

TITLE OF THE INVENTION

PROCESS TO MAKE FLUOROOLEFINS BY CATALYTIC HYDROFLUORINATION
OF HYDROCHLOROCARBONS OR HYDROCHLOROOLEFINS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/565,058 filed March 14, 2024, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention is directed to processes for preparing hydrofluoroolefin (HFOs) and/or hydrochlorofluoroolefin (HCFOs) from a hydrochloroolefin (HCO) or hydrochlorocarbon (HCC), and compositions thereof.

BACKGROUND OF THE INVENTION

[0003] The fluorocarbon industry has been working for the past few decades to find replacement refrigerants for the ozone depleting chlorofluorocarbons (CFCs) and 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 (ODP) and thus are not affected by the current regulatory phase-out as a result of the Montreal Protocol. In addition to ozone depleting concerns, global warming is another environmental concern in many of these applications. HFC refrigerants such as HFC-134a and HFC-125 respectively have global warming potentials (GWP) of 1,300 and 3,170 according to the UN's IPCC Fifth Assessment Report (AR5).

[0004] This regulatory landscape is continuously evolving, taking into consideration properties beyond just ODP and GWP. More particularly, there is a need for refrigerant compositions that not only meet low ODP standards and have low global warming potentials, but that also exhibit low or no flammability, provide

superior performance in a variety of applications and which meet the standards of evolving regulations.

[0005] There is a need in this art for new refrigerants that meet evolving regulations as well as provide heat transfer and refrigerant characteristics that meet or exceed the effectiveness of conventional refrigerants.

[0006] Some hydrofluoroolefins, such as 2,3,3,3-tetrafluoropropene (HFO-1234yf), are such kind of new refrigerants. Chlorofluoroolefins (CFOs) such as 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and HFOs such as 3,3,3-trifluoropropene (HFO-1243zf) are useful intermediates for the production of HFO-1234yf. Some processes to produce HCFO-1233xf from 1,1,2,3-tetrachloro-1-propene (HCO-1230xa) and to produce HFO-1243zf from 1,1,1,3-tetrachloropropane (HCC-250fb) involve using a metal oxide catalyst, such as a chromium oxide catalyst. Although chromium oxide catalysts are highly efficient, they are expensive, have limited availability, and can be toxic to the environment. Therefore, a need exists for alternative approaches that are more cost effective and much more environmentally friendly. The present invention provides such an alternative approach, namely by an innovative process of converting an HCC or HCO starting material to an HFO and/or HCFO, and more particularly converting HCO-1230xa to HCFO-1233xf and converting HCC-250fb to HFO-1243zf.

SUMMARY OF THE INVENTIONS

[0007] In some embodiments, the present invention relates to processes for preparing hydrofluoroolefin (HFOs) and/or hydrochlorofluoroolefin (HCFOs) from a hydrochlorocarbons (HCC) or hydrochloroolefin (HCO). Generally, the process comprises hydrofluorinating an HCC or HCO under conditions suitable to produce a product stream comprising HFO and/or HCFO products and optionally reaction intermediates and optionally unreacted starting materials. More particularly, the process comprises hydrofluorinating an HCC or HCO with an effective amount of hydrogen fluoride (HF) and in the presence of a catalyst, preferably a metal doped catalyst, under conditions suitable to produce a product stream comprising HFO and/or HCFO products.

[0008] In one embodiment, the HCO starting material used in the processes of the present invention is HCO-1230xa.

[0009] In one embodiment, the HFOs and/or HCFOs produced by processes of the present invention include one or more compounds selected from HCFO-1233xf, HFO-1234yf, HFO-1243zf and HCFO-1232xf.

[0010] In one embodiment, the HCO starting material used in the processes of the present invention is HCO-1230xa and the product stream produced by the processes comprises HCFO-1233xf.

[0011] In some embodiments, the present invention relates to processes for producing HCFO-1233xf from HCO-1230xa in the presence of a catalyst.

[0012] Certain embodiments of the invention disclosed herein relate to vapor phase processes for converting, preferably selectively converting, HCO-1230xa by hydrofluorination to HCFO-1233xf in the presence of a catalyst.

[0013] One embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HCFO-1233xf and at least one additional compound selected from HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

[0014] One embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HCFO-1233xf and HCFC-244bb and at least one additional compound selected from HFO-1243zf, HFO-1234yf, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

[0015] Another embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HCFO-1233xf, HCFC-244bb, HFO-1234yf, and at least one additional compound selected from HFO-1243zf, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

[0016] Another embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HCFO-1233xf and at least two additional compounds selected from HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

[0017] One embodiment disclosed herein relates to compositions which comprise, consist essentially of or consist of HCFO-1233xf and at least one additional compound selected from HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇, wherein the total amount of the additional compounds is about 10% or less based on the total amount of the composition.

[0018] In one embodiment, the HCC starting material used in the processes of the present invention is HCC-250fb.

[0019] In one embodiment, the HCC starting used in the processes of the present invention is HCC-250fb and the product stream produced by the processes comprises HFO-1243zf.

[0020] In some embodiments, the present invention relates to processes for producing HFO-1243zf from HCC-250fb in the presence of a catalyst.

[0021] Certain embodiments of the invention disclosed herein relate to vapor phase processes for converting, preferably selectively converting, HCC-250fb by hydrofluorination to HFO-1243zf in the presence of a catalyst.

[0022] One embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HFO-1243zf and at least one additional compound selected from HCFO-1233xf, HCFC-253fb, HCC-250fb, HCFO-1242zf and HCFO-1241 isomers.

[0023] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, suitable methods and materials are described below. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

DETAILED DESCRIPTION OF THE DRAWINGS

[0024] Fig. 1 illustrates a system according to one embodiment of the present invention.

[0025] The foregoing summary and the following detailed description and drawings are exemplary and explanatory only and are not restrictive of the invention, as defined in the appended claims. Other features and benefits of any one or more of the embodiments will be apparent from the following detailed description, drawings and from the claims.

DETAILED DESCRIPTION OF THE INVENTION

[0026] Before addressing details of embodiments described herein, certain terms are defined or clarified as follows.

[0027] The term "hydro(halo)alkane," as used herein means a molecule containing hydrogen, carbon, and optionally fluorine and/or chlorine and/or bromine and/or iodine, with no carbon-carbon double bond (halo- fluoro, chloro, bromo, iodo). Examples are described throughout the instant specification. The term hydro(halo)alkane encompasses both alkanes and halogen substituted alkanes.

[0028] The term "hydrochloroolefin," as used herein, means unsaturated organic compounds composed of hydrogen, chlorine and carbon.

[0029] The term "hydrofluoroolefin," as used herein, means unsaturated organic compounds composed of hydrogen, fluorine and carbon.

[0030] The term "hydrochlorofluoroolefin," as used herein, means unsaturated organic compounds composed of hydrogen, chlorine, fluorine and carbon.

[0031] The term "hydrochlorocarbon," as used herein, means saturated organic compounds composed of hydrogen, chlorine, and carbon.

[0032] 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 is true (or present).

[0033] The transitional phrase “consisting essentially of” is used to define a composition, method that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention, especially the mode of action to achieve the desired result of any of the processes of the present invention. The term ‘consisting essentially of’ occupies a middle ground between “comprising” and “consisting of.”

[0034] The transitional phrase “consisting of” excludes any element, step, or ingredient not specified. If in the claim such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase “consists of” appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

[0035] Where applicants have defined an invention or a portion thereof with an open-ended term such as “comprising,” it should be readily understood that (unless otherwise stated) the description should be interpreted to also include such an invention using the terms “consisting essentially of” or “consisting of.”

[0036] 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.

[0037] When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and/or lower preferable values, this is to be understood as specifically disclosing all ranges

formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed.

Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

[0038] As used herein GC/FID peak area correlates to the amount of a compound present as a proportion of the total area of all detected peaks. FID area% can be converted to mol% using a response factor either calculated or measured. See <https://www.chromatographytoday.com/news/gc-mdgc/32/breaking-news/what-is-a-response-factor/31169>.

[0039] As used herein, the term “about” is meant to account for variations due to experimental error (e.g., plus or minus approximately 10% of the indicated value- $\pm 1\%$, $\pm 2\%$, ± 3 , ... $\pm 10\%$, or between $\pm 1\%$ of a stated value and $\pm 10\%$ of the stated value and all ranges therebetween). All measurements reported herein are understood to be modified by the term “about,” whether or not the term is explicitly used, unless explicitly stated otherwise.

[0040] Compounds referred to in this disclosure may be referred to by code, based on fluorochemical naming convention, chemical structure and/or chemical name. For convenience and reference, selected compounds with codes, structures and chemical names are provided in Table 1.

Table 1

Code	Name	Formula
HCC-250fb	1,1,1,3-tetrachloropropane	$\text{CCl}_3\text{CH}_2\text{CH}_2\text{Cl}$
HCFC-244bb	2-chloro-1,1,1,2-tetrafluoropropane	$\text{CF}_3\text{CClFCH}_3$
CO-1110	Tetrachloroethene	$\text{CCl}_2=\text{CCl}_2$
HCO-1230xa	1,1,2,3-tetrachloro-1-propene	$\text{CCl}_2=\text{CClCH}_2\text{Cl}$
HCFO-1233xf	2-chloro-3,3,3-trifluoropropene	$\text{CF}_3\text{CCl}=\text{CH}_2$
HCFO-1241	1,1-dichloro-2-fluoro propene-1	$\text{C}_3\text{H}_3\text{Cl}_2\text{F}$
HFO-1234yf	2,3,3,3-tetrafluoropropene	$\text{CF}_3\text{CF}=\text{CH}_2$
HCFO-1242zf	3-chloro-3,3-difluoropropene	$\text{CClF}_2\text{CH}=\text{CH}_2$

Code	Name	Formula
HFO-1243zf	3,3,3-trifluoropropene	$\text{CF}_3\text{CH}=\text{CH}_2$
HCFO-1232xf	2,3-dichloro-3,3-difluoropropene	$\text{CClF}_2\text{CCl}=\text{CH}_2$
		$\text{C}_6\text{H}_2\text{F}_8$
		$\text{C}_6\text{H}_3\text{F}_7$
		$\text{C}_6\text{H}_3\text{ClF}_6$
		$\text{C}_6\text{H}_3\text{ClF}_6$
		$\text{C}_6\text{H}_2\text{ClF}_7$
		$\text{C}_6\text{H}_2\text{ClF}_7$
		$\text{C}_6\text{H}_3\text{Cl}_2\text{F}_7$

[0041] Some of the compounds present in the compositions of the present invention may exist as different configurational isomers or stereoisomers. The present invention is intended to include all single configurational isomers, single stereoisomers or any combination or mixture thereof. Single isomers or multiple isomers of the same compound may be used in any proportion.

[0042] In some embodiments, the present invention relates to processes for preparing HFOs and/or HCFOs from a starting material selected from an HCO or HCC. Generally, the process comprises hydrofluorinating an HCO or HCC under conditions suitable to produce a product stream comprising HFO and/or HCFO products and optionally reaction intermediates and optionally unreacted starting materials. More particularly, the process comprises hydrofluorinating an HCO or HCC with an effective amount of hydrogen fluoride (HF) and in the presence of a catalyst, preferably a metal doped catalyst, more preferably a metal doped alumina catalyst, most preferably a zinc doped alumina catalyst, under conditions suitable to produce a product stream comprising HFO and/or HCFO products.

[0043] In one embodiment, the starting material used in the processes of the present invention is HCO-1230xa or HCC-250fb.

[0044] In one embodiment, the HFOs and/or HCFOs produced by processes of the present invention include one or more compounds selected from HCFO-1233xf, HFO-1234yf, HFO-1243zf and HCFO-1232xf.

[0045] In one embodiment, the HCO used in the processes of the present invention is HCO-1230xa and the product stream produced by the processes comprises HCFO-1233xf.

[0046] In some embodiments, the present invention relates to processes for producing HCFO-1233xf from HCO-1230xa in the presence of a catalyst.

[0047] Certain embodiments of the invention disclosed herein relate to vapor phase processes for converting HCO-1230xa by hydrofluorination to HCFO-1233xf in the presence of a catalyst.

[0048] Another embodiment disclosed herein relates to a process of converting a starting material selected from an HCO and HCC to an HFO and/or HCFO with hydrogen fluoride and in the presence of a metal doped alumina oxide catalyst, wherein the doping metal comprises zinc.

[0049] In one embodiment, the HCC used in the processes of the present invention is HCC-250fb and the product stream produced by the processes comprises HFO-1243zf.

[0050] In some embodiments, the present invention relates to processes for producing HFO-1243zf from HCC-250fb in the presence of a catalyst.

[0051] Certain embodiments of the invention disclosed herein relate to vapor phase processes for converting HCC-250fb by hydrofluorination to HFO-1243zf in the presence of a catalyst.

[0052] It will be understood by those skilled in the art that while certain aspects of the present invention disclosed herein may refer to the specific embodiment of the starting material being HCO-1230xa and the product comprising HCFO-1233xf or the specific embodiment of the starting material being HCC-250fb and the product comprising HFO-1243zf, the present invention has broader applicability to the production of HFOs and/or HCFOs by hydrofluorination of an HCO or HCC in the presence of a metal doped alumina catalyst, and thus the parameters disclosed herein (e.g., reaction pressure, temperature, mole ratios and the like) are not limited to the specific embodiment of conversion of HCO-1230xa to HCFO-1233xf or of HCC-250fb to HFO-1243zf by hydrofluorination.

[0053] In some embodiments, hydrofluorination catalysts which may be used for the conversion of the HCO (e.g., HCO-1230xa) or HCC (e.g., HCC-250fb) to HCFOs (e.g., HCFO-1233xf) and/or HFOs (e.g., HFO-1234yf and/or HFO-1243zf) comprise Group IIB metals and/or Group IIIA, and more particularly a Group IIB metal and a Group IIIA metal.

[0054] In some embodiments, the catalyst comprises metal doped aluminum oxide.

[0055] In preferred embodiments, the catalyst comprises zinc (Zn) and aluminum (Al) compounds.

[0056] In one embodiment, the Zn is doped to alumina. In some embodiments, the catalyst comprises zinc doped aluminum oxide.

[0057] In some embodiments, the catalyst comprises aluminum oxide doped with a zinc compound. For example, the catalyst may comprise aluminum oxide doped with a zinc compound selected from zinc halide, zinc oxide, zinc hydroxide, zinc acetate, and the like as well as combinations thereof.

[0058] In one embodiment, the catalyst comprises from about 99 to about 90 wt.% alumina and about 1 to about 8 wt.% zinc or zinc compounds. In one embodiment, the catalyst is 2.5%Zn/Al₂O₃.

[0059] The catalyst may be readily regenerated by any means known in the art if it becomes deactivated.

[0060] Another embodiment disclosed herein relates to a process of converting HCO-1230xa to HCFO-1233xf, preferably in the vapor phase, in the presence of a metal doped alumina oxide catalyst, wherein the doping metal preferably comprises zinc or zinc compounds.

[0061] Another embodiment disclosed herein relates to a process of converting HCC-250fb to HFO-1243zf, preferably in the vapor phase, in the presence of a metal doped alumina oxide catalyst, wherein the doping metal preferably comprises zinc or zinc compounds.

[0062] Optionally, in some embodiments, the catalyst can be pretreated (preactivated) with HF or a HF/N₂ mixture. This pretreatment can be accomplished,

for example, by placing the catalyst in a suitable container and thereafter, passing HF over the catalyst at an elevated temperature. In one embodiment, such container can be the reactor used to perform the hydrofluorination reaction. In one embodiment, the pretreatment temperature is from about 100°C to about 500°C, or from about 150°C to about 450°C, preferably about 450°C.

[0063] In certain embodiments, contact/reaction of the starting material (e.g., HCO-1230xa or HCC-250fb) and HF is conducted in a catalyst filled reactor or reaction zone which is heated to or maintained at a temperature in the range of about 150°C to about 400°C, about 200°C to about 350°C, about 250°C to about 325°C, or about 280°C to about 330°C and all ranges therebetween, including endpoints. In some embodiments, the temperature for the hydrofluorination reaction is selected from one of about 150°C, about 155°C, about 160°C, about 165°C, about 170°C, about 175°C, about 185°C, about 195°C, about 200°C, about 205°C, about 210°C, about 215°C, about 220°C, about 225°C, about 230°C, about 235°C, about 240°C, about 245°C, about 250°C, about 255°C, about 260°C, about 265°C, about 270°C, about 275°C, about 280°C, about 285°C, about 290°C, about 295°C, about 300°C, about 305°C, about 310°C, about 315°C, about 320°C, about 325°C, about 330°C, or about 335°C, about 345°C, about 350°C, about 355°C, about 360°C, about 365°C, about 370°C, about 375°C, about 380°C, about 385°C, about 390°C, about 395°C, and about 400°C, and all values and ranges within and between about 150°C to about 400°C.

[0064] In certain catalytic vapor phase embodiments, contact of the starting material, preferably HCO-1230xa or HCC-250fb, and HF is conducted at a temperature range with limits between two of:

- a. about 150°C is equal to 150°C $\pm$ 1% $\pm$ 2%, $\pm$ 3%, $\pm$ 4%, $\pm$ 5%, $\pm$ 6%, $\pm$ 7%, $\pm$ 8%, $\pm$ 9% or $\pm$ 10% of 150°C,
- b. about 200°C is equal to 200°C $\pm$ 1% $\pm$ 2%, $\pm$ 3%, $\pm$ 4%, $\pm$ 5%, $\pm$ 6%, $\pm$ 7%, $\pm$ 8%, $\pm$ 9% or $\pm$ 10% of 200°C,
- c. about 240°C is equal to 240°C $\pm$ 1% $\pm$ 2%, $\pm$ 3%, $\pm$ 4%, $\pm$ 5%, $\pm$ 6%, $\pm$ 7%, $\pm$ 8%, $\pm$ 9% or $\pm$ 10% of 240°C,
- d. about 280°C is equal to 280°C $\pm$ 1% $\pm$ 2%, $\pm$ 3%, $\pm$ 4%, $\pm$ 5%, $\pm$ 6%, $\pm$ 7%, $\pm$ 8%, $\pm$ 9% or $\pm$ 10% of 280°C,

- e. about 300°C is equal to 300°C $\pm$ 1% $\pm$ 2%, $\pm$ 3%, $\pm$ 4%, $\pm$ 5%, $\pm$ 6%, $\pm$ 7%, $\pm$ 8%, $\pm$ 9% or $\pm$ 10% of 330°C
- f. about 350°C is equal to 200°C $\pm$ 1% $\pm$ 2%, $\pm$ 3%, $\pm$ 4%, $\pm$ 5%, $\pm$ 6%, $\pm$ 7%, $\pm$ 8%, $\pm$ 9% or $\pm$ 10% of 350°C, and
- g. about 400°C is equal to 400°C $\pm$ 1% $\pm$ 2%, $\pm$ 3%, $\pm$ 4%, $\pm$ 5%, $\pm$ 6%, $\pm$ 7%, $\pm$ 8%, $\pm$ 9% or $\pm$ 10% of 400°C.

[0065] One embodiment of the present invention relates to a process of contacting HCO-1230xa and HF, in the presence of a catalyst, preferably a metal doped alumina catalyst, at sufficient temperatures to produce HCFO-1233xf.

[0066] Certain embodiments of the invention disclosed herein relate to vapor phase processes for selectively converting HCO-1230xa in the presence of HF to HCFO-1233xf in the presence of a catalyst, preferably a metal doped alumina catalyst, at temperatures ranging from 150°C to 400°C.

[0067] One embodiment of the present invention relates to a process of contacting HCC-250fb and HF, in the presence of a catalyst, preferably a metal doped alumina catalyst, at sufficient temperatures to produce HFO-1243zf.

[0068] Certain embodiments of the invention disclosed herein relate to vapor phase processes for selectively converting HCC-250fb in the presence of HF to HFO-1243zf in the presence of a catalyst, preferably a metal doped alumina catalyst, at temperatures ranging from 150°C to 400°C.

[0069] In certain embodiments, contact of the starting material (e.g., HCO-1230xa or HCC-250fb) and HF to produce certain HCFOs and/or HFOs is conducted at subatmospheric pressure, including but not limited to about 0 psig to about 100 psig.

[0070] In some embodiments, the reaction pressure for the vapor phase catalytic hydrofluorination of HCO-1230xa to produce HCFO-1233xf or vapor phase catalytic hydrofluorination of HCC-250fb to produce HFO-1243zf is between about 0 psig and about 100 psig.

[0071] In certain embodiments, contact of the HCO (e.g., HCO-1230xa) or HCC (e.g., HCC-250fb) and HF is conducted at an HF:organic mole ratio in the range of

between about 5:1 and about 40:1, or between about 5:1 and about 30:1, or between about 10:1 and about 20:1, and all ratios therebetween.

[0072] In some embodiments, the HF:organic mole ratio, and more particularly the HF:HCO-1230xa ratio for the vapor phase catalytic hydrofluorination of HCO-1230xa to produce HCFO-1233xf, or the HF:HCC-250fb ratio for the vapor phase catalytic hydrofluorination of HCC-250fb to produce HFO-1243zf, is in the range of between about 5:1 and about 40:1, or between about 5:1 and about 30:1, or between about 10:1 and about 20:1, and all ratios therebetween.

[0073] In some catalytic vapor phase embodiments of the present invention, conversion of HCO-1230xa to HCFO-1233xf or conversion of HCC-250fb to HFO-1243zf in the presence of HF ranges between about 90% and about 100%. Another embodiment disclosed herein relates to a process of selectively converting HCO-1230xa to greater than about 90% HCFO-1233xf. Another embodiment disclosed herein relates to a process of selectively converting HCC-250fb to greater than about 90% HFO-1243zf. One embodiment of the present invention relates to a process of contacting HCO-1230xa and HF at sufficient temperatures to produce greater than about 90% HCFO-1233xf. One embodiment of the present invention relates to a process of contacting HCC-250fb and HF at sufficient temperatures to produce greater than about 90% HFO-1243zf.

[0074] In some embodiments of the present invention, reaction of the starting material and HF is conducted in a reactor or reaction zone heated to or maintained at a temperature of from about 150°C to about 400°C, or between about 200°C and about 350°C, and at a pressure of between about 0 psig and about 100 psig, in the presence of a catalyst, preferably a zinc doped alumina catalyst, with an HF:HCO mole ratio between about 5:1 and about 40:1, or from about 5:1 to about 30:1, to produce one or more HCFOs and/or HFOs preferably in an amount of about 90% or greater.

[0075] In some embodiments of the present invention, reaction of HCO-1230xa and HF is conducted in a reactor or reaction zone heated to or maintained at a temperature of from about 150°C to about 400°C, or between about 200°C and about 350°C, and at a pressure of between about 0 psig and about 100 psig, in the presence of a catalyst, preferably a zinc doped alumina catalyst, with an HF:HCO-

1230xa mole ratio between about 5:1 and about 40:1, or from about 5:1 to about 30:1, to produce HCFO-1233xf preferably in an amount of about 90% or greater.

[0076] In some embodiments of the present invention, reaction of HCC-250fb and HF is conducted in a reactor or reaction zone heated to or maintained at a temperature of from about 150°C to about 400°C, or between about 200°C and about 350°C, and at a pressure of between about 0 psig and about 100 psig, in the presence of a catalyst, preferably a zinc doped alumina catalyst, with an HF: HCC-250fb mole ratio between about 5:1 and about 40:1, or from about 5:1 to about 30:1, to produce HFO-1243zf preferably in an amount of about 90% or greater.

[0077] One embodiment disclosed herein relates to vapor phase hydrofluorination processes which produce one or more HCFOs and/or HFOs by contacting the starting material at a temperature of from about 150°C to about 400°C, or between about 200°C and about 350°C, and at a pressure of between about 0 psig and about 100 psig, in the presence of a catalyst, preferably a zinc doped alumina catalyst, with an HF:organic mole ratio between about 5:1 and about 40:1, or from about 5:1 to about 30:1, wherein conversion of the HCO or HCC to HCFOs and/or HFOs in the presence of HF is about 90% or greater.

[0078] One embodiment disclosed herein relates to vapor phase hydrofluorination processes which produce HCFO-1233xf by contacting HCO-1230xa and HF at a temperature of from about 150°C to about 400°C, or between about 200°C and about 350°C, and at a pressure of between about 0 psig and about 100 psig, in the presence of a catalyst, preferably a zinc doped alumina catalyst, with an HF:HCO-1230xa mole ratio between about 5:1 and about 40:1, or from about 5:1 to about 30:1, wherein conversion of HCO-1230xa to HCFO-1233xf in the presence of HF is about 90% or greater.

[0079] One embodiment disclosed herein relates to vapor phase hydrofluorination processes which produce HFO-1243zf by contacting HCC-250fb and HF at a temperature of from about 150°C to about 400°C, or between about 200°C and about 350°C, and at a pressure of between about 0 psig and about 100 psig, in the presence of a catalyst, preferably a zinc doped alumina catalyst, with an HF: HCC-250fb mole ratio between about 5:1 and about 40:1, or from about 5:1 to about 30:1,

wherein conversion of HCC-250fb to HFO-1243zf in the presence of HF is about 90% or greater.

[0080] Fig. 1 illustrates one embodiment for the conversion of an HCO, such as HCO-1230xa, to an HCFO, such as HCFO-1233xf, and/or for the conversion of an HCC, such as HCC-250fb, to an HFO, such as HFO-1243zf, using system 100. The starting material (e.g., HCO-1230xa or HCC-250fb) feed flows from line 102 and is conveyed by pump 104 to and through optional vaporizer 110 in which the organic feed is heated to about 200°C, optionally with a flow of nitrogen, and discharged from the vaporizer 110 through line 114 to be combined with HF feed 112 in mixer 116 (or instead of mixer 116, the organic feed and HF lines can be connected through valving directly to the reactor 120 and combined therein). The combined organic/HF feed is fed into a heated reactor 120 having a catalyst bed (optionally containing a suitable inert packing) using any system suitable for heating, controlling and regulating temperatures ranging from between about room temperature and 700°C, at a temperature suitable for the hydrofluorination of the HCO, such as HCO-1230xa, or HCC, such as HCC-250fb. The product mixture from reactor 120 is discharged through line 124 or optionally transferred through line 124 into and through a treating system 130, e.g., scrubbers (via scrubbing fluid 132), distillation columns (not shown), etc. to purify and recover at least one HFO and/or HCFO in line 134, preferably to purify and recover at least one of HCFO-1232xf and/or HCFO-1233xf in line 134 or to purify and recover at least HFO-1243zf in line 134.

[0081] Reactors suitable for either liquid phase reactions or for vapor phase reactions can be used. Preferably, reactors suitable for vapor phase reactions are used. In the vapor phase, a heated reactor is used, and the reactor is provided with suitable heat control. A number of reactor configurations are possible including packed bed tube or column reactors, optionally containing suitable inert packing such as Monel™ or Hastelloy™ nickel alloy turnings or wool, or other material inert to halogenated species. E.g., HCl and HF which allows efficient mixing of starting materials.

[0082] Reactor configurations whether containing the suitable packing or free of any packing can be operated in batch, semi-batch or continuous modes. In addition to the reactors disclosed herein, preheaters and vaporizers, heat exchangers, feed

and effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, and valving associated with reactors, heat exchangers, vessels, columns, and units that are used in the processes of various embodiments disclosed herein should be constructed of materials resistant to corrosion.

[0083] One embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HCFO-1233xf and at least one additional compound selected from HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, $C_6H_2F_8$, $C_6H_3F_7$, $C_6H_3ClF_6$ isomers, CO-1110, $C_6H_2ClF_7$ isomers and $C_6H_3Cl_2F_7$, or two or more of the additional compounds.

[0084] One embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HCFO-1233xf and HCFC-244bb and at least one additional compound selected from HFO-1243zf, HFO-1234yf, HCFO-1232xf, HCO-1230xa, $C_6H_2F_8$, $C_6H_3F_7$, $C_6H_3ClF_6$ isomers, CO-1110, $C_6H_2ClF_7$ isomers and $C_6H_3Cl_2F_7$, or two or more of the additional compounds.

[0085] Another embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HCFO-1233xf, HCFC-244bb, HFO-1234yf, and at least one additional compound selected from HFO-1243zf, HCFO-1232xf, HCO-1230xa, $C_6H_2F_8$, $C_6H_3F_7$, $C_6H_3ClF_6$ isomers, CO-1110, $C_6H_2ClF_7$ isomers and $C_6H_3Cl_2F_7$, or two or more of the additional compounds.

[0086] One embodiment disclosed herein relates to compositions which comprise, consist essentially of or consist of HCFO-1233xf and at least one additional compound selected from HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, $C_6H_2F_8$, $C_6H_3F_7$, $C_6H_3ClF_6$ isomers, CO-1110, $C_6H_2ClF_7$ isomers and $C_6H_3Cl_2F_7$, wherein the total amount of the additional compounds is about 10% or less based on the total amount of the composition.

[0087] One embodiment of the present invention disclosed herein relates to a composition comprising, consisting essentially of, or consisting of HFO-1243zf and at least one additional compound selected from HCFO-1233xf, HCFC-253fb, HCC-250fb, HCFO-1242zf and HCFO-1241 isomers.

[0088] The following Examples are provided to illustrate certain aspects of the invention and shall not limit the scope of the appended claims.

EXAMPLES

Example 1: Preparation of 2.5% Zn/Al₂O₃ catalyst

[0089] A 2.5% Zn/Al₂O₃ catalyst is prepared by soaking 24 g Al₂O₃ in an aqueous solution containing 2.73 g zinc nitrate hexahydrate in 19.22 g D.I. water. The mixture is in a vacuum oven at 110°C overnight to remove the water and the dried catalyst contains 2.5 wt% zinc.

Example 2: Hydrofluorination of 1230xa to 1233xf using 2.5%Zn/Al₂O₃ catalyst

[0090] A 2.5% Zn/Al₂O₃ catalyst was prepared by soaking Al₂O₃ in an aqueous solution containing the appropriate amount of zinc salt. Excess water was removed by placing the sample in a vacuum oven at 110°C. 6ml 12-20mesh of the prepared 2.5%Zn/Al₂O₃ catalyst was loaded into a 12 inches long Inconel (0.5 inch OD) tube reactor. The catalyst was activated by HF starting from 150°C to 450°C. HCO-1230xa was fed by a pump and went through a vaporizer at 200°C with N₂ and then was mixed with HF and flowed through the reactor with the catalyst bed. The HCO-1230xa-HF reaction was tested at the conditions listed in Table 2 below. The reactor effluent was analyzed by a GC-MS-FID and shows that HCFO-1233xf was produced at high concentrations at various conditions (see, e.g., Table 3).

Table 2

Temp C	Pres- sure psi	1230xa ml/hr	N2 Sccm	HF sccm	HF/org mol ratio	GC FID area%			
						1233xf	1232xf	1230xa	Others
240	2.4	0.15	11.99	5.51	10.41	97.01%	0.00%	0.00%	2.99%
240	2.4	0.15	11.99	5.51	10.41	97.15%	0.00%	0.00%	2.85%
260	2.3	0.15	11.99	5.51	10.41	96.09%	0.00%	0.00%	3.91%
260	2.3	0.15	11.99	5.51	10.41	96.59%	0.00%	0.15%	3.25%
240	0.9	0.15	11.99	5.51	10.41	95.19%	0.00%	0.00%	4.81%
240	0.9	0.15	11.99	5.51	10.41	96.74%	0.00%	0.32%	2.94%
240	0.9	0.15	11.99	5.51	10.41	94.84%	0.00%	0.56%	4.60%
260	0.9	0.15	11.99	5.51	10.41	96.91%	0.00%	0.30%	2.80%
280	0.9	0.15	11.99	5.51	10.41	97.45%	0.00%	0.00%	2.55%
280	0.9	0.15	11.99	5.51	10.41	97.28%	0.00%	0.00%	2.72%
300	0.9	0.15	11.99	5.51	10.41	97.29%	0.00%	0.00%	2.71%
300	0.9	0.15	11.99	5.51	10.41	97.34%	0.00%	0.00%	2.66%
310	0.9	0.15	11.99	5.51	10.41	97.36%	0.00%	0.19%	2.46%
310	0.9	0.15	11.99	5.51	10.41	97.35%	0.00%	0.15%	2.50%
320	0.9	0.15	11.99	5.51	10.41	97.15%	0.00%	0.23%	2.63%
320	0.9	0.15	11.99	5.51	10.41	96.95%	0.00%	0.23%	2.82%

Temp C	Pres- sure psi	1230xa ml/hr	N2 Sccm	HF sccm	HF/org mol ratio	GC FID area%			
						1233xf	1232xf	1230xa	Others
330	0.8	0.15	11.99	5.53	10.43	96.94%	0.00%	0.38%	2.67%
330	0.7	0.15	11.99	5.53	10.43	96.41%	0.00%	0.31%	3.28%
180	0.8	0.25	27.96	6.02	6.84	91.15%	0.00%	0.00%	8.85%
180	0.8	0.25	27.96	6.02	6.84	91.34%	0.00%	0.00%	8.66%
180	0.8	0.25	27.96	6.02	6.84	91.36%	0.00%	0.00%	8.64%
200	0.8	0.25	27.96	6.02	6.84	93.24%	0.00%	0.00%	6.76%
200	0.9	0.25	27.96	6.02	6.84	93.56%	0.00%	0.00%	6.44%
220	0.9	0.25	27.96	6.02	6.84	95.35%	0.00%	0.00%	4.65%
220	0.8	0.25	27.96	6.02	6.84	95.41%	0.00%	0.00%	4.59%
240	0.9	0.25	27.96	6.00	6.82	96.37%	0.00%	0.00%	3.63%
240	0.8	0.25	27.96	6.01	6.83	96.67%	0.00%	0.00%	3.33%

Table 3: Detailed GC analysis at 240°C with HF/Organic ratio at 10.4:1

Compounds	FID area%
1243zf/1234yf	0.1576%
244bb	0.2715%
1233xf	96.6894%
C6H2F8	0.0287%
C6H3F7	0.1183%
C6H3ClF6	0.7634%
1110	0.2217%
C6H3ClF6	0.1178%
C6H2ClF7	0.4499%
C6H2ClF7	0.1515%
C6H3Cl2F7	1.0101%
others	0.0202%

Example 3: Hydrofluorination of 250fb to 1243zf using 2.5%Zn/Al₂O₃ catalyst

[0091] 4ml 2.5% Zn/Al₂O₃ catalyst was loaded into a 12 inches long Inconel (0.5 inch OD) tube reactor. The catalyst was activated by HF starting from 150°C to 450°C. HCC-250fb was fed by a pump and went through a vaporizer at 200°C with N₂ and then was mixed with HF and flowed through the reactor with the catalyst bed. The HCC250fb-HF reaction was tested at the conditions listed in Table 4 below. The reactor effluent was analyzed by a GC-MS-FID and shows that HFO-1243zf was produced at high concentrations at various conditions.

Table 4

Temp C	Pres- sure psig	250fb ml/hr	N2 sccm	HF sccm	HF/org mol ratio	Mole Percents				
						1243zf	1233xf	253fb	250fb	others
200	2.0	0.22	30	7.03	16	96.49%	0.00%	0.00%	0.00%	3.51%
200	2.0	0.22	30	7.03	16	97.58%	0.85%	0.55%	0.00%	1.02%
200	2.0	0.22	30	7.03	16	98.69%	0.00%	0.53%	0.00%	0.78%
220	1.9	0.22	30	7.03	16	97.60%	0.31%	0.83%	0.00%	1.26%
220	1.9	0.22	30	7.03	16	97.30%	0.29%	1.38%	0.00%	1.02%
240	2.0	0.22	30	7.03	16	96.07%	0.35%	2.22%	0.00%	1.36%
240	2.0	0.22	30	7.03	16	96.57%	0.30%	2.13%	0.00%	1.00%
260	2.0	0.22	30	7.03	16	95.86%	0.36%	2.04%	0.00%	1.74%
280	2.0	0.22	30	7.03	16	97.42%	0.00%	0.99%	0.00%	1.59%
280	2.0	0.22	30	7.03	16	97.41%	0.35%	1.02%	0.00%	1.22%
300	2.0	0.22	30	7.03	16	97.21%	0.42%	0.58%	0.00%	1.78%
300	2.0	0.22	30	7.03	16	97.18%	0.00%	0.84%	0.00%	1.98%
320	2.0	0.22	30	7.03	16	97.63%	0.00%	0.26%	0.00%	2.11%

Other Embodiments

[0092] Embodiment 1. A process of converting a starting material selected from a hydrochloroolefin and a hydrochlorocarbon to one or more hydrofluoroolefins and/or hydrochlorofluoroolefins, the process comprising contacting the starting material with hydrogen fluoride in the presence of a metal doped alumina catalyst.

[0093] Embodiment 2. The process of Embodiment 1, where the doping metal is zinc and/or zinc compounds.

[0094] Embodiment 3. The process of Embodiment 2, wherein the catalyst comprises 1 to 8 wt % of zinc as zinc and/or zinc compounds.

[0095] Embodiment 4. The process of any of Embodiments 1-3, wherein the hydrochloroolefin is 1,1,2,3-tetrachloro-1-propene (HCO-1230xa)

[0096] Embodiment 5. The process of any of Embodiments 1-4, wherein the hydrochlorofluoroolefin produced by the process is 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf).

[0097] Embodiment 6. The process of any of Embodiments 1-5, wherein a product stream of the process comprises HCFO-1233xf and at least one additional compound selected from HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

[0098] Embodiment 7. The process of any of Embodiments 1-3, wherein the hydrochlorocarbon is 1,1,1,3-tetrachloropropane (HCC-250fb).

[0099] Embodiment 8. The process of any of Embodiments 1-3 and 7, wherein the hydrofluoroolefin produced by the process is 3,3,3-trifluoropropene (HFO-1243zf).

[0100] Embodiment 9. The process of any of Embodiments 1-3 and 7-8, wherein a product stream of the process comprises HFO-1243zf and at least one additional compound selected from HCFO-1233xf, HCFC-253fb, HCC-250fb, HCFO-1242zf and HCFO-1241 isomers.

[0101] Embodiment 10. The process of any of Embodiments 1-9, wherein selectivity of the one or more hydrofluoroolefins and/or hydrochlorofluoroolefins is greater than about 90%.

[0102] Embodiment 11. The process of any of Embodiments 1-10, wherein the hydrogen fluoride:starting material mole ratio is in the range of between about 5:1 and about 40:1, preferably about 5:1 and about 30:1, more preferably about 10:1 and about 20:1.

[0103] Embodiment 12. The process of any of Embodiments 1-11, wherein a reaction zone for contacting the starting material with hydrogen fluoride is heated to a temperature in the range of between about 150°C and about 400°C, preferably between about 200°C to about 350°C.

[0104] Embodiment 13. A process comprising contacting HCO-1230xa and HF in a reaction zone containing a zinc doped alumina catalyst and producing HCFO-1233xf.

[0105] Embodiment 14. The process of Embodiment 13, wherein the reaction zone is heated to a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C.

[0106] Embodiment 15. A process to produce HCFO-1233xf, the process comprising contacting HCO-1230xa and HF in a reaction zone heated to a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C, wherein the reaction zone contains a zinc doped alumina.

[0107] Embodiment 16. The process of any of Embodiments 13-15, wherein selectivity of HCFO-1233xf is greater than about 90%.

[0108] Embodiment 17. The process of any of Embodiments 13-16, wherein the hydrogen fluoride:HCO-1230xa mole ratio is in the range of between about 5:1 and about 40:1, preferably about 5:1 and about 30:1, more preferably about 10:1 and about 20:1.

[0109] Embodiment 18. A process comprising contacting HCC-250fb and HF in a reaction zone containing a zinc doped alumina catalyst and producing HFO-1243zf.

[0110] Embodiment 19. The process of Embodiment 18, wherein the reaction zone is heated to a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C.

[0111] Embodiment 20. A process to produce HFO-1243zf, the process comprising contacting HCC-250fb and HF in a reaction zone heated to a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C, wherein the reaction zone contains a zinc dope alumina.

[0112] Embodiment 21. The process of any of Embodiments 18 to 20, wherein selectivity of HFO-1243zf is greater than about 90%.

[0113] Embodiment 22. The process of any of Embodiments 18 to 21, wherein the hydrogen fluoride:HCC-250fb mole ratio is in the range of between about 5:1 and about 40:1, preferably about 5:1 and about 30:1, more preferably about 10:1 and about 20:1.

[0114] Embodiment 23. The process of any of Embodiments 1 to 22, wherein the process is carried out in the vapor phase.

[0115] Embodiment 24. The process of any of Embodiments 1 to 23, wherein the process is carried out at a pressure of between about 0 psig and about 100 psig.

[0116] Embodiment 25. A vapor phase process of producing HCFO-1233xf, the process contacting HCO-1230xa and HF at a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C, in the presence of a catalyst comprising zinc and aluminum compounds, at an HF:HCO-1230xa mole

ratio of from about 5:1 to about 40:1, preferably from about 5:1 to about 30:1, and at a pressure of between about 0 psig and about 100 psig.

[0117] Embodiment 26. A vapor phase process of producing HFO-1243zf, the process contacting HCC-250fb and HF at a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C, in the presence of a catalyst comprising zinc and aluminum compounds, at an HF:HCC-250fb mole ratio of from about 5:1 to about 40:1, preferably from about 5:1 to about 30:1, and at a pressure of between about 0 psig and about 100 psig.

[0118] Embodiment 27. The vapor phase process of any of Embodiments 25 to 26, wherein the catalyst comprises zinc doped aluminum oxide.

[0119] Embodiment 28. A composition comprising HCFO-1233xf and at least one additional compound selected from the group consisting of HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

[0120] Embodiment 29. A composition comprising HCFO-1233xf and HCFC-244bb and at least one additional compound selected from the group consisting of HFO-1243zf, HFO-1234yf, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

[0121] Embodiment 30. A composition comprising HCFO-1233xf, HFO-1234yf and HCFC-244bb and at least one additional compound selected from the group consisting of HFO-1243zf, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

[0122] Embodiment 31. A composition comprising HFO-1243zf and at least one additional compound selected from the group consisting of HCFO-1233xf, HCFC-253fb, HCC-250fb, HCFO-1242zf and HCFO-1241 isomers.

[0123] Although certain aspects, embodiments and principals have been described above, it is understood that this description is made only way of example and not as limitation of the scope of the invention or appended claims. The foregoing various aspects, embodiments and principals can be used alone and in combinations with each other.

CLAIMS

What is claimed is:

1. A process of converting a starting material selected from a hydrochloroolefin and a hydrochlorocarbon to one or more hydrofluoroolefins and/or hydrochlorofluoroolefins, the process comprising contacting the starting material with hydrogen fluoride in the presence of a metal doped alumina catalyst.
2. The process of claim 1, where the doping metal is zinc and/or zinc compounds.
3. The process of claim 2, wherein the catalyst comprises 1 to 8 wt % of zinc as zinc and/or zinc compounds.
4. The process of any of claims 1-3, wherein the hydrochloroolefin is 1,1,2,3-tetrachloro-1-propene (HCO-1230xa)
5. The process of any of claims 1-4, wherein the hydrochlorofluoroolefin produced by the process is 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf).
6. The process of any of claims 1-5, wherein a product stream of the process comprises HCFO-1233xf and at least one additional compound selected from HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.
7. The process of any of claims 1-3, wherein the hydrochlorocarbon is 1,1,1,3-tetrachloropropane (HCC-250fb).
8. The process of any of claims 1-3 and 7, wherein the hydrofluoroolefin produced by the process is 3,3,3-trifluoropropene (HFO-1243zf).
9. The process of any of claims 1-3 and 7-8, wherein a product stream of the process comprises HFO-1243zf and at least one additional compound selected from HCFO-1233xf, HCFC-253fb, HCC-250fb, HCFO-1242zf and HCFO-1241 isomers.
10. The process of any of claims 1-9, wherein selectivity of the one or more hydrofluoroolefins and/or hydrochlorofluoroolefins is greater than about 90%.

11. The process of any of claims 1-0, wherein the hydrogen fluoride:starting material mole ratio is in the range of between about 5:1 and about 40:1, preferably about 5:1 and about 30:1, more preferably about 10:1 and about 20:1.
12. The process of any of claims 1-11, wherein a reaction zone for contacting the starting material with hydrogen fluoride is heated to a temperature in the range of between about 150°C and about 400°C, preferably between about 200°C to about 350°C.
13. A process comprising contacting HCO-1230xa and HF in a reaction zone containing a zinc doped alumina catalyst and producing HCFO-1233xf.
14. The process of claim 13, wherein the reaction zone is heated to a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C.
15. A process to produce HCFO-1233xf, the process comprising contacting HCO-1230xa and HF in a reaction zone heated to a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C, wherein the reaction zone contains a zinc dope alumina.
16. The process of any of claims 13-15, wherein selectivity of HCFO-1233xf is greater than about 90%.
17. The process of any of claims 13-16, wherein the hydrogen fluoride:HCO-1230xa mole ratio is in the range of between about 5:1 and about 40:1, preferably about 5:1 and about 30:1, more preferably about 10:1 and about 20:1.
18. A process comprising contacting HCC-250fb and HF in a reaction zone containing a zinc doped alumina catalyst and producing HFO-1243zf.
19. The process of claim 18, wherein the reaction zone is heated to a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C.
20. A process to produce HFO-1243zf, the process comprising contacting HCC-250fb and HF in a reaction zone heated to a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C, wherein the reaction zone contains a zinc dope alumina.

21. The process of any of claims 18 to 20, wherein selectivity of HFO-1243zf is greater than about 90%.
22. The process of any of claims 18 to 21, wherein the hydrogen fluoride:HCC-250fb mole ratio is in the range of between about 5:1 and about 40:1, preferably about 5:1 and about 30:1, more preferably about 10:1 and about 20:1.
23. The process of any of claims 1 to 22, wherein the process is carried out in the vapor phase.
24. The process of any of claims 1 to 23, wherein the process is carried out at a pressure of between about 0 psig and about 100 psig.
25. A vapor phase process of producing HCFO-1233xf, the process contacting HCO-1230xa and HF at a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C, in the presence of a catalyst comprising zinc and aluminum compounds, at an HF:HCO-1230xa mole ratio of from about 5:1 to about 40:1, preferably from about 5:1 to about 30:1, and at a pressure of between about 0 psig and about 100 psig.
26. A vapor phase process of producing HFO-1243zf, the process contacting HCC-250fb and HF at a temperature from about 150°C to about 400°C, preferably from about 200°C to about 350°C, in the presence of a catalyst comprising zinc and aluminum compounds, at an HF:HCC-250fb mole ratio of from about 5:1 to about 40:1, preferably from about 5:1 to about 30:1, and at a pressure of between about 0 psig and about 100 psig.
27. The vapor phase process of any of claims 25 to 26, wherein the catalyst comprises zinc doped aluminum oxide.
28. A composition comprising HCFO-1233xf and at least one additional compound selected from the group consisting of HFO-1243zf, HFO-1234yf, HCFC-244bb, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.
29. A composition comprising HCFO-1233xf and HCFC-244bb and at least one additional compound selected from the group consisting of HFO-1243zf, HFO-

1234yf, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.

30. A composition comprising HCFO-1233xf, HFO-1234yf and HCFC-244bb and at least one additional compound selected from the group consisting of HFO-1243zf, HCFO-1232xf, HCO-1230xa, C₆H₂F₈, C₆H₃F₇, C₆H₃ClF₆ isomers, CO-1110, C₆H₂ClF₇ isomers and C₆H₃Cl₂F₇.
31. A composition comprising HFO-1243zf and at least one additional compound selected from the group consisting of HCFO-1233xf, HCFC-253fb, HCC-250fb, HCFO-1242zf and HCFO-1241 isomers.