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(54) **Eljárás 2,3,3,3-tetrafluorpropén előállítására**

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VERFAHREN ZUR HERSTELLUNG VON 2,3,3,3-TETRAFLUORPROPEN

PROCÉDÉ DE FABRICATION DE 2,3,3,3-TETRAFLUOROPROPÈNE

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Description

Field of the Disclosure

[0001] This disclosure relates in general to methods of synthesis of fluorinated olefins.

Description of the Related Art

[0002] The fluorocarbon industry has been working for the past few decades to find replacement refrigerants for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being phased out as a result of the Montreal Protocol. The solution for many applications has been the commercialization of hydrofluorocarbon (HFC) compounds for use as refrigerants, solvents, fire extinguishing agents, blowing agents and propellants. These new compounds, such as HFC refrigerants, HFC-134a and HFC-125 being the most widely used at this time, have zero ozone depletion potential and thus are not affected by the current regulatory phase-out as a result of the Montreal Protocol.

[0003] In addition to ozone depleting concerns, global warming is another environmental concern in many of these applications. Thus, there is a need for compositions that meet both low ozone depletion standards as well as having low global warming potentials. Certain hydrofluoroolefins are believed to meet both goals. Thus there is a need for manufacturing processes that provide halogenated hydrocarbons and fluoroolefins that contain no chlorine that also have a low global warming potential. There is also considerable interest in developing new refrigerants with reduced global warming potential for the mobile air-conditioning market.

[0004] HFC-1234yf ($CF_3CF=CH_2$) and HFC-1234ze ($CF_3CH=CHF$), both having zero ozone depletion and low global warming potential, have been identified as potential refrigerants. U. S. Patent Publication No. 2006/0106263 A1 discloses the production of HFC-1234yf by a catalytic vapor phase dehydrofluorination of $CF_3CF_2CH_3$ or CF_3CHFCH_2F, and of HFC-1234ze (mixture of *E*- and Z- isomers) by a catalytic vapor phase dehydrofluorination of $CF_3CH_2CHF_2$.

[0005] International patent application WO 2007/056194 A1 discloses methods for producing fluorinated organic compounds, including hydrofluoropropenes, which comprises converting a compound of formula CF_3CHFCH_2F to at least one compound of formula CF_3CZCHZ where Z independently is H or F.

[0006] International patent application WO 2008/008350 A2 discloses a process for making $CF_3CF=CH_2$. The process involves contacting $CF_3CF_2CH_3$ with a chromium oxyfluoride catalyst to obtain a product mixture comprising $CF_3CF=CH_2$, and recovering $CF_3CF=CH_2$ from the product mixture.

[0007] International patent application WO 96/41679 A1 and European patent application EP 1 495 801 A1 both relate to processes for the production of vinyl fluoride comprising contacting 1,1-difluoroethane in the vapor phase with a trivalent chromium catalyst.

[0008] There is a continuing need for more selective and efficient manufacturing processes for the production of HFC-1234yf.

SUMMARY

[0009] In one aspect, disclosed is a process for the manufacture of 2,3,3,3-tetrafluoropropene comprising: dehydrofluorinating 1,1,1,2,3-pentafluoropropane in the presence of a dehydrofluorination catalyst comprised of chromium (III) oxide, and alkali metal, to produce a product mixture comprising 2,3,3,3-tetrafluoropropene; and recovering said 2,3,3,3-tetrafluoropropene from the product mixture produced in the dehydrofluorination.

[0010] The foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as defined in the appended claims.

DETAILED DESCRIPTION

[0011] In one aspect, disclosed is the use of a catalyst comprising chromium(III)oxide and an alkali metal to dehydrofluorinate CF3CHFCH2F (HFC-245eb) to produce 2,3,3,3-tetrafluoropropene.

[0012] In another aspect, disclosed is a process for the manufacture of 2,3,3,3-tetrafluoropropene comprising: dehydrofluorinating 1,1,1,2,3-pentafluoropropane in the presence of a dehydrofluorination catalyst comprised of chromium (III) oxide, and alkali metal, to produce a product mixture comprising 2,3,3,3-tetrafluoropropene; and recovering said 2,3,3,3-tetrafluoropropene from the product mixture produced in the dehydrofluorination. In one embodiment, the product mixture comprising 2,3,3,3-tetrafluoropropene further comprises less than 20 parts per hundred on a molar basis of 1,1,1,2,2-pentafluoropropane. In another embodiment, the product mixture comprising 2,3,3,3-tetrafluoropropene further comprises less than 10 parts per hundred on a molar basis of 1,1,1,2,2-pentafluoropropane. In one embodiment, the dehydrofluorination catalyst comprises chromium (III) oxide and at least 1000 ppm alkali metal. In another embodiment, the dehydrofluorination catalyst comprises chromium (III) oxide and at least 3000 ppm alkali metal. In yet another embodiment, the dehydrofluorination catalyst comprises chromium oxide and at least 5000 ppm alkai metal. In yet another embodiment, the dehydrofluorination catalyst comprises chromium oxide and at least 1000 ppm potassium. In yet another embodiment, the dehydrofluorination catalyst comprises from 0.1% to 3% boron and at least 3000 ppm of alkali metal. In another embodiment, the dehydrofluorination catalyst comprises from 0.5% to 2% boron and at least 3000 ppm of alkali metal. In yet another embodiment, the dehydrofluorination catalyst comprises from 0.5% to 2% boron and at least 3000 ppm of sodium. In yet another embodiment, the dehydrofluorination catalyst comprises from 0.5% to 2% boron and at least 2000 ppm of potassium.

[0013] Other features and benefits of any one or more of the embodiments will be apparent from the following detailed description, and from the claims.

[0014] Before addressing details of embodiments described below, some terms are defined or clarified.

[0015] The catalytic dehydrofluorination of hydrofluorocarbons to produce hydrofluoroolefins is ordinarily carried out in the vapor phase using a dehydrofluorination catalyst. Vapor phase dehydrofluorination catalysts are well known in the art. These catalysts include, but are not limited to, alumina, aluminum fluoride, fluorided alumina, metal compounds on aluminum fluoride, metal compounds on fluorided alumina; chromium oxides, fluorided chromium oxides, and cubic chromium trifluoride; oxides, fluorides, and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc and/or aluminum; lanthanum oxide and fluorided lanthanum oxide; carbon, acid-washed carbon, activated carbon, three dimensional matrix carbonaceous materials; and metal compounds supported on carbon. The metal compounds are oxides, fluorides, and oxyfluorides of at least one metal selected from the group consisting of sodium, potassium, rubidium, cesium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, chromium, iron, cobalt, rhodium, nickel, copper, zinc, and mixtures thereof.

[0016] In the preparation of HFC-1234yf by dehydrofluorination of CF_3CHFCH_2F, it is possible to obtain either HFC-1234yf or HFC-1234ze, depending on which pair of adjacent fluorine and hydrogen atoms are eliminated. Generally, HFC-1234yf is the predominant product, although depending on reaction conditions, yields of HFC-1234ze can be as much 10 pph or more compared to HFC-1234yf. It has also been found that another by-product of the catalytic dehydrofluorination of CF_3CHFCH_2F (HFC-245eb) is $CF_3CF_2CH_3$ (HFC-245cb) which can be very difficult to separate from HFC-1234yf. This product is believed to arise via the re-addition of hydrogen fluoride to HFC-1234yf in the direction opposite to that it was eliminated by. Although HFC-245cb can be catalytically dehydrofluorinated to HFC-1234yf, in practice the dehydrofluorination of HFC-245cb requires higher temperatures and a different catalyst. Depending upon the catalyst and reaction conditions, the amount of HFC-245cb produced by isomerization can be as much as from 30 to 60 parts per hundred of HFC-1234yf, resulting in significant yield losses. Selectivity for the production of HFC-1234yf can be expressed as parts per hundred of the by-product relative to the amount of HFC-1234yf. By way of example, a product mixture formed from the dehydrofluorination of HFC-245eb comprising 60% HFC-1234yf, 20% HFC-245cb and 3% HFC-1234ze would have 33 pph HFC-245cb and 5 pph HFC-1234ze.

[0017] It is possible to dehydrofluorinate CF_3CHFCH_2F (HFC-245eb) to HFC-1234yf with high selectivity and very little formation of HFC-245cb using a catalyst comprising chromium (III) oxide, and alkali metal. In one embodiment, the alkali metal is at least one of sodium, potassium and cesium, or mixtures thereof.

[0018] In one embodiment, the catalyst comprises chromium (III) oxide, and an amount of alkali metal effective to produce 2,3,3,3-tetrafluoro-1-propene while producing less than 20 pph on a molar basis of 1,1,1,2,2-pentafluoropropane. The effective amount of alkali metal required will be dependent upon how it is distributed within the catalyst composition. The effective amount of alkali metal required is also dependent on which alkali metal is chosen. An effective amount of cesium is less than an effective amount of potassium, which is less than an effective amount of sodium.

[0019] In one embodiment, the dehydrofluorination catalyst comprises chromium (III) oxide and at least 1000 ppm alkali metal. In another embodiment, the dehydrofluorination catalyst comprises chromium (III) oxide and at least 3000 ppm alkali metal. In yet another embodiment, the dehydrofluorination catalyst comprises chromium oxide and at least 5000 ppm alkali metal. In yet another embodiment, the dehydrofluorination catalyst comprises chromium oxide and at least 1000 ppm potassium. In another embodiment, the dehydrofluorination catalyst comprises from 0.1% to 3% boron and at least 3000 ppm of alkali metal. In another embodiment, the dehydrofluorination catalyst comprises from 0.5% to 2% boron and at least 3000 ppm of alkali metal. In yet another embodiment, the dehydrofluorination catalyst comprises from 0.5% to 2% boron and at least 3000 ppm of sodium. In yet another embodiment, the catalyst comprises chromium (III) oxide, from 0.5% to 2% boron, and at least 2000 ppm potassium. In one embodiment, the catalyst is a chromium composition known as Guignet's green pigment.

[0020] In one embodiment, the dehydrofluorination catalyst may be prepared by slurrying preformed pellets or particles of chromium (III) oxide catalyst in an aqueous solution of an alkali metal salt, such as sodium carbonate, potassium carbonate or cesium carbonate. The slurry is then allowed to dry.

[0021] In another embodiment, the dehydrofluorination catalyst may be prepared by slurrying chromium (III) oxide powder with an aqueous solution of an alkali metal salt, such as sodium carbonate, potassium carbonate or cesium carbonate. The slurry is then allowed to dry. In one embodiment, the dehydrofluorination catalyst is then pressed, ground into particles, and sieved to 12/20 mesh (1.680 mm/0.841 mm) particles.

[0022] In yet another embodiment, the catalyst may be prepared by fusing a mixture of from 3 parts to 16 parts boric acid and 1 part potassium dichromate at from 500-800°C, cooling the mixture in air, crushing the solid to produce a powder, hydrolysis, filtering, drying, milling and screening. Numerous, examples of the preparation of Guignet's green can be found in the art, including U.S. Patent 3,413,363.

[0023] The physical shape of the catalyst is not critical and may, for example, include pellets, powders or granules.

[0024] In one embodiment, the catalytic dehydrofluorination may be suitably conducted with the temperature set point of the reactor in the range of from 250 °C to 350 °C. In another embodiment, the catalytic dehydrofluorination is conducted with the temperature set point of the reactor in the range of from 250°Cto 300 °C. In one embodiment, the contact time is typically from 1 to 450 seconds. In another embodiment, the contact time is from 10 to 120 seconds.

[0025] The reaction pressure can be subatmospheric, atmospheric or superatmospheric. Generally, near atmospheric pressures are preferred. However, the dehydrofluorination can be beneficially run under reduced pressure (i.e., pressures less than one atmosphere).

[0026] In one embodiment, the catalytic dehydrofluorination is carried out in the presence of an inert gas such as nitrogen, helium, or argon. The addition of an inert gas can be used to increase the extent of dehydrofluorination. Of note are processes where the mole ratio of inert gas to hydrofluorocarbon undergoing dehydrofluorination is from 5:1 to 0.5:1. In one embodiment, nitrogen is the inert gas.

[0027] Reaction product HFC-1234yf and any unconverted HFC-245eb are recovered from the effluent leaving the reactor. The unconverted HFC-245eb can be recycled back to the reactor to produce additional HFC-1234yf. In one embodiment of this invention, the unconverted HFC-245eb is recycled back to the reactor as its azeotrope with HF. Published PCT Application WO 2008/002501 filed June 27, 2006 is disclosing an azeotrope of HF/HFC-245eb. U.S. Patent 7,423,188 discloses an azeotrope of the E- isomer of HFC-1234ze and HF and a method to separate the HFC-1234ze from the azeotrope, and U.S. Patent 7,476,771 discloses an azeotrope of HFC-1234yf and HF and a method to separate the HFC-1234yf from the azeotrope. HFC-1234ze may be recovered as a HF/HFC-1234ze azeotrope. Similarly, HFC-1234yf may be recovered as a HF/HFC-1234yf azeotrope. Pure HFC-1234ze and pure HFC-1234yf can be further recovered from their HF azeotropes by using methods similar to those described in U.S. Patent 7,423,188 and U.S. Patent 7,476,771 .

[0028] The reactor, or reactor bed, distillation columns, and their associated feed lines, effluent lines, and associated units used in applying the processes of this invention should be constructed of materials resistant to hydrogen fluoride. Typical materials of construction, well-known to the fluorination art, include stainless steels, in particular of the austenitic type, the well-known high nickel alloys, such as Monel™ nickel-copper alloys, Hastelloy™ nickel-based alloys and, Inconel™ nickel-chromium alloys, and copper-clad steel.

[0029] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0030] Also, use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0031] Group numbers corresponding to columns within the Periodic Table of the elements use the "New Notation" convention as seen in the CRC Handbook of Chemistry and Physics, 81st Edition (2000-2001).

EXAMPLES

[0032] The concepts described herein will be further described in the following examples. In the examples the following abbreviations or codes may be used:

CT = contact time
1234yf = $CF_3CF{=}CH_2$
245eb = CF_3CHFCH_2F
1234ze = $CF_3CH{=}CHF$
245cb = $CF_3CF_2CH_3$

Example 1

[0033] Example 1 demonstrates the dehydrofluorination of 1,1,1,2,3-pentafluoropropane over a chromium oxide catalyst further comprising boron, potassium and sodium.

[0034] An Inconel™ tube (5/8 inch = 1.59 cm OD) was filled with 6 cc (4.9 gm) of hydrated chromic oxide (also known as Guignet's Green) in extrudate form, which was crushed and sieved to 12/20 mesh (1.680 mm/0.841 mm). A typical analysis of this catalyst indicated the following composition: 54.5% Cr, 1.43% B, 3400 ppm Na, 120 ppm K. The temperature of the catalyst bed was raised to 325°C and purged with nitrogen (38 sccm, 6.3 x 10^{-7} m^3/sec) for 120 minutes and then at 300°C for 80 minutes. Then the flow of nitrogen was reduced to 27 sccm (4.5 x 10^{-7} m^3/sec) and HF was fed at 9 sccm (1.5×10^{-7} m^3/sec) for 500 minutes. The flow of nitrogen was then lowered to 19 sccm (3.2×10^{-7} m^3/sec) and the flow of HF was raised to 15 sccm (2.5×10^{-7} m^3/sec) for 25 minutes. The flow of nitrogen was then lowered to 11 sccm (1.8×10^{-7} m^3/sec) and the flow of HF was raised to 21 sccm (3.5 x 10^{-7} m^3/sec) for 30 minutes. The flow of nitrogen was then lowered to 4 sccm (6.7 x 10^{-8} m^3/sec) and the flow of HF was raised to 27 sccm (4.5 x 10^{-7} m^3/sec) for 30 minutes. The flow of nitrogen was then discontinued and the flow of HF was raised to 30 sccm (5.0×10^{-7} m^3/sec) for 160 minutes. After this activation period, the catalyst bed temperature was changed to reaction conditions.

[0035] The reactor temperature was stabilized at temperatures from 250°C to 302°C, as indicated in the table below, and CF_3CHFCH_2F was fed at 6.4 sccm (1.1×10^{-7} m^3/sec). The CF_3CHFCH_2F was vaporized at 41°C while passing nitrogen through the vaporizer at 6.4 sccm (1.1×10^{-7} m^3/sec). Part of the reactor effluent was passed through a series of valves and analyzed by GCMS. The results in Table 1 are an average of at least two GC injections at each set of conditions. Amounts for 245cb, and 1234ze are expressed as mole parts per hundred of 2,3,3,3-tetrafluoropropene produced.

Table 1

Mole % 1234yf	245cb (pph)	1234ze (pph)	245eb (%)	Temp °C	CT (sec)
71.7	8.9	5.2	17.5	302	28
47.9	6.1	4.0	46.6	275	28
28.9	4.5	2.8	68.4	250	28

Example 2

[0036] Example 2 demonstrates the dehydrofluorination of 1,1,1,2,3-pentafluoropropane over chromium oxide catalysts further comprising varying amounts of boron, potassium and sodium.

[0037] An Inconel™ tube (1/2 inch = 1.27 cm OD) was filled with 6 cc (4.9 gm) of hydrated chromic oxide in extrudate form, which was crushed and sieved to 12/20 mesh (1.680 mm/0.841 mm). Composition of the catalysts with respect to B, Na and K are as indicated in Table 2. The temperature of the catalyst bed was raised to 300°C and purged with nitrogen (30 cc/min) for 200 minutes. Then the flow of nitrogen was reduced to 60 cc/min and HF was fed at 20 cc/min for 60 minutes. The temperature was increased to 325°C for 300 minutes. The flow of nitrogen was then lowered to 30 cc/min and the flow of HF was raised to 30 cc/min for 30 minutes. The flow of nitrogen was then lowered to 12 cc/min and the flow of HF was raised to 48 cc/min for 60 minutes. The flow of nitrogen was then discontinued and the flow of HF was raised to 48 cc/min for 30 minutes. The reactor temperature was then decreased to 250°C for 30 minutes. Afterwards HF was turned off and the reactor was purged with 30 cc/min of nitrogen. The reactor temperature was then stabilized at 300°C, the flow of nitrogen was turned off, and CF_3CHFCH_2F was fed at 3.2 ml/hr (12 cc/min). The CF_3CHFCH_2F was vaporized at 175°C. Part of the reactor effluent was passed through a series of valves and analyzed by GCMS. Amounts for 245cb and 1234ze are expressed as mole parts per hundred of 2,3,3,3-tetrafluoropropene produced.

Table 2

% B	Na ppm	K ppm	Mole % 1234yf	245cb (pph)	1234ze (pph)	245eb (%)	Temp °C	CT (sec)
1.1	3225	135	58.1	28,5	2.7	23.20	300	30
1.6	49	17000	53.7	10.0	2	39.2	300	30
1.6	4550	150	52.8	15.5	2.9	36.68	300	30

Example 3

[0038] Example 3 demonstrates the dehydrofluorination of 1,1,1,2,3-pentafluoropropane over chromium oxide catalysts further comprising varying amounts of added potassium.

[0039] Chromium oxide catalyst which had a starting composition of 55.8% Cr, 175 ppm Na, 60 ppm K, 53 ppm Cu and 20 ppm Zn was doped with varying levels of potassium. Composition of the catalysts with respect to amount of K added is indicated in Table 3.

[0040] An Inconel™ tube (1/2 inch = 1.27 cm OD) was filled with 6 cc (4.9 gm) of catalyst which had been prepared as follows. Hydrated chromic oxide in extrudate form, which was crushed and sieved to 12/20 mesh (1.680 mm/0.841 mm) was doped with varying levels of potassium by slurrying catalyst with an aqueous potassium carbonate solution containing enough potassium to provide the indicated potassium levels. The solution was then evaporated to dryness, and the resulting catalyst was dried at 200°C for 3 hours. After charging the reactor tube, the temperature of the catalyst bed was raised to 300°C and purged with nitrogen (30 cc/min) for 200 minutes. Then the flow of nitrogen was reduced to 60 cc/min and HF was fed at 20 cc/min for 60 minutes. The temperature was increased to 325°C for 300 minutes. The flow of nitrogen was then lowered to 30 cc/min and the flow of HF was raised to 30 cc/min for 30 minutes. The flow of nitrogen was then lowered to 12 cc/min and the flow of HF was raised to 48 cc/min for 60 minutes. The flow of nitrogen was then discontinued and the flow of HF was raised to 48 cc/min for 30 minutes. The reactor temperature was then decreased to 250°C for 30 minutes. Afterwards HF was turned off and the reactor was purged with 30 cc/min of nitrogen. The reactor temperature was then stabilized at 300°C, the flow of nitrogen was turned off, and CF_3CHFCH_2F was fed at 3.2 ml/hr (12 cc/min). The CF_3CHFCH_2F was vaporized at 175°C. Part of the reactor effluent was passed through a series of valves and analyzed by GCMS. Amounts for 245cb and 1234ze are expressed as mole parts per hundred of 2,3,3,3-tetrafluoropropene produced.

Table 3

K added - ppm	1234ze (pph)	245eb (%)	1234yf (%)	245cb (pph)
100	12.97	9.73	31.01	45.60
5000	5.30	11.83	73.4	9.47
6500	3.87	34.7	58.55	2.88
10000	0.73	82.41	16.52	0

Example 4 (comparative example)

[0041] Example 3 demonstrates the dehydrofluorination of 1,1,1,2,3-pentafluoropropane over a gamma alumina dehydrofluorination catalyst.

[0042] A batch of gamma alumina (BASF) (6 cc, 3.19 gm) was activated as the catalyst in Example 1 described above. The temperature of the reactor was controlled to temperatures from 249°C to 299°C, as indicated in the table below, and CF_3CHFCH_2F was fed at 6.4 sccm (1.1×10^{-7} m^3/sec). The CF_3CHFCH_2F was vaporized at 41 °C while passing nitrogen through the vaporizer at 6.4 sccm (1.1×10^{-7} m^3/sec). Part of the reactor effluent was passed through a series of valves and analyzed by GCMS. The results in Table 4 are an average of at least two GC injections at each set of conditions. Amounts for 245cb and 1234ze are expressed as mole parts per hundred of 2,3,3,3-tetrafluoropropene produced.

Table 4

Mole % 1234yf	245cb (pph)	1234ze (pph)	245eb (%)	Temp °C	CT (sec)
68.7	32.5	8.0	2.9	299	28
64.4	43.3	6.1	3.3	276	28
57.3	46.9	3.3	13.5	249	28

Example 5 (comparative example)

[0043] Example 5 demonstrates the dehydrofluorination of 1,1,1,2,3-pentafluoropropane over an alpha chromium oxide catalyst.

[0044] A batch of alpha chromium oxide (6 cc, 8.51 gm) as described in US 5,036,036 was activated as the catalyst in Example 1 described above. Analysis of the catalyst indicated the following composition: 55.8% Cr, 0% B, 175 ppm Na, 60 ppm K. The temperature of the reactor was controlled to temperatures from 249°C to 298°C, as indicated in the table below, and CF_3CHFCH_2F was fed at 6.4 sccm (1.1×10^{-7} m^3/sec). The $CF_3CHClCH_2CCl_2CF_3$ was vaporized at 41°C while passing nitrogen through the vaporizer at 5.4 sccm (9.5×10^{-8} m^3/sec). Part of the reactor effluent was passed through a series of valves and analyzed by GCMS. The results in Table 5 are an average of at least two GC injections at each set of conditions. Amounts for 245cb and 1234ze are expressed as mole parts per hundred of 2,3,3,3-tetrafluoropropene produced.

