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[54] PROCESS FOR THE MANUFACTURE OF
1,1,1-TRIFLUORODICHLOROETHANE AND
1,1,1,2-TETRAFLUROCHLOROETHANE

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[52] U.S. Cl. 570/169; 423/595;
570/168

[58] Field of Search 570/168, 169; 423/595

[56] References Cited

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[57] ABSTRACT

An improved gas-phase process for the manufacture of 1,1,1-trifluorodichloroethane and/or 1,1,1,2-tetrafluorochloroethane by contacting a suitable tetrahaloethylene and/or pentahaloethane with hydrogen fluoride in the presence of Cr₂O₃, prepared by pyrolysis of (NH₄)₂Cr₂O₇, the reaction being conducted under controlled conditions whereby the production of pentafluoroethane is minimized.

11 Claims, No Drawings

**PROCESS FOR THE MANUFACTURE OF
1,1,1-TRIFLUORODICHLOROETHANE AND
1,1,1,2-TETRAFLUOROCHLOROETHANE**

FIELD OF THE INVENTION

An improved process for the manufacture of 1,1,1-trifluorodichloroethane and/or 1,1,1,2-tetrafluoro-
chloroethane, more particularly, a gas-phase reaction of
a suitable tetrahaloethylene and/or pentahaloethane
with hydrogen fluoride in the presence of a Cr₂O₃ cata-
lyst prepared by pyrolysis of ammonium dichromate,
the reaction being conducted under controlled condi-
tions whereby the production of pentafluoroethane is
minimized.

BACKGROUND OF THE INVENTION

Canadian Pat. No. 1,196,345 (1985) describes a pro-
cess for the preparation of CF₃CHXY (X=H, F; Y=H,
F, Cl, Br, I) by addition of HF to the corresponding
ethylene in the presence of chromium oxyfluoride at
20°-200° C., especially 60°-180° C.

U.S. Pat. No. 3,755,477 describes a process for pro-
ducing fluorinated aliphatic hydrocarbons which com-
prises fluorinating a halogenated aliphatic hydrocarbon,
including tetrachloroethylene and chlorotrifluoroethyl-
ene, by reaction in the gas phase with HF in the pres-
ence of a steam-treated and calcined chromium oxide
catalyst prepared by a multi-step process. Example 23,
column 5, shows tetrachloroethylene as a raw material
with formation of CF₃CHCl₂ (20%), CF₃CHClF
(20%), CF₃CHF₂ (30%), and CF₃CClF₂ (20%) at 10/1
HF/C₂Cl₄ mol ratio, 5.4 seconds contact time and 360°
C. reaction temperature. Example 24, column 5, shows
chlorotrifluoroethylene as a raw material with forma-
tion of CF₂=CF₂ (20%) and CF₃CHClF (13%) at 1.8/1
HF/C₂ClF₃ mol ratio, 4 seconds contact time and 320°
C. reaction temperature. In these examples, less desir-
able pentafluorinated products are obtained in a greater
amount than the desired tri- and tetrafluoro products.

U.S. Pat. No. 3,258,500 describes a process for the
catalytic vapor phase reaction of HF with halohydro-
carbons, including tetrachloroethylene and chlorotrifluoro-
ethylene, employing a catalyst that consists essen-
tially of a heat-activated anhydrous chromium (III)
oxide which may be supported on alumina. This catalyst
is highly active. Example 17, column 14 showing fluori-
nation of tetrachloroethylene with this catalyst, like
that of the above '477 patent, produces large quantities
of the less desirable highly fluorinated pentafluoro-
ethane. At 400° C. the product distribution is 35.0%
pentafluoroethane, 9.2% 1-chloro-1,2,2,2-tetrafluoro-
ethane, and 3.5% 1,1-dichloro-2,2,2-trifluoroethane. At
300° C. the product distribution is 38.3% 1-chloro-
1,2,2,2-tetrafluoroethane, 25.4% pentafluoroethane, and
16.0% 1,1-dichloro-2,2,2-trifluoroethane. Example 20,
column 15, shows that chlorotrifluoroethylene yields
CF₃CHF₂ as the major product at 400° C.

