aliphatic hydrocarbons. This reaction was found to be primarily useful in replacing one or two non-fluorine halogens on a single carbon with fluorine.<sup>1,5</sup>

Swarts failed in his attempts to produce aliphatic  $-CF_3$  groups with his indirect fluorination techniques, but was able to prepare phenyl fluoroform,  $CF_3C_6H_5$ . By combining substitution steps with electrolysis, Swarts was able to prepare a large number of new fluorocarbon compounds, including *o*-trifluorotoluidine, trifluoroacetic acid, and pure hexafluorethane. He also discovered a second useful fluorination agent, mercurous fluoride.<sup>5</sup>

In France, at about the same time, Meslans and his co-workers also studied fluorination with antimony and mercury fluorides, as well as silver and zinc fluorides.<sup>2</sup>

In America in the 1920s, a number of researchers, most notably Henne, Midgley and Renoll, began intensive studies of the properties of fluorocarbons, particularly incompletely fluorinated species, and chlorofluorocarbons. These researchers, and others, also experimented with various means of producing fluorocarbons based on the work of Meslans and Swarts.<sup>6-15</sup>



Henne and Midgley discovered that the boiling points, inertness, and other properties of a number of fluoro- and chlorofluoro-derivatives of methane and ethane, particularly dichlorodifluoromethane, made them nearly ideal refrigerants. This discovery was patented in 1930, and the compounds were subsequently manufactured by the E. I. duPont Nemours Company under the trade name of "Freons". This represented the first commercial application of fluorocarbons. The industrial process was based on the Swarts reaction, utilizing anhydrous HF and a catalyst consisting of a mixture of  $\text{SbF}_3$  and  $\text{SbF}_5$  for fluorination of chlorinated hydrocarbons.<sup>16-17</sup>

In 1934, a major advance in direct fluorination techniques was made by Fredehagen and Cadenbach, who reported that a copper mesh packing in a tubular reactor would serve to moderate the reaction between fluorine and hydrocarbons.<sup>18</sup>

In 1937 various researchers, including Bigelow, Calfee, Fukuhara, Hadley and Young studied the vapor-phase fluorination of methane and ethane over a copper screen packing, producing a variety of incompletely-fluorinated products as well as  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ . That same year, American chemists Simons and Block discovered that mercury salts would promote a smooth reaction of fluorine with carbon over a heated carbon bed.<sup>18-21</sup>

With the advent of World War II and the subsequent initiation of the Manhattan Project to develop the atomic bomb, a search was begun for lubricants, dilutant gases, sealants and heat-transfer media which would be inert to the highly reactive uranium hexafluoride

used in the diffusion process for concentration of  $^{235}\text{U}$ . The discovery that saturated fluorocarbons met this criteria gave impetus to an investigation into practical methods of production.<sup>22</sup>

Two processes for the production of saturated fluorocarbons were developed from this research. The first, referred to as the catalytic process, consisted of direct fluorination of various hydrocarbons in the vapor phase over a silver-plated copper packing. The second method, called the metallic fluoride process, utilized high-valence-state metal fluorides, such as  $\text{CoF}_3$ , as the fluorinating agent, with elemental fluorine being used to prepare these high-valence-state fluorides. Following the war, attempts to adapt these two processes to economical commercial applications failed, and substitution-type reactions became established as the principal method used in industry.<sup>20-24</sup>

### Heterogeneous Fluorination Catalysts

Catalysts for the vapor-phase fluorination of halogenated hydrocarbons have been appearing in the patent literature since the mid-1930s. A major advantage to such a process over one employing a homogeneous antimony pentahalide catalyst is the elimination of the necessity for separation of the catalyst from the product mixture. In the liquid-phase process utilizing an antimony catalyst, a quantity of the volatile antimony compound is inevitably lost during separation and purification steps.

The first heterogeneous catalysts for vapor-phase fluorination of halocarbons utilized metal salts on various types of solid

supports, such as crushed coke or charcoal. One early patent, in 1935, also mentions the use of a low-porosity alumina support. The metal salts were deposited on the support by precipitation, by coating with a paste of the metal salt, or by impregnation with a solution of the metal salt.<sup>24-34</sup>

These early heterogeneous catalysts were characterized by rather low activities. Since the objective of the majority of these processes was to produce fluorocarbons containing at least two fluorine atoms per carbon, for use as refrigerants, it was generally necessary to utilize high temperatures to obtain a significant conversion. These high temperatures often resulted in loss of products and reactants through thermal cracking.<sup>24-34</sup>

An example of a catalyst of this type is given by Benning, Park and Krahler, who patented a catalyst consisting of  $\text{CrF}_3$  on activated charcoal. With a feedstock composed of anhydrous HF and  $\text{CClF}_3$  in a 3.1 to 1 ratio, at  $880^\circ\text{C}$  and a residence time of 11-12 seconds, they reportedly produced a product consisting of 88.5%  $\text{CF}_4$  and 11.5%  $\text{CClF}_3$ , utilizing this chromium fluoride catalyst. It is not stated in their report if any material is lost through cracking.<sup>24</sup>

In the early 1950s, aluminum fluoride, alone or in combination with various other metal fluorides, was found to be significantly more active as a fluorination catalyst than any heterogeneous catalyst previously studied. Several techniques were found to be effective in preparation of such catalysts, including fluorination of porous alumina or aluminum chloride with anhydrous hydrogen fluoride.

Other metal fluorides were included by impregnation of alumina with solutions of metal salts prior to fluorination, or by pelletizing mixtures of  $\text{AlF}_3$  and the desired metal fluorides.<sup>25-34</sup>

A number of examples of catalysts of this type were given by Ruh and Davis in their patent of 1956. They reported that an effective fluorination catalyst could be prepared by impregnating a porous alumina with a solution of a nickel salt of a concentration sufficient to result in a 5% nickel content in the final catalyst, followed by fluorination of the wet mixture with anhydrous HF at room temperature. This catalyst could be activated at  $350^\circ\text{C}$  in a stream of anhydrous HF.<sup>25</sup>

The authors claim that the presence of water during the initial fluorination of the catalyst results in conversion of the alumina to a mixture of  $\text{AlF}_3$  and two incompletely fluorinated species,  $\text{Al}(\text{OH})\text{F}_2$  and  $\text{Al}(\text{OH})_2\text{F}$ , which they refer to as the basic aluminum fluorides. The catalyst activation step evidently involves conversion of a portion of these basic aluminum fluorides to  $\text{AlF}_3$ , but Ruh and Davis state that the presence of basic aluminum fluorides is essential to catalytic activity.<sup>25</sup>

Passage of a mixture of anhydrous HF and  $\text{CH}_2\text{Cl}_2$ , at a ratio of 4.8 to 1, a temperature of  $450^\circ\text{C}$ , and a contact time of 1.9 seconds, through a bed of the above catalyst reportedly resulted in a 29.6% yield of  $\text{CH}_2\text{F}_2$ , a 22.6% yield of  $\text{CH}_2\text{ClF}$ , and a 12.4% yield of an unidentified fluorocarbon. Conversion based on  $\text{CH}_2\text{Cl}_2$  was 65.9%, while 23.3% of the organic materials were apparently lost through

thermal cracking.<sup>25</sup>

A patent report by Miller and Calfee, also in 1956, claims the invention of an aluminum fluoride catalyst for vapor-phase fluorination of  $\text{CCl}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and several chloroethanes. The catalyst was reported to have been prepared from aluminum chloride and anhydrous HF, then activated by heating to 250-350°C in a stream of dry  $\text{N}_2$  or anhydrous HF for several hours. The authors mention that activation accompanies the removal of any waters of hydration remaining in the  $\text{AlF}_3$ . The use of  $\text{AlF}_3$  alone as a catalyst in this report tends to contradict the claim of Ruh and Davis that basic aluminum fluorides are required for activity.<sup>26</sup>

The above catalyst produced a 40% yield of  $\text{CH}_2\text{F}_2$  and a 60% yield of  $\text{CH}_2\text{ClF}$ , at 400°C and a feed consisting of HF and  $\text{CH}_2\text{Cl}_2$  in a 1.25 to 1 ratio. Conversion based on  $\text{CH}_2\text{Cl}_2$  was reported to be 23%.<sup>26</sup>

Additional examples of heterogeneous fluorination catalysts are given in Table I. The column in Table I labeled "Material Balance" refers to the total percentage of organic materials recovered in relation to the halogenated hydrocarbons input.

#### Modern Production and Uses of Fluorocarbons

Between 80 and 90% of all commercially produced fluorocarbons are either  $\text{CF}_2\text{Cl}_2$  or  $\text{CFC}_1_3$ . As of 1974, use of  $\text{CF}_2\text{Cl}_2$ , or mixtures of  $\text{CF}_2\text{Cl}_2$  and  $\text{CFC}_1_3$ , as aerosol propellants accounted for approximately 40% of the total fluorocarbon market, while about 30% of the total production went for use as refrigerants (mainly  $\text{CF}_2\text{Cl}_2$ ).