[0045] Analysis of the alpha chromium oxide catalyst indicated it comprised 55.8% chromium, 53 ppm copper, 120 ppm iron, 175 ppm sodium, 60 ppm potassium, 23 ppm manganese, and 20 ppm zinc.

Table 5

Mole % 1234yf	245cb (pph)	1234ze (pph)	245eb (%)	Temp °C	CT (sec)
65.5	34.5	11	4.1	298	31
61.8	46.3	8.1	4.1	277	31
57.7	59.4	5.2	4.6	249	31

Example 6 (comparative example)

[0046] Example 6 demonstrates the dehydrofluorination of 1,1,1,2,3-pentafluoropropane over an chromium oxide gel catalyst.

[0047] A batch of chromium oxide gel (6 cc, 7.47 gm) obtained from BASF was activated as the catalyst in Example 1 described above. The temperature of the reactor was controlled to temperatures from 249°C to 298°C, as indicated in the table below, and CF_3CHFCH_2F was fed at 6.4 sccm (1.1×10^{-7} m^3/sec). The $CF_3CHClCH_2CCl_2CF_3$ was vaporized at 41°C while passing nitrogen through the vaporizer at 5.4 sccm (9.5×10^{-8} m^3/sec). Part of the reactor effluent was passed through a series of valves and analyzed by GCMS. The results in Table 6 are an average of at least two GC injections at each set of conditions. Amounts for 245cb and 1234ze are expressed as mole parts per hundred of 2,3,3,3-tetrafluoropropene produced.

Table 6

Mole % 1234yf	245cb (pph)	1234ze (pph)	245eb (%)	Temp °C	CT (sec)
69.0	33.9	6.4	1.8	299	31
64.4	47.0	4.0	1.5	277	31
59.5	63.4	1.5	0.9	248	31

Example 7 (comparative example)

[0048] Example 7 demonstrates the dehydrofluorination of 1,1,1,2,3-pentafluoropropane over an chromium oxide gel catalyst.

[0049] A batch of chromium oxide gel (6 cc, 5.9 gm) obtained from Synetix (CPA200A) was activated as the catalyst in Example 1 described above. The temperature of the reactor was controlled to temperatures from 251°C to 301°C, as indicated in the table below, and CF_3CHFCH_2F was fed at 6.4 sccm (1.1×10^{-7} m^3/sec). The $CF_3CHClCH_2CCl_2CF_3$ was vaporized at 41°C while passing nitrogen through the vaporizer at 5.4 sccm ($9.5 x 10^{-8}$ m^3/sec). Part of the reactor effluent was passed through a series of valves and analyzed by GCMS. The results in Table 7 are an average of at least two GC injections at each set of conditions. Amounts for 245cb and 1234ze are expressed as mole parts per hundred of 2,3,3,3-tetrafluoropropene produced.

[0050] Analysis of the chromium oxide gel catalyst indicated it comprised 62.9% chromium, 350 ppm copper, 198 ppm sodium, 145 ppm iron and 50 ppm potassium.

Table 7

Mole % 1234yf	245cb (pph)	1234ze (pph)	245eb (%)	Temp °C	CT (sec)
70.8	30.5	6.2	1.8	301	31
65.9	43.6	3.9	1.5	276	31
67.3	42.6	1.9	1.3	251	31

Claims

1. A process for the manufacture of 2,3,3,3-tetrafluoropropene comprising: (a) dehydrofluorinating 1,1,1,2,3-pentafluoropropane in the presence of a dehydrofluorination catalyst comprised of chromium (III) oxide, and an alkali metal in an amount effective to produce a product mixture comprising 2,3,3,3-tetrafluoropropene and less than 20 parts per hundred an a molar basis of 1,1,1,2,2-pentafluoropropane; and (b) recovering said 2,3,3,3-tetrafluoropropene from the product mixture produced in (a).

2. A process of claim 1, wherein said product mixture comprising 2,3,3,3-tetrafluoropropene comprises less than 10 parts per hundred on a molar basis of 1,1,1,2,2-pentafluoropropane.

3. The process of claim 1, wherein said dehydrofluorination catalyst comprises from 0.1% to 2% alkali metal disposed on the surface of said catalyst.

4. The process of claim 1, wherein said dehydrofluorination catalyst comprises from 0.1 % to 1 % alkali metal disposed on the surface of said catalyst.

5. The process of claim 1, wherein said dehydrofluorination catalyst comprises from 0.1% to 1% potassium disposed on the surface of said catalyst.

6. The process of claim 1, wherein said dehydrofluorination catalyst comprises from 0.5% to 2% alkali metal dispersed throughout the particles of said catalyst.

7. The process of claim 1, wherein said dehydrofluorination catalyst comprises from 0.1% to 3% boron and at least 3000 ppm of alkali metal.

8. The process of claim 1, wherein said dehydrofluorination catalyst comprises from 0.5% to 2% boron and at least 3000 ppm of sodium.

9. The process of claim 1, wherein said dehydrofluorination catalyst comprises from 0.5% to 2% boron and at least 2000 ppm potassium.

10. The process of claim 1, wherein the temperature of the catalyst is maintained at a set point of from 250°C to 350°C.

11. The process of claim 8, wherein the temperature of the catalyst is maintained at a set point of from 250°C to 300.C.

12. Use of a catalyst comprising chromium (III) oxide and an alkali metal to dehydrofluorinate CF3CHFCH2F (HFC-245eb) to produce 2,3,3,3-tetrafluoropropene (HFC-1234yf).

Patentansprüche

1. Verfahren für die Herstellung von 2,3,3,3-Tetrafluorpropen, umfassend: (a) das Dehydrofluorieren von 1,1,1,2,3-Pentafluorpropan in Gegenwart eines Dehydrofluorierungskatalysators, der aus Chrom(III)oxid und einem Alkalimetall in einer Menge besteht, die wirksam ist, eine Produktmischung herzustellen, die 2,3,3,3-Tetrafluorpropen und weniger als 20 Teile pro hundert, auf molekularer Basis, 1,1,1,2,2-Pentafluorpropan umfasst; und (b) das Gewinnen des 2,3,3,3-Tetrafluorpropens aus der in (a) hergestellten Produktmischung.

2. Verfahren nach Anspruch 1, wobei die Produktmischung, die 2,3,3,3-Tetrafluorpropen umfasst, weniger als 10 Teile pro hundert, auf molarer Basis, 1,1,1,2,2-Pentafluorpropan umfasst.

3. Verfahren nach Anspruch 1, wobei der Dehydrofluorierungskatalysator 0,1 % bis 2 % Alkalimetall umfasst, das sich auf der Oberfläche des Katalysators befindet.

4. Verfahren nach Anspruch 1, wobei der Dehydrofluorierungskatalysator 0,1 % bis 1 % Alkalimetall umfasst, das sich auf der Oberfläche des Katalysators befindet.

5. Verfahren nach Anspruch 1, wobei der Dehydrofluorierungskatalysator 0,1 % bis 1 % Kalium umfasst, das sich auf

der Oberfläche des Katalysators befindet.

6. Verfahren nach Anspruch 1, wobei der Dehydrofluorierungskatalysator 0,5 % bis 2 % Alkalimetall umfasst, das über die Teilchen des Katalysators dispergiert ist.

7. Verfahren nach Anspruch 1, wobei der Dehydrofluorierungskatalysator 0,1 % bis 3 % Bor und mindestens 3000 ppm Alkalimetall umfasst.

8. Verfahren nach Anspruch 1, wobei der Dehydrofluorierungskatalysator 0,5 % bis 2 % Bor und mindestens 3000 ppm Natrium umfasst.

9. Verfahren nach Anspruch 1, wobei der Dehydrofluorierungskatalysator 0,5 % bis 2 % Bor und mindestens 2000 ppm Kalium umfasst.

10. Verfahren nach Anspruch 1, wobei die Temperatur des Katalysators bei einem Sollwert von 250 °C bis 350 °C gehalten wird.

11. Verfahren nach Anspruch 1, wobei die Temperatur des Katalysators bei einem Sollwert von 250 °C bis 300 °C gehalten wird.

12. Verwendung eines Katalysators, der Chrom(III)oxid und ein Alkalimetall umfasst, zum Dehydrofluorieren von CF3CHFCH2F (HCF-245eb), um 2,3,3,3-Tetrafluorpropen (HFC-1234-yf) herzustellen

Revendications

1. Procédé de fabrication de 2,3,3,3-tétrafluoropropène comprenant: (a) la déshydrofluoration de 1,1,1,2,3-pentafluoropropane en présence d'un catalyseur de déshydrofluoration composé d'oxyde de chrome (III), et d'un métal alcalin en une quantité efficace pour produire un mélange de produits comprenant du 2,3,3,3-tétrafluoropropène et moins de 20 parties pour cent sur une base molaire de 1,1,1,2,2-pentafluoropropane; et (b) la récupération dudit 2,3,3,3-tétrafluoropropène du mélange de produits produit en (a).

2. Procédé selon la revendication 1, dans lequel ledit mélange de produits comprenant du 2,3,3,3-tétrafluoropropène comprend moins de 10 parties pour cent sur une base molaire de 1,1,1,2,2-pentafluoropropane.

3. Procédé selon la revendication 1, dans lequel ledit catalyseur de déshydrofluoration comprend de 0,1 % à 2 % de métal alcalin disposé sur la surface dudit catalyseur.

4. Procédé selon la revendication 1, dans lequel ledit catalyseur de déshydrofluoration comprend de 0,1 % à 1 % de métal alcalin disposé sur la surface dudit catalyseur.

5. Procédé selon la revendication 1, dans lequel ledit catalyseur de déshydrofluoration comprend de 0,1 % à 1 % de potassium disposé sur la surface dudit catalyseur.

6. Procédé selon la revendication 1, dans lequel ledit catalyseur de déshydrofluoration comprend de 0,5 % à 2 % de métal alcalin dispersé à travers les particules dudit catalyseur.

7. Procédé selon la revendication 1, dans lequel ledit catalyseur de déshydrofluoration comprend de 0,1 % à 3 % de bore et au moins 3 000 ppm de métal alcalin.

8. Procédé selon la revendication 1, dans lequel ledit catalyseur de déshydrofluoration comprend de 0,5 % à 2 % de bore et au moins 3 000 ppm de sodium.

9. Procédé selon la revendication 1, dans lequel ledit catalyseur de déshydrofluoration comprend de 0,5 % à 2 % de bore et au moins 2 000 ppm de potassium.

10. Procédé selon la revendication 1, dans lequel la température du catalyseur est maintenue à un point de consigne de 250°C à 350°C.

11. Procédé selon la revendication 8, dans lequel la température du catalyseur est maintenue à un point de consigne de 250°C à 300°C.

12. Utilisation d'un catalyseur comprenant de l'oxyde de chrome (III) et un métal alcalin pour déshydrofluorer le CF3CHFCH2F (HFC-245eb) afin de produire du 2,3,3,3-tétrafluoropropène (HFC-1234yf).

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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- WO 2007056194 A1 **[0005]**
- WO 2008008350 A2 **[0006]**
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Non-patent literature cited in the description

- CRC Handbook of Chemistry and Physics. 2000 **[0031]**

Szabadalmi igénypontok

1. Eljárás 2,3,3,3-tetrafluorpropén előállítására, amely tartalmazza: (a) 1,1,1,2,3-pentafluorpropán dehidrofluorozását dehidrofluorozási katalizátor jelenlétében, amely áll króm (III) oxidból és alkáli fémből, olyan mennyiségben, amely hatásos termék keverék előállítására, amely tartalmaz 2,3,3,3-tetrafluorpropént és kevesebb, mint 20 részt százanként, moláris alapon 1,1,1,2,2-pentafluorpropánt; és (b) a 2,3,3,3-tetrafluorpropén visszanyerését az (a)-ban előállított termék keverékből.

2. Az 1. igénypont szerinti eljárás, ahol a termék keverék, amely tartalmaz 2,3,3,3-tetrafluorpropént, kevesebb, mint 10 részt százanként 1,1,1,2,2-pentafluorpropánt tartalmaz, moláris alapon.

3. Az 1. igénypont szerinti eljárás, ahol a dehidrofluorozási katalizátor tartalmaz 0,1%-2% alkáli fémet, amely a katalizátor felületén van elhelyezve.

4. Az 1. igénypont szerinti eljárás, ahol a dehidrofluorozási katalizátor tartalmaz 0,1 %-1 % alkáli fémet, amely a katalizátor felületén van elhelyezve.

5. Az 1. igénypont szerinti eljárás, ahol a dehidrofluorozási katalizátor tartalmaz 0,1%-1% káliumot, amely a katalizátor felületén van elhelyezve.

6. Az 1. igénypont szerinti eljárás, ahol a dehidrofluorozási katalizátor tartalmaz 0,5% -2% alkáli fémet, amely a katalizátor részecskéin át vannak diszpergálva.

7. Az 1. igénypont szerinti eljárás, ahol a dehidrofluorozási katalizátor tartalmaz 0,1% -3% bórt és legalább 3000 ppm alkáli fémet.

8. Az 1. igénypont szerinti eljárás, ahol a dehidrofluorozási katalizátor tartalmaz 0.5%-2% bórt és legalább 3000 ppm nátriumot.

9. Az 1. igénypont szerinti eljárás, ahol a dehidrofluorozási katalizátor tartalmaz 0,5%.2% bórt és legalább 2000 ppm káliumot.

10. Az 1. igénypont szerinti eljárás, ahol a katalizátor hőmérséklete 250°C-350°C előírt hőmérsékleten van tartva.

11. A 8. igénypont szerinti eljárás, ahol a katalizátor hőmérséklete 250°C-300°C előírt hőmérsékleten van tartva.

12. Katalizátor felhasználása, amely tartalmaz króm (III) oxiot és alkáli fémet, hogy dehidrofluorozza CF3CHFCH2F (HFC-245eb)-et, 2,3,3,3-tetrafluorpropén (HFC-1234yf) előállítására.