GB No. 1,000,485 describes a process for the prepara-
tion of organic fluorinated compounds by fluorination
of halo-olefins in the gaseous phase and at a temperature
preferably within the range of 200° C. to 400° C. The
catalyst consists essentially of partially fluorinated alu-
mina impregnated with one or more polyvalent metal
halides. The polyvalent metal may be chromium, cobalt,
nickel or manganese. The total content of polyvalent
metal halide, expressed as oxide, is not more than
15% by weight of the partially fluorinated (70-80%)

alumina expressed as alumina. Example 4 (Table 4)
shows that reaction of tetrachloroethylene with HF
over such catalyst yields CF₃CHCl₂ as the major prod-
uct at 220°-290° C. In addition, the patent states that, if
fluorination of the catalyst is excessive, the activity of
the catalyst is impaired (page 3, column 2, lines 85-87).

The references do not disclose how to favor the pro-
duction of 1,1,1-trifluorodichloroethane over 1,1,1,2-
tetrafluoroethane while maximizing the produc-
tion of these two compounds taken together over the
production of more highly fluorinated products.

The process of the instant invention achieves the
desired high degree of selectivity by minimizing the
formation of the pentafluoroethane through catalyst
selection and control of the reaction variables, as dis-
cussed below and illustrated in the Examples.

SUMMARY OF THE INVENTION

What has been discovered is a process for the prepa-
ration of 1,1,1-trifluorodichloroethane and/or 1,1,1,2-
tetrafluoroethane by fluorination of a tetrahalo-
ethylene, C₂Cl_{4-x}F_x, wherein x=0 to 3, and/or a pen-
tahaloethane, C₂HCl_{5-x}F_x, wherein x=0 to 2, compris-
ing contacting in the gaseous phase at effective temper-
ature, mol ratio, and contact time, said tetrahaloethyl-
ene and/or pentahaloethane with HF and Cr₂O₃, said
Cr₂O₃ prepared by pyrolysis of (NH₄)₂Cr₂O₇, said con-
tacting producing a product stream containing 1,1,1-tri-
fluorodichloroethane and/or 1,1,1,2-tetrafluoro-
chloroethane and pentafluoroethane, wherein the
amount of said 1,1,1-trifluorodichloroethane and/or
1,1,1,2-tetrafluoroethane is greater than the
amount of pentafluoroethane produced, and, thereafter,
separating the 1,1,1-trifluorodichloroethane and/or
1,1,1,2-tetrafluoroethane from the product
stream.

DETAILS OF THE INVENTION

The tetrahaloethylene of this invention is defined by
the formula C₂Cl_{4-x}F_x, wherein x=0 to 3, and includes
CCl₂=CCl₂, CClF=CCl₂, CClF=CClF, CF₂=CCl₂,
and CF₂=CClF and mixtures of these. The pentahalo-
ethanes of this invention are defined by the formula
C₂HCl_{5-x}F_x, wherein x=0 to 2, and includes
CCl₃CHCl₂, CCl₂FCHCl₂, CCl₃CHClF, CCl₂FCHCl₂,
and CCl₂FCHClF and mixtures of these. The tetrahalo-
ethylenes and pentahaloethanes of this invention are
known to the art.

The Cr₂O₃ catalyst of this invention is prepared by
pyrolysis of ammonium dichromate. By pyrolysis is
meant heating ammonium dichromate to a sufficient
temperature and for a sufficient time to cause the fol-
lowing reaction to occur to substantial completion:



For example, ammonium dichromate may be heated in
a continuous kiln at 500°-700° C., preferably 540°-640
C., for 5-20 minutes so that it will undergo an internal
oxidation-reduction reaction to produce mainly water,
nitrogen and Cr₂O₃. After the water and nitrogen are
driven off, the remaining fine powder of Cr₂O₃ may be
cooled and compacted so as to increase its bulk density
for ease of handling. For example, a bulk density of
approximately 400-560 kg/m³ may be desirable, prefer-
ably 448-512 kg/m³.

The Cr_2O_3 obtained may contain low levels of contaminants which are present as a result of the manufacturing process for the original $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. Although not totally destructive of catalyst efficacy, potassium as a contaminant has an adverse effect on the activity and life of the catalyst of this invention. It is desirable for potassium levels to be 100 ppm by weight or less. The level may be reduced by a water washing step. While the conditions are not critical, the water washing step can include forming a slurry containing 5–15% Cr_2O_3 , preferably 10%, and deionized water. Stirring of this water slurry can be carried out at 35°–65° C. for at least one hour, preferably two or more hours. The solids are then recovered by filtration, suitably on a plate and frame filter press. The filter cake can be analyzed for potassium. If its level is 100 ppm by weight or less (dry basis), the solids are, thereafter, dried. If not, the washing step can be repeated to obtain a desired level of potassium.

The form of the catalyst is not critical and may be used as pellets, powders or granules.

For example, if the catalyst is desired to be in the pellet form, 5–15%, preferably 10%, of chromium acetate and 1–5%, preferably 2%, of graphite can be added to the dried solids as pelletization aids. The chromium acetate can be added in aqueous solution of 30–70%, preferably 50% concentration. The resultant paste can be milled to mix the ingredients and then pelletized to the desired size, preferably 0.32 cm \times 0.32 cm cylinders. The pellets can be dried at 80°–120° C., preferably 105° C., for 8–48 hours, preferably 16–24 hours. The Cr_2O_3 pellets then have a bulk density of 1120–1440 kg/m³ for the preferred pellet size and a surface area of 40–57 m²/g, preferably 45–55 m²/g. Pore volume is 0.15–0.3 cc/g, the potassium content is 100 ppm or less.

Generally, the resulting Cr_2O_3 will be pretreated with HF. It is thought that this converts some of the surface chrome oxide to chrome oxy-fluoride. This pretreatment can be accomplished by placing the Cr_2O_3 in a suitable container, which can be the reactor to be used to perform the reaction of the instant invention, and thereafter, passing HF over the pyrolyzed and dried Cr_2O_3 so as to partially saturate the Cr_2O_3 with HF. This is conveniently carried out by passing HF over the Cr_2O_3 for a period of time of, for example, about 15 to 300 minutes at a temperature of, for example, about 200° C. to about 450° C. The purpose of this pretreatment is to prevent damage to the catalyst due to possible high temperature excursions and resultant coking of the catalyst if the reactants, tetrahaloethylene and/or pentahaloethane, were contacted with the catalyst without first having conditioned some of the surface chrome oxide with HF. Nevertheless, this pretreatment is not essential; initial process conditions and equipment could be selected so as to avoid the problem of high temperature and coking of the catalyst.

The contacting of the reactants with HF in the presence of the catalyst, preferably pretreated, of the instant invention is performed at effective temperature, mol ratio and contact time. By effective temperature, mol ratio and contact time is meant the temperatures, mol ratios, and contact times which produce a product stream which contains an amount of 1,1,1-trifluorodichloroethane and/or 1,1,1,2-tetrafluorochloroethane which is greater than the amount of pentafluoroethane produced. The temperature can be, for example, about 225° C. to 400° C., preferably about 225° C. to 250° C., with a contact time, for example, of about 0.1 to 100

seconds, preferably about 10 to 90 seconds, and most preferably about 15 to 90 seconds.

The molar ratio of HF to the reactants can range, for example, from about 1/1 to 20/1, preferably about 3/1 to 10/1, and most preferably about 4/1 to 6/1.

In general, the higher the temperature, the greater the HF/reactant mol ratio, and the longer the contact time, the greater is the conversion of the reactants to fluorinated products and the greater is the degree of fluorination of the raw material. The above variables can be balanced, one against the other, so that formation of CF_3CHCl_2 is favored over CF_3CHClF , and the production of these two compounds taken together is maximized and that of more highly fluorinated products minimized.

A key feature of the invention is that through catalyst selection and process control, as described herein, the desired tri- and tetrafluoro products can be obtained as the major products at high reactant conversions, normally greater than 30%. Preferably, the reaction variables are controlled so as to keep the production of the pentafluoro product below about 10 area percent, as determined gas chromatographically, of the products produced. Thus, as illustrated in the Examples with tetrachloroethylene, the tri- and tetrafluoro products are obtained in very high yields while the production of higher fluorinated products is minimized, even at high conversions of tetrachloroethylene.

Intermediates formed during the course of the reaction, such as CHClFCClF_2 , $\text{CHCl}_2\text{CClF}_2$, $\text{CClF}=\text{CCl}_2$ and $\text{CHCl}_2\text{CCl}_2\text{F}$ can be recycled to the reactor for the production of additional CF_3CHCl_2 and CF_3CHClF . In addition, CF_3CHCl_2 can be recycled to the reactor for the production of additional CF_3CHClF when this is desired.

The reaction of the reactants with HF may be conducted in any suitable reactor, including fixed and fluidized bed reactors. The reaction vessel should be constructed from materials which are resistant to the corrosive effects of hydrogen fluoride such as "Hastelloy" and "Inconel".

The pentachloroethane may be fed directly to the reactor or may be prepared in-situ in the reactor by contemporaneously feeding trichloroethylene, chlorine and HF to the reactor containing the catalyst of this invention.

Pressure is not critical Atmospheric and superatmospheric pressures are the most convenient and are therefore preferred.

The fluorinated alkanes produced by the instant invention have utility as blowing agents, propellants and refrigerants. They can also be used as starting materials for the preparation of other useful compounds. For example, CF_3CHClF can be used to prepare 1,1,1,2-tetrafluoroethane.

EXAMPLES

In the following illustrative Examples all parts and percentages are by weight and all temperatures are Centigrade unless otherwise stated. All reactions used commercial HF containing only trace amounts of water.

The pyrolyzed Cr_2O_3 catalyst used in the following Examples was prepared using ammonium dichromate having the following specifications:

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Insolubles	less than	0.2%
Iron	less than	100 ppm
Chloride	less than	100 ppm
Sulfate	less than	500 ppm
Alkali	less than	2000 ppm
pH (8 wt % aqueous sol).		3.2-4.0

The preparation, drying and compacting of the Cr_2O_3 used in the following Examples were performed according to the following procedure:

A rotating continuous kiln, 18 inches in diameter and 17 feet long, was electrically heated to 570° - 620° C. At this point the heater was turned off and ammonium dichromate was fed into the kiln at a feed rate of 280 lb/hr (residence time=8 minutes). The conversion of ammonium dichromate to Cr_2O_3 was essentially quantitative. The heat generated from the internal oxidation-reduction reaction to produce water, nitrogen and Cr_2O_3 was sufficient to maintain the desired reaction temperature. After the water and nitrogen were driven off, the remaining fine powder of Cr_2O_3 was cooled and compacted to a bulk density of approximately 448-512 kg/cubic meter.

PROCEDURE FOR PRETREATMENT

The reactor (0.5 inch ID, 12 inch long "Inconel" pipe) was charged with the amount of catalyst as described in the following Examples and placed in a sand bath. The bath was gradually heated to 400° while nitrogen gas at a flow rate of 50 ml/minute was passed through the reactor to remove traces of water. The temperature was lowered to 200° , and HF and nitrogen gas (1:4 molar ratio) were passed through the reactor. The nitrogen flow was decreased with time until neat HF was being passed through the reactor. At this point, the temperature was gradually raised to 450° and maintained there for 15 to 300 minutes.

PROCEDURE FOR FLUORINATION

The temperature was then decreased, while maintaining the HF flow, to the indicated values and, thereafter, $\text{CCl}_2=\text{CCl}_2$ flow was started. The flows of HF and $\text{CCl}_2=\text{CCl}_2$ were adjusted to give the indicated molar ratios and contact times.

The reactor effluent was scrubbed with aqueous potassium hydroxide to remove HCl and HF, and sampled on-line with a gas chromatograph using a 20 foot, long one-eighth inch diameter column containing "Krytox" perfluorinated polyether on an inert support and a helium carrier gas flow of 35 cc/minute.

EXAMPLES 1-7

The Procedures for Pretreatment and Fluorination were followed using 38.1 g (30 cc) of Cr_2O_3 with a potassium content of 60 ppm as the initial catalyst charge in the form of crushed pellets (40-80 mesh). The results are given in the Table.

TABLE

	Example						
	1	2	3	4	5	6	7
Temperature	300°	300°	250°	225°	225°	225°	250°
HF/ C_2Cl_4 mol ratio	4/1	4/1	4/1	6/1	10/1	6/1	6/1

TABLE -continued

	Example						
	1	2	3	4	5	6	7
Contact time (sec.)	15	30	60	60	60	90	90
Conversion (percent)	79.8	89.4	97.8	94.9	90.4	98.3	99.5
	Area Percent						
CF_3CHCl_2	65.3	57.9	76.1	73.1	74.2	78.3	68.3
CF_3CHClF	11.8	13.2	14.5	10.0	10.0	12.4	20.2
CF_3CHF_2	10.7	15.1	5.4	0.1	0.1	0.1	8.0
$\text{CF}_3\text{CHCl}_2 + \text{CF}_3\text{CHClF}$	77.1	71.1	90.6	83.1	84.2	90.7	88.5

We claim:

1. A process for the preparation of 1,1,1-trifluorodichloroethane and/or 1,1,1,2-tetrafluorochloroethane by fluorination of a tetrahaloethylene, $\text{C}_2\text{Cl}_{4-x}\text{F}_x$, wherein $x=0$ to 3, and/or pentahaloethane, $\text{C}_2\text{HCl}_{5-x}\text{F}_x$, wherein $x=0$ to 2, comprising contacting in the gaseous phase at effective temperature, mol ratio and contact time, said tetrahaloethylene and/or pentahaloethane with HF and Cr_2O_3 , said Cr_2O_3 prepared by pyrolysis of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, said contacting producing a product stream containing 1,1,1-trifluorodichloroethane and/or 1,1,1,2-tetrafluorochloroethane and pentafluoroethane, wherein the amount of said 1,1,1-trifluorodichloroethane and/or 1,1,1,2-tetrafluorochloroethane produced is greater than the amount of pentafluoroethane produced and, thereafter, separating the 1,1,1-trifluorodichloroethane and/or 1,1,1,2-tetrafluorochloroethane from the product stream.
2. The process of claim 1 wherein the tetrahaloethylene is tetrachloroethylene.
3. The process of claim 1 wherein the HF is contacted with the tetrahaloethylene and/or pentahaloethane at a mol ratio of about 1/1 to about 20/1, at a temperature of about 225° C. to about 400° C., and a contact time of about 0.1 seconds to about 100 seconds.
4. The process of claim 3 wherein the HF is contacted with the tetrahaloethylene and/or pentahaloethane at a mol ratio of about 3/1 to about 10/1, at a temperature of about 225° C. to about 250° C., and a contact time of about 10 seconds to about 90 seconds.
5. The process of claim 4 wherein the HF is contacted with the tetrahaloethylene and/or pentahaloethane at a mol ratio of about 4/1 to about 6/1, at a temperature of about 225° C. to about 250° C., and a contact time of about 15 seconds to about 90 seconds.
6. The process of claim 1 wherein conversion of the tetrahaloethylene and/or pentahaloethane to fluorinated products is between about 30% and 100%.
7. The process of claim 1 wherein the amount of pentafluoroethane in the product stream is less than 10 area percent by gas chromatography.
8. The process of claim 1 further comprising the step of recycling at least a portion of starting materials and underfluorinated products.
9. The process of claim 1 wherein the Cr_2O_3 contains 100 ppm potassium or less.
10. The process of claim 1 wherein before the contacting step, the Cr_2O_3 is given a pretreatment by passing hydrogen fluoride gas over it.
11. The process of claim 10 wherein the pretreatment is carried out for about 15 to about 300 minutes at about 200° C. to about 450° C.

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