TABLE I

Examples of Heterogeneous Catalysts for Vapor-Phase  
Fluorination of Halogenated Hydrocarbons from Patent Literature

Catalyst	Temperature	Contact Time (sec.)	Feed	Conversion	Yields	Material Balance	Reference
CrF <sub>3</sub> on Activated Carbon	880°C	11-12	HF/CClF <sub>3</sub> 3.1:1	---	Product recovered 88.5% CF <sub>4</sub> and 11.5% CClF <sub>3</sub>	---	24
5% Ni on Alumina	290-310°C	---	HF/CBr <sub>4</sub> 7.2:1	90.1%	92.5% CBrF <sub>3</sub>	92.5%	25
5% Ni on Alumina	350-390°C	---	HF/CBr <sub>4</sub> 3.4:1	---	64.1% of feed converted to CBrF <sub>4</sub>	Lower than previous	25
5% Ni on Alumina	400°C	4.8	HF/CH <sub>2</sub> Br <sub>2</sub> 4.0:1	66.2%	CH <sub>2</sub> F <sub>2</sub> 45.7% CH <sub>2</sub> BrF 24.4%	81.4%	25
5% Ni on Alumina	450°C	1.9	HF/CH <sub>2</sub> Cl <sub>2</sub> 4.8:1	65.9%	CH <sub>2</sub> F <sub>2</sub> 29.6% CH <sub>2</sub> FCl 22.6%	76.7%	25
5% Ni on Alumina	400°C	2.9	HF/CHCl <sub>3</sub> 8.9:1	99.2%	CHF <sub>3</sub> 90.7% CHClF <sub>2</sub> 3.0% CHCl <sub>2</sub> F 0.7%	94.5%	25

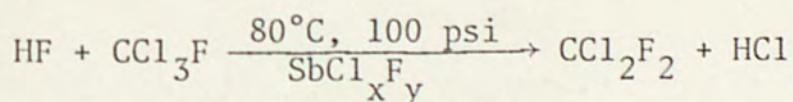
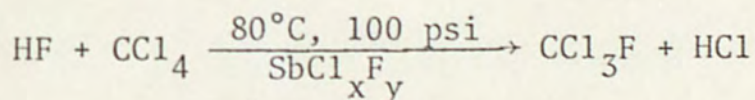
TABLE I (cont.)

Catalyst	Temperature	Contact Time (sec.)	Feed	Conversion	Yields	Material Balance	Reference
Alumina (AlF <sub>3</sub> )	350°C	3.4	HF/CCl <sub>4</sub> 4.1:1	100%	CF <sub>4</sub>	92.7%	25
					CClF <sub>3</sub>	0.2%	
					CCl <sub>2</sub> F <sub>2</sub>	76.8%	
Alumina (AlF <sub>3</sub> )	295°C	---	HF/CHCl <sub>3</sub> 1.8:1	90%	CClF <sub>3</sub>	100%	26
					CCl <sub>2</sub> F <sub>2</sub>	3.9%	
					CCl <sub>3</sub> F	32.0%	
Alumina (AlF <sub>3</sub> )	350°C	---	HF/CHCl <sub>3</sub> 1.8:1	97%	CHF <sub>3</sub>	---	26
						100.0%	
Alumina (AlF <sub>3</sub> )	400°C	---	HF/CH <sub>2</sub> Cl <sub>2</sub> 1.3:1	23%	CH <sub>2</sub> F <sub>2</sub>	100%	26
					CH <sub>2</sub> FCl	60.0%	
						40.0%	

Fluorocarbons also find increasing use in fluorocarbon plastics, such as polytetrafluoroethylene, as solvents, as foam-blowing agents for production of foamed plastics, and in a variety of miscellaneous applications. Not all one- and two-carbon fluorocarbons or chlorofluorocarbons find uses in industry, although all have been classified as useful refrigerants, mainly because those in common use have superior combinations of properties.<sup>35-37</sup>

Dichlorodifluoromethane and trichlorofluoromethane are produced commercially by liquid-phase fluorination of carbon tetrachloride with a partially-fluorinated antimony pentahalide catalyst and anhydrous HF. In spite of the many patented gas-phase processes utilizing heterogeneous catalysts, the processes in current use are very similar to that originally developed by duPont for Freon manufacture following the discoveries of Midgley and Henne.<sup>35-37</sup>

The reactions which take place in production of  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$  from  $\text{CCl}_4$  are



Where  $x + y = 5$  for the antimony catalyst. Dichlorodifluoromethane is generally obtained in about 80% yield, the remaining products being almost exclusively trichlorofluoromethane.<sup>35</sup>

Chlorodifluoromethane, which is pyrolyzed to form tetrafluoroethylene for use in the manufacture of polytetrafluoroethylene,



is obtained from fluorination of chloroform by a similar process.<sup>35</sup>

Other commercial fluorocarbons are generally prepared by analogous Swarts-type halogen-exchange reactions.<sup>35-37</sup>

### General Chemical and Physical Properties of Fluoromethanes and Chlorofluoromethanes

As would be expected, the extremely high electronegativity and small atomic radius of fluorine endows fluorine-containing compounds with a number of unusual properties. Since fluorine is the most electronegative element, the carbon-fluorine bond is the most strongly polarized, and has the highest degree of ionic character, of all carbon-halogen bonds. In spite of this, the relatively short carbon-fluorine bond length results in a lower bond dipole moment than for the carbon-chlorine bond (See Table II).<sup>38-41</sup>

Table III compares molecular weights and boiling points for the fluoromethanes, chlorofluoromethanes, and chloromethanes. It can be seen that the boiling points of the chloromethanes increase with increasing molecular weight, following the general rule, but that the fluoromethanes show a decrease in boiling point as molecular weight and degree of fluorination increase, with the exception of difluoromethane. The explanation for this behavior lies in the fact that transmission of electronic effects through the carbon center, due to the extreme polarization of the carbon-fluorine bond, allows a type of hydrogen bonding in incompletely fluorinated fluorocarbons. Difluoromethane is capable of a maximal number of such interactions, and thus has the highest boiling point of the series. Tetrafluoromethane,

TABLE II

Electronegativity Difference, Percent Ionic Character,  
Dipole Moment and Bond Length for Carbon-Halogen Bond

	<u>Carbon-Halogen Bond Length (Å)</u>	<u>Dipole Moment (Debye)</u>	<u>Pauling Electronegativity Difference</u>	<u>Percent Ionic Character</u>
CH <sub>3</sub> -F	1.38	1.79	1.5	43%
CH <sub>3</sub> -Cl	1.77	1.87	0.5	12%
CH <sub>3</sub> -Br	1.93	1.80	0.3	2%
CH <sub>3</sub> -I	2.18	1.65	0.0	0%

TABLE III

Comparison of Boiling Points and Molecular Weights for Fluoromethanes, Chlorofluoromethanes and Chloromethanes

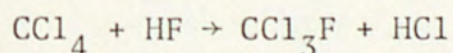
<u>Fluorocarbon</u>	<u>Mol. Wt.</u>	<u>B.P.</u>	<u>Chlorofluorocarbon</u>	<u>Mol. Wt.</u>	<u>B.P.</u>	<u>Chlorocarbon</u>	<u>Mol. Wt.</u>	<u>B.P.</u>
$\text{CH}_3\text{F}$	34.0	-78.4	----	----	----	$\text{CH}_3\text{Cl}$	50.5	-24.2
$\text{CH}_2\text{F}_2$	52.0	-51.6	$\text{CH}_2\text{ClF}$	64.5	-9.1	$\text{CH}_2\text{Cl}_2$	84.9	40.0
$\text{CHF}_3$	70.0	-82.2	$\text{CHCl}_2\text{F}$	102.9	9.0	$\text{CHCl}_3$	119.4	61.7
			$\text{CHClF}_2$	86.5	-40.8			
$\text{CF}_4$	88.0	-129	$\text{CCl}_2\text{F}_2$	120.9	-29.8	$\text{CCl}_4$	153.8	76.5
			$\text{CCl}_3\text{F}$	137.4	23.8			
			$\text{CClF}_3$	104.5	-81.1			

which is symmetrical, could then be expected to have the lowest boiling point of the series. The incompletely-halogenated chlorofluoromethanes exhibit similar behavior.<sup>38-41</sup>

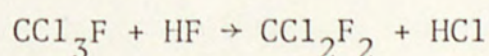
Although fluorocarbons would be expected to be relatively inert on the basis of the strength of the carbon-fluorine bond, saturated fluorocarbons exhibit an unusual inertness in many reactions that are apparently favored by thermodynamics, such as hydrolysis of  $\text{CF}_4$ . This effect has been attributed to the very low polarizability of fluorine in fluorocarbons and to the fact that the small atomic radius of fluorine and the relatively small bond length of the carbon-fluorine bond allows a shielding of the carbon center from attacking species.<sup>38-41</sup>

Chlorofluoromethanes, in general, have chemical properties intermediate to those of fluoromethanes and chloromethanes, with chemical inertness decreasing and toxicity increasing as the number of chlorines increases.<sup>16,38</sup>

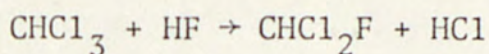
Values for enthalpy changes at  $350^\circ\text{C}$  for vapor-phase reactions producing common fluorocarbons and for the fluorination of dichloromethane are given below:



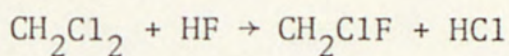
$$\Delta H = -2.2 \text{ kcal/mol}$$



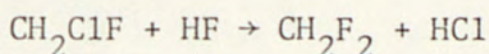
$$\Delta H = -4.3 \text{ kcal/mol}$$



$$\Delta H = -4.3 \text{ kcal/mol}$$



$$\Delta H = -7.6 \text{ kcal/mol}$$



$$\Delta H = +7.1 \text{ kcal/mol}$$

It can be seen that these fluorination reactions, with the exception of the fluorination of  $\text{CH}_2\text{ClF}$ , are exothermic, but not greatly so. Enthalpy values for chloromethanes and fluoromethanes were obtained by interpolation from tabularized data published by Stull, Westrum, and Sinke. A lack of published thermochemical data for chlorofluorocarbons in general at temperatures above  $100^\circ\text{C}$ , and an almost total lack of thermochemical data for  $\text{CH}_2\text{ClF}$ , necessitated estimations of enthalpy values for these compounds based on the data that was available.<sup>37,42-43</sup>

As was mentioned in the previous section, fluorocarbons and chlorofluorocarbons are produced commercially by variations of the halogen-exchange reaction first discovered by Swarts. The mechanism of fluorination of chlorinated hydrocarbons by an antimony pentahalide catalyst apparently involves the formation of an intermediate hexacoordinate antimony complex from the chlorinated hydrocarbon and  $\text{SbCl}_3\text{F}_2$ , followed by a fluorine transfer, either intramolecularly, or

from HF or a second  $\text{SbCl}_3\text{F}_2$  molecule (See Figure 1). Current information supports the mechanism involving intramolecular fluorine transfer. Following such a transfer,  $\text{SbCl}_3\text{F}_2$  would be regenerated by reaction of HF with  $\text{SbCl}_4\text{F}$ . Presumably, other fluorination catalysts involving metals capable of forming this type of complex would act by a similar mechanism.<sup>38</sup>

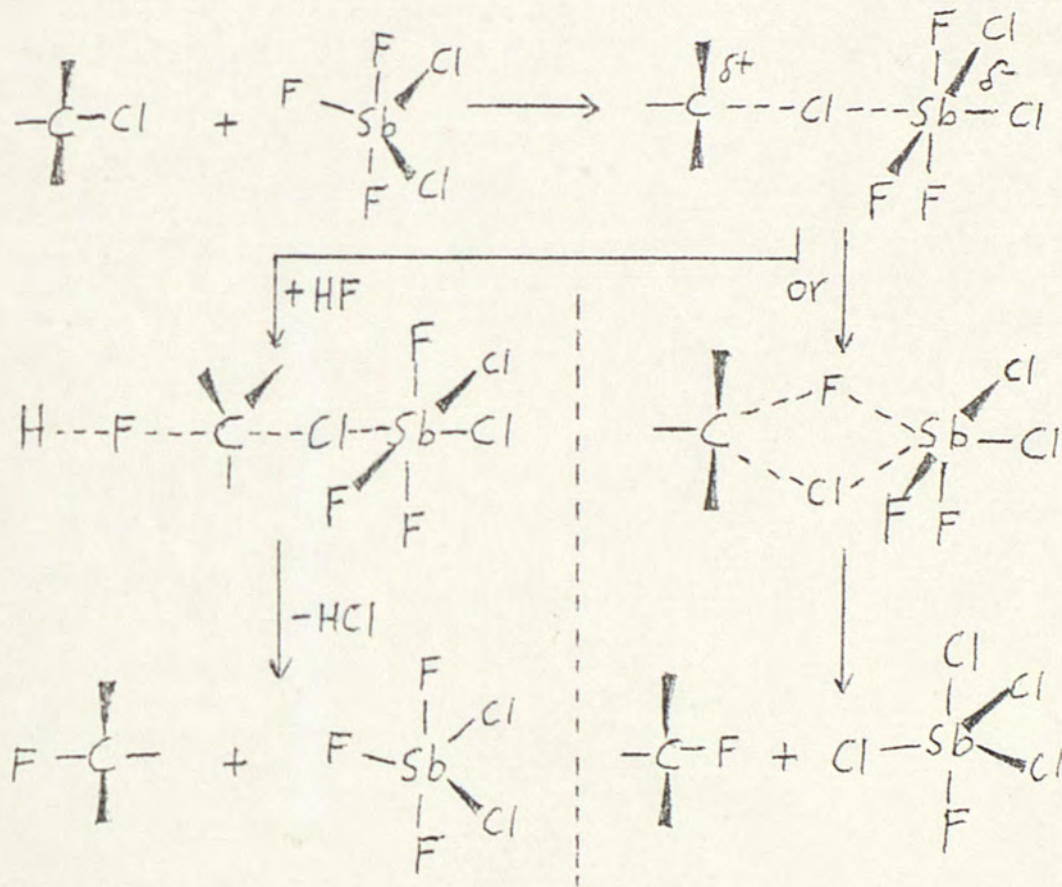


FIGURE 1. - Proposed Mechanisms for Swarts Reaction.

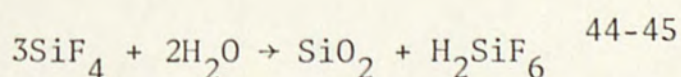
### HF Production and the Fluorocarbon Industry

All present day large-scale industrial processes for fluorocarbon production utilize only anhydrous HF. This is due to several

factors: first, commercial production of HF is geared to the anhydrous product. Second, appreciable amounts of water would tend to promote the decomposition of the antimony pentahalide catalyst commonly used in fluorocarbon production. Also, aqueous HF produces a corrosive environment different from that of anhydrous HF.<sup>44-45</sup>

A survey of the literature revealed that currently patented heterogeneous fluorination catalysts were also specific for anhydrous HF. This is apparently due to the fact that these patented processes were evaluated as potential industrial processes, and as mentioned above, industry produces and utilizes anhydrous HF. Additional reasons may include the fact that early fluorocarbon researchers observed that water deactivated some metal fluoride catalysts, and the fact that some heterogeneous catalysts are best activated in a stream of dry gas.<sup>10, 25-26, 44-45</sup>

Hydrogen fluoride is manufactured by reaction of sulfuric acid with acid-grade fluorspar ( $\text{CaF}_2$ ), yielding HF and  $\text{CaSO}_4$ . Specifications of acid-grade fluorspar call for low levels of silica, since silica will react with HF to produce water and  $\text{SiF}_4$ . This reaction lowers the yield of HF, and increases product drying requirements. The silicon tetrafluoride by-product cannot be released in quantity into the environment, and must be removed from process effluents. This is commonly done by absorbing the  $\text{SiF}_4$  into water, resulting in the formation of hexafluorosilicic acid by the reaction



$\text{SiF}_4$  is also produced as a by-product of the phosphate industry during acidification of phosphate rock with sulfuric acid, due to the presence of silica and fluoroapatite,  $\text{Ca}_7\text{F}(\text{PO}_4)_3$ .<sup>44</sup>

Natural deposits of fluorspar in the United States contain moderate to large amounts of silica. Manufacturers of HF must therefore either upgrade domestic fluorspar, which raises production costs, or import acid-grade material.<sup>44-45</sup>

Concern over diminishing world deposits of acid-grade fluorspar and difficulties encountered in disposal of  $\text{H}_2\text{SiF}_6$  have motivated a number of companies to explore the possibilities of utilizing  $\text{H}_2\text{SiF}_6$  for HF production. A number of patents currently exist which utilize a variety of approaches to the problem. These include formation of  $\text{NH}_4\text{F}$  or  $\text{KF}$  from  $\text{H}_2\text{SiF}_6$  followed by electro dialysis, heating  $\text{H}_2\text{SiF}_6$  with  $\text{H}_2\text{SO}_4$ , reduction of  $\text{H}_2\text{SiF}_6$  with hydrogen, and others.<sup>44-47</sup>

The electro dialysis process, and many of the other processes which produce HF from  $\text{H}_2\text{SiF}_6$ , produce hydrofluoric acid of varying concentrations rather than anhydrous HF. Since HF forms a 38% azeotrope with water, conversion of hydrofluoric acid from these alternative processes to the conventional anhydrous form may prove costly. This fact should motivate research into the feasibility of utilizing hydrofluoric acid directly in, for example, fluorocarbon production.<sup>45</sup>

#### Purpose of This Project

Dow Chemical U.S.A., which funded this project, has an interest in the possibility of utilizing aqueous hydrofluoric acid, along the lines of the discussion in the previous section of this paper, to



produce various fluorocarbons and/or chlorofluorocarbons.

The purpose of this research project was to evaluate the possibility of producing chlorofluoromethane from dichloromethane and 38% hydrofluoric acid. To this end, the vapor-phase fluorination of dichloromethane with 38% hydrofluoric acid was studied, utilizing a number of heterogeneous catalyst systems consisting, in general, of one or more metal fluorides on an activated carbon or alumina support, under a variety of reaction conditions.

## EXPERIMENTAL

### Fluorination Apparatus

The fluorination apparatus consisted basically of a preheater with inlets for hydrofluoric acid, dichloromethane, and nitrogen, a tubular reactor, and an HF scrubber unit. A diagram of this apparatus is given in Figure 2.

The preheater section consisted of a nine-inch section of 3/4 inch monel pipe fitted with four 1/4 inch monel entrance ports. Two entrance ports were located at each end of the pipe section and the other two attached to the lower side. Four-inch lengths of 1/4 inch diameter monel tubing, insulated with wrappings of asbestos tape, were attached to the side ports. One-eighth-inch Teflon feed lines from the syringe pump, which served to deliver the hydrofluoric acid and dichloromethane to the system, were connected to the two side tubes. A loop of monel tubing, intended to prevent any HF from flowing out of the preheater, was connected to the inlet end fitting of the preheater. Through this tubing, a flow of nitrogen, controlled by a Brooks rotameter with a type 1355-07C1AA tube, entered the preheater.

