

TITLE OF THE INVENTION

PROCESS OF PRODUCING FLUOROOLEFIN COMPOSITIONS BY CATALYTIC
HYDRODECHLORINATION OF HYDROCHLOROFLUOROCARBONS AND
COMPOSITIONS THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/565,052 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 producing fluoroolefins, more particularly difluoroolefins, by catalytic hydrodechlorination of hydrochlorofluorocarbons (HCFCs), 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).

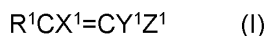
[0004] This regulatory landscape is continuously evolving, taking into consideration properties beyond just ODP and GWP. More particularly, there is a need for refrigerant compositions that not only meet low ODP standards and have low global warming potentials, but that also exhibit low or no flammability, 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 fluoroolefins, such as 1,1-difluoropropene (HFO-1252zc) ($\text{CF}_2=\text{CHCH}_3$) and E/Z-1,2-difluoroethylene (E/Z-HFO-1132) ($\text{CFH}=\text{CFH}$), are such potential new refrigerants. There continues to be need for effective and efficient processes for preparing low GWP and low or zero ODP fluoroolefin compounds and processes for making these low GWP and low or zero ODP fluoroolefin compounds, as well as compositions thereof.

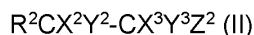
SUMMARY OF THE INVENTION

[0007] In an embodiment, the present invention is directed to a method of producing a fluoroolefin compound of formula (I):



[0008] In the compound of formula (I), R^1 represents a H, Cl, F or a C1-C4 alkyl group, X^1 is H, F or Cl, Y^1 is H, F or Cl, and Z^1 is H, Cl or F.

[0009] In an embodiment, a method of producing a fluoroolefin of formula (I) comprises contacting a compound of formula (II) with hydrogen:



[0010] In the compound of formula (II), R^2 represents a H, Cl, F or a C1-C4 alkyl group, X^2 is H, F, Cl or Br, Y^3 is H, Cl, Br, or F, X^3 and Y^2 are the same or different and are each independently Cl or Br, and Z^2 is H, Cl or F.

[0011] 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 INVENTION

[0012] 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.

[0013] 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).

[0014] 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.”

[0015] 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.

[0016] 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.”

[0017] 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.

[0018] 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.

[0019] 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 response factors either calculated or measured. See <https://www.chromatographytoday.com/news/gc-mdgc/32/breaking-news/what-is-a-response-factor/31169>.

[0020] 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. $\pm 1\%$, $\pm 2\%$, $\pm 3\%$, ... $\pm 10\%$). 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.

[0021] 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.

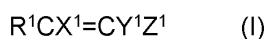
TABLE 1

Code	Name	Formula
HCFC-132	1,2-dichloro-1,2-difluoroethane	CHClFCHClF
HFC-152a	1,1-difluoroethane	CHF ₂ CH ₃
HCFC-242	trichlorodifluoropropane	C ₃ H ₃ F ₂ Cl ₃
HCFC-243 isomer	dichlorotrifluoropropane	C ₃ H ₃ F ₃ Cl ₂
HCFC-252dc	1,2-dichloro-1,1-difluoropropane	CClF ₂ CHClCH ₃

Code	Name	Formula
HCFC-253db	2-chloro-1,1,1-trifluoropropane	CF ₃ CHClCH ₃
HCFC-262db	2-chloro-1,1-difluoropropane	CHF ₂ CHClCH ₃
HCFC-262fc	1-chloro-1,1-difluoropropane	CH ₃ CH ₂ CClF ₂
HFC-263fb	1,1,1- trifluoropropane	CF ₃ CH ₂ CH ₃
HFC-272fb	1,1- difluoropropane	CH ₃ CH ₂ CF ₂ H
HCFO-1223xd	1,2-dichloro-3,3,3-trifluoropropene	CF ₃ CCl=CHCl
HCCO-1230xa	1,1,2,3-tetrachloro-1-propene	CCl ₂ =CClCH ₂ Cl
HCFO-1232xf	2,3-dichloro-3,3-difluoropropene	CClCF ₂ CCl=CH ₂
HCFO-1233xf	2-chloro-3,3,3-trifluoropropene	CF ₃ CCl=CH ₂
HCFO-1241xb	1,2-dichloro-1-fluoropropene (E/Z)	CH ₃ CCl=CClF
HCFO-1242zf	3-chloro-3,3-difluoro-1-propene	CClF ₂ CH=CH ₂
HFO-1243zf	3,3,3-Trifluoropropene	CF ₃ CH=CH ₂
HCFO-1251zb	1-chloro-1-fluoropropene (E/Z)	CH ₃ CH=CClF
HFO-1252zc	1,1-difluoropropene	CH ₃ CH=CF ₂
HFO-1261ze	1-fluoropropene (E/Z)	CH ₃ CH=CHF
HCFO-1335	monochloropentafluorobutene	C ₄ H ₂ ClF ₅
HCFO-1371	chlorofluorobutene	C ₄ H ₆ ClF
--	Acetone	CH ₃ COCH ₃
--	Isopropanol	CH ₃ CH(OH)CH ₃
--	Propylene	CH ₃ CH=CH ₂
HFO-1132	1,2-difluoroethylene (E/Z)	CHF=CHF
HCFO-1122a	1-chloro-1,2-difluoroethylene (E/Z)	CClF=CHF
CFO-1122	1,2-dichloro-1,2-difluoroethylene (E/Z)	CClF=CClF

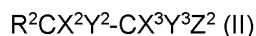
[0022] Some of the compounds present in the compositions of the present invention may exist as different configurational isomers or stereoisomers. Examples of such compounds include, but are not limited to, HCFO-1241xb and HCFO-1251zb. The present invention is intended to include all single configurational isomers, single stereoisomers or any combination or mixture thereof. Single isomers or multiple isomers of the same compound may be used in any proportion.

[0023] In some embodiments, the present invention is directed to a method of producing a fluoroolefin of formula (I):



[0024] In the compound of formula (I), R¹ represents a H, Cl, F or a C1-C4 alkyl group, X¹ is H, F or Cl, Y¹ is H, F or Cl, and Z¹ is H, Cl or F.

[0025] In some embodiments, a method of producing a fluoroolefin of formula (I) comprises contacting a compound of formula (II) with hydrogen:



[0026] In the compound of formula (II), R^2 represents a H, Cl, F or a C1-C4 alkyl group, X^2 is H, F, Cl or Br, Y^3 is H, Cl, Br, or F, X^3 and Y^2 are the same or different and are each independently Cl or Br, and Z^2 is H, Cl or F.

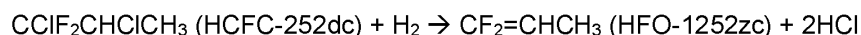
[0027] Preferably, the contacting of the compound of formula (II) with H_2 is performed in the vapor phase. Also preferably, the contacting is performed in the presence of a catalyst in an amount sufficient to form a composition comprising a compound of formula (I).

[0028] In some embodiments, the compound of formula (I) includes 1,1-difluoropropene (HFO-1252zc) ($CF_2=CHCH_3$) or E/Z-1,2-difluoroethylene (E/Z-HFO-1132) ($CHF=CHF$), or E/Z-1-chloro-1,2-difluoroethylene (E/Z-HCFO-1122a) ($CClF=CHF$) or E/Z-1,2-dichloro-1,2-difluoroethylene (E/Z-CFO-1112) ($CClF=CClF$).

[0029] In some embodiments, the compound of formula (II) includes 1,2-dichloro-1,1-difluoropropane (HCFC-252dc) or 1,2-dichloro-1,2-difluoroethane (HCFC-132).

[0030] In some embodiments, the present invention relates to processes for producing (making) HFO-1252zc and compositions thereof. In some embodiments, the present invention relates to processes for producing (making) HFO-1252zc and compositions thereof from HCFC-252dc.

[0031] In some embodiments, the present invention relates to making HFO-1252zc and involves the following reaction:



[0032] In some embodiments, the feed composition which is contacted with H_2 to form HFO-1252zc comprises, consists essentially of, or consists of HCFC-252dc and one or more additional compounds selected from HCFC-262fc, HCFO-1233xf, HCFO-1242zf, acetone, HCFC-262db, HCFC-253db, HCFO-1223xd, C_4H_6ClF , HCFO-1232xf, E-HCFO-1241xb, Z-HCFO-1241xb and HCFO-1335. In some embodiments, the HCFC-252dc constitutes about 0.1 wt% to about 99.9 wt.%, or about 40 wt.% to about

99.9 wt.%, or about 90 wt.% to about 99.9 wt.%, based on the total weight of the composition, inclusive of all integers and ranges therebetween.

[0033] In some embodiments, the total amount of additional compounds of the HCFC-252dc feed composition may be between greater than 0 and about 15 wt.% expressed by GC-FID peak area percent, e.g., the total amount of the composition, and all values and ranges therebetween. In some embodiments, the total amount of additional compounds of the HCFC-252dc feed composition may be between greater than 0 and less than one of 15 percent, 14 percent, 13 percent, 12 percent, 11 percent, 10 percent, 9 percent, 9 percent, 7 percent, 6 percent, 5 percent, 4 percent, 3 percent, 2 percent, or 1 percent and all values and ranges therebetween.

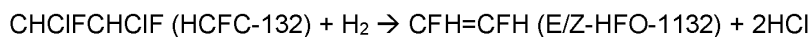
[0034] In some embodiments, the total amount of additional compounds of the HCFC-252dc feed composition may be between greater than 0 and less than 0.1 percent, greater than 0 and less than 0.01 percent, between greater than 0.0001 and less than 0.3 percent, greater than 0.0001 and less than 0.2 percent, greater than 0.0001 and less than 0.1 percent, greater than 0.0001 and less than 0.01 percent, or greater than 0.0001 and less than 0.001 percent based on the total amount of the composition and all values and ranges therebetween.

[0035] In some embodiments, each additional compound of the HCFC-252dc feed composition may be present in an amount of between greater than 0 and less than 4 percent, or less than 3 percent, or less than 2 percent, or less than 1 percent, or less than 0.5 percent, or less than 0.1 percent, or less than 0.01 percent, or less than 0.005 percent, or greater than 0.001 and less than 4 percent, or less than 3 percent, or less than 2 percent, or less than 1 percent, or less than 0.5 percent, or less than 0.1 percent, or less than 0.01 percent, or less than 0.005 percent, based on the total amount of the feed composition *with the proviso* that the total amount of the additional compounds is greater than 0.0001 and less than 15%, greater than 0.0001 and less than 10%, greater than 0.0001 and less than 8%, greater than 0.0001 and less than 7%, greater than 0.0001 and less than 6%, greater than 0.0001 and less than 5%, greater than 0.0001 and less than 4%, greater than 0.0001 and less than 3%, greater than 0.0001 and less than 2%, greater than 0.0001 and less than 1%, greater than 0.0001 and less than 0.5%, or greater than 0.0001 and less than 0.1.

[0036] One embodiment of the invention disclosed herein relates to processes of contacting HCFC-252dc with hydrogen in the vapor phase, in the presence of a catalyst, to form a product mixture or composition comprising HFO-1252zc. More particularly, in certain embodiments disclosed herein, HCFC-252dc is converted to HFO-1252zc by hydrodechlorination in the vapor phase in the presence of a catalyst.

[0037] In some embodiments, the present invention relates to processes for producing (making) E-HFO-1132 and Z-HFO-1132 and compositions thereof. In some embodiments, the present invention relates to processes for producing (making) E-HFO-1132 and Z-HFO-1132 and compositions thereof from HCFC-132.

[0038] In some embodiments, the present invention relates to making E/Z-HFO-1132 and involves the following reaction:



[0039] In some embodiments, the feed composition which is contacted with H₂ to form E/Z-HFO-1132 comprises, consists essentially of, or consists of HCFC-132 and one or more additional compounds selected from HCFC-132C (1,1-dichloro-1,2-difluoroethane), HCFC-132a (1,1-dichloro-2,2-difluoroethane), CFO-1112 (1,2-dichloro-1,2-difluoroethylene), CFO-1112a (1,1-dichloro-2,2-difluoroethylene), HCFC-142 (1-chloro-2,2-difluoroethane), HCFC-142a (1-chloro-1,2-difluoroethane) and HFC-152 (1,2-difluoroethane). In some embodiments, the HCFC-132 constitutes about 0.1 wt% to about 99.9 wt.%, or about 40 wt.% to about 99.9 wt.%, or about 90 wt.% to about 99.9 wt.%, based on the total weight of the composition, inclusive of all integers and ranges therebetween.

[0040] In some embodiments, the total amount of additional compounds of the HCFC-132 feed composition may be between greater than 0 and about 15 wt.% expressed by GC-FID peak area percent, e.g., the total amount of the composition, and all values and ranges therebetween. In some embodiments, the total amount of additional compounds of the HCFC-132 feed composition may be between greater than 0 and less than one of 15 percent, 14 percent, 13 percent, 12 percent, 11 percent, 10 percent, 9 percent, 9 percent, 7 percent, 6 percent, 5 percent, 4 percent, 3 percent, 2 percent, or 1 percent and all values and ranges therebetween.

[0041] In some embodiments, the total amount of additional compounds of the HCFC-132 feed composition may be between greater than 0 and less than 0.1 percent, greater than 0 and less than 0.01 percent, between greater than 0.0001 and less than 0.3 percent, greater than 0.0001 and less than 0.2 percent, greater than 0.0001 and less than 0.1 percent, greater than 0.0001 and less than 0.01 percent, or greater than 0.0001 and less than 0.001 percent based on the total amount of the composition and all values and ranges therebetween.

[0042] In some embodiments, each additional compound of the HCFC-132 feed composition may be present in an amount of between greater than 0 and less than 4 percent, or less than 3 percent, or less than 2 percent, or less than 1 percent, or less than 0.5 percent, or less than 0.1 percent, or less than 0.01 percent, or less than 0.005 percent, or greater than 0.001 and less than 4 percent, or less than 3 percent, or less than 2 percent, or less than 1 percent, or less than 0.5 percent, or less than 0.1 percent, or less than 0.01 percent, or less than 0.005 percent, based on the total amount of the feed composition *with the proviso* that the total amount of the additional compounds is greater than 0.0001 and less than 15%, greater than 0.0001 and less than 10%, greater than 0.0001 and less than 8%, greater than 0.0001 and less than 7%, greater than 0.0001 and less than 6%, greater than 0.0001 and less than 5%, greater than 0.0001 and less than 4%, greater than 0.0001 and less than 3%, greater than 0.0001 and less than 2%, greater than 0.0001 and less than 1%, greater than 0.0001 and less than 0.5%, or greater than 0.0001 and less than 0.1.

[0043] One embodiment of the invention disclosed herein relates to processes of contacting HCFC-132 with hydrogen in the vapor phase, in the presence of a catalyst, to form a product mixture or composition comprising HFO-1132(E) and HFO-1132(Z). More particularly, in certain embodiments disclosed herein, HCFC-132 is converted to HFO-1132(E) and HFO-1132(Z) by hydrodechlorination in the vapor phase in the presence of a catalyst.

[0044] Reactors suitable for vapor phase reactions can be used. In some embodiments, 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, 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. For example, the vapor phase reactor and other components may be made of or packed with materials such as, but not limited to, Hastelloy®, nickel-chromium alloys commercially available from Special Metals Corp. under the trademark Inconel® (hereinafter Inconel®) or nickel-copper alloys commercially available from Special Metals Corp. (New Hartford, N.Y.) under the trademark Monel® or other nickel alloy turnings or wool, or other material inert to the reactants.

[0045] In certain embodiments, the reaction to effect hydrodechlorination of the feed compound (i.e., the compound of formula (II), such as HCFC-252dc or HCFC-132) with H₂ is carried out in the presence of a catalyst. In some embodiments, hydrogenation catalysts which may be used comprise Group IB and/or IIB metals, and more particularly a Group IB metal and a Group IIB metal. In preferred embodiments, hydrogenation catalysts which may be used comprise copper (Cu) and zinc (Zn). The catalyst may be unsupported or supported. In one embodiment, the Cu-Zn metal is carried on a support, such as aluminum oxide, SiC or carbon, preferably carbon. In certain embodiments, the metal catalyst is supported on carbon and the carbon support/carrier comprises carbon, acid-washed carbon, activated carbon, three-dimensional matrix carbonaceous materials. In one embodiment, the catalyst is Zn-Cu/C. In one embodiment, the catalyst comprises from about 2 to about 20 wt.% copper and about 0.5 to about 10 wt.% zinc. In one embodiment, the catalyst is 3%Zn-8%Cu/C. The catalyst may be readily regenerated by any means known in the art if it becomes deactivated.

[0046] It has been found that the use of a Zn-Cu catalyst for catalytic hydrodechlorination of a compound of formula (II) (e.g., HCFC-252dc and/or HCFC-132) is effective for the production of a compound of formula (I) (e.g., HFO-1252zc and/or E/Z-HFO-1132) with high selectivity.

[0047] In some embodiments, for example where R¹ is a C1-C4 alkyl group, such as HFO-1252zc formed by the hydrodechlorination of HCFC-252dc, the product selectivity to R¹CX¹=CY¹Z¹ is at least about 70 mol%, or at least about 80 mol%, or at least about

90 mol%, or at least about 95 mol%, or at least about 96 mol%, or at least about 97 mol%.

[0048] In some embodiments, for example where R^1 is H, F or Cl, such as E/Z-HCFO-1132 formed by the hydrodechlorination of HCFC-132, the product selectivity to $R^1CX^1=CY^1Z^1$ is at least about 30 mol%, or at least about 32 mol%, or at least about 34 mol%, or at least about 36 mol%, or at least about 38 mol%, or at least about 40 mol%.

[0049] The term “product selectivity to $R^1CX^1=CY^1Z^1$ ”, as used herein, means the molar percentage of $R^1CX^1=CY^1Z^1$ obtained in the process compared to the total molar amounts of all products obtained.

[0050] Optionally, the catalyst can be pretreated (preactivated) with H_2 . This pretreatment can be accomplished, for example, by placing the catalyst in a suitable container and thereafter, passing H_2 over the catalyst at elevated temperature. In one embodiment, such container can be the reactor used to perform the hydrodechlorination reaction. Where the metals packing of the reactor has catalytic activity, H_2 may be passed over the metals packing surface for activation thereof. In one embodiment, the pretreatment time is from about 15 to about 300 minutes, preferably about 120 minutes, and the pretreatment temperature is from about 100°C to about 500°C, or from about 200°C to about 450°C, preferably about 450°C.

[0051] In one embodiment, a heated reactor is used for the reaction of H_2 with the formula (II) compound (e.g., HCFC-252dc or HCFC-132). A number of reactor configurations are possible including horizontal or vertical orientation of the reactor as well as the sequence of reaction of the formula (II) compound with H_2 . In one embodiment of the invention, the formula (II) compound may be initially vaporized and fed to the reactor as a gas. In one embodiment, the reactor may be empty. In another embodiment, the reactor is filled with a suitable packing such as nickel-based alloys such as Hastelloy®, nickel-chromium alloys commercially available from Special Metals Corp. under the trademark Inconel® (hereinafter Inconel®) or nickel-copper alloys commercially available from Special Metals Corp. (New Hartford, N.Y.) under the trademark Monel® or other nickel alloy turnings or wool, or other material which is inert to the reactants and products and which allows efficient mixing of the formula (II) compound and H_2 vapor. It will be understood by those skilled in the art that a pre-reactor could be utilized.

[0052] In some embodiments, an inert diluent gas is used as a carrier gas for the $R^2CX^2Y^2-CX^3Y^3Z^2$ compound (e.g., HCFC-252dc or HCFC-132). In one embodiment, the carrier gas is selected is HCl, nitrogen, argon, helium, carbon dioxide or fluorinated carbons. In some embodiments, the carrier gas is mixed and vaporized with the formula (II) compound and H_2 in the reactor.

[0053] In some embodiments, the molar ratio of H_2 to $R^2CX^2Y^2-CX^3Y^3Z^2$ for the vapor-phase reaction is from about 1:1 to about 50:1. In one embodiment, $R^2CX^2Y^2-CX^3Y^3Z^2$ is HCFC-252dc, and the molar ratio of H_2 to the total amount of the HCFC-252dc in the vapor phase reactor is from about 1:1 to about 50:1. In another embodiment, $R^2CX^2Y^2-CX^3Y^3Z^2$ is HCFC-132, and the molar ratio of H_2 to the total amount of the HCFC-132 in the vapor phase reactor is from about 5:1 to about 40:1.

[0054] Suitable temperatures for the vapor-phase hydrodechlorination of $R^2CX^2Y^2-CX^3Y^3Z^2$ (e.g., HCFC-252dc or HCFC-132) with H_2 in the presence of the catalyst are from about 60°C to about 300°C, or from about 180°C to about 280°C.

[0055] Suitable reactor pressures for the vapor-phase hydrodechlorination of the $R^2CX^2Y^2-CX^3Y^3Z^2$ (e.g., HCFC-252dc or HCFC-132) compound with H_2 in the presence of the catalyst are from about 0 to about 200 psig, or from about 10 to about 150 psig.

[0056] Suitable reaction times for the vapor-phase hydrodechlorination of $R^2CX^2Y^2-CX^3Y^3Z^2$ (e.g., HCFC-252dc or HCFC-132) with H_2 in the presence of the catalyst may vary from about 5 seconds to about 300 seconds, or from about 10 seconds to about 120 seconds.

[0057] In all embodiments disclosed herein, the product stream comprising the $R^2CX^2Y^2-CX^3Y^3Z^2$ compound (e.g., HFO-1252zc, E-HFO-1132 and/or Z-HFO-1132) may include additional members including unreacted precursor materials, e.g., HCFC-252dc for HFO-1252dc and HCFC-132 for E/Z-HFO-1132.

[0058] In some embodiments, the amount of HFO-1252zc produced is greater than about 10%, preferably greater than about 20%, more preferably greater than about 30%, most preferably greater than about 35%, based on the total amount of the product mixture. In some embodiments, the amount of E-HFO-1132 and Z-HFO-1132 produced is greater than about 1%, or greater than about 2%, preferably greater than about 3%,

more preferably greater than about 4%, most preferably greater than about 5%, based on the total amount of the product mixture.

[0059] In some embodiments, the processes of the present invention further comprise separation and/or purification (e.g., distillation, fractionation, adsorption, absorption, and the like, or a combination of any such methods) to recover the desired product or enhance the content of the desired product ($R^1CX^1=CY^1Z^1$; e.g., HFO-1252zc, E-HFO-1132 and/or Z-HFO-1132) from the mixture produced by the hydrodechlorination reaction.

[0060] Certain embodiments of the invention disclosed herein relates to compositions comprising, consisting essentially of, or consisting of R-1252zc which further include one or more additional members comprising hydrofluorocarbons (HFCs), hydrochlorocarbons (HCCs), hydrofluorochlorocarbons (HCFCs), hydrofluoroolefins (HFOs) and hydrofluorochloroolefins (HFCOs).

[0061] Certain embodiments of the invention disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HFO-1252zc and one or more additional compounds selected from propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-1241xb, HCFC-242 and HCFC-262db.

[0062] Certain embodiments of the invention disclosed herein relates to compositions comprising, consisting essentially of, or consisting of greater than about 10%, preferably greater than about 20%, more preferably greater than about 30%, most preferably greater than about 35% of HFO-1252zc, based on the total amount of the composition, and further including one or more additional compounds selected from propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-1241xb, HCFC-242 and HCFC-262db.

[0063] In some embodiments, under the reaction conditions disclosed herein, for example, a mixture of H_2 and HCFC-252dc is converted by the catalytic vapor-phase hydrodechlorination process to a reaction mixture comprising HCl and a composition comprising HFO-1252zc and one or more additional compounds selected from propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-

1241xb, HCFC-242 and HCFC-262db. In some embodiments, the HFO-1252zc constitutes about 0.1 wt% to about 99.9 wt.%, or about 20 wt.% to about 40 wt% based on the total weight of the composition, inclusive of all integers and ranges therebetween.

[0064] One embodiment of the invention disclosed herein is a composition comprising, consisting essentially of, or consisting of HFO-1252zc, wherein the HFO-1252zc is present in an amount greater than greater than about 20%, or greater than about 30%, or greater than about 35%, and less than about 100%, or less than about 50%, or less than about 40%, and all values and ranges therebetween.

[0065] Certain embodiments of the invention disclosed herein relates to compositions comprising, consisting essentially of, or consisting of E-HFO-1132 and Z-HFO-1132, which further include one or more additional members comprising HFCs, HCCs, HCFCs, HFOs and HFCOs.

[0066] Certain embodiments of the invention disclosed herein relate to compositions comprising, consisting essentially of, or consisting of E-HFO-1132, Z-HFO-1132 and one or more additional compounds selected from F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HCFC-142b, HFO-1132a, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a.

[0067] Certain embodiments of the invention disclosed herein relates to compositions comprising, consisting essentially of, or consisting of greater than about 3%, preferably greater than about 4%, more preferably greater than about 5% of E-HFO-1132 and Z-HFO-1132, based on the total amount of the composition, and further including one or more additional compounds selected from F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HCFC-142b, HFO-1132a, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a.

[0068] In some embodiments, under the reaction conditions disclosed herein, for example, a mixture of H₂ and HCFC-132 is converted by the catalytic vapor-phase hydrodechlorination process to a reaction mixture comprising HCl and a composition comprising E-HFO-1132 and Z-HFO-1132 and one or more additional compounds selected from F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HCFC-142b, HFO-1132a, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a. In some embodiments, the E-HFO-1132 and Z-HFO-1132 constitute about 0.1 wt% to about 10 wt.%, or about

1 wt.% to about 5 wt.%, or about 3 wt.% to about 5 wt.%, based on the total weight of the composition, inclusive of all integers and ranges therebetween.

[0069] One embodiment of the invention disclosed herein is a composition comprising, consisting essentially of, or consisting of E-HFO-1132 and Z-HFO-1132, wherein the E-HFO-1132 and Z-HFO-1132 are present in an amount greater than greater than about 1%, or greater than about 2%, or greater than about 3%, or greater than about 4%, or greater than about 5%, and less than about 100%, or less than about 20%, or less than about 10%, and all values and ranges therebetween.

[0070] In a preferred embodiment, compositions according to the present invention are free of or substantially free of Group A Fluorinated Substances. In one embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that (i) contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it); and (ii) meets the criterion for persistence in soil/sediment and water established in Annex XIII (Section 1.1.1) of the European Union's REACH Regulation (<https://reachonline.eu/reach/en/annex-xiii-1-1.1-1.1.1.html> as accessed on May 2, 2023) and referenced in the Annex XV Restriction Report dated March 22, 2023, the disclosure of which is hereby incorporated by reference (<https://echa.europa.eu/documents/10162/f605d4b5-7c17-7414-8823-b49b9fd43aea> as accessed on May 2, 2023).

[0071] In another embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that has a Henry's Law constant $\leq 250 \text{ Pa}\cdot\text{m}^3/\text{mol}$ and contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it).

[0072] In embodiments, Group A Fluorinated Substances include, but are not limited to, TFA.

[0073] The phrase "free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by gas chromatography with a flame ionization detector, gas chromatography with a mass detector by analysis of a gas sample or liquid sample, and/or ion chromatography by analysis of a water sample after bubbling the thermal fluid through water. Such methodologies are well known to those skilled in

the art. The phrase "substantially free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is > 0 wt.% and ≤ 5 wt.%, or > 0 wt.% and ≤ 4 wt.%, or > 0 wt.% and ≤ 3 wt.%, or > 0 wt.% and ≤ 2 wt.%, or > 0 wt.% and ≤ 1 wt.%, and all values and ranges therebetween, when measured by gas chromatographic (GC) techniques, for example gas chromatography (GC) with a flame ionization or electron-capture detector, or GC coupled with a mass detector (gas chromatography/mass spectral (GC/MS) method), by ion chromatograph(IC) or ion chromatography mass spectrometry (IC-MS) techniques, or by high-performance liquid chromatography (HPLC) or high-performance liquid chromatography mass spectrometry (HPLC-MS) techniques. The TFA analytical standard may be used in either gas chromatography or ion chromatography and is available from, for example, Sigma Aldrich.

[0074] In a preferred embodiment, degradation products of compositions according to the present invention are free of or substantially free of Group A Fluorinated Substances. The phrase "free of" as used herein with respect to the formation of Group A Fluorinated Substances as degradation products of the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques. The phrase "substantially free of" as used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is $> 0\%$ and $\leq 5\%$, or $> 0\%$ and $\leq 4\%$, or $> 0\%$ and $\leq 3\%$, or $> 0\%$ and $\leq 2\%$, or $> 0\%$ and $\leq 1\%$, and all values and ranges therebetween, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques.

[0075] Certain embodiments of the invention disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HFO-1252zc or E/Z-HFO-1132, and are free of or substantially free of Group A Fluorinated Substances. In some embodiments, compositions of the present invention comprise, consist essentially of, or

consist of HFO-1252zc or E/Z-HFO-1132, and degradation products of such compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0076] Certain embodiments of the invention disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HFO-1252zc or E/Z-HFO-1132 and one or more additional members selected from HFCs, HCCs, HCFCs, HFOs, HFCOs, C₂-C₄ alkanes, and C₂-C₄ alkenes. In some embodiments, such compositions are free of or substantially free of Group A Fluorinated Substances and/or degradation products of such compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0077] Certain embodiments of the invention disclosed herein relate to blend compositions comprising, consisting essentially of, or consisting of HFO-1252zc or E/Z-HFO-1132 and one or more refrigerant compounds selected from HFCs, HCCs, HCFCs, HFOs, HFCOs, C₂-C₄ alkanes, and C₂-C₄ alkenes. In some embodiments, such blend compositions are free of or substantially free of Group A Fluorinated Substances and/or degradation products of such blend compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0078] Certain embodiments of the invention disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HFO-1252zc and one or more additional members selected from propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-1241xb, HCFC-242 and HCFC-262db, and which are free of or substantially free of Group A Fluorinated Substances, and/or degradation products of such compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0079] Certain embodiments of the invention disclosed herein relate to blend compositions comprising HFO-1252zc, one or more other refrigerant compounds, and one or more additional members selected from propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-1241xb, HCFC-242 and HCFC-262db. In some embodiments, such blend compositions are free of or substantially free of Group

A Fluorinated Substances and/or degradation products of such blend compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0080] Certain embodiments of the invention disclosed herein relate to compositions comprising, consisting essentially of, or consisting of E-HFO-1132, Z-HFO-1132 and one or more additional members selected from F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HFO-1132a, HCFC-142b, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a, and which are free of or substantially free of Group A Fluorinated Substances, and/or degradation products of such compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0081] Certain embodiments of the invention disclosed herein relate to blend compositions comprising HFO-1132, Z-HFO-1132, one or more other refrigerant compounds, and one or more additional members selected from F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HFO-1132a, HCFC-142b, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a. In some embodiments, such blend compositions are free of or substantially free of Group A Fluorinated Substances and/or degradation products of such blend compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0082] In some embodiments, at least a portion of any of the compositions disclosed herein comprises reclaimed materials.

[0083] Aspects of the present invention will now be described with reference to the following Examples.

**Example 1: Hydrodechlorination of
HCFC-252dc to HFO-1252zc with 12% Cu/C catalyst**

[0084] In a 12-inches long Inconel (0.5-inch OD) reactor tube, 6ml of 12% Cu/C catalyst was loaded. The 12% Cu/C catalyst was activated at 450°C with H₂ for 2 hours. Then, HCFC-252dc and H₂ were fed into the reactor and tested at the reaction conditions listed in Table 2 below. The reactor effluent was analyzed by GC-MS-FID.

TABLE 2

T C	Pressure psi	252dc cc/hr	N2 sccm	H2 sccm	H2/252dc mol ratio	GC		
						1252zc	262	1251
180	20.0	0.30	4.99	7.07	6.37	7.28%	0.00%	0.00%
180	20.0	0.30	4.99	7.07	6.37	5.80%	0.00%	0.00%
180	20.0	0.30	4.99	7.07	6.37	5.32%	0.00%	0.00%
200	20.0	0.30	5.04	7.08	6.38	10.69%	0.33%	0.00%
200	20.0	0.30	5.04	7.08	6.38	9.50%	0.28%	0.00%
230	20.0	0.30	5.04	7.08	6.38	26.08%	4.32%	0.22%
230	20.0	0.30	5.04	7.08	6.38	25.37%	4.25%	0.23%
260	20.0	0.30	5.04	7.06	6.36	51.13%	30.42%	2.78%
260	20.0	0.30	5.04	7.06	6.36	51.26%	28.48%	2.80%
240	20.0	0.30	6.01	7.06	6.36	25.54%	2.43%	0.00%
240	20.0	0.30	6.01	7.06	6.36	23.08%	2.05%	0.00%
240	20.0	0.30	6.01	7.06	6.36	22.90%	2.05%	0.00%
240	20.0	0.30	6.01	7.07	6.37	22.57%	1.95%	0.00%
240	20.0	0.30	6.01	7.07	6.37	24.17%	2.20%	0.00%
240	20.0	0.30	6.01	7.08	6.38	21.63%	1.79%	0.00%
250	20.0	0.30	12.37	7.08	6.38	26.98%	2.05%	0.00%
250	20.0	0.30	12.38	7.08	6.38	35.41%	2.93%	0.00%
250	20.0	0.30	12.22	7.06	6.36	24.29%	1.75%	0.00%

TABLE 2 (Continued)

T C	Pressure psi	GC					252dc conversion	1252zc selectivity
		1251	252dc	1250	1241xb	others		
180	20.0	0.08%	91.60%	0.08%	0.07%	0.89%	8.40%	86.70%
180	20.0	0.07%	93.13%	0.07%	0.07%	0.87%	6.87%	84.46%
180	20.0	0.06%	93.63%	0.06%	0.07%	0.87%	6.37%	83.41%
200	20.0	0.04%	88.40%	0.06%	0.05%	0.43%	11.60%	92.15%
200	20.0	0.04%	89.56%	0.06%	0.06%	0.51%	10.44%	90.99%
230	20.0	0.00%	68.97%	0.00%	0.00%	0.41%	31.03%	84.03%
230	20.0	0.00%	69.75%	0.00%	0.00%	0.40%	30.25%	83.87%
260	20.0	3.40%	11.19%	0.18%	0.00%	0.91%	88.81%	57.57%
260	20.0	3.50%	12.88%	0.20%	0.00%	0.87%	87.12%	58.84%
240	20.0	0.29%	71.41%	0.00%	0.00%	0.32%	28.59%	89.36%
240	20.0	0.28%	74.24%	0.00%	0.00%	0.35%	25.76%	89.60%
240	20.0	0.22%	74.47%	0.00%	0.00%	0.35%	25.53%	89.71%
240	20.0	0.21%	74.88%	0.00%	0.00%	0.39%	25.12%	89.87%
240	20.0	0.21%	73.05%	0.00%	0.00%	0.38%	26.95%	89.68%
240	20.0	0.19%	75.98%	0.00%	0.00%	0.41%	24.02%	90.04%
250	20.0	0.26%	70.40%	0.00%	0.00%	0.31%	29.60%	91.15%
250	20.0	0.27%	61.15%	0.00%	0.00%	0.24%	38.85%	91.14%
250	20.0	0.32%	73.28%	0.00%	0.00%	0.36%	26.72%	90.89%

Example 2: Hydrodechlorination of HCFC-252dc to HFO-1252zc with 3%Zn-8%Cu/C catalyst

[0085] In a 12-inches long Inconel (0.5-inch OD) reactor tube, 6ml of 1/8" pellets of 3%Zn-8%Cu/C catalyst was loaded. The catalyst was activated at 450°C with H₂ for 2 hours. Then, HCFC-252dc and H₂ were fed into the reactor and tested at the reaction conditions listed in Table 3 below. The reactor effluent was analyzed by GC-MS-FID, and a detailed GC analysis of the product at 8 hours is provided in Table 4.

TABLE 3

Time hr	T C	P psi	252dc cc/hr	252dc sccm	N2 sccm	H2 sccm	H2/252dc mol ratio
1	180	20.0	0.17	0.63	2.06	12.01	19.06
2	180	20.0	0.17	0.63	2.06	12.01	19.06
3	180	20.1	0.17	0.63	2.06	12.01	19.06
4	200	20.0	0.17	0.63	2.06	12.05	19.13
5	200	20.1	0.17	0.63	2.06	12.05	19.13
6	220	20.0	0.17	0.63	2.06	12.05	19.13
7	220	20.1	0.17	0.63	2.06	12.05	19.13
8	240	20.0	0.17	0.63	2.06	12.05	19.13
9	240	20.0	0.17	0.63	2.06	12.05	19.13
10	220	20.1	0.17	0.63	2.06	12.05	19.13
11	220	20.1	0.17	0.63	2.09	12.01	19.06
12	220	20.0	0.17	0.63	2.09	12.05	19.13
13	220	20.0	0.17	0.63	2.09	12.05	19.13
14	220	20.0	0.17	0.63	2.09	12.05	19.13
15	220	20.0	0.17	0.63	2.09	12.01	19.06
16	220	20.0	0.17	0.63	2.09	12.05	19.13
17	220	20.0	0.17	0.63	2.09	12.05	19.13
18	230	20.1	0.17	0.63	10.30	9.00	14.29
19	230	20.1	0.17	0.63	10.33	9.00	14.29
20	230	20.0	0.17	0.63	10.42	9.00	14.29
21	230	20.1	0.17	0.63	10.30	9.00	14.29
22	230	20.0	0.17	0.63	10.36	9.00	14.29
23	230	20.1	0.17	0.63	10.30	9.00	14.29
25	240	20.1	0.17	0.63	10.36	9.00	14.29
26	240	20.1	0.17	0.63	10.35	9.00	14.29
27	240	20.0	0.17	0.63	10.32	9.01	14.30
28	240	20.0	0.17	0.63	10.45	9.01	14.30
29	240	20.0	0.17	0.63	10.33	9.01	14.30
30	180	20.0	0.17	0.63	2.10	12.05	19.13
31	180	20.0	0.17	0.63	2.10	12.05	19.13

TABLE 3 (Continued)

Time hr	T C	P psi	GC-FID area%					
			1252zc	1243zf	262fc	E-1251zb	Z-1251zb	272fb
1	180	20.0	20.83%	0.03%	0.39%	0.12%	0.06%	0.00%
2	180	20.0	22.20%	0.00%	0.38%	0.12%	0.06%	0.00%
3	180	20.1	21.92%	0.05%	0.33%	0.12%	0.06%	0.00%
4	200	20.0	24.42%	0.04%	0.45%	0.11%	0.05%	0.00%
5	200	20.1	24.96%	0.05%	0.37%	0.11%	0.05%	0.00%
6	220	20.0	29.53%	0.05%	0.81%	0.14%	0.06%	0.00%
7	220	20.1	29.84%	0.05%	0.96%	0.14%	0.06%	0.00%
8	240	20.0	36.90%	0.06%	3.68%	0.25%	0.11%	0.08%
9	240	20.0	33.27%	0.06%	4.27%	0.27%	0.11%	0.09%
10	220	20.1	24.23%	0.00%	1.18%	0.17%	0.08%	0.00%
11	220	20.1	23.04%	0.00%	1.16%	0.16%	0.07%	0.00%
12	220	20.0	22.91%	0.00%	1.09%	0.15%	0.07%	0.00%
13	220	20.0	22.48%	0.00%	1.08%	0.15%	0.07%	0.00%
14	220	20.0	22.04%	0.00%	1.06%	0.16%	0.07%	0.00%
15	220	20.0	22.28%	0.00%	1.10%	0.16%	0.07%	0.00%
16	220	20.0	21.78%	0.00%	1.10%	0.15%	0.07%	0.00%
17	220	20.0	21.83%	0.00%	1.10%	0.16%	0.07%	0.00%
18	230	20.1	30.80%	0.06%	1.71%	0.26%	0.09%	0.00%
19	230	20.1	28.04%	0.00%	1.61%	0.24%	0.08%	0.00%
20	230	20.0	25.63%	0.05%	1.53%	0.24%	0.08%	0.00%
21	230	20.1	25.54%	0.00%	1.47%	0.23%	0.08%	0.00%
22	230	20.0	23.86%	0.00%	1.35%	0.23%	0.08%	0.00%
23	230	20.1	26.43%	0.00%	1.46%	0.25%	0.09%	0.00%
25	240	20.1	29.93%	0.00%	3.00%	0.38%	0.11%	0.06%
26	240	20.1	27.67%	0.00%	2.56%	0.35%	0.10%	0.05%
27	240	20.0	30.00%	0.00%	2.88%	0.39%	0.11%	0.06%
28	240	20.0	29.36%	0.00%	2.95%	0.38%	0.10%	0.06%
29	240	20.0	30.57%	0.00%	3.07%	0.41%	0.11%	0.06%
30	180	20.0	20.35%	0.00%	0.22%	0.13%	0.05%	0.00%
31	180	20.0	20.70%	0.00%	0.20%	0.12%	0.04%	0.00%

TABLE 3 (Continued)

Time hr	T C	P psi	GC-FID area%					252dc conversion	1252zc Selectivity
			242	252dc	1241xb	262db	Others		
1	180	20.0	0.10%	78.32%	0.00%	0.11%	0.02%	21.68%	96.08%
2	180	20.0	0.08%	77.07%	0.00%	0.07%	0.02%	22.93%	96.83%
3	180	20.1	0.09%	77.39%	0.00%	0.05%	0.00%	22.61%	96.95%
4	200	20.0	0.07%	74.78%	0.03%	0.04%	0.00%	25.22%	96.82%
5	200	20.1	0.08%	74.29%	0.04%	0.05%	0.00%	25.71%	97.09%
6	220	20.0	0.07%	69.27%	0.04%	0.05%	0.00%	30.73%	96.09%
7	220	20.1	0.08%	68.87%	0.00%	0.00%	0.00%	31.13%	95.85%
8	240	20.0	0.06%	58.87%	0.00%	0.00%	0.00%	41.13%	89.72%
9	240	20.0	0.08%	61.86%	0.00%	0.00%	0.00%	38.14%	87.22%
10	220	20.1	0.09%	74.25%	0.00%	0.00%	0.00%	25.75%	94.11%
11	220	20.1	0.09%	75.49%	0.00%	0.00%	0.00%	24.51%	94.00%
12	220	20.0	0.08%	75.70%	0.00%	0.00%	0.00%	24.30%	94.26%
13	220	20.0	0.09%	76.12%	0.00%	0.00%	0.00%	23.88%	94.16%

Time hr	T C	P psi	GC-FID area%					252dc conversion	1252zc Selectivity
			242	252dc	1241xb	262db	Others		
14	220	20.0	0.09%	76.59%	0.00%	0.00%	0.00%	23.41%	94.12%
15	220	20.0	0.09%	76.30%	0.00%	0.00%	0.00%	23.70%	93.97%
16	220	20.0	0.09%	76.81%	0.00%	0.00%	0.00%	23.19%	93.94%
17	220	20.0	0.09%	76.75%	0.00%	0.00%	0.00%	23.25%	93.90%
18	230	20.1	0.08%	67.00%	0.00%	0.00%	0.00%	33.00%	93.33%
19	230	20.1	0.08%	69.94%	0.00%	0.00%	0.00%	30.06%	93.28%
20	230	20.0	0.10%	72.38%	0.00%	0.00%	0.00%	27.62%	92.78%
21	230	20.1	0.08%	72.61%	0.00%	0.00%	0.00%	27.39%	93.24%
22	230	20.0	0.09%	74.40%	0.00%	0.00%	0.00%	25.60%	93.19%
23	230	20.1	0.07%	71.71%	0.00%	0.00%	0.00%	28.29%	93.43%
25	240	20.1	0.08%	66.44%	0.00%	0.00%	0.00%	33.56%	89.21%
26	240	20.1	0.08%	69.18%	0.00%	0.00%	0.00%	30.82%	89.77%
27	240	20.0	0.09%	66.47%	0.00%	0.00%	0.00%	33.53%	89.46%
28	240	20.0	0.08%	67.08%	0.00%	0.00%	0.00%	32.92%	89.17%
29	240	20.0	0.08%	65.69%	0.00%	0.00%	0.00%	34.31%	89.12%
30	180	20.0	0.08%	79.01%	0.04%	0.13%	0.00%	20.99%	96.93%
31	180	20.0	0.08%	78.77%	0.00%	0.07%	0.00%	21.23%	97.52%

TABLE 4

Compounds	FID area%
Propylene	0.0036%
1261ze	0.0215%
1252zc	36.9513%
1243zf	0.0124%
262fc	3.6660%
1251zb	0.2458%
1251zb	0.1051%
272fb	0.0831%
243 isomer	0.0610%
252dc	58.7544%
1241xb	0.0296%
1241xb	0.0107%
262db	0.0259%
others	0.0296%

[0086] The results show HFO-1252zc is produced with higher selectivity using a Zn-Cu/C catalyst rather than a Cu/C catalyst. Also, the stability of a Zn-Cu/C catalyst is much better than a Cu/C catalyst. Using a Zn-Cu/C catalyst, the product selectivity to HFO-1252zc is about 90 mol% or greater, about 93 mol% or greater, about 94 mol% or greater, about 95 mol% or greater, about 96 mol% or greater, or about 97 mol% or greater.

**Example 3: Hydrodechlorination of
HCFC-132 to HFO-1132 with 3%Zn-8%Cu/C catalyst**

[0087] In a 12-inches long Inconel (0.5-inch OD) reactor tube, 6ml of 1/8" pellets of 3%Zn-8%Cu/C catalyst was loaded. The catalyst was activated at 450°C with H₂ for 2 hours. Then, HCFC-132 and H₂ were fed into the reactor and tested at the reaction conditions provided in Table 5 below. The reactor effluent was analyzed by GC-MS-FID, the detailed GC analysis result at the 9th hour of reaction time is provided in Table 6.

Table 5

Time hr	T C	P psig	HCFC132 cc/hr	H2 sccm	GC-FID area%				
					1132-E	1132-Z	132	122a	others
1	240	18.0	0.17	19	1.09%	2.15%	88.86%	2.69%	5.21%
2	240	20.1	0.17	19	1.09%	2.01%	90.57%	2.41%	3.13%
3	240	20.2	0.17	19	1.24%	2.25%	92.05%	2.11%	2.72%
4	250	20.8	0.17	19	1.42%	2.51%	92.15%	1.98%	2.85%
5	250	21.1	0.17	19	1.53%	2.78%	92.07%	2.03%	2.60%
6	250	21.3	0.17	19	1.63%	2.96%	91.67%	2.24%	2.41%
7	260	21.9	0.17	19	1.69%	3.09%	90.52%	2.41%	3.19%
8	260	22.4	0.17	19	1.75%	3.25%	89.78%	2.63%	3.46%
9	260	22.9	0.17	19	1.77%	3.30%	88.96%	2.83%	4.00%

Table 6

Detailed GC analysis result at 9th hour of reaction time

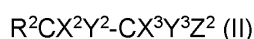
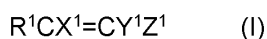
Compounds	GC-FID
FC-13	0.0194%
1132-E	1.6591%
1132-Z	3.0950%
F-12	0.1151%
1122a-E	1.3380%
1122a-Z	1.3411%
21	0.0544%
142b	0.1724%
132	88.9600%
113	0.2363%
122a	2.8124%
others	0.1969%

[0088] The process of the present invention therefore provides a method to produce (make) a fluoroolefin compound R¹CX¹=CY¹Z¹, such as HFO-1252zc or E/Z-HFO-1132,

using a low-cost catalyst that is effective for production of the fluoroolefin compound with high selectivity.

Additional Embodiments

[0089] Embodiment 1. A process of making a fluoroolefin of formula (I), the process comprising contacting a compound of formula (II) with hydrogen in the vapor phase in the presence of a catalyst comprising a Group IB metal and a Group IIB metal:



[0090] wherein in formula (I), R^1 represents a H, Cl, F or a C1-C4 alkyl group, X^1 is H, F or Cl, Y^1 is H, F or Cl, and Z^1 is H, Cl or F, and wherein in formula (II), R^2 represents a H, Cl, F or a C1-C4 alkyl group, X^2 is H, F, Cl or Br, Y^3 is H, Cl, Br, or F, X^3 and Y^2 are the same or different and are each independently Cl or Br, and Z^2 is H, Cl or F.

[0091] Embodiment 2. The process of Embodiment 1, wherein the catalyst comprises zinc and copper.

[0092] Embodiment 3. The process of any of Embodiments 1 to 2, wherein the catalyst is carried on a support material selected from the group consisting of alumina, SiC and carbon.

[0093] Embodiment 4. The process of Embodiment 3, wherein the support material is carbon.

[0094] Embodiment 5. The process of any of Embodiments 1 to 4, wherein the catalyst contains zinc in the range of 1% to 10% and copper in the range of 3% to 15%.

[0095] Embodiment 6. The process of any of Embodiments 1 to 5, wherein the catalyst is 3%Zn-8%Cu/C.

[0096] Embodiment 7. The process of any of Embodiments 1 to 6, wherein the catalyst is pre-activated with H_2 .

[0097] Embodiment 8. The process of Embodiment 7, wherein the pre-activation with H_2 occurs at a temperature of from about 100°C to about 500°C.

[0098] Embodiment 9. The process of any of Embodiments 1 to 8, wherein the compound of formula (II) comprises 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

[0099] Embodiment 10. The process of Embodiment 9, wherein a feed composition comprising the HCFC-252dc further comprises one or more additional compounds selected from the group consisting of HFC-262fc, HCFO-1233xf, HCFO-1242zf, acetone, HCFC-262db, HCFC-253db, HCFO-1223xd, C₄H₆ClF, HCFO-1232xf, E-HCFO-1241xb, Z-HCFO-1241xb and HFO-1335.

[0100] Embodiment 11. The process of any of Embodiments 1 to 10, wherein the compound of formula (I) comprises 1,1-difluoropropene (HFO-1252zc).

[0101] Embodiment 12. The process of Embodiment 11, wherein a product composition comprising the HFO-1252zc further comprises one or more additional compounds selected from the group consisting of propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-1241xb, HCFC-242 and HCFC-262db.

[0102] Embodiment 13. The process of any of Embodiments 1 to 8, wherein a product selectivity to R¹CX¹=CY¹Z¹ is at least about 30 mol%, or at least about 32 mol%, or at least about 34 mol%, or at least about 36 mol%, or at least about 38 mol%, or at least about 40 mol%, and less than 100 mol%.

[0103] Embodiment 14. The process of any of Embodiments 1 to 8 and 13, wherein the compound of formula (II) comprises 1,2-dichloro-1,2-difluoroethane (HCFC-132).

[0104] Embodiment 15. The process of Embodiment 14, wherein a feed composition comprising the HCFC-132 further comprises one or more additional compounds selected from the group consisting of HCFC-132C (1,1-dichloro-1,2-difluoroethane), HCFC-132a (1,1-dichloro-2,2-difluoroethane), CFO-1112 (1,2-dichloro-1,2-difluoroethylene), CFO-1112a (1,1-dichloro-2,2-difluoroethylene), HCFC-142 (1-chloro-2,2-difluoroethane), HCFC-142a (1-chloro-1,2-difluoroethane) and HFC-152 (1,2-difluoroethane).

[0105] Embodiment 16. The process of any of Embodiments 1 to 8 and 13 to 15, wherein the compound of formula (I) comprises E/Z-1,2-difluoroethylene (E/Z-HFO-1132).

[0106] Embodiment 17. The process of Embodiment 16, wherein a product composition comprises E-HFO-1132 and Z-HFO-1132, and further comprises one or more additional compounds selected from the group consisting of F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HCFC-142b, HFO-1132a, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a.

[0107] Embodiment 18. The process of any of Embodiments 1 to 17, wherein hydrodechlorination of the $R^1CX^1=CY^1Z^1$ is conducted at a temperature between about 60°C and about 300°C, preferably between about 180°C and about 280°C.

[0108] Embodiment 19. The process of any of Embodiments 1 to 18, wherein hydrodechlorination of the $R^1CX^1=CY^1Z^1$ is conducted at a pressure between about 0 and about 200 psig, preferably between about 10 and about 150 psig.

[0109] Embodiment 20. A composition comprising HCFC-252dc and one or more additional compounds selected from the group consisting of HFC-262fc, HCFO-1233xf, HCFO-1242zf, acetone, HCFC-262db, HCFC-253db, HCFO-1223xd, C_4H_6ClF , HCFO-1232xf, E-HCFO-1241xb, Z-HCFO-1241xb and HFO-1335.

[0110] Embodiment 21. A composition comprising HFO-1252zc and one or more additional compounds selected from the group consisting of propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-1241xb, HCFC-242 and HCFC-262db.

[0111] Embodiment 22. A composition comprising HCFC-132 and one or more additional compounds selected from the group consisting of HCFC-132C (1,1-dichloro-1,2-difluoroethane), HCFC-132a (1,1-dichloro-2,2-difluoroethane), CFO-1112, CFO-1112a, HCFC-142 (1-chloro-2,2-difluoroethane), HCFC-142a (1-chloro-1,2-difluoroethane) and HFC-152.

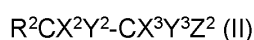
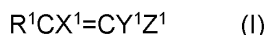
[0112] Embodiment 23. A composition comprising E-HFO-1132, Z-HFO-1132 and one or more additional compounds selected from the group consisting of F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HCFC-142b, HFO-1132a, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a.

[0113] 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 making a fluoroolefin of formula (I), the process comprising contacting a compound of formula (II) with hydrogen in the vapor phase in the presence of a catalyst comprising a Group IB metal and a Group IIB metal:



wherein in formula (I), R^1 represents a H, Cl, F or a C1-C4 alkyl group, X^1 is H, F or Cl, Y^1 is H, F or Cl, and Z^1 is H, Cl or F, and

wherein in formula (II), R^2 represents a H, Cl, F or a C1-C4 alkyl group, X^2 is H, F, Cl or Br, Y^3 is H, Cl, Br, or F, X^3 and Y^2 are the same or different and are each independently Cl or Br, and Z^2 is H, Cl or F.

2. The process of claim 1, wherein the catalyst comprises zinc and copper.
3. The process of any of claims 1 to 2, wherein the catalyst is carried on a support material selected from the group consisting of alumina, SiC and carbon.
4. The process of claim 3, wherein the support material is carbon.
5. The process of any of claims 1 to 4, wherein the catalyst contains zinc in the range of 1% to 10% and copper in the range of 3% to 15%.
6. The process of any of claims 1 to 5, wherein the catalyst is 3%Zn-8%Cu/C.
7. The process of any of claims 1 to 6, wherein the catalyst is pre-activated with H_2 .
8. The process of claim 7, wherein the pre-activation with H_2 occurs at a temperature of from about 100°C to about 500°C.
9. The process of any of claims 1 to 8, wherein the compound of formula (II) comprises 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).
10. The process of claim 9, wherein a feed composition comprising the HCFC-252dc further comprises one or more additional compounds selected from the group consisting of HFC-262fc, HCFO-1233xf, HCFO-1242zf, acetone, HCFC-262db,

HCFC-253db, HCFO-1223xd, C₄H₆ClF, HCFO-1232xf, E-HCFO-1241xb, Z-HCFO-1241xb and HFO-1335.

11. The process of any of claims 1 to 10, wherein the compound of formula (I) comprises 1,1-difluoropropene (HFO-1252zc).
12. The process of claim 11, wherein a product composition comprising the HFO-1252zc further comprises one or more additional compounds selected from the group consisting of propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-1241xb, HCFC-242 and HCFC-262db.
13. The process of any of claims 1 to 8, wherein a product selectivity to R¹CX¹=CY¹Z¹ is at least about 30 mol%, or at least about 32 mol%, or at least about 34 mol%, or at least about 36 mol%, or at least about 38 mol%, or at least about 40 mol%, and less than 100 mol%.
14. The process of any of claims 1 to 8 and 13, wherein the compound of formula (II) comprises 1,2-dichloro-1,2-difluoroethane (HCFC-132).
15. The process of claim 14, wherein a feed composition comprising the HCFC-132 further comprises one or more additional compounds selected from the group consisting of HCFC-132C (1,1-dichloro-1,2-difluoroethane), HCFC-132a (1,1-dichloro-2,2-difluoroethane), CFO-1112 (1,2-dichloro-1,2-difluoroethylene), CFO-1112a (1,1-dichloro-2,2-difluoroethylene), HCFC-142 (1-chloro-2,2-difluoroethane), HCFC-142a (1-chloro-1,2-difluoroethane) and HFC-152 (1,2-difluoroethane).
16. The process of any of claims 1 to 8 and 13 to 15, wherein the compound of formula (I) comprises E/Z-1,2-difluoroethylene (E/Z-HFO-1132).
17. The process of claim 16, wherein a product composition comprises E-HFO-1132 and Z-HFO-1132, and further comprises one or more additional compounds selected from the group consisting of F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HCFC-142b, HFO-1132a, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a.

18. The process of any of claims 1 to 17, wherein hydrodechlorination of the $R^1CX^1=CY^1Z^1$ is conducted at a temperature between about 60°C and about 300°C, preferably between about 180°C and about 280°C.
19. The process of any of claims 1 to 18, wherein hydrodechlorination of the $R^1CX^1=CY^1Z^1$ is conducted at a pressure between about 0 and about 200 psig, preferably between about 10 and about 150 psig.
20. A composition comprising HCFC-252dc and one or more additional compounds selected from the group consisting of HFC-262fc, HCFO-1233xf, HCFO-1242zf, acetone, HCFC-262db, HCFC-253db, HCFO-1223xd, C_4H_6ClF , HCFO-1232xf, E-HCFO-1241xb, Z-HCFO-1241xb and HFO-1335.
21. A composition comprising HFO-1252zc and one or more additional compounds selected from the group consisting of propylene, HFO-1261ze, HFO-1243zf, HCFC-262fc, E-HCFO-1251zb, Z-HCFO-1251zb, HFC-272fb, HCFC-243 isomer(s), HCFC-252dc, E-HCFO-1241xb, Z-HCFO-1241xb, HCFC-242 and HCFC-262db.
22. A composition comprising HCFC-132 and one or more additional compounds selected from the group consisting of HCFC-132C (1,1-dichloro-1,2-difluoroethane), HCFC-132a (1,1-dichloro-2,2-difluoroethane), CFO-1112, CFO-1112a, HCFC-142 (1-chloro-2,2-difluoroethane), HCFC-142a (1-chloro-1,2-difluoroethane) and HFC-152.
23. A composition comprising E-HFO-1132, Z-HFO-1132 and one or more additional compounds selected from the group consisting of F-12, FC-13, HCFC-21, CFC-113, HCFC-122a, HCFC-132, HCFC-142b, HFO-1132a, HFO-1141, E-HCFO-1122a and Z-HCFO-1122a.