

## Description

An improved process for the manufacture of 1,1,1-trifluorodichloroethane (FC-123) and 1,1,1,2-tetrafluorochloroethane (FC-124), more particularly, a gas-phase reaction of a suitable tetrahaloethylene with hydrogen fluoride in the presence of a selected metal on a high fluorine content alumina support, the reaction being conducted under controlled conditions whereby the production of pentafluoroethane is minimized.

Canadian Patent No. 1,196,345 describes a process for the preparation of  $\text{CF}_3\text{CHXY}$  ( $\text{X} = \text{H}, \text{F}; \text{Y} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) by addition of HF to the corresponding ethylene in the presence of chromium oxyfluoride at 20-200°C, especially 60-180°C.

U.S. 3,755,477 describes a process for producing fluorinated aliphatic hydrocarbons which comprises fluorinating a halogenated aliphatic hydrocarbon, including tetrachloroethylene and chlorotrifluoroethylene, by reaction in the gas phase with hydrogen fluoride in the presence of a steam-treated and calcined chromium oxide catalyst prepared by a multi-step process. Example 23, col. 5, shows tetrachloroethylene as a raw material with formation of  $\text{CF}_3\text{CHCl}_2$  (20%),  $\text{CF}_3\text{CHClF}$  (20%),  $\text{CF}_3\text{CHF}_2$  (30%), and  $\text{CF}_3\text{CClF}_2$  (20%) at 10/1 HF/ $\text{C}_2\text{Cl}_4$  mol ratio, 5.4 seconds contact time and 360°C reaction temperature. Example 24, col. 5, shows chlorotrifluoroethylene as a raw material with formation of  $\text{CF}_2=\text{CF}_2$  (20%) and  $\text{CF}_3\text{CHClF}$  (13%) at 1.8/1 HF/ $\text{C}_2\text{ClF}_3$  mol ratio, 4 seconds contact time and 320°C reaction temperature. In these examples, less desirable pentafluorinated products are obtained in a greater amount than the desired tri- and tetrafluoro products.

U.S. 3,258,500 describes a process for the catalytic vapor phase reaction of HF with haloalkanes, including tetrachloroethylene including chlorotrifluoroethylene, employing a catalyst that consists essentially of a heat-activated anhydrous chromium (III) oxide which may be supported on alumina. This catalyst is highly active. Example 17, col. 14, shows fluorination of tetrachloroethylene with this catalyst, like that of the above '477 patent, produces large quantities of the less desirable highly fluorinated pentafluoroethane. At 400°C the product distribution is 35.0% pentafluoroethane, 9.2% 1-chloro-1,2,2,2-tetrafluoroethane, 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, col. 15, shows chlorotrifluoroethylene yields  $\text{CF}_3\text{CHF}_2$  as the major product at 400°C.

GB 1,000,485 describes a process for the preparation of organic fluorinated compounds by fluorination of halo-olefins in the gaseous phase and at a temperature preferably within the range 200°C to 400°C. The catalyst consists essentially of partially fluorinated alumina 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 reaction of tetrachloroethylene with HF over such catalyst yields  $\text{CF}_3\text{CHCl}_2$  as the major product 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 produce selectively both 1,1,1-trifluorochloroethane and 1,1,1,2-tetrafluorochloroethane while minimizing the production of the pentafluoroethanes, especially at high tetrahaloethylene conversions.

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 discussed below and illustrated in the Examples.

What has been discovered is a process for the preparation of 1,1,1-trifluorodichloroethane and 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, comprising contacting in the gaseous phase at 300°C to 450°C said tetrahaloethylene and HF with a catalyst comprising a metal in an oxidation state greater than zero, said metal selected from the group consisting of chromium, manganese, nickel, and cobalt, and mixtures thereof, on a support consisting essentially of aluminum, oxygen, and fluorine in such proportions that the fluorine content corresponds to an  $\text{AlF}_3$  content of at least 90% by weight of the catalyst composition exclusive of the metal, said  $\text{AlF}_3$  content being obtained by pretreatment with HF.

The tetrahaloethylene of this invention defined by the formula  $\text{C}_2\text{Cl}_{4-x}\text{F}_x$ , wherein  $x = 0$  to 3, includes  $\text{CCl}_2=\text{CCl}_2$ ,  $\text{CClF}=\text{CCl}_2$ ,  $\text{CClF}=\text{CClF}$ ,  $\text{CF}_2=\text{CCl}_2$ , and  $\text{CF}_2=\text{CClF}$ , and mixtures of these. Tetrachloroethylene is preferred.

By a high fluorine content alumina support is meant a composition comprising aluminum, oxygen and fluorine in such proportions that the total fluorine content of the catalyst composition taken as  $\text{AlF}_3$  corresponds to at least 90 weight percent, exclusive of the supported metal, preferably 95 weight percent  $\text{AlF}_3$  or more.

The remainder of the support may include alumina or aluminum oxyfluoride. The high  $\text{AlF}_3$  content support can be prepared in-situ by exhaustive fluorination of alumina impregnated with at least one chromium, manganese, nickel, or cobalt compound which may be in the form of the oxide, oxyhalide, halide or pseudohalide or such other form which is convertible to the fluoride or oxyfluoride under the conditions of the HF pretreatment

step described herein. The halides include fluorides, chlorides, or bromides. The pseudohalides include cyanides, cyanates and thiocyanates. The preferred metals are manganese, nickel and cobalt. The most preferred metal is cobalt.

The total content of chromium, manganese, nickel, or cobalt expressed as the divalent oxide is not more than 20% by weight of the supported catalyst.

The catalyst of the instant invention can be prepared prior to reaction with the tetrahaloethylene, by impregnating  $Al_2O_3$  with the desired metal compound and treatment with HF at elevated temperatures until the desired degree of fluorination is obtained, e.g., at about 200 degrees Centigrade to about 450 degrees Centigrade. The treatment with HF can conveniently be done in the reactor which is to be used for contacting tetrachloroethylene with HF.

A suitable catalyst may be prepared, for example, as follows:

A quantity of  $Al_2O_3$  is impregnated with a solution of a catalytically effective amount of one or more metal halides or pseudohalides of chromium, manganese, nickel, or cobalt. By catalytically effective amount is meant an amount of the metal expressed as the divalent oxide between 0.02 to 20 weight percent of the alumina support, preferably 0.1 to 5 weight percent. The impregnated  $Al_2O_3$  can be dried until essentially all moisture is removed, e.g., for about 18 hours at about 100°C. The dried catalyst is then transferred to the reactor to be used. The temperature is then gradually increased to about 400°C while maintaining a flow of  $N_2$  through the reactor to remove any remaining traces of moisture from the catalyst and the reactor. The temperature is then lowered to about 200°C and HF diluted with  $N_2$  is passed through the reactor. The  $N_2$  can be gradually reduced until only HF is being passed through the reactor. At this point the temperature can be increased to about 450°C and held at that temperature to convert the impregnated  $Al_2O_3$  to a fluoride content corresponding to at least 90%  $AlF_3$ , e.g., for 15 to 300 minutes, depending on the HF flow and the catalyst volume.

The reaction of the tetrahaloethylene with HF in the presence of the catalyst of the instant invention is conducted at 300°C to 450°C, preferably about 300°C to 400°C, and most preferably about 325°C to 350°C, with a contact time of 5 to 100 seconds, preferably about 10 to 90 seconds, and most preferably about 15 to 60 seconds.

The molar ratio of HF to the tetrahaloethylene can range from 1/1 to 20/1, preferably about 3/1 to 10/1, and most preferably about 4/1 to 7/1.

In general, with a given catalyst composition, the higher the temperature, the greater the HF/tetrahaloethylene mol ratio, and the longer the contact time, the greater is the conversion of the tetrahaloethylene to fluorinated products. The above variables can be balanced, one against the other, so that formation of FC-123 is favored over FC-124 and the production of these two compounds taken together is maximized and that of higher 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 tetrahaloethylene conversions, normally between 30% and 90%. Preferably, the reaction variables are controlled so as to keep the production of the pentafluoro product below 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 minimizing the production of higher fluorinated products even at high conversions of tetrachloroethylene.

Intermediates formed during the course of the reaction, such as  $CHF_2CClF_2$ ,  $CHClFCClF_2$ ,  $CHCl_2CClF_2$ ,  $CClF=CCl_2$ , and  $CHCl_2CCl_2F$ , can be recycled to the reactor for the production of additional FC-123 and FC-124. In addition, FC-123 can be recycled to the reactor for the production of additional FC-124 when this is desired.

The reaction of the tetrahaloethylene 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.

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

The fluorinated alkanes produced by the invention have utility as blowing agents and refrigerants. They can also be used as starting materials for the preparation of other useful compounds. For example, FC-124 can be used to prepare 1,1,1,2-tetrafluoroethane.

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.

#### General Procedure for Fluorination

The reactor (a 12.7mm (0.5 inch) ID, 305mm (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 and 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. The fluorine content of the catalyst composition corresponded to an  $\text{AlF}_3$  content, exclusive of the metal, of at least 95%.

The temperature was then decreased 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 Hewlett Packard HP 5890 gas chromatograph using a 6.1m (20 foot) long, 3.18mm (one-eighth inch) diameter, column containing "Krytox" perfluorinated polyether on an inert support and a helium flow of 35 cc/minute. Gas chromatographic conditions were 70° for 3 minutes followed by temperature programming to 180° at a rate of 6°/minute.

#### EXAMPLES 1 - 2

The General Procedure for Fluorination was followed using 19.8 g. (30 cc) of  $\text{NiCl}_2/\text{Al}_2\text{O}_3$  (2%  $\text{NiCl}_2$ ) as the initial catalyst charge. The results of the reaction of HF with  $\text{CCl}_2=\text{CCl}_2$  over the prepared catalyst are given in Table 1.

**TABLE 1**  
**Example**

|                                                              | <u>1</u>            | <u>2</u> |
|--------------------------------------------------------------|---------------------|----------|
| Temp. °C                                                     | 325                 | 350      |
| HF/ $\text{C}_2\text{Cl}_4$<br>(mol ratio)                   | 5/1                 | 6/1      |
| Contact Time<br>(sec.)                                       | 45                  | 30       |
| Conversion %                                                 | 58.7                | 61.2     |
|                                                              | <u>Area Percent</u> |          |
| $\text{CF}_3\text{CHCl}_2$                                   | 70.0                | 60.6     |
| $\text{CF}_3\text{CHClF}$                                    | 12.4                | 20.3     |
| $\text{CF}_3\text{CHF}_2$                                    | 0.5                 | 1.3      |
| $\text{CF}_3\text{CHCl}_2$ plus<br>$\text{CF}_3\text{CHClF}$ | 82.4                | 80.9     |

#### EXAMPLES 3 - 4

The General Procedure for Fluorination was followed using 19.5 g. (30 cc) of  $\text{MnCl}_2/\text{Al}_2\text{O}_3$  (1.87%  $\text{MnCl}_2$ ) as the initial catalyst charge. The results of the reaction of HF with  $\text{CCl}_2=\text{CCl}_2$  over the prepared catalyst are given in Table 2.

**TABLE 2**

| <b>Example</b>                                                  |          |          |
|-----------------------------------------------------------------|----------|----------|
|                                                                 | <b>3</b> | <b>4</b> |
| Temp. °C                                                        | 350      | 375      |
| HF/C <sub>2</sub> Cl <sub>4</sub><br>(mol ratio)                | 6/1      | 10/1     |
| Contact Time<br>(sec.)                                          | 30       | 25       |
| Conversion %                                                    | 70.4     | 61.5     |
| <b>Area Percent</b>                                             |          |          |
| CF <sub>3</sub> CHCl <sub>2</sub>                               | 67.8     | 58.5     |
| CF <sub>3</sub> CHClF                                           | 18.5     | 17.6     |
| CF <sub>3</sub> CHF <sub>2</sub>                                | 1.0      | 1.1      |
| CF <sub>3</sub> CHCl <sub>2</sub> plus<br>CF <sub>3</sub> CHClF | 86.3     | 76.1     |

**EXAMPLES 5 - 9**

The General Procedure for Fluorination was followed using 18.4 g. (30 cc) of CoCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (2.0% CoCl<sub>2</sub>) as the initial catalyst charge. The results of the reaction of HF with CCl<sub>2</sub>=CCl<sub>2</sub> over the prepared catalyst are given in Table 3.

**TABLE 3**

| Example                                                         |      |      |      |      |      |
|-----------------------------------------------------------------|------|------|------|------|------|
|                                                                 | 5    | 6    | 7    | 8    | 9    |
| Temp. °C                                                        | 350  | 350  | 350  | 350  | 350  |
| HF/C <sub>2</sub> Cl <sub>4</sub><br>(mol ratio)                | 7/1  | 10/1 | 5/1  | 5/1  | 3/1  |
| Contact Time<br>(sec.)                                          | 13.2 | 19.3 | 31.8 | 17.6 | 25.7 |
| Conversion %                                                    | 87.3 | 90.3 | 86.8 | 75.7 | 60.0 |
| Area Percent                                                    |      |      |      |      |      |
| CF <sub>3</sub> CHCl <sub>2</sub>                               | 56.5 | 52.8 | 53.6 | 57.8 | 52.1 |
| CF <sub>3</sub> CHClF                                           | 37.2 | 41.1 | 39.4 | 32.2 | 32.9 |
| CF <sub>3</sub> CHF <sub>2</sub>                                | 1.6  | 2.1  | 2.2  | 1.5  | 2.5  |
| CF <sub>3</sub> CHCl <sub>2</sub> plus<br>CF <sub>3</sub> CHClF | 93.7 | 93.9 | 93.0 | 90.0 | 85.0 |

**EXAMPLES 10 - 13**

The General Procedure for Fluorination was followed using 20.4 g. (30 cc) of CrCl<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> (5.2% CrCl<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>) as the initial catalyst charge. The results of the reaction of HF with CCl<sub>2</sub>=CCl<sub>2</sub> over the prepared catalyst are given in Table 4.

**TABLE 4**

|                                                                 | Example |      |      |      |
|-----------------------------------------------------------------|---------|------|------|------|
|                                                                 | 10      | 11   | 12   | 13   |
| Temp. °C                                                        | 425     | 350  | 350  | 350  |
| HF/C <sub>2</sub> Cl <sub>4</sub><br>(mol ratio)                | 4/1     | 4/1  | 5/1  | 6/1  |
| Contact Time<br>(sec.)                                          | 15      | 60   | 60   | 60   |
| Conversion %                                                    | 62.1    | 78.3 | 78.1 | 80.3 |
| Area Percent                                                    |         |      |      |      |
| CF <sub>3</sub> CHCl <sub>2</sub>                               | 31.4    | 50.8 | 49.6 | 46.1 |
| CF <sub>3</sub> CHClF                                           | 22.2    | 28.5 | 29.7 | 33.3 |
| CF <sub>3</sub> CHF <sub>2</sub>                                | 9.8     | 6.9  | 7.3  | 7.2  |
| CF <sub>3</sub> CHCl <sub>2</sub> plus<br>CF <sub>3</sub> CHClF | 53.6    | 79.3 | 79.3 | 79.4 |

**Claims**

Claims for the following Contracting States: CH, DE, ES, FR, GB, LI, NL, SE, IT

1. A process for the preparation of 1,1,1-trifluorodichloroethane and 1,1,1,2-tetrafluorochloroethane by fluorination of a tetrahaloethylene, C<sub>2</sub>Cl<sub>4-x</sub>F<sub>x</sub>, wherein x = 0 to 3, comprising contacting in the gaseous phase at 300°C to 450°C said tetrahaloethylene and HF with a catalyst comprising at least one metal in an oxidation state greater than zero, said metal selected from the group consisting of chromium, manganese, nickel and cobalt, wherein in the case of chromium it is present in the form of chromium fluoride or chromium oxyfluoride, on a support comprising aluminum, oxygen and fluorine in such proportions that the fluorine content corresponds to an AlF<sub>3</sub> content of at least 90% by weight of the catalyst composition exclusive of the metal, said AlF<sub>3</sub> content being obtained by pretreatment with HF.

2. A process as claimed in claim 1 wherein the tetrahaloethylene is tetrachloroethylene.

3. A process as claimed in claim 1 or claim 2 wherein the catalyst contains 0.02 to 20 weight percent of metal expressed as the divalent oxide.

4. A process as claimed in claim 3 wherein the catalyst contains 0.1 to 5 weight percent of metal expressed as the divalent oxide.

5. A process as claimed in any one of the preceding claims wherein the HF is contacted with the tetrahaloethylene at a mol ratio of 1:1 to 20:1 at a temperature of 300°C to 400°C, and a contact time of 5 to 100 seconds.

6. A process as claimed in any one of the preceding claims wherein conversion of the tetrahaloethylene to fluorinated products is between 30% and 95%.

7. A process as claimed in any one of the preceding claims wherein the metal is selected from the group consisting of manganese, nickel and cobalt.

8. A process as claimed in any one of the preceding claims wherein the temperature, the mol ratio to HF to the tetrahaloethylene, and the contact time are controlled to yield a product stream having a CF<sub>3</sub>CHCl<sub>2</sub> content greater than that of CF<sub>3</sub>CHClF, and the combined total of CF<sub>3</sub>CHCl<sub>2</sub> and CF<sub>3</sub>CHClF is greater than that of

**TABLE 4**

|  |                                                                 | Example      |      |      |      |
|--|-----------------------------------------------------------------|--------------|------|------|------|
|  |                                                                 | 10           | 11   | 12   | 13   |
|  | Temp. °C                                                        | 425          | 350  | 350  | 350  |
|  | HF/C <sub>2</sub> Cl <sub>4</sub><br>(mol ratio)                | 4/1          | 4/1  | 5/1  | 6/1  |
|  | Contact Time<br>(sec.)                                          | 15           | 60   | 60   | 60   |
|  | Conversion %                                                    | 62.1         | 78.3 | 78.1 | 80.3 |
|  |                                                                 | Area Percent |      |      |      |
|  | CF <sub>3</sub> CHCl <sub>2</sub>                               | 31.4         | 50.8 | 49.6 | 46.1 |
|  | CF <sub>3</sub> CHClF                                           | 22.2         | 28.5 | 29.7 | 33.3 |
|  | CF <sub>3</sub> CHF <sub>2</sub>                                | 9.8          | 6.9  | 7.3  | 7.2  |
|  | CF <sub>3</sub> CHCl <sub>2</sub> plus<br>CF <sub>3</sub> CHClF | 53.6         | 79.3 | 79.3 | 79.4 |

**Claims**

Claims for the following Contracting States: CH, DE, ES, FR, GB, LI, NL, SE, IT

1. A process for the preparation of 1,1,1-trifluorodichloroethane and 1,1,1,2-tetrafluorochloroethane by fluorination of a tetrahaloethylene, C<sub>2</sub>Cl<sub>4-x</sub>F<sub>x</sub>, wherein x = 0 to 3, comprising contacting in the gaseous phase at 300°C to 450°C said tetrahaloethylene and HF with a catalyst comprising at least one metal in an oxidation state greater than zero, said metal selected from the group consisting of chromium, manganese, nickel and cobalt, wherein in the case of chromium it is present in the form of chromium fluoride or chromium oxyfluoride, on a support comprising aluminum, oxygen and fluorine in such proportions that the fluorine content corresponds to an AlF<sub>3</sub> content of at least 90% by weight of the catalyst composition exclusive of the metal, said AlF<sub>3</sub> content being obtained by pretreatment with HF.

2. A process as claimed in claim 1 wherein the tetrahaloethylene is tetrachloroethylene.

3. A process as claimed in claim 1 or claim 2 wherein the catalyst contains 0.02 to 20 weight percent of metal expressed as the divalent oxide.

4. A process as claimed in claim 3 wherein the catalyst contains 0.1 to 5 weight percent of metal expressed as the divalent oxide.

5. A process as claimed in any one of the preceding claims wherein the HF is contacted with the tetrahaloethylene at a mol ratio of 1:1 to 20:1 at a temperature of 300°C to 400°C, and a contact time of 5 to 100 seconds.

6. A process as claimed in any one of the preceding claims wherein conversion of the tetrahaloethylene to fluorinated products is between 30% and 95%.

7. A process as claimed in any one of the preceding claims wherein the metal is selected from the group consisting of manganese, nickel and cobalt.

8. A process as claimed in any one of the preceding claims wherein the temperature, the mol ratio to HF to the tetrahaloethylene, and the contact time are controlled to yield a product stream having a CF<sub>3</sub>CHCl<sub>2</sub> content greater than that of CF<sub>3</sub>CHClF, and the combined total of CF<sub>3</sub>CHCl<sub>2</sub> and CF<sub>3</sub>CHClF is greater than that of



CF<sub>3</sub>CHF<sub>2</sub> in the product stream.

9. A process as claimed in any one of the preceding claims wherein the amount of the CF<sub>3</sub>CHF<sub>2</sub> in the product stream is less than ten percent.

10. A process as claimed in any one of the preceding claims further comprising the step of recycling at least a portion of CF<sub>3</sub>CHCl<sub>2</sub> produced to the contacting step for conversion to additional CF<sub>3</sub>CHClF.

#### Claims for the following Contracting States: AT, BE, LU, GR

1. A process for the preparation of 1,1,1-trifluorodichloroethane and 1,1,1,2-tetrafluorochloroethane by fluorination of a tetrahaloethylene, C<sub>2</sub>Cl<sub>4-x</sub>F<sub>x</sub>, wherein x = 0 to 3, comprising contacting in the gaseous phase at 300°C to 450°C said tetrahaloethylene and HF with a catalyst comprising at least one metal in an oxidation state greater than zero, said metal selected from the group consisting of chromium, manganese, nickel and cobalt, on a support comprising aluminum, oxygen and fluorine in such proportions that the fluorine content corresponds to an AlF<sub>3</sub> content of at least 90% by weight of the catalyst composition exclusive of the metal, said AlF<sub>3</sub> content being obtained by pretreatment with HF.

2. A process as claimed in claim 1 wherein the tetrahaloethylene is tetrachloroethylene.

3. A process as claimed in claim 1 or claim 2 wherein the catalyst contains 0.02 to 20 weight percent of metal expressed as the divalent oxide.

4. A process as claimed in claim 3 wherein the catalyst contains 0.1 to 5 weight percent of metal expressed as the divalent oxide.

5. A process as claimed in any one of the preceding claims wherein the HF is contacted with the tetrahaloethylene at a mol ratio of 1:1 to 20:1 at a temperature of 300°C to 400°C, and a contact time of 5 to 100 seconds.

6. A process as claimed in any one of the preceding claims wherein conversion of the tetrahaloethylene to fluorinated products is between 30% and 95%.

7. A process as claimed in any one of the preceding claims wherein the metal is selected from the group consisting of manganese, nickel and cobalt.

8. A process as claimed in any one of the preceding claims wherein the temperature, the mol ratio to HF to the tetrahaloethylene, and the contact time are controlled to yield a product stream having a CF<sub>3</sub>CHCl<sub>2</sub> content greater than that of CF<sub>3</sub>CHClF, and the combined total of CF<sub>3</sub>CHCl<sub>2</sub> and CF<sub>3</sub>CHClF is greater than that of CF<sub>3</sub>CHF<sub>2</sub> in the product stream.

9. A process as claimed in any one of the preceding claims wherein the amount of the CF<sub>3</sub>CHF<sub>2</sub> in the product stream is less than ten percent.

10. A process as claimed in any one of the preceding claims further comprising the step of recycling at least a portion of CF<sub>3</sub>CHCl<sub>2</sub> produced to the contacting step for conversion to additional CF<sub>3</sub>CHClF.

#### Patentansprüche

Patentansprüche für folgende Vertragsstaaten: CH, DE, ES, FR, GB, LI, NL, SE, IT

1. Verfahren zur Herstellung von 1,1,1-Trifluorodichlorethan und 1,1,1,2-Tetrafluorochlorethan durch Fluorierung eines Tetrahalogenethylen, C<sub>2</sub>Cl<sub>4-x</sub>F<sub>x</sub>, worin x = 0 bis 3 ist, bei dem man das Tetrahalogenethylen und HF in der Gasphase bei 300 °C bis 450 °C mit einem Katalysator in Kontakt bringt, der mindestens ein Metall in einem Oxidationszustand von mehr als 0 enthält, wobei das Metall ausgewählt wird aus der Gruppe, bestehend aus Chrom, Mangan, Nickel und Kobalt, und im Falle von Chrom dieses in der Form von Chromfluorid oder Chromoxyfluorid enthalten ist, auf einem Träger, der Aluminium, Sauerstoff und Fluor in solchen Mengenteilen enthält, daß der Fluorgehalt einem AlF<sub>3</sub>-Gehalt von mindestens 90 Gew.-% der Katalysatorzusammensetzung, ausschließend das Metall, entspricht und der AlF<sub>3</sub>-Gehalt durch Vorbehandlung mit HF erhalten wurde.

2. Verfahren nach Anspruch 1, worin das Tetrahalogenethylen Tetrachlorethylen ist.

3. Verfahren nach Anspruch 1 oder 2, bei dem der Katalysator 0,02 bis 20 Gew.-% Metall, ausgedrückt als zweiwertiges Oxid, enthält.

4. Verfahren nach Anspruch 3, bei dem der Katalysator 0,1 bis 5 Gew.-% Metall enthält, ausgedrückt als zweiwertiges Oxid.

5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das HF mit dem Tetrahalogenethylen bei einem Molverhältnis von 1:1 bis 20:1 bei einer Temperatur von 300 °C bis 400 °C und einer Kontaktzeit



von 5 bis 100 Sekunden kontaktiert wird.

6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Umwandlung des Tetrahalogenethylen in fluorierte Produkte zwischen 30 % und 95 % liegt.

7. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Metall ausgewählt wird aus der Gruppe, bestehend aus Mangan, Nickel und Kobalt.

8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Temperatur, das Molverhältnis von HF zu Tetrahalogenethylen und die Kontaktzeit so gelenkt werden, daß ein Produktstrom entsteht, der einen  $\text{CF}_3\text{CHCl}_2$ -Gehalt von mehr als dem von  $\text{CF}_3\text{CHClF}$  hat und die kombinierte Gesamtmenge von  $\text{CF}_3\text{CHCl}_2$  und  $\text{CF}_3\text{CHClF}$  größer ist als die von  $\text{CF}_3\text{CHF}_2$  im Produktstrom ist.

9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Menge an  $\text{CF}_3\text{CHF}_2$  im Produktstrom niedriger ist als 10 %.

10. Verfahren nach einem der vorhergehenden Ansprüche, weiter umfassend die Stufe des Recyclen von mindestens einem Teil von  $\text{CF}_3\text{CHCl}_2$ , das in der Kontaktierstufe erzeugt wurde, für die Umwandlung zu weiterem  $\text{CF}_3\text{CHClF}$ .

#### Patentansprüche für folgende Vertragsstaaten: AT, BE, LU, GR

1. Verfahren zur Herstellung von 1,1,1-Trifluorodichlorethan und 1,1,1,2-Tetrafluorochlorethan durch Fluorierung eines Tetrahalogenethylen,  $\text{C}_2\text{Cl}_{4-x}\text{F}_x$ , worin  $x = 0$  bis 3 ist, bei dem man das Tetrahalogenethylen und HF in der Gasphase bei 300 °C bis 450 °C mit einem Katalysator in Kontakt bringt, der mindestens ein Metall in einem Oxidationszustand von mehr als 0 enthält, wobei das Metall ausgewählt wird aus der Gruppe, bestehend aus Chrom, Mangan, Nickel und Kobalt, auf einem Träger, der Aluminium, Sauerstoff und Fluor in solchen Mengenanteilen enthält, daß der Fluorgehalt einem  $\text{AlF}_3$ -Gehalt von mindestens 90 Gew.-% der Katalysatorzusammensetzung, ausschließend das Metall, entspricht und der  $\text{AlF}_3$ -Gehalt durch Vorbehandlung mit HF erhalten wurde.

2. Verfahren nach Anspruch 1, worin das Tetrahalogenethylen Tetrachlorethylen ist.

3. Verfahren nach Anspruch 1 oder 2, bei dem der Katalysator 0,02 bis 20 Gew.-% Metall, ausgedrückt als zweiwertiges Oxid, enthält.

4. Verfahren nach Anspruch 3, bei dem der Katalysator 0,1 bis 5 Gew.-% Metall enthält, ausgedrückt als zweiwertiges Oxid.

5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das HF mit dem Tetrahalogenethylen bei einem Molverhältnis von 1:1 bis 20:1 bei einer Temperatur von 300 °C bis 400 °C und einer Kontaktzeit von 5 bis 100 Sekunden kontaktiert wird.

6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Umwandlung des Tetrahalogenethylen in fluorierte Produkte zwischen 30 % und 95 % liegt.

7. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Metall ausgewählt wird aus der Gruppe, bestehend aus Mangan, Nickel und Kobalt.

8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Temperatur, das Molverhältnis von HF zu Tetrahalogenethylen und die Kontaktzeit so gelenkt werden, daß ein Produktstrom entsteht, der einen  $\text{CF}_3\text{CHCl}_2$ -Gehalt von mehr als dem von  $\text{CF}_3\text{CHClF}$  hat und die kombinierte Gesamtmenge von  $\text{CF}_3\text{CHCl}_2$  und  $\text{CF}_3\text{CHClF}$  größer ist als die von  $\text{CF}_3\text{CHF}_2$  im Produktstrom ist.

9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Menge an  $\text{CF}_3\text{CHF}_2$  im Produktstrom niedriger ist als 10 %.

10. Verfahren nach einem der vorhergehenden Ansprüche, weiter umfassend die Stufe des Recyclen von mindestens einem Teil von  $\text{CF}_3\text{CHCl}_2$ , das in der Kontaktierstufe erzeugt wurde, für die Umwandlung zu weiterem  $\text{CF}_3\text{CHClF}$ .

#### Revendications

#### Revendications pour les Etats contractants suivants: CH, DE, ES, FR, GB, LI, NL, SE, IT

1. Un procédé pour la préparation de 1,1,1-trifluorodichloroéthane et de 1,1,1,2-tétrafluorochloroéthane par fluoration d'un tétrahalogénoéthylène,  $\text{C}_2\text{Cl}_{4-x}\text{F}_x$  où  $x = 0$  à 3, consistant à mettre en contact, en phase gazeuse entre 300°C et 450°C, ledit tétrahalogénoéthylène et HF avec un catalyseur comprenant au moins un métal à un degré d'oxydation supérieur à zéro, ledit métal étant choisi dans le groupe formé par le chrome, le manganèse, le nickel et le cobalt, où dans le cas du chrome celui-ci est présent sous la forme de fluorure de chrome ou d'oxyfluorure de chrome, sur un support comprenant de l'aluminium, de l'oxygène et du fluor en des pro-



portions telles que la teneur en fluor corresponde à une teneur en  $\text{AlF}_3$  d'au moins 90 % en poids de la composition de catalyseur à l'exclusion du métal, ladite teneur en  $\text{AlF}_3$  étant obtenue par prétraitement avec HF.

2. Un procédé tel que revendiqué dans la revendication 1, dans lequel le tétrahalogénoéthylène est le tétrachloroéthylène.

3. Un procédé tel que revendiqué dans la revendication 1 ou la revendication 2, dans lequel le catalyseur contient 0,02 à 20 pour cent en poids de métal exprimé en oxyde divalent.

4. Un procédé tel que revendiqué dans la revendication 3, dans lequel le catalyseur contient 0,1 à 5 pour cent en poids de métal exprimé en oxyde divalent.

5. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel le HF est mis en contact avec le tétrahalogénoéthylène en un rapport molaire de 1:1 à 20:1 à une température de 300°C à 400°C, et avec un temps de contact de 5 à 100 secondes.

6. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel le taux de conversion du tétrahalogénoéthylène en produits fluorés est compris entre 30 % et 95 %.

7. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel le métal est choisi dans le groupe formé par le manganèse, le nickel et le cobalt.

8. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel la température, le rapport molaire de HF au tétrahalogénoéthylène et le temps de contact sont réglés pour donner un courant de produit ayant une teneur en  $\text{CF}_3\text{CHCl}_2$  supérieure à celle de  $\text{CF}_3\text{CHClF}$ , et le total de  $\text{CF}_3\text{CHCl}_2$  et  $\text{CF}_3\text{CHClF}$  réunis est supérieur à celui de  $\text{CF}_3\text{CHF}_2$  dans le courant de produit.

9. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel la quantité de  $\text{CF}_3\text{CHF}_2$  dans le courant de produit est inférieure à dix pour cent.

10. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, comprenant de plus l'étape de recyclage d'au moins une portion du  $\text{CF}_3\text{CHCl}_2$  produit vers l'étape de mise en contact pour la conversion en  $\text{CF}_3\text{CHClF}$  supplémentaire.

#### Revendications pour les Etats contractants suivants: AT, BE, LU, GR

1. Un procédé pour la préparation de 1,1,1-trifluorodichloroéthane et de 1,1,1,2-tétrafluorochloroéthane par fluoration d'un tétrahalogénoéthylène,  $\text{C}_2\text{Cl}_{4-x}\text{F}_x$  où  $x = 0$  à 3, consistant à mettre en contact, en phase gazeuse entre 300°C et 450°C, ledit tétrahalogénoéthylène et HF avec un catalyseur comprenant au moins un métal à un degré d'oxydation supérieur à zéro, ledit métal étant choisi dans le groupe formé par le chrome, le manganèse, le nickel et le cobalt, sur un support comprenant de l'aluminium, de l'oxygène et du fluor en des proportions telles que la teneur en fluor corresponde à une teneur en  $\text{AlF}_3$  d'au moins 90 % en poids de la composition de catalyseur à l'exclusion du métal, ladite teneur en  $\text{AlF}_3$  étant obtenue par prétraitement avec HF.

2. Un procédé tel que revendiqué dans la revendication 1, dans lequel le tétrahalogénoéthylène est le tétrachloroéthylène.

3. Un procédé tel que revendiqué dans la revendication 1 ou la revendication 2, dans lequel le catalyseur contient 0,02 à 20 pour cent en poids de métal exprimé en oxyde divalent.

4. Un procédé tel que revendiqué dans la revendication 3, dans lequel le catalyseur contient 0,1 à 5 pour cent en poids de métal exprimé en oxyde divalent.

5. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel le HF est mis en contact avec le tétrahalogénoéthylène en un rapport molaire de 1:1 à 20:1 à une température de 300°C à 400°C, et avec un temps de contact de 5 à 100 secondes.

6. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel le taux de conversion du tétrahalogénoéthylène en produits fluorés est compris entre 30 % et 95 %.

7. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel le métal est choisi dans le groupe formé par le manganèse, le nickel et le cobalt.

8. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel la température, le rapport molaire de HF au tétrahalogénoéthylène et le temps de contact sont réglés pour donner un courant de produit ayant une teneur en  $\text{CF}_3\text{CHCl}_2$  supérieure à celle de  $\text{CF}_3\text{CHClF}$ , et le total de  $\text{CF}_3\text{CHCl}_2$  et  $\text{CF}_3\text{CHClF}$  réunis est supérieur à celui de  $\text{CF}_3\text{CHF}_2$  dans le courant de produit.

9. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel la quantité de  $\text{CF}_3\text{CHF}_2$  dans le courant de produit est inférieure à dix pour cent.

10. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, comprenant de plus l'étape de recyclage d'au moins une portion du  $\text{CF}_3\text{CHCl}_2$  produit vers l'étape de mise en contact pour la conversion en  $\text{CF}_3\text{CHClF}$  supplémentaire.