The preheater section was wrapped with #20 nichrome wire over a layer of asbestos tape, and insulated with approximately 1 1/2 inches of asbestos tape. A 1/8 inch diameter copper tube between the first layer of asbestos and the preheater tubing served as the preheater thermowell. Temperature was monitored with a Bailey Instruments model Bat-8 electronic thermometer equipped with a seven-junction

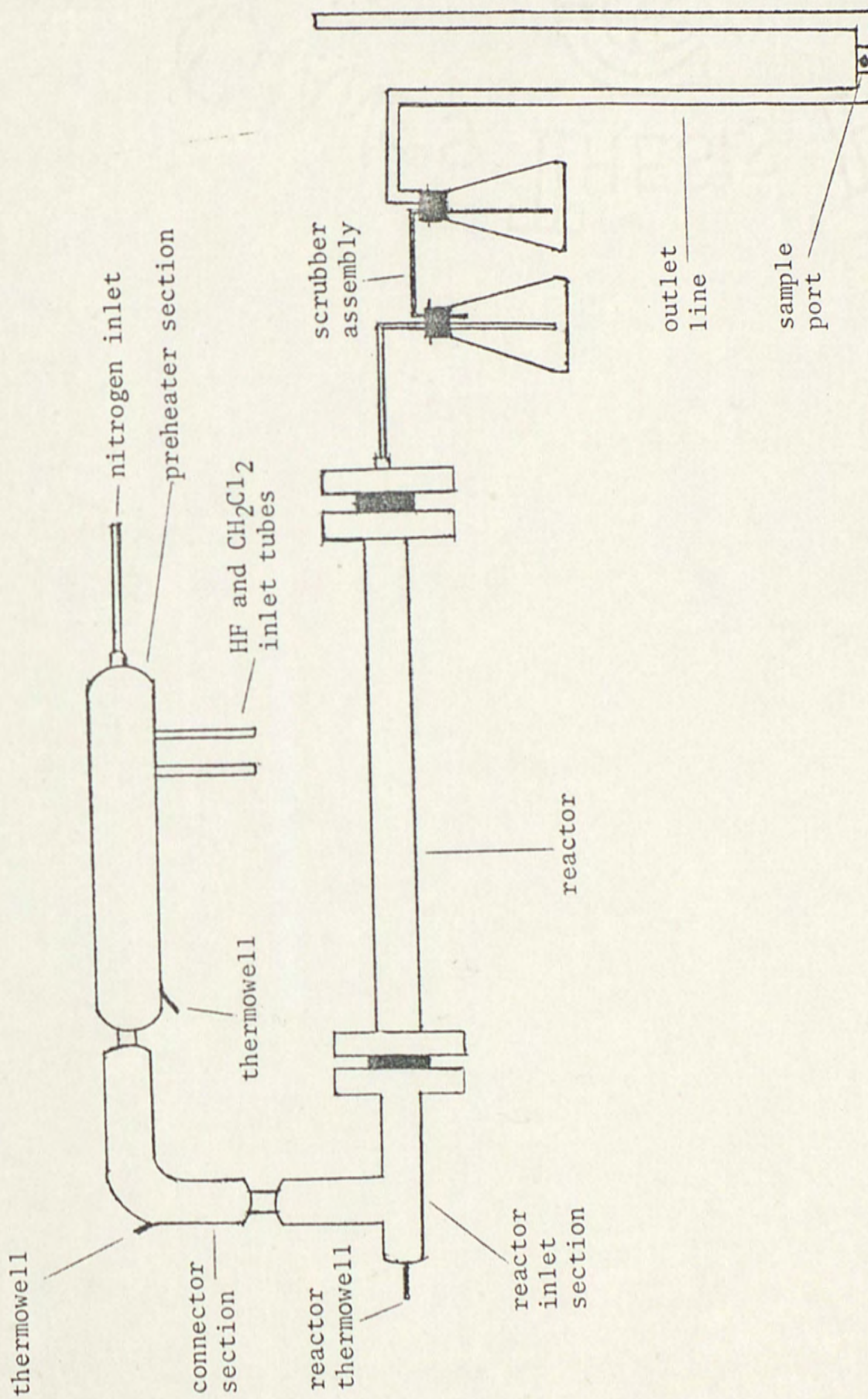


FIGURE 2. - Fluorination Apparatus.

switchbox and copper-constantan thermocouple leads.

The preheater outlet lead into a 90° connector section, consisting of a six inch length of 1/4 inch diameter monel tubing, wrapped with a nichrome wire heating element and asbestos insulation. This section was equipped with a thermocouple well similar to that described for the preheater section.

The lower end of the connector section was attached to the reactor inlet section by means of a monel "T" connector (Swagelok). The other end of the "T" served as access to, and support for, the reactor bed thermocouple well. The inlet section was heated with a double wrapping of #20 asbestos-insulated nichrome wire, and insulated with asbestos tape. As with the other sections, a thermocouple well was installed for temperature monitoring.

The reactor consisted of a 14 inch length of 3/4 inch outside diameter, 0.53 inch inside diameter monel pipe, with four-inch diameter flanges welded to each end. Mating flanges with attached 1/4 inch fittings (Swagelok) were employed to both seal the reactor and to adapt it to the inlet and outlet lines.

The reactor seal was established by means of spiraflex #300 stainless steel gaskets placed between the mating flanges. The reactor tube was heated by means of a Lindberg Sola Basic type 55035 tube furnace. A wrapping of asbestos tape at each end of the reactor tube served to center the reactor in the tube furnace and to prevent the escape of heat at the furnace ends. A 1/8 inch monel thermocouple well ran the entire length of the reactor, allowing measurement of

catalyst bed temperature. The reactor flanges were heated by means of Briskeat heating tapes and insulated with a heavy wrapping of asbestos tape. A 1/4 inch diameter, four inch long monel tube, heated by the same heating tape that heated the reactor outlet flange lead from the reactor outlet to the scrubber inlet.

The scrubber assembly consisted of two plastic (Nalgene) 125 ml erlenmeyer flasks set up in series so that reactor products would bubble through a 20% NaOH solution. The two flasks were immersed in a water bath which was heated by a Blue M immersion heater.

A 1/4 inch diameter monel outlet line, heated with a heating tape, lead from the scrubber outlet and extended about six inches from the fume hood in which the apparatus was enclosed, then looped sharply back into the hood, where outlet gases were finally discharged. A sample port in the section of the line outside the fume hood, equipped with a septum with a rigid Teflon support disk, allowed sample collection without the hood being opened.

The syringe pump employed for delivery of dichloromethane and 38% hydrofluoric acid was a Harvard Apparatus Compact Infusion Pump, Model 971. Hamilton Gas-Tite glass syringes with Teflon-coated plungers were utilized for  $\text{CH}_2\text{Cl}_2$  deliver, while Plastipak plastic syringes were used for hydrofluoric acid.

Power was supplied to the various heating elements and heating tapes by individual variable transformers.

#### Analytical

Analysis of the fluorination reactor outlet stream was performed

with a Hewlett-Packard model 5710A gas chromatograph equipped with a flame-ionization detector, a 5706A dual differential electrometer, and a Linear Instruments integrating chart recorder.

The column utilized in the gas chromatograph was a six-foot length of 1/8 inch diameter copper tubing packed with a mixture of 50% Porapak Q and 50% Porapak QS (Waters Associates). The column was initially conditioned at 180°C for two days at a helium carrier flow rate of 10 ml per minute.

The syringes used for gas sampling were Plastipak Ice Tuberculin syringes, graduated to 1/10 ml. This type of syringe was utilized because the large sample size allowed the use of a relatively high attenuation setting on the gas chromatograph, which prevented baseline noise from masking any smaller peaks, and also, because glass/metal syringes, in spite of the two-stage scrubber system, had a rather limited lifetime in this application due to residual HF.

Analysis of the reactor outlet stream was carried out using a temperature program which initially held the G.C. column at 100°C for a period of two minutes, then caused the temperature to increase at a rate of 32°C per minute to 150°C, this temperature being maintained until all peaks had eluted.

Typically, the reactor effluent samples taken during a run produced the series of peaks given in Table IV using the above temperature program and a helium carrier flow of 30.0 ml per minute.

Table IV

Peak Residence Times  
for Reactor Effluent Chromatograms

<u>Peak Number</u>	<u>Retention Time (min.)</u>	<u>Peak Size</u>
1	0.70	variable
2	1.40	major
3	2.53	trace
4	2.66	major
5	2.97	major
6	3.80	trace
7	4.93	trace
8	6.70	major

Comparisons of the retention times for various standards with this data, and the use of internal standards lead to the peak identifications given in Table V. Peaks six and seven are apparently due to two of a number of possible fluorochloroethylenes or fluorochloroethanes formed as a by-product of thermal cracking. Total areas of peaks three, six and seven were generally much less than 1% of the combined areas of all peaks.

Table VPeak Identities for  
Reactor Effluent Chromatograms

<u>Peak Number</u>	<u>Identity</u>
1	CH <sub>4</sub>
2	CH <sub>2</sub> F <sub>2</sub>
3	CH <sub>3</sub> F
4	CH <sub>2</sub> ClF
5	CH <sub>3</sub> Cl
6	----
7	----
8	CH <sub>2</sub> Cl <sub>2</sub>

Standard samples for preparation of calibration curves for the conversion of chromatogram peak areas to molar quantities were prepared as follows: a gas sample bottle, generally 1125 milliliters in volume, fitted with a double rubber septum, was thoroughly flushed with dry nitrogen and sealed. A volume of gas equal to the quantity of undiluted gaseous standard to be used was withdrawn from the sample bottle, followed by injection of the standard into the bottle via a Hamilton Gas-Tite syringe. Mixing was facilitated by a stirring bar previously placed in the sample bottle. In the case of dichloromethane, which is a liquid at room temperature, the desired quantity of liquid sample was injected into a sample bottle from which a quantity of gas equal to the volume of the vaporized CH<sub>2</sub>Cl<sub>2</sub> was withdrawn.

To insure that changes in the response of the G.C. flame-ioniza-



tion detector would not effect the calibration curve, standard gas samples of dichloromethane vapor were used to provide a reference for detector adjustment.

Linear regression analysis of calibration data for  $\text{CH}_4$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_2\text{FCl}$ ,  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  yielded straight lines, with correlation coefficients greater than 0.99, in the range of standard concentrations employed, approximately  $5 \times 10^{-5}$  to  $5 \times 10^{-3}$  moles per liter of gas.

### Catalyst Preparation

Catalysts utilized in this project were prepared by the incipient wetness technique, which involves dissolution of the metal salts to be deposited on the support in an amount of solvent just sufficient to saturate the support without leaving any free liquid, followed by impregnation of the support with this solution, and drying. This technique helps assure that the metal salts are deposited in the pores of the support for maximal surface area and number of active sites.

The supports used in catalyst preparation were Darco 12-20 mesh activated charcoal (MC/B) and 8-14 mesh alumina (MC/B). Preliminary preparation of the carbon support involved drying at a temperature of 100-120°C overnight followed by screening over a 40-mesh wire sieve to remove fines. Due to the presence of fine dust clinging to the surface of the alumina granules, preliminary preparation for this support involved screening over a 40-mesh sieve, washing by shaking with a large excess of deionized water, drying at approximately 120°C for a minimum of twelve hours, and screening for a second time.

The wet point of the two supports, the point at which the support is saturated with solvent, as determined by slow addition of deionized water or metal salt solution to a quantity of the dry support until free liquid first appeared, was found to vary somewhat, depending upon the particular metal salt solution being used for impregnation. In general, 1.2 to 1.4 milliliters of solution per gram of support were utilized for impregnation of carbon, while approximately one milliliter of solvent per gram of support was used in the case of alumina.

A general procedure used for preparation of such catalysts is as follows: first, the required amount of metal salt, the chloride or nitrate of the metal of interest, was weighed out. This amount was calculated on the basis of a particular number of moles of metal per gram of support. Since a constant volume of catalyst was packed for each catalyst system studied, this procedure helped insure that the same number of metal atoms would be present in the same catalyst bed volume. After the salt was weighed out, it was dissolved in a suitable quantity of solvent. Solvents used included deionized water, dilute HCl, and dilute HNO<sub>3</sub>. The dilute acid solutions were used in cases in which some possibility of hydrolysis of the salt in water existed. Next, the metal salt solution was added slowly to the proper quantity of support material as the support was stirred vigorously. After addition of the impregnating solution, the catalyst was dried at 100-140°C for a minimum of twelve hours.

Data concerning the preparation of the various catalysts studied

is summarized in Table VI. Typical examples of the preparation of a carbon-supported and an alumina-supported catalyst are given below.

An alumina-supported chromium catalyst was prepared as follows: 8.447 grams of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (Fisher Reagent Grade) dissolved in 30 milliliters of water was added slowly to 45.00 grams of 8-14 mesh alumina (MC/B) which had been previously washed, dried, and screened as described above, as the alumina was stirred rapidly. The resulting mixture was dried at  $140^\circ\text{C}$  for about 48 hours.

A chromium catalyst supported on carbon was prepared by adding a solution consisting of 16.94 grams of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (Fisher Reagent Grade) in 70 milliliters of water to 53.06 grams of Darco 12-20 mesh activated charcoal (MC/B) as the charcoal was stirred rapidly. The mixture was dried at  $140^\circ\text{C}$  for approximately 48 hours.

The procedure used in packing a given catalyst into the reactor tube was as follows: a monel screen plug (40 mesh), perforated to allow access of the reactor thermocouple well, was positioned 1.5 inches from the inlet end of the reactor. The inlet flange plate was then attached. With the bed thermocouple tube positioned in the center of the reactor, the catalyst was poured into the reactor tube as the reactor was tapped with a metal rod, to assure close packing of the catalyst. When the catalyst bed reached a depth of 11.0 inches, the second screen plug was put in place to retain the catalyst. The outlet end flange plate was bolted in position, the reactor placed in the tube furnace, and the inlet attached to the connector section.

Table VI  
Catalyst Preparation Data

Catalyst Number	Metal Salt	Weight of Metal Salt Used (grams)	Source of Metal Salt	Solvent	Support	Weight of Support Used (grams)
1	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	---	---	---	Alumina	---
2	---	---	---	---	Activated Charcoal	---
3	$\text{NiCl}_3 \cdot 6\text{H}_2\text{O}$	15.12	Baker	$\text{H}_2\text{O}$	Activated Charcoal	53.84
4	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	16.94	Baker	$\text{H}_2\text{O}$	"	53.06
5	"	33.88	"	"	"	53.06
6	"	64.00	"	"	"	54.78
7	$\text{K}_2\text{Cr}_2\text{O}_7$	7.790	MC/B	"	"	50.00
8	$\text{AgNO}_3$	8.154	"	"	"	40.00
9	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	13.85	"	"	"	40.00
10	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	15.37	"	"	"	30.00
11	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ *	10.74	Baker	"	"	40.00
12	$\text{HgNO}_3 \cdot \text{H}_2\text{O}$	13.47	"	5% $\text{HNO}_3$	"	40.00

Table VI (cont.)

Catalyst Number	Metal Salt	Weight of Metal Salt Used (grams)	Source of Metal Salt	Solvent	Support	Weight of Support Used (grams)
13	$\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	16.45	Fisher	5% $\text{HNO}_3$	Activated Charcoal	40.00
14	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	8.183	"	$\text{H}_2\text{O}$	"	40.00
15	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	16.37	"	"	"	40.00
16	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	12.97	"	10% $\text{HCl}$	"	40.00
17	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	5.300	Alpha	15% $\text{HCl}$	"	16.89
18	$\text{ZnCl}_2$	6.541	Fisher	$\text{H}_2\text{O}$	"	40.00
19	$\text{NaCl}$	2.805	"	"	"	40.00
20	$\text{CaCl}_2$	5.328	Baker	"	"	40.00

With a Swagelok plug fitting blocking the outlet end of the reactor, and the hydrofluoric acid and dichloromethane feed lines closed off, the apparatus would be leak tested by pressurizing to about four p.s.i.g. with nitrogen and observing the ability of the apparatus to hold pressure.

The scrubber flasks would each be filled with about 100 ml of 50% sodium hydroxide solution and connected to the reactor outlet. The preheater would be raised to about 250°C while the inlet, connector and reactor sections were heated to about 350°C. Then 25 ml of 38% hydrofluoric acid (50 ml in the case of an alumina-supported catalyst) would then be run into the system, over a period of about 30 minutes, with a nitrogen flush of about 50 ml per minute. After the hydrofluoric acid flow was stopped, the nitrogen flush would be maintained for at least 30 additional minutes with the system at the given temperatures to assure that no condensation of water or hydrofluoric acid occurred when the system cooled down.

#### Fluorination Run Procedures

The first runs made with a new catalyst were those at lower temperatures and shorter residence times, to minimize aging effects due to catalyst carbonation. In the evaluation of catalysts in terms of variations in activities and yields with variations in temperature and residence time, the pivot point technique was employed. This involved varying either run temperature or residence time with respect to a set of central reference conditions, termed the "pivot point". This reference point was chosen as a run temperature of 350°C and a

syringe pump setting of 19 (residence time approximately seven seconds) based upon literature data and the results of preliminary runs.

At the beginning of a run or series of runs, the variable transformers were set at the level required to bring the preheater, connector, and inlet sections to the required temperature. The preheater was generally maintained at approximately 200°C, since higher temperatures resulted in significant pressure surges due to flash vaporization of feed materials. Connector and inlet sections were set to the reactor temperature, while reactor flange heating tapes were allowed to reach a level about 50°C higher than the reactor. The scrubber assembly was maintained at 50-55°C to prevent condensation of  $\text{CH}_2\text{Cl}_2$  in the system, while the scrubber outlet was regulated at 60°C to prevent any condensation of water vapor from the scrubber.

The temperature of the reactor was regulated by setting the tube furnace control to a point slightly above the desired temperature, then manually cycling the reactor temperature about the desired run temperature by means of an on/off switch. This procedure was made necessary by the inability of the tube furnace temperature control to maintain a set temperature, and allowed control to  $\pm 2^\circ\text{C}$ .

When the apparatus had stabilized at the desired temperature, the pump syringes were filled with dichloromethane (Malinkrodt Analytical Reagent grade) and 38% hydrofluoric acid (prepared by dilution of Malinkrodt Analytical Reagent grade 48% hydrofluoric acid). With a nitrogen flow of 51.0 ml per minute, the syringe pump was initially set to a high rate to fill the feed lines and preheater

inlet tubes, this requiring about 4 ml of each liquid. The pump rate was then set to the required level for the run.

The mole ratio of HF to  $\text{CH}_2\text{Cl}_2$  for most runs was 1.4 to 1, this resulting from the relative sizes of the syringes used. Residence times were determined by the particular pump setting used in a run. Due to the fact that the Harvard Apparatus Syringe pump had discrete rather than continuous pump rate settings, run sequences in which residence time was held constant while temperature was varied were, by necessity, made at the same flow settings. This resulted in some variation of the actual residence time due to the change in the volume of the products and the reactants with temperature.

As a run progressed, 0.500 ml samples of reactor effluent gas were withdrawn from the sample port and analyzed on the gas chromatograph. Samples were generally taken at 15 minute intervals, which corresponds roughly to the cycle time of the G.C. Run times were generally limited to 1 1/2 to 2 hours to minimize the effects of catalyst aging on subsequent runs.



## RESULTS AND DISCUSSION

### Alumina-Supported Catalysts

Table VII shows the results obtained in runs with a chromium-alumina catalyst at various temperatures and contact times. The column labeled "Material Balance" refers to the percentage of the original dichloromethane feed which leaves the reactor as a gaseous product or as unreacted  $\text{CH}_2\text{Cl}_2$ . The material balance serves as an indication of the amount of feed that underwent thermal cracking to carbon and thus as a general indication of the rate of catalyst carbonization.

The column on Table VII labeled "Percent Yield of Other Cracking Products" refers to the combined yield of all products of thermal cracking other than  $\text{CH}_3\text{Cl}$ :  $\text{CH}_4$ ,  $\text{CH}_3\text{F}$ , carbon and any two-carbon fluorocarbons. The yield of  $\text{CH}_3\text{Cl}$ , also a cracking product, is given separately due to the fact that it is a major component of the reactor effluent of some runs. Thermal cracking of  $\text{CH}_2\text{Cl}_2$  will be discussed in detail in the next section.

Two points should be noted from the results given in Table VII: first, the activity of the catalyst is considerably lower than that observed for vapor phase fluorinations with anhydrous hydrogen fluoride (see Table I). Second, the yield of the desired product,  $\text{CH}_2\text{ClF}$ , is low, with production of difluoromethane and methyl chloride tending to be favored. Qualitative runs made earlier with the clean alumina support only and with a chromium-nickel alumina-supported

Table VII  
Results for Alumina-Supported Catalyst

Catalyst	Metal Content (moles metal per gram sup- port, $\times 10^{-5}$ )	Resi- dence Time (sec.)	HF/CH <sub>2</sub> Cl <sub>2</sub> Ratio	Run Temper- ature (°C)	Conver- sion	Mater- ial Balance	Yield CH <sub>2</sub> ClF	Yield CH <sub>2</sub> F <sub>2</sub>	Yield CH <sub>3</sub> Cl	Yield Other Cracking Products
1. Cr/ Alumina	0.704	6.6	1.4/1	300	9%	100%	29%	31%	40%	0%
"	"	3.5	"	350	12%	100%	2%	73%	24%	0%
"	"	6.1	"	350	13%	100%	16%	44%	39%	0%
"	"	7.7	"	350	14%	100%	37%	34	29%	0%
"	"	8.8	"	400	30%	95%	11%	47	24%	18%

catalyst showed similar behavior.

Surface area and pore volume determinations made at Dow Chemical Company, Louisiana Division, for samples of clean alumina and for the used chromia-alumina catalyst produced the following results:

Table VIII

Surface Areas and Pore Volumes for  
Alumina and Cr/Alumina Catalyst

	<u>Surface Area</u> (m <sup>2</sup> /gram)	<u>Total Pore</u> <u>Volume (cm<sup>3</sup>/gm)</u>
Alumina	224	0.272
Used Cr/Alumina Catalyst	15	0.013

This data shows a severe loss of catalyst surface area, which would explain the low activity observed for this catalyst system. The high material balances obtained for runs with this catalyst tend to indicate that buildup of carbon from thermal cracking was not the cause of this surface area loss.

The loss in surface area may then result from the unique ability of aqueous HF to fluorinate the alumina. The patent reports mentioned previously indicate that fluorination of alumina with anhydrous HF results in no such drastic loss of surface area.

Data reported concerning the formation of aluminum fluorides, Al(OH)F<sub>2</sub> and Al(OH)<sub>2</sub>F are formed to some degree during fluorination of alumina if the support is wet, and suggests that partial conversion of these to AlF<sub>3</sub> optimizes catalyst activity. If the presence of a

relatively large amount of water, due to the use of aqueous HF, favors the formation of one or both of these species over  $\text{AlF}_3$ , the resulting crystal structure on the support surface may have a lower surface area than in a case in which  $\text{AlF}_3$  predominates.

### Carbon-Supported Catalysts

Table IX summarizes the results obtained in runs involving Cr, Ni, Co, La, Ag, Cu, Sn, Hg(I), Hg(II), Sn, Ru, Zn, Na and Ca salts impregnated on carbon, and with the clean carbon support.

The data from the runs utilizing the carbon support without any impregnated metal salts indicates that carbon has a low degree of activity as a fluorination catalyst, but a considerably greater activity as a cracking catalyst. The production of a significant quantity of methyl chloride in the cracking reaction suggest the following free-radical mechanism:<sup>48</sup>

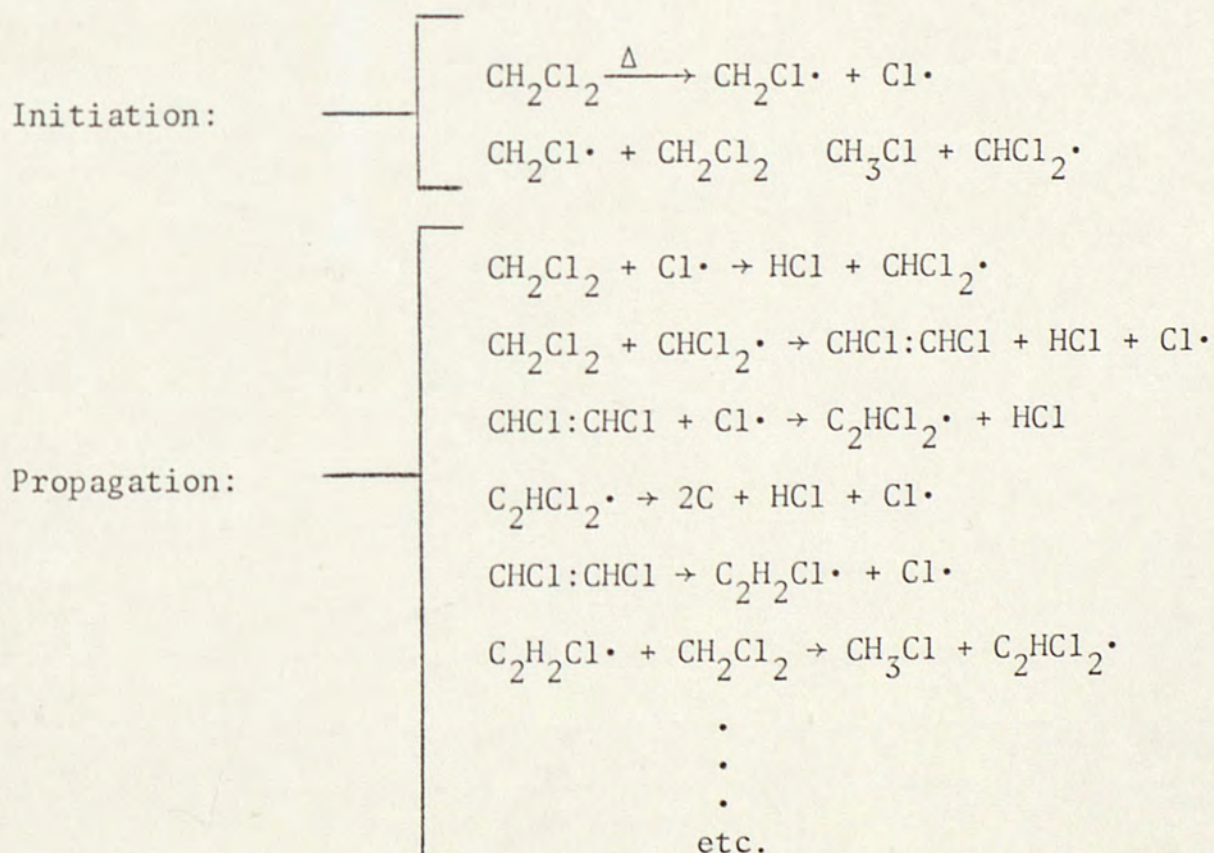


Table IX  
Results for Carbon-Supported Catalysts

Catalyst	Metal Content (moles metal per gram sup- port, x 10 <sup>-5</sup> )	Resi- dence time (sec.)	HF/CH <sub>2</sub> Cl <sub>2</sub> Ratio	Run Temper- ature (°C)	Conver- sion	Mater- ial Balance	Yield CH <sub>2</sub> ClF	Yield CH <sub>2</sub> F <sub>2</sub>	Yield CH <sub>3</sub> Cl	Yield Other Cracking Products
2. C only	----	5.5	1.4/1	250	1%	99%	0%	0%	79%	21%
"	----	6.0	"	275	10%	91%	4%	3%	7%	86%
"	----	6.6	"	300	18%	89%	23%	6%	8%	63%
"	----	7.2	"	325	43%	77%	24%	12%	9%	55%
"	----	3.5	"	350	56%	53%	11%	3%	1%	84%
"	----	7.7	"	350	92%	33%	18%	7%	3%	73%
"	----	12.3	"	350	70%	53%	20%	10%	4%	66%
"	----	8.8	"	400	98%	27%	14%	8%	2%	75%
3. Ni/C	1.20	3.5	"	350	62%	62%	18%	11%	9%	62%
"	"	6.1	"	350	29%	97%	44%	27%	17%	13%
"	"	7.7	"	350	34%	86%	29%	22%	9%	40%
4. Cr/C	1.20	6.6	"	300	42%	89%	9%	48%	15%	28%
"	"	10.5	"	300	32%	100%	17%	63%	20%	1%
"	"	3.5	"	350	29%	100%	20%	64%	14%	3%
"	"	6.1	"	350	54%	84%	24%	35%	11%	31%
"	"	7.7	"	350	62%	70%	17%	29%	7%	48%
"	"	12.3	"	350	90%	25%	16%	1%	0%	84%
"	"	8.8	"	400	91%	32%	10%	12%	1%	77%
"	"	2.6	2.7/1	350	60%	64%	4%	28%	9%	59%
"	"	4.6	"	350	67%	60%	5%	27%	8%	60%
"	"	5.8	"	350	64%	68%	5%	35%	10%	50%

Table IX (cont.)

Catalyst	Metal Content (moles metal per gram sup- port, $\times 10^{-5}$ )	Resi- dence Time (sec.)	HF/CH <sub>2</sub> Cl <sub>2</sub> Ratio	Run Temper- ature (°C)	Conver- sion	Mater- ial Balance	Yield CH <sub>2</sub> ClF	Yield CH <sub>2</sub> F <sub>2</sub>	Yield CH <sub>3</sub> Cl	Yield Other Cracking Products
5. Cr/C	2.40	3.5	1.4/1	350	68%	90%	20%	58%	7%	16%
"	"	6.1	"	350	42%	100%	36%	45%	18%	2%
"	"	7.7	"	350	71%	51%	6%	20%	5%	69%
6. Cr/C	4.40	7.7	1.4/1	350	52%	83%	22%	36%	9%	34%
"	"	8.8	"	400	62%	74%	21%	27%	6%	46%
7. Cr(VI)/C	1.10	7.7	1.4/1	350	76%	18%	11%	7%	2%	80%
8. Ag/C	1.20	6.6	1.4/1	300	15%	92%	35%	7%	4%	55%
"	"	10.5	"	300	56%	54%	14%	4%	1%	81%
"	"	7.0	"	320	66%	43%	11%	3%	1%	86%
"	"	11.2	"	320	88%	24%	10%	3%	1%	86%
"	"	3.5	"	350	11%	96%	44%	14%	2%	40%
"	"	7.7	"	350	95%	18%	11%	2%	1%	87%
"	"	12.3	"	350	75%	25%	20%	6%	1%	73%
"	"	8.8	"	400	97%	2%	10%	4%	1%	85%
9. Co/C	1.20	6.6	1.4/1	300	18%	95%	47%	12%	14%	27%
"	"	3.5	"	350	51%	59%	10%	3%	6%	82%
"	"	7.7	"	350	61%	52%	14%	4%	2%	80%
"	"	12.3	"	350	76%	42%	5%	6%	2%	77%
"	"	8.8	"	400	93%	16%	5%	2%	1%	92%

Table IX (cont.)

Catalyst	Metal Content (moles metal per gram sup- port, $\times 10^{-5}$ )	Resi- sence Time (sec.)	HF/CH <sub>2</sub> Cl <sub>2</sub> Ratio	Run Temper- ature (°C)	Conver- sion	Mater- ial Balance	Yield CH <sub>2</sub> ClF	Yield CH <sub>2</sub> F <sub>2</sub>	Yield CH <sub>3</sub> Cl	Yield Other Cracking Products
10. La/C	1.20	3.5	1.4/1	350	89%	32%	8%	10%	2%	80%
"	"	6.1	"	350	99%	24%	8%	11%	1%	81%
"	"	7.7	"	350	97%	32%	15%	12%	2%	72%
11. Sn/C	1.20	6.6	1.4/1	300	35%	76%	24%	3%	4%	69%
"	"	3.5	"	350	22%	88%	36%	7%	3%	54%
"	"	7.7	"	350	45%	73%	32%	6%	1%	59%
"	"	12.3	"	350	72%	52%	27%	5%	1%	66%
12. Hg(I)/C	1.20	6.6	1.4/1	300	----	----	----	----	----	----
13. Hg(II)/C	1.20	5.5	1.4/1	250	50%	53%	4%	1%	1%	95%
"	"	6.1	"	275	78%	43%	11%	15%	1%	74%
14. Cu/C	1.20	6.6	1.4/1	300	58%	47%	5%	1%	3%	91%
"	"	3.5	"	350	21%	92%	39%	11%	12%	38%
"	"	5.5	"	350	27%	88%	26%	10%	16%	46%
"	"	7.7	"	350	78%	35%	14%	3%	1%	83%
"	"	12.3	"	350	96%	18%	12%	2%	1%	85%
"	"	8.8	"	400	97%	25%	11%	4%	6%	77%
15. Cu/C	2.40	5.5	1.4/1	350	63%	43%	8%	1%	1%	91%
"	"	7.7	"	350	52%	63%	21%	5%	3%	71%
"	"	12.3	"	350	70%	49%	18%	5%	3%	73%
"	"	8.8	"	400	98%	26%	14%	5%	2%	79%

Table IX (cont.)

Catalyst	Metal Content (moles metal per gram sup- port, $\times 10^{-3}$ )	Resi- dence Time (sec.)	HF/CH <sub>2</sub> Cl <sub>2</sub> Ratio	Run Temper- ature (°C)	Conver- sion	Mater- ial Balance	Yield CH <sub>2</sub> ClF	Yield CH <sub>2</sub> F <sub>2</sub>	Yield CH <sub>3</sub> Cl	Yield Other Cracking Products
16. Fe/C	1.20	6.6	1.4/1	300	92%	22%	10%	4%	2%	85%
"	"	3.5	"	350	61%	41%	3%	1%	1%	96%
17. Ru/C	1.20	5.5	1.4/1	250	8%	96%	41%	1%	12%	46%
"	"	5.8	"	265	10%	97%	18%	10%	13%	29%
"	"	6.1	"	275	38%	75%	26%	5%	3%	66%
"	"	6.6	"	300	100%	14%	10%	2%	1%	86%
18. Zn/C	1.20	5.5	1.4/1	250	1%	100%	0%	0%	0%	0%
"	"	6.1	"	275	5%	98%	19%	4%	34%	43%
"	"	6.6	"	300	22%	88%	16%	11%	16%	57%
"	"	3.5	"	350	26%	88%	27%	11%	14%	48%
"	"	7.7	"	350	59%	58%	15%	6%	6%	72%
"	"	12.3	"	350	68%	48%	13%	5%	4%	77%
"	"	8.8	"	400	94%	21%	8%	4%	1%	87%
19. Na/C	1.20	6.6	1.4/1	300	3%	100%	65%	18%	17%	0%
"	"	3.5	"	350	19%	90%	27%	12%	7%	54%
"	"	7.7	"	350	47%	69%	22%	7%	4%	66%
"	"	12.3	"	350	98%	22%	15%	4%	2%	80%
"	"	8.8	"	400	67%	58%	24%	8%	2%	66%
20. Ca/C	1.20	6.1	1.4/1	275	12%	91%	10%	3%	15%	72%
"	"	6.6	"	300	5%	100%	46%	18%	36%	0%
"	"	3.5	"	350	30%	82%	20%	10%	11%	59%
"	"	7.7	"	350	27%	90%	32%	13%	16%	38%



Termination of the chains could take place by a variety of radical-coupling reactions. Data collected by Hoare, Norrish and Whittingham indicates that  $\text{CHCl}_2\cdot$  is the chain carrier and not  $\text{CH}_2\text{Cl}\cdot$ .<sup>48</sup>

The results obtained for runs with the clean carbon support alone indicate that production of a practical carbon-supported catalyst requires the discovery of a metal fluoride or combination of metal fluorides which, when impregnated on a carbon support, result in a catalyst which is active below the temperature at which significant cracking of  $\text{CH}_2\text{Cl}_2$  on carbon occurs, or which has a reduced cracking activity in general. Thermal cracking not only results in lower yields of desired products, but also deposits carbon on the catalyst surface, reducing activity. This is particularly serious in the case of a carbon-supported catalyst, as carbon deposits cannot be burned off the carbon support as they often can for alumina-supported catalysts.

Since the majority of patented fluorination catalysts utilize nickel, chromium, or both, the first metal fluoride/carbon catalysts studied consisted of salts of these metals impregnated on the carbon support.

The data presented in Table IX for the Ni/C catalyst appears to indicate that this catalyst has a higher activity at lower contact times. This drop in conversion was apparently due, in actuality, to rapid buildup of carbon deposits on the catalyst. Qualitative runs for Ni/C and Ni-Cr/C catalysts for long periods of time at the same contact time supports this theory.

The Cr/C catalyst produced somewhat better results than the Ni/C catalyst in terms of material balance and activity loss, although a definite loss in activity can be noted following the initial run. The ratio of production of  $\text{CH}_2\text{F}_2$  to the desired product,  $\text{CH}_2\text{ClF}$ , is even greater than that observed for the Cr/alumina catalyst, except at the high-temperature, long-residence-time runs where cracking predominates. Surface-area studies on the carbon support and the Cr/C catalyst showed that the surface area of the used catalyst was severely reduced, apparently by carbon deposited on the catalyst surface by thermal cracking.

Table X

Surface Areas and Pore Volumes for  
Activated Charcoal and Cr/Carbon Catalyst

	<u>Surface Area</u> ( $\text{m}^2/\text{gram}$ )	<u>Total Pore Volume</u> ( $\text{cm}^3/\text{gram}$ )
Activated Charcoal	592	0.562
Used Cr/Carbon Catalyst	99	0.212

Runs with a Cr/C catalyst with a higher HF to  $\text{CH}_2\text{Cl}_2$  ratio resulted in even lower yields of  $\text{CH}_2\text{ClF}$  than observed in previous Cr/C catalyst runs. The higher relative HF concentration apparently results in the production of the more highly-fluorinated species, as might be expected. The higher acid concentration also appeared to enhance the cracking process.

An increase in the metal content of the chromium catalyst

resulted, in general, in increased cracking, and a lower yield of the difluorinated product relative to the initial Cr/C catalyst was observed.

A further increase in metal content resulted in a reduction in thermal cracking, an enhanced yield of  $\text{CH}_2\text{ClF}$ , and a lower overall conversion relative to the previous catalyst. This apparently indicates that the optimum metal content, in terms of maximal catalyst activity, had been exceeded, and that any additional metal content would result in lower catalyst surface areas and thus lower activity.

Since it is mentioned in the patent literature that catalyst systems containing chromium oxyfluorides appear to be more active as fluorination catalysts than those containing only  $\text{CrF}_3$ ,<sup>27</sup> a carbon support was impregnated with  $\text{K}_2\text{Cr}_2\text{O}_7$  in an attempt to prepare potassium fluorochromate,  $\text{KCrOF}_3$ , by a procedure similar to one given by Mellor, involving the reaction of  $\text{K}_2\text{Cr}_2\text{O}_7$  and hydrofluoric acid. The resulting catalyst exhibited an extremely high activity toward the cracking reaction, with reduced fluorination activity in comparison to the other chromium catalysts.<sup>49</sup>

A silver catalyst produced a 5:1 ratio of  $\text{CH}_2\text{ClF}$  to  $\text{CH}_2\text{F}_2$  at  $300^\circ\text{C}$  and a residence time of 6.6 seconds, and a 3:1 ratio at  $350^\circ\text{C}$  and a residence time of 3.5 seconds. But the actual yields of  $\text{CH}_2\text{ClF}$  were, respectively, only 35 and 44%, at relatively low conversions, due to thermal cracking.

Results similar to those obtained for the silver catalyst were observed in runs with a cobalt catalyst. A run at  $300^\circ\text{C}$  with a

residence time of 6.6 seconds produced a 4:1 ratio of  $\text{CH}_2\text{ClF}$  to  $\text{CH}_2\text{F}_2$ , but with a higher yield of cracking products than the desired product,  $\text{CH}_2\text{ClF}$ . Runs at higher temperatures exhibited an even greater degree of thermal cracking.

A recent German article<sup>33</sup> prompted the preparation and testing of a lanthanum catalyst. This catalyst was characterized by a high conversion, but very low yields of fluorocarbons due to severe cracking.

A catalyst consisting of tin on a carbon support produced the highest ratios of  $\text{CH}_2\text{ClF}$  to  $\text{CH}_2\text{F}_2$ , at a conversion of over 10%, of any catalyst studied, ranging from 6:1 at 300°C and a 6.6 second residence time to 5:1 at 350°C and a residence time of 12.3 seconds. But yields of cracking products exceeded that of  $\text{CH}_2\text{ClF}$  by a significant margin at all run temperatures.

A catalyst prepared with mercurous nitrate exhibited such a high initial cracking activity and such a rapid loss of overall activity that no quantitative results were obtained. A catalyst containing  $\text{Hg(II)}$  also caused severe cracking, even at a run temperature of 250°C. When the reactor tube was opened following runs with these two catalysts, metallic mercury was found in each case. This phenomena has been observed by previous researchers, and is apparently due to the reduction of  $\text{Hg(I)}$  and  $\text{Hg(II)}$  by carbon.<sup>50</sup>

Another interesting observation concerning the  $\text{Hg(II)}$  catalyst is the fact that very little methyl chloride was produced in spite of extensive cracking. This effect was observed for a number of other

catalysts. Apparently, methyl chloride also undergoes thermal cracking with these catalysts.

A copper catalyst produced an overall yield of  $\text{CH}_2\text{ClF}$  of 39%, with a conversion of 21%, at a run temperature of  $350^\circ\text{C}$  and a residence time of 3.5 seconds. This was the largest actual quantity of  $\text{CH}_2\text{ClF}$  produced by any catalyst system.

Runs with a copper catalyst with twice the metal content of the previous one produced poorer yields of  $\text{CH}_2\text{ClF}$  and higher yields of cracking products, rather than the reverse. This suggests that copper also catalyzes the cracking reaction.

To gain information on catalyst lifetimes, an extended run was made with a fresh bed of the first copper catalyst, at a temperature of  $350^\circ\text{C}$  and a residence time of 3.5 seconds. The catalyst showed an initial high cracking activity, which dropped off very rapidly over the first hour of the run. There were no corresponding changes in the quantities of fluorocarbon produced, these remaining approximately constant over that time period. This behavior helps to explain the poor yields at  $300^\circ\text{C}$  for the first copper catalyst. After about 1 1/2 hours, a decrease in catalyst activity relative to fluorocarbon production was noted. After five hours of running at the specified conditions, fluorocarbon production had dropped to about one-half its initial level.

An iron catalyst was found, in general, to be highly active in catalyzing the cracking reaction, but to have little ability to catalyze the fluorination reaction.

A ruthenium catalyst was found to be capable of producing a 48% yield of chlorofluoromethane at the relatively low run temperature of 265°C, but conversion in this case was only 10%. In common with other catalysts studied, cracking predominated at higher temperatures.

A zinc catalyst, prepared and tested in order to compare its properties with those of the mercury catalysts, as it is in the same column of the periodic table as mercury, exhibited properties which differed little from those of the carbon alone, exhibiting some cracking and little fluorination.

Recent reports of the use of calcium fluoride and sodium bifluoride,  $\text{NaHF}_2$ , as fluorinating agents<sup>34,51-52</sup> lead to the preparation of sodium and calcium catalysts on a carbon support in the hope that they would show cracking activities different from catalysts prepared with other metals. The sodium catalyst produced a 65% yield of  $\text{CH}_2\text{ClF}$  at 300°C, but with a conversion of only 3%. At higher temperatures, cracking became severe. At the same temperature, the calcium catalyst produced a 46% yield of  $\text{CH}_2\text{ClF}$ , but a conversion of only 5%. Again, higher temperatures resulted in a rapid increase in cracking.

At this point, it was concluded that the evaluation of the most promising fluorination catalysts was complete, and the project was terminated.

#### Sources of Experimental Error

The major source of error in this project was found to be the random fluctuations in total chromatogram peak areas during a run.

This fluctuation was apparently due mainly to irregularities in the infusion rates of  $\text{CH}_2\text{Cl}_2$  and hydrofluoric acid, caused by a relatively small degree of intermittent binding of the syringe plungers, and to a lesser extent to the flash vaporization effects in the preheater section. The latter problem was minimized by running the preheater section at a temperature substantially lower than the reactor section. Relative error in results from this source ranged typically from about one to four percent.

Another source of error is in the calibration curves used for conversion of peak areas to molar quantities. In this case, it was estimated that these calibration curves induced from one-half to one percent error in the final results.

Error due to effluent sampling technique was estimated to be approximately one-half of one percent.

### CONCLUSIONS

Examination of the results obtained in this project lead to the following conclusions:

1. The severe surface-area loss of alumina-supported catalysts during fluorination with aqueous HF, and the accompanying low catalytic activities makes them weak candidates for consideration as potentially useful fluorination catalysts.
2. Although several of the carbon-supported catalysts produced substantial amounts of the desired product, chlorofluoromethane, the low yields due to the competing thermal cracking reaction would tend to make their application to an industrial process economically unattractive.
3. The apparent short lifetime of the significantly active catalysts due to carbonization, and the absence of a reasonable method for removal of this deposit or otherwise reactivating the carbon-supported catalysts, renders them impractical for fluorination of dichloromethane from this standpoint also.
4. The fact that some catalysts did display significant fluorination activity with hydrofluoric acid indicates that they might be useful for the fluorination of chlorinated hydrocarbons that are less susceptible to thermal cracking than dichloromethane.
5. It is suggested that the project be continued with other



chlorinated hydrocarbons as feed materials.

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