

**TITLE OF THE INVENTION**

PROCESSES TO PRODUCE HFO-1252ZC  
FROM HCFO-1233XF AND HBFO-1233XFB

**CROSS REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/527,160 filed July 17, 2023, and U.S. Provisional Application 63/565,029 filed March 14, 2024, the disclosure of each of which is incorporated herein by reference in its entirety.

**FIELD OF THE INVENTION**

[0002] The present invention is directed to processes for producing difluoroolefins, compositions and uses thereof.

**BACKGROUND OF THE INVENTION**

[0003] Many industries have been working for the past few decades to find replacements for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). The CFCs and HCFCs have been employed in a wide range of applications, including their use as aerosol propellants, refrigerants, cleaning agents, expansion agents for thermoplastic and thermoset foams, heat transfer media, gaseous dielectrics, fire extinguishing and suppression agents, power cycle working fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, and displacement drying agents. In the search for replacements for these versatile compounds, many industries have turned to the use of hydrofluorocarbons (HFCs).

[0004] Although HFCs do not contribute to the destruction of stratospheric ozone, they contribute to the "greenhouse effect", i.e., global warming. As a result of their contribution to global warming, HFCs have come under scrutiny, and their widespread use may also be limited in the future.

[0005] The regulatory landscape is continuously evolving, taking into consideration properties beyond just ozone depletion potential (ODP) and global warming potential (GWP). More particularly, there is a need for refrigerant compositions that not only

meet low ODP standards and have low GWP, but that also exhibit low or no flammability, provide superior performance in a variety of applications and which meet the standards of evolving regulations.

**[0006]** 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.

**[0007]** Some fluoropropenes, such as 1,1-difluoropropene (HFO-1252zc), are such potential new refrigerants. There continues to be need for effective and efficient processes for preparing 1,1-difluoropropene (HFO-1252zc) and intermediates and compositions thereof.

### **SUMMARY OF THE INVENTION**

**[0008]** In some embodiments, the present invention relates to processes for producing 1,1-difluoropropene (HFO-1252zc,  $\text{CF}_2=\text{CHCH}_3$ ) through at least one intermediate selected from 2-chloro-1,1,1-trifluoropropane (HCFC-253db,  $\text{CF}_3\text{CHClCH}_3$ ); 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB,  $\text{CF}_3\text{CHBrCH}_3$ ); 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf,  $\text{CF}_3\text{CCl}=\text{CH}_2$ ), or 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB,  $\text{CF}_3\text{CBr}=\text{CH}_2$ ).

**[0009]** In some embodiments, the present invention relates to providing a fluoroolefin, converting the fluoroolefin to a halogenated hydrocarbon which has halogens on adjacent carbon atoms, and dehalogenating the adjacent carbon atoms to form HFO-1252zc.

**[0010]** In some embodiments, the present invention relates to a method for making HFO-1252zc from a precursor of the formula  $\text{CF}_3\text{CX}=\text{CH}_2$ , wherein X is selected from Cl, Br or I.

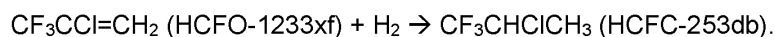
**[0011]** In some embodiments, the present invention relates to a method for making a compound of the formula  $\text{CF}_3\text{CHXCH}_3$  by contacting a compound of the formula  $\text{CF}_3\text{CX}=\text{CH}_2$  with hydrogen in the presence of a catalyst, wherein X is selected from Cl, Br or I.

**[0012]** In some embodiments, the present invention relates to a method for making HFO-1252zc by reaction of a compound of the formula  $\text{CF}_3\text{CHXCH}_3$  with a metal

such as Zn or Mg, or by reaction of a compound of the formula  $\text{CF}_3\text{CHXCH}_3$  with hydrogen in the presence of a catalyst, wherein X is selected from Cl, Br or I.

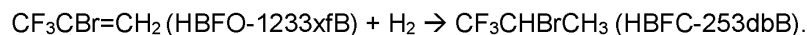
**[0013]** In some embodiments, the method comprises two steps to convert a precursor or starting material to HFO-1252zc. In some embodiments, the first step comprises converting the precursor  $\text{CF}_3\text{CX}=\text{CH}_2$  to an intermediate compound of the formula  $\text{CF}_3\text{CHXCH}_3$  by reaction with  $\text{H}_2$  in the presence of a catalyst, wherein X is selected from Cl, Br or I. In some embodiments, the second step comprises converting the intermediate  $\text{CF}_3\text{CHXCH}_3$  to HFO-1252zc by reaction with a metal such as Zn or Mg, or by reaction with  $\text{H}_2$  in the presence of a catalyst.

**[0014]** In some embodiments, the  $\text{CF}_3\text{CX}=\text{CH}_2$  compound is HCFO-1233xf and the  $\text{CF}_3\text{CHXCH}_3$  compound is HCFC-253db, as shown in the following reaction:



**[0015]** In some embodiments, the present invention relates to processes for producing HCFC-253db from HCFO-1233xf, and compositions thereof.

**[0016]** In some embodiments, the  $\text{CF}_3\text{CX}=\text{CH}_2$  compound is HBFO-1233xfB and the  $\text{CF}_3\text{CHXCH}_3$  compound is HBFC-253dbB, as shown in the following reaction:

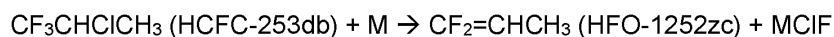


**[0017]** In some embodiments, the present invention relates to processes for producing HBFC-253dbB from HBFO-1233xfB, and compositions thereof.

**[0018]** In some embodiments, the  $\text{CF}_3\text{CHXCH}_3$  compound which is converted with hydrogen to HFO-1252zc is HCFC-253db, as shown in the following reaction:



**[0019]** In some embodiments, the  $\text{CF}_3\text{CHXCH}_3$  compound which is converted with a metal to HFO-1252zc is HCFC-253db, as shown in the following reaction, where M represents the metal which is preferably selected from Zn, Mg or a combination thereof:

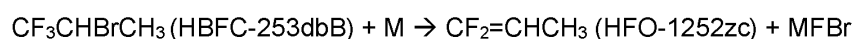


**[0020]** In some embodiments, the present invention relates to processes for producing HFO-1252zc from HCFC-253db, and compositions thereof.

[0021] In some embodiments, the  $\text{CF}_3\text{CHXCH}_3$  compound which is converted with hydrogen to HFO-1252zc is HBFC-253dbB, as shown in the following reaction:



[0022] In some embodiments, the  $\text{CF}_3\text{CHXCH}_3$  compound which is converted with a metal to HFO-1252zc is HBFC-253db, as shown in the following reaction, where M represents the metal which is preferably selected from Zn, Mg or a combination thereof:



[0023] In some embodiments, the present invention relates to processes for producing HFO-1252zc from HBFC-253dbB, and compositions thereof.

[0024] In some embodiments, the present invention relates to processes for producing HFO-1252zc from HCFO-1233xf or HBFO-1233xfB, and compositions thereof.

[0025] In some embodiments, the present invention relates to processes for producing HFO-1252zc from HCFO-1233xf or HBFO-1233xfB and HCFC-253db or HBFC-253dbB, and compositions thereof.

[0026] One embodiment of the invention disclosed herein relates to a process of converting HCFO-1233xf through the intermediate HCFC-253db to form HFO-1252zc.

[0027] One embodiment of the invention disclosed herein relates to a process of converting HBFO-1233xfB through the intermediate HBFC-253dbB to form HFO-1252zc.

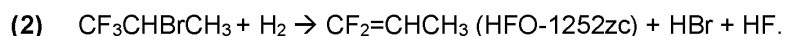
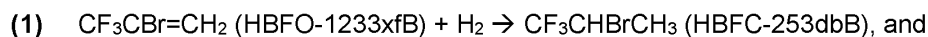
[0028] In certain embodiments disclosed herein, HFO-1252zc is prepared according to any of the following two-step reaction schemes:

- (1)  $\text{CF}_3\text{CCl}=\text{CH}_2 \text{ (HCFO-1233xf)} + \text{H}_2 \rightarrow \text{CF}_3\text{CHClCH}_3 \text{ (HCFC-253db)}$  and
- (2)  $\text{CF}_3\text{CHClCH}_3 + \text{H}_2 \rightarrow \text{CF}_2=\text{CHCH}_3 \text{ (HFO-1252zc)} + \text{HCl} + \text{HF}.$

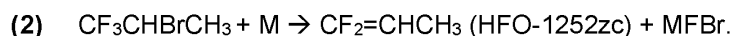
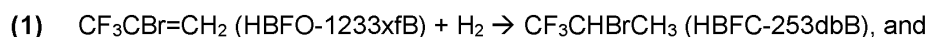
OR

- (1)  $\text{CF}_3\text{CCl}=\text{CH}_2 \text{ (HCFO-1233xf)} + \text{H}_2 \rightarrow \text{CF}_3\text{CHClCH}_3 \text{ (HCFC-253db)},$  and
- (2)  $\text{CF}_3\text{CHClCH}_3 + \text{M} \rightarrow \text{CF}_2=\text{CHCH}_3 \text{ (HFO-1252zc)} + \text{MCIF}.$

OR



OR



wherein M is a metal, and more particularly a reactive metal, such as zinc, magnesium or a combination thereof.

**[0029]** Certain embodiments relate to a composition comprising HCFO-1233xf, HBFO-1233xfB, 1,1,1-trifluoropropane (HFC-263fb,  $\text{CF}_3\text{CH}_2\text{CH}_3$ ), HCFC-253db, and HBFC-253dbB.

**[0030]** Certain embodiments relate to a composition comprising up to about 10 mole percent HFC-263fb and up to about 99.5 mole percent HCFC-253db, based on a total composition of 100%.

**[0031]** Certain embodiments relate to a composition comprising HCFO-1233xf, up to about 10 mole percent HFC-263fb and up to about 99.5 mole percent HCFC-253db, based on a total composition of 100 mole percent, wherein the term “about” is defined as 10 mole percent of the indicated value selected from one of:  $\pm 1\%$ ,  $\pm 2\%$ ,  $\pm 3\%$ ,  $\pm 4\%$ ,  $\pm 5\%$ ,  $\pm 6\%$ ,  $\pm 7\%$ ,  $\pm 8\%$ ,  $\pm 9\%$  or  $\pm 10\%$ .

**[0032]** Certain embodiment disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB),

3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

**[0033]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc), wherein at least HFO-1252zc is present in the composition.

**[0034]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HFC-252dc), wherein at least HFO-1252zc and HFO-1243zf are present.

**[0035]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of at least two or more compounds selected

from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc), wherein at least HFO-1252zc and HFO-1261ze are present.

**[0036]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of at least two or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc), wherein at least HFO-1252zc and HFC-263fb are present.

**[0037]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HCFC-253db, HFC-263fb, HCFO-1233xf and HFO-1252zc.

**[0038]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HCFC-253db, HFC-263fb, HFO-1243zf, HCFO-1233xf, HFO-1252zc, HFO-1261ze, HBFC-253dbB and HBFO-1233xfB.

[0039] Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HFO-1252zc in amounts of greater than 0 and up to about 10%, about 20%, about 30% or about 40% or higher, based on the total amount of the composition, wherein the term “about” is defined as the indicated value and  $\pm 1\%$ ,  $\pm 2\%$ ,  $\pm 3$ ,  $\pm 4\%$ ,  $\pm 5\%$ ,  $\pm 6$ ,  $\pm 7\%$ ,  $\pm 8\%$ ,  $\pm 9$  or  $\pm 10\%$ .

[0040] Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of from about 10 to about 50 mole percent, about 10 to about 40 mole percent, about 10 to about 30 mole percent or about 10 to about 20 mole percent HFO-1252zc, based on the total amount of the composition, wherein the term “about” is defined as the indicated value and  $\pm 1\%$ ,  $\pm 2\%$ ,  $\pm 3$ ,  $\pm 4\%$ ,  $\pm 5\%$ ,  $\pm 6$ ,  $\pm 7\%$ ,  $\pm 8\%$ ,  $\pm 9$  or  $\pm 10\%$ .

[0041] One embodiment disclosed herein relates to a system including a first reactor and an optional second reactor, the reactors being independently configured. The first and/or second reactors can be operated in the vapor and/or liquids phases consistent with the reactions disclosed herein.

[0042] 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.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0043] Fig. 1 depicts serially arranged first and optional second reactors.

[0044] Fig. 2 illustrates an NMR analysis during reaction at 60°C.

#### **DETAILED DESCRIPTION OF THE INVENTION**

[0045] The foregoing summary and the following detailed description 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 and from the claims.

**[0046]** Before addressing details of embodiments described herein, certain terms are defined or clarified as follows.

**[0047]** The term “about”, as used herein, means the indicated value and  $\pm 1\%$ ,  $\pm 2\%$ ,  $\pm 3$ ,  $\pm 4\%$ ,  $\pm 5\%$ ,  $\pm 6$ ,  $\pm 7\%$ ,  $\pm 8\%$ ,  $\pm 9$  or  $\pm 10\%$ .

**[0048]** 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.

**[0049]** The term “dehydrohalogenation,” as used herein, means loss of HX from a hydrohaloalkane, where X=F, Cl, Br, I, where H and X are on adjacent carbons in the hydrohaloalkane. For example, the term “dehydrofluorination,” “dehydrofluorinating” or “dehydrofluorinated,” as used herein, means a process during which hydrogen and fluorine on adjacent carbons in a molecule are removed; the term “dehydrochlorination,” “dehydrochlorinating,” or “dehydrochlorinated,” as used herein, means a process during which hydrogen and chlorine on adjacent carbons in a molecule are removed.

**[0050]** The term “dehalogenation” as used herein, means the loss of halogen without the loss of a hydrogen, e.g., the loss of halogens on adjacent carbon atoms.

**[0051]** 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).

**[0052]** 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.”

**[0053]** 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.

**[0054]** 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.”

**[0055]** 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.

**[0056]** 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.

**[0057]** 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.

**[0058]** 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.

**[0059]** 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: LISTING OF SELECT COMPOUNDS**

| Code        | Name (ASHRAE Designation)                           | Formula             |
|-------------|-----------------------------------------------------|---------------------|
| R-243       | dichlorotrifluoropropane isomers (HCFC-243 isomers) | $C_3H_3Cl_2F_3$     |
| R-252dc     | 1,2-dichloro-1,1-difluoropropane (HCFC-252dc)       | $CClF_2CHClCH_3$    |
| R-253db     | 2-chloro-1,1,1-trifluoropropane (HCFC-253db)        | $CF_3CHClCH_3$      |
| R-263fb     | 1,1,1-trifluoropropane (HFC-263fb)                  | $CF_3CH_2CH_3$      |
| R-30        | dichloromethane (HCC-30)                            | $CH_2Cl_2$          |
| R-374       | tetrafluorobutane (HFC-374)                         | $C_4H_6F_4$         |
| R-E-1132    | E-1, 2-difluoroethene (E-HFO-1132)                  | $E-CHF=CHF$         |
| R-Z-1132    | Z-1, 2-difluoroethene (Z-HFO-1132)                  | $Z-CHF=CHF$         |
| R-1242zf    | 3-chloro-3,3-difluoropropene (HCFO-1242zf)          | $CClF_2CH=CH_2$     |
| R-1243zf    | 3,3,3-trifluoropropene (HFO-1243zf)                 | $CF_3CHCH_2$        |
| R-1233xf    | 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf)       | $CF_3CCl=CH_2$      |
| R-1251      | chlorofluoropropene (HCFO-1251)                     | $CH_3CF=CHCl$       |
| R-1252      | difluoropropene isomers (HFO-1252 isomers)          | $C_3H_4F_2$         |
| R-1252zc    | 1,1-difluoropropene (HFO-1252zc)                    | $CH_3CH=CF_2$       |
| R-1261ze    | 1-fluoropropene (HFO-1261ze)                        | $CH_3CH=CHF$        |
| R-1345      | pentafluorobutene isomers (HFO-1345 isomers)        | $C_4H_3F_5$         |
| R-253db(Br) | 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB)        | $CF_3CHBrCH_3$      |
|             | Dibromotrifluoropropane                             | $C_3H_3Br_2F_3$     |
| R-1233xfB   | 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB)       | $CF_3CBr=CH_2$      |
| R-1242xfB   | 2-bromo-3,3-difluoropropene (HBFO-1242xfB)          | $CF_2HCBBr=CH_2$    |
|             | Methanol                                            | $CH_3OH$            |
|             | Acetone                                             | $(CH_3)_2CO$        |
| R-290       | propane (HC-290)                                    | $CH_3CH_2CH_3$      |
| R-1270      | propylene (HCO-1270)                                | $CH_3CH=CH_2$       |
|             | 2-methoxy-propane                                   | $CH_3OCH(CH_3)CH_3$ |

| Code    | Name (ASHRAE Designation)   | Formula                                                         |
|---------|-----------------------------|-----------------------------------------------------------------|
| R-280da | 2-chloropropane (HCC-280da) | CH <sub>3</sub> CHClCH <sub>3</sub>                             |
|         | 2-butene                    | CH <sub>3</sub> CH=CHCH <sub>3</sub>                            |
| R-600   | butane (HC-600)             | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> |

### Processes

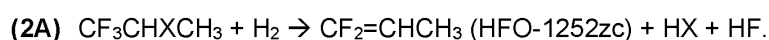
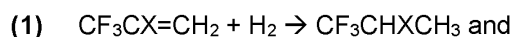
**[0060]** In some embodiments, the present invention relates to a method for making HFO-1252zc from a precursor of the formula CF<sub>3</sub>CX=CH<sub>2</sub>, wherein X is selected from Cl, Br or I.

**[0061]** In some embodiments, the present invention relates to a method for making a compound of the formula CF<sub>3</sub>CHXCH<sub>3</sub> by contacting a compound of the formula CF<sub>3</sub>CX=CH<sub>2</sub> with hydrogen in the presence of a catalyst, wherein X is selected from Cl, Br or I.

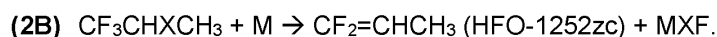
**[0062]** In some embodiments, the present invention relates to a method for making HFO-1252zc by reaction of a compound of the formula CF<sub>3</sub>CHXCH<sub>3</sub> with a metal such as Zn or Mg, or by reaction of a compound of the formula CF<sub>3</sub>CHXCH<sub>3</sub> with hydrogen in the presence of a catalyst, wherein X is selected from Cl, Br or I.

**[0063]** In some embodiments, the method comprises two steps to convert a precursor or starting material to HFO-1252zc. In some embodiments, the first step comprises converting the precursor CF<sub>3</sub>CX=CH<sub>2</sub> to an intermediate compound of the formula CF<sub>3</sub>CHXCH<sub>3</sub> by reaction with H<sub>2</sub> in the presence of a catalyst, wherein X is selected from Cl, Br or I. In some embodiments, the second step comprises converting the intermediate CF<sub>3</sub>CHXCH<sub>3</sub> to HFO-1252zc by reaction with a metal such as Zn or Mg, or by reaction with H<sub>2</sub> in the presence of a catalyst.

**[0064]** In other embodiments disclosed herein, the CF<sub>3</sub>CHXCH<sub>3</sub> compound is prepared according to the following step (1) and/or HFO-1252zc is prepared in a two-step process according to the following two-step reaction scheme:



OR



wherein X is selected from Cl, Br or I, and wherein M is selected from Zn or Mg or combinations thereof.

**[0065]** In embodiments of the two-step process, the  $\text{CF}_3\text{CX}=\text{CH}_2$  compound is a precursor and the  $\text{CF}_3\text{CHXCH}_3$  compound is an intermediate.

**[0066]** In some embodiments, conversion of the  $\text{CF}_3\text{CX}=\text{CH}_2$  compound to the  $\text{CF}_3\text{CHXCH}_3$  compound is conducted in the vapor phase or in the liquid phase.

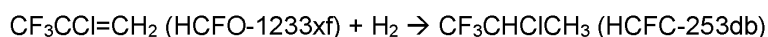
**[0067]** In some embodiments, conversion of the  $\text{CF}_3\text{CX}=\text{CH}_2$  compound to the  $\text{CF}_3\text{CHXCH}_3$  compound is conducted in the presence of a catalyst selected from Pd, Pt, Ni, Cu, Au or combinations thereof, with or without a support selected from carbon,  $\text{Al}_2\text{O}_3$  or SiC.

**[0068]** In some embodiments, conversion of the  $\text{CF}_3\text{CHXCH}_3$  compound to HFO-1252zc is conducted in the vapor phase with hydrogen in the presence of a catalyst selected from Cu, Ni, Au or combinations thereof, with or without a support selected from carbon,  $\text{Al}_2\text{O}_3$  or SiC.

**[0069]** In some embodiments, conversion of the  $\text{CF}_3\text{CHXCH}_3$  compound to HFO-1252zc is conducted in the liquid phase by reaction with a metal, such as Zn or Mg, optionally in the presence of a catalyst and/or optionally in the presence of a solvent.

**[0070]** In some embodiments, the  $\text{CF}_3\text{CX}=\text{CH}_2$  compound is HCFO-1233xf and the  $\text{CF}_3\text{CHXCH}_3$  compound is HCFC-253db.

**[0071]** In certain embodiments disclosed herein, the present invention relates to processes using HCFO-1233xf as the starting material to produce HCFC-253db according to the following reaction, and compositions thereof:



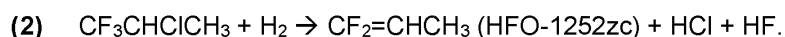
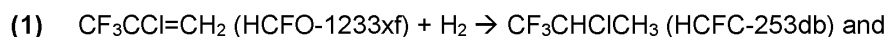
**[0072]** In certain embodiments disclosed herein, the present invention relates to processes of converting HCFC-253db to HFO-1252zc according to either of the following reactions, and compositions thereof:



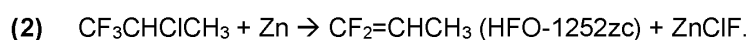
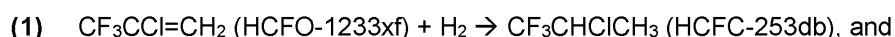
OR



**[0073]** In certain embodiments disclosed herein, the present invention relates to a two-step process using HCFO-1233xf as the starting material to produce HFO-1252zc according to either of the following two step reaction schemes, and compositions thereof:



OR



**[0074]** One embodiment of the invention disclosed herein relates to a process of converting HCFO-1233xf through the intermediate HCFC-253db to form HFO-1252zc.

**[0075]** Hydrogenation of HCFO-1233xf to HCFC-253db can be conducted in the vapor or liquid phase. Reaction of HCFO-1233xf with hydrogen is also referred to as hydrogenation or hydrogenolysis.

**[0076]** The hydrogenation reaction of HCFO-1233xf to HCFC-253db is conducted in the vapor phase at temperatures ranging from about 20°C to about 80°C, preferably about 20°C and about 60°C. In certain embodiments disclosed herein, HCFO-1233xf is converted to HCFC-253db at a temperature of about 20°C, about 30°C, about 40°C, about 50°C, about 60°C, about 70°C, or about 80°C, and all values and ranges therebetween.

**[0077]** The hydrogenation reaction of HCFO-1233xf to HCFC-253db is conducted in the liquid phase at temperatures ranging from about 20°C to about 120°C, preferably about 30°C and about 110°C. In certain embodiments disclosed herein, HCFO-1233xf is converted to HCFC-253db at a temperature of about 20°C, about 30°C, about 40°C, about 50°C, about 60°C, about 70°C, about 80°C, about 90°C, about 100°C, about 110°C, or about 120°C, and all values and ranges therebetween.

**[0078]** In some embodiments, the reaction between HCFO-1233xf and hydrogen is conducted in the vapor phase at pressures of 0 psig to about 250 psig, including all values and ranges therebetween.

**[0079]** In some embodiments, a molar ratio of hydrogen:HCFO-1233xf for the vapor phase conversion of HCFO-1233xf to HCFC-235db is in the range of from about 0.5:1 to about 3:1, preferably from about 1:1 to about 2:1.

**[0080]** In some embodiments, a molar ratio of hydrogen:HCFO-1233xf for the liquid phase conversion of HCFO-1233xf to HCFC-235db is in the range of from about 0.5:1 to about 2:1, preferably from about 0.8:1 to about 1.2:1.

**[0081]** In certain embodiments disclosed herein, the reaction between HCFO-1233xf and hydrogen is optionally conducted in the presence of diluent, such as nitrogen.

**[0082]** In certain embodiments disclosed herein, HCFO-1233xf is converted to HCFC-253db in the vapor or liquid phase, in the presence of a catalyst, and more particularly a hydrogenation catalyst.

**[0083]** In certain embodiments, the hydrogenation catalyst to convert HCFO-1233xf to HCFC-253db by reaction with hydrogen comprises a metal catalyst. In some embodiments, the catalyst comprises a metal selected from Pd, Pt, Ni, Cu, Au or combinations thereof, with or without a support selected from carbon, graphite (e.g., SiC) or a metal oxide (e.g.,  $\text{Al}_2\text{O}_3$ ). In some embodiments, the catalyst has been treated with hydrogen. In some embodiments, the catalyst is Pd/ $\text{Al}_2\text{O}_3$  or Pd/C.

**[0084]** The amount of catalyst (e.g., palladium) on the support can range from 0.01 wt.% to 10 wt.%, based on the total weight of the support and catalyst. In certain embodiments disclosed herein, the amount of catalyst (e.g., palladium) on the support is up to and including 0.005 wt.%, 0.01 wt.%, 0.02 wt.%, 0.03 wt.%, 0.04 wt.%, 0.05 wt.%, 0.06 wt.%, 0.07 wt.%, 0.08 wt.%, 0.09 wt.%, 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.5 wt.%, or 2.0 wt.%, 3.0 wt.%, 4.0 wt.%, 5.0 wt.%, 6.0 wt.%, 7.0 wt.%, 8.0 wt.%, 9.0 wt.%, 10 wt.% and all values and ranges therebetween including, but not limited to, 0.005 wt.% to 0.05 wt.%, 0.01 wt.% to 0.1 wt.%, 0.01 wt.% to 0.5 wt.%, 0.01 wt.% to 1.0 wt.%, or 0.01 wt.% to 2.0 wt.%, 0.02 wt.% to 5.0 wt.%, 0.02 wt.% to 10.0 wt.%, based on the total weight of the support and catalyst.

**[0085]** In some embodiments, for conversion of HCFO-1233xf to HCFC-253db in the vapor phase, the amount of catalyst on the support ranges from about 0.01 wt.%

to about 0.1 wt.%, preferably from about 0.02 wt.% to about 0.05 wt.%, based on the total weight of the support and catalyst, inclusive of all values and ranges therebetween.

**[0086]** In some embodiments, the catalyst for the vapor hydrogenation reaction of HCFO-1233xf is a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, wherein the Pd loading is in the range of 0.01 wt.% to 0.05 wt.%.

**[0087]** In some embodiments, for conversion of HCFO-1233xf to HCFC-253db in the liquid phase, the amount of catalyst on the support ranges from about 0.1 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst, inclusive of all values and ranges therebetween.

**[0088]** In some embodiments, the catalyst for the liquid phase hydrogenation reaction of HCFO-1233xf is a Pd/C catalyst, wherein the Pd loading is in the range of 0.1 wt.% to 10 wt.%.

**[0089]** Hydrogenation catalysts supported on low ash carbon are described in U.S. Pat. No. 5,136,113, the disclosure of which is incorporated herein by reference in its entirety, and also may be used for the conversion of HCFO-1233xf to HCFC-253db.

**[0090]** In certain embodiments disclosed herein, the HCFO-1233xf reaction with hydrogen to form HCFC-253db is conducted in the presence of a catalyst preferably comprising a metal on a support, such as Pd on a support, preferably Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C, optionally in the presence of nitrogen, wherein for a liquid phase process, the amount of catalyst on the support ranges from about 0.01 wt.% to about 10 wt.%, and for a vapor phase process, the amount of catalyst on the support ranges from about 0.01 wt.% to about 0.1 wt.%.

**[0091]** In certain embodiments disclosed herein, the HCFO-1233xf reaction with hydrogen to form HCFC-253db is conducted in the liquid phase at a temperature between about 20°C to about 120°C, preferably about 30°C and about 110°C, in the presence of a catalyst preferably comprising a metal on a support, such as Pd on a support, preferably Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C, and preferably where the amount of catalyst on the support ranges from about 0.1 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, and optionally in the presence of nitrogen. Preferably, a molar ratio of hydrogen:HCFO-1233xf for the liquid phase conversion of HCFO-1233xf to

HCFC-235db is in the range of from about 0.5:1 to about 2:1, more preferably from about 0.8:1 to about 1.2:1.

**[0092]** In certain embodiments disclosed herein, the HCFO-1233xf reaction with hydrogen to form HCFC-253db is conducted in the vapor phase at a temperature between about 20°C and about 120°C, preferably between about 30°C and about 110°C, in the presence of a catalyst preferably comprising a metal on a support, such as Pd on a support, preferably Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C, and preferably where the amount of catalyst on the support ranges from about 0.01 wt. % to about 0.1 wt. %, preferably from about 0.02 wt. % to about 0.05 wt. %, and optionally in the presence of nitrogen. Preferably, a molar ratio of hydrogen:HCFO-1233xf for the vapor phase conversion of HCFO-1233xf to HCFC-235db is in the range of from about 0.5:1 to about 3:1, more preferably from about 1:1 to about 2:1.

**[0093]** In certain embodiments, the present invention relates to conversion of HCFC-253db to HFO-1252zc by contacting the HCFC-253db with hydrogen. More particularly, HCFC-253db is converted to HFO-1252zc by removal of the halogens on adjacent carbons to form a double bond by hydrogenation. The removal of the adjacent halogens is considered hydrodehalogenation.

**[0094]** In some embodiments, the HCFC-253db is an intermediate formed by step (1) of the above reaction scheme which converts HCFO-1233xf to HCFC-253db, such that the present invention provides a multi-step integrated process to form HFO-1252zc from HCFO-1233xf.

**[0095]** In certain embodiments, conversion of HCFC-253db to HFO-1252zc is conducted in the vapor phase with hydrogen.

**[0096]** In certain embodiments disclosed herein, HCFC-253db is converted to HFO-1252zc in the vapor phase with H<sub>2</sub> at temperatures between about 200°C and about 500°C, preferably between about 300°C and about 450°C.

**[0097]** In certain embodiments disclosed herein, HCFC-253db is converted to HFO-1252zc in the vapor phase with H<sub>2</sub> at a temperature of 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, about 335°C, about 340°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, about 400°C, about 405°C, about 410°C, about 415°C, about 420°C, about 425°C, about 430°C, about 435°C, about 440°C, about 445°C, about 450°C, about 455°C, about 460°C, about 465°C, about 470°C, about 475°C, about 480°C, about 485°C, about 490°C, about 495°C, or about 500°C and all values and ranges therebetween.

**[0098]** In certain embodiments disclosed herein, HCFC-253db is converted to HFO-1252zc in the vapor phase with H<sub>2</sub> at pressures of 0 psig to about 250 psig, including all values and ranges therebetween.

**[0099]** In some embodiments, a molar ratio of hydrogen:HCFC-253db for the vapor phase conversion of HCFC-253db is in the range of about 5:1 to about 40:1, preferably about 10:1 to about 30:1.

**[0100]** In certain embodiments disclosed herein, the reaction between HCFC-253db and hydrogen is optionally conducted in the presence of diluent, such as nitrogen.

**[0101]** In certain embodiments disclosed herein, HCFC-253db is converted to HFO-1252zc in the vapor phase with H<sub>2</sub> in the presence of a catalyst. In some embodiments, the catalyst for the conversion of HCFC-253db to HFO-1252zc comprises a metal selected from Ni, Cu, Au or combinations thereof, with or without a support, such as carbon, graphite (e.g., SiC) or a metal oxide (e.g., Al<sub>2</sub>O<sub>3</sub>). In some embodiments, the catalyst has been treated with hydrogen. In some embodiments, the catalyst is Au/C or Cu/C.

**[0102]** The amount of catalyst on the support can range from about 2 wt.% to about 10 wt.%, based on the total weight of the support and catalyst. In certain embodiments disclosed herein, the amount of catalyst on the support is up to and including 2.0 wt.%, 3.0 wt.%, 4.0 wt.%, 5.0 wt.%, 6.0 wt.%, 7.0 wt.%, 8.0 wt.%, 9.0 wt.%, 10 wt.% and all values and ranges therebetween based on the total weight of the support and catalyst.

**[0103]** In some embodiments, the catalyst for the vapor phase conversion of HCFC-253db to HFO-1252zc is an Au/C catalyst, wherein the Au loading is in the range of about 2 wt.% to about 10 wt.%.

**[0104]** Hydrogenation catalysts supported on low ash carbon are described in U.S. Pat. No. 5,136,113, the disclosure of which is incorporated herein by reference in its entirety and may be used for the conversion of HCFC-253db to HFO-1252zc.

**[0105]** In certain embodiments disclosed herein, reaction of HCFC-253db with hydrogen to form HFO-1252zc is conducted in the vapor phase at a temperature between about 200°C and about 500°C, preferably between about 300°C and about 450°C, in the presence of a catalyst preferably comprising a metal on a support, such as Au or Cu on a support, and preferably where the amount of catalyst on the support ranges from 2 wt.% to 10 wt.%, and optionally in the presence of nitrogen. Preferably, a molar ratio of hydrogen:HCFC-253db for the vapor phase conversion of HCFC-235db is in the range of about 5:1 to about 40:1, more preferably about 10:1 to about 30:1.

**[0106]** In certain embodiments, the present invention relates to conversion of HCFC-253db to HFO-1252zc by contacting the HCFC-253db with a metal, such as Zn, Mg or a combination thereof. More particularly, HCFC-253db is converted to HFO-1252zc with a metal by removal of the halogens on adjacent carbons to form a double bond. The removal of the adjacent halogens is considered dehalogenation.

**[0107]** In some embodiments, the HCFC-253db is an intermediate formed by step (1) of the above reaction scheme which converts HCFO-1233xf to HCFC-253db, such that the present invention provides a multi-step integrated process to form HFO-1252zc from HCFO-1233xf.

**[0108]** In certain embodiments, conversion of HCFC-253db to HFO-1252zc is conducted in the liquid phase by a metal, such as Zn or Mg or a combination thereof. In some embodiments, the metal is a reactive metal.

**[0109]** In some embodiments, reaction of HCFC-253db and the metal (e.g., zinc) occurs in the liquid phase at temperatures of between about 50°C and about 180°C, preferably between about 80°C and about 150°C.

[0110] In some embodiments, reaction of HCFC-253db and the metal (e.g., zinc) occurs in the liquid phase at a temperature of about 50°C, about 55°C, about 60°C, about 65°C, about 70°C, about 75°C, about 80°C, about 85°C, about 90°C, about 95°C, about 100°C, about 105°C, about 110°C, about 115°C, about 120°C, about 125°C, about 130°C, about 135°C, about 140°C, about 145°C, about 150°C, about 155°C, about 160°C, about 165°C, about 170°C, about 175°C, or about 180°C, and all values and ranges therebetween.

[0111] In certain embodiments, reaction of HCFC-253db and the metal (e.g., zinc) occurs under autogenous pressure.

[0112] In some embodiments, a molar ratio of metal:HCFC-253db for the liquid phase conversion of HCFC-253db is in the range of about 1:1 to about 5:1, preferably about 1.05:1 to about 3:1.

[0113] In some embodiments, the metal is activated by an acid, and more particularly is activated by contact with an acid before used for reaction with HCFC-253db.

[0114] In some embodiments, the metal is zinc, and more particularly zinc powder. In some embodiments, the zinc is activated by an acid, such as HCl. In certain embodiments disclosed herein, zinc powder is activated with HCl (e.g., aqueous or in an alcohol) and is then used to convert HCFC-253db to HFO-1252zc.

[0115] In some embodiments, the reaction of HCFC-253db and the metal (e.g., zinc) is conducted in the absence of a catalyst.

[0116] In some embodiments, the reaction of HCFC-253db and the metal (e.g., zinc) is conducted in the presence of a catalyst. In some embodiments, the catalyst is selected from zinc salt, ammonium salt and phosphonium salt. In some embodiments, the catalyst comprises a zinc salt selected from zinc acetate and  $\text{ZnCl}_2$ . In some embodiments, the catalyst comprises an ammonium salt, such as tetrabutylammonium bromide.

[0117] In some embodiments, the reaction of HCFC-253db and the metal (e.g., zinc) is conducted in the presence of a solvent. In some embodiments, the solvent is selected from alcohol, amide, pyridine and ether. In certain embodiments

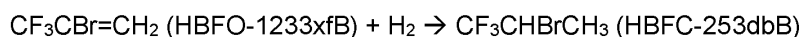
disclosed herein, the solvent comprises an alcohol selected from methanol, ethanol, propanol, isopropanol and ethylene glycol.

**[0118]** In some embodiments, the reaction of HCFC-253db and the metal (e.g., zinc) is conducted in the liquid phase in the presence of a catalyst and a solvent.

**[0119]** In other embodiments, the present invention relates to liquid phase reaction of HCFC-253db and zinc at a temperature between about 50°C and about 180°C, preferably from about 80°C to about 150°C, in the presence of a catalyst preferably selected from a zinc salt (e.g., ZnCl<sub>2</sub> or zinc acetate), ammonium salt (e.g., tetrabutylammonium bromide) or phosphonium salt, and in the presence of a solvent preferably selected from alcohol, amide, pyridine and ether, and more preferably an alcohol solvent selected from methanol, ethanol, propanol, isopropanol and ethylene glycol. In some embodiments, the zinc used for this reaction has been activated by an acid, for example zinc powder which has been activated with HCl (e.g., aqueous or in an alcohol). Preferably, a molar ratio of metal:HCFC-253db for the liquid phase conversion of HCFC-253db is in the range of about 1:1 to about 5:1, more preferably about 1.05:1 to about 3:1

**[0120]** In some embodiments, the CF<sub>3</sub>CX=CH<sub>2</sub> compound is HBFO-1233xfB and the CF<sub>3</sub>CHXCH<sub>3</sub> compound is HBFC-253dbB.

**[0121]** In certain embodiments disclosed herein, the present invention relates to processes using HBFO-1233xfB as the starting material to produce HBFC-253dbB according to the following reaction, and compositions thereof:



**[0122]** In certain embodiments disclosed herein, the present invention relates to processes of converting HBFC-253dbB to HFO-1252zc according to either of the following reactions, and compositions thereof:

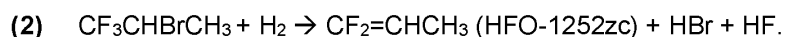
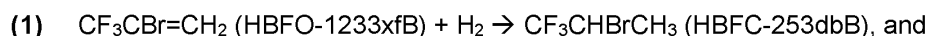


OR

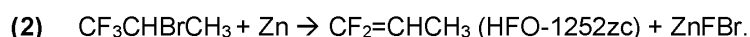
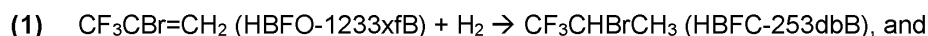


**[0123]** In certain embodiments disclosed herein, the present invention relates to a two-step process using HBFO-1233xfB as the starting material to produce HFO-

1252zc according to either of the following two step reaction schemes, and compositions thereof:



OR



**[0124]** One embodiment of the invention disclosed herein relates to a process of converting HBFO-1233xfB through the intermediate HBFC-253dbB to form HFO-1252zc.

#### Discussion of 1233xfB $\rightarrow$ 253dbB

**[0125]** Hydrogenation of HBFO-1233xfB to HBFC-253dbB can be conducted in the vapor or liquid phase. Reaction of HBFO-1233xfB with hydrogen is also referred to as hydrogenation or hydrogenolysis.

**[0126]** The hydrogenation reaction of HBFO-1233xfB to HBFC-253dbB is conducted in the vapor phase at temperatures ranging from about 30°C to about 130°C, preferably about 60°C and about 110°C. In certain embodiments disclosed herein, HCFO-1233xf is converted to HCFC-253db or HBFO-1233xfB is converted to HBFC-253dbB at a temperature of about 30°C, about 40°C, about 50°C, about 60°C, about 70°C, about 80°C, about 90°C, about 100°C, about 110°C, about 120°C, or about 130°C, and all values and ranges therebetween.

**[0127]** The hydrogenation reaction of HBFO-1233xfB to HBFC-253dbB is conducted in the liquid phase at temperatures ranging from about 40°C to about 120°C, preferably about 60°C and about 100°C. In certain embodiments disclosed herein, HBFO-1233xfB is converted to HBFC-253dbB at a temperature of about 40°C, about 50°C, about 60°C, about 70°C, about 80°C, about 90°C, about 100°C, about 110°C, or about 120°C, and all values and ranges therebetween.

**[0128]** In some embodiments, the reaction between HBFO-1233xfB and hydrogen is conducted in the vapor phase at pressures of 0 psig to about 250 psig, including all values and ranges therebetween.

**[0129]** In some embodiments, a molar ratio of hydrogen:HBFO-1233xfB for the vapor phase conversion of HBFO-1233xfB to HBFC-253dbB is in the range of about 1:1 to about 10:1, preferably about 2:1 to about 8:1.

**[0130]** In some embodiments, a molar ratio of hydrogen:HBFO-1233xfB for the liquid phase conversion of HBFO-1233xfB to HBFC-253dbB is in the range of about 0.5:1 to about 3:1, preferably about 0.8:1 to about 2:1.

**[0131]** In certain embodiments disclosed herein, the reaction between HBFO-1233xfB and hydrogen is optionally conducted in the presence of diluent, such as nitrogen.

**[0132]** In certain embodiments disclosed herein, HBFO-1233xfB is converted to HBFC-253dbB in the vapor or liquid phase, in the presence of a catalyst, and more particularly a hydrogenation catalyst.

**[0133]** In certain embodiments, the hydrogenation catalyst to convert HBFO-1233xfB to HBFC-253dbB by reaction with hydrogen comprises a metal catalyst. In some embodiments, the catalyst comprises a metal selected from Pd, Pt, Ni, Cu, Au or combinations thereof, with or without a support selected from carbon, graphite (e.g., SiC) or a metal oxide (e.g.,  $\text{Al}_2\text{O}_3$ ). In some embodiments, the catalyst has been treated with hydrogen. In some embodiments, the catalyst is Pd/ $\text{Al}_2\text{O}_3$  or Pd/C.

**[0134]** The amount of catalyst (e.g., palladium) on the support can range from 0.1 wt.% to 10 wt.%, based on the total weight of the support and catalyst. In certain embodiments disclosed herein, the amount of catalyst (e.g., palladium) on the support is up to and including 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.5 wt.%, or 2.0 wt.%, 3.0 wt.%, 4.0 wt.%, 5.0 wt.%, 6.0 wt.%, 7.0 wt.%, 8.0 wt.%, 9.0 wt.%, 10 wt.% and all values and ranges therebetween based on the total weight of the support and catalyst.

**[0135]** In some embodiments, for conversion of HBFO-1233xfB to HBFC-253dbB in the vapor phase, the amount of catalyst on the support ranges from about 0.1 wt.% to about 1.0 wt.%, more preferably about 0.2 wt.% to about 0.8 wt.%, based on the total weight of the support and catalyst, inclusive of all values and ranges therebetween.

**[0136]** In some embodiments, the catalyst for the vapor hydrogenation reaction of HBFO-1233xfB is a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, wherein the Pd loading is in the range of 0.1 wt.% to 1.0 wt.%.

**[0137]** In some embodiments, for conversion of HBFO-1233xfB to HBFC-253dbB in the liquid phase, the amount of catalyst on the support ranges from about 0.1 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst, inclusive of all values and ranges therebetween.

**[0138]** In some embodiments, the catalyst for the liquid phase hydrogenation reaction of HBFO-1233xfB is a Pd/C catalyst, wherein the Pd loading is in the range of 0.1 wt.% to 10 wt.%.

**[0139]** Hydrogenation catalysts supported on low ash carbon are described in U.S. Pat. No. 5,136,113, the disclosure of which is incorporated herein by reference in its entirety, and also may be used for the conversion of HBFO-1233xfB to HBFC-253dbB.

**[0140]** In certain embodiments disclosed herein, the HBFO-1233xfB reaction with hydrogen to form HBFC-253dbB is conducted in the presence of a catalyst preferably comprising a metal on a support, such as Pd on a support, preferably Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C, optionally in the presence of nitrogen, wherein for a liquid phase process, the amount of catalyst on the support ranges from 0.1 wt.% to 10 wt.%, and for a vapor phase process, the amount of catalyst on the support ranges from about 0.1 wt.% to about 1 wt.%.

**[0141]** In certain embodiments disclosed herein, the HBFO-1233xfB reaction with hydrogen to form HBFC-253dbB is conducted in the liquid phase at a temperature between about 40°C and about 120°C, preferably between about 60°C and about 100°C, in the presence of a catalyst preferably comprising a metal on a support, such as Pd on a support, preferably Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C, and preferably where the amount of catalyst on the support ranges from about 0.1 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, and optionally in the presence of nitrogen. Preferably, a molar ratio of hydrogen:HBFO-1233xfB for the liquid phase conversion of HBFO-1233xfB to HBFC-253dbB is in the range of about 0.5:1 to about 3:1, more preferably about 0.8:1 to about 2:1.

**[0142]** In certain embodiments disclosed herein, the HBFO-1233xfB reaction with hydrogen to form HBFC-253dbB is conducted in the vapor phase at a temperature between about 30°C and about 130°C, preferably between about 60°C and about 110°C, in the presence of a catalyst preferably comprising a metal on a support, such as Pd on a support, preferably Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C, and preferably where the amount of catalyst on the support ranges from about 0.1 wt. % to about 1.0 wt. %, more preferably about 0.2 wt. % to about 0.8 wt. %, and optionally in the presence of nitrogen. Preferably, a molar ratio of hydrogen:HBFO-1233xfB for the vapor phase conversion of HBFO-1233xfB to HBFC-253dbB is in the range of about 1:1 to about 10:1, more preferably about 2:1 to about 8:1.

**[0143]** In certain embodiments, the present invention relates to conversion of HBFC-253dbB to HFO-1252zc by contacting the HBFC-253dbB with hydrogen. More particularly, HBFC-253dbB is converted to HFO-1252zc by removal of the halogens on adjacent carbons to form a double bond by hydrogenation. The removal of the adjacent halogens is considered hydrodehalogenation.

**[0144]** In some embodiments, the HBFC-253dbB is an intermediate formed by step (1) of the above reaction scheme which converts HBFO-1233xfB to HBFC-253dbB, such that the present invention provides a multi-step integrated process to form HFO-1252zc from HBFO-1233xfB.

**[0145]** In certain embodiments, conversion of HBFC-253dbB to HFO-1252zc is conducted in the vapor phase with hydrogen.

**[0146]** In certain embodiments disclosed herein, HBFC-253dbB is converted to HFO-1252zc in the vapor phase with H<sub>2</sub> at temperatures between about 200°C and about 500°C, preferably between about 300°C and about 450°C.

**[0147]** In certain embodiments disclosed herein, HBFC-253dbB is converted to HFO-1252zc in the vapor phase with H<sub>2</sub> at a temperature of 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, about 335°C, about 340°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, about 400°C, about 405°C, about 410°C, about 415°C, about 420°C, about 425°C, about 430°C, about 435°C, about 440°C, about 445°C, about 450°C, about 455°C, about 460°C, about 465°C, about 470°C, about 475°C, about 480°C, about 485°C, about 490°C, about 495°C, or about 500°C and all values and ranges therebetween.

**[0148]** In certain embodiments disclosed herein, HBFC-253dbB is converted to HFO-1252zc in the vapor phase with H<sub>2</sub> at pressures of 0 psig to about 250 psig, including all values and ranges therebetween.

**[0149]** In some embodiments, a molar ratio of hydrogen:HBFC-253dbB for the vapor phase conversion of HBFC-253dbB is in the range of about 5:1 to about 40:1, preferably about 10:1 to about 30:1.

**[0150]** In certain embodiments disclosed herein, the reaction between HBFC-253dbB and hydrogen is optionally conducted in the presence of diluent, such as nitrogen.

**[0151]** In certain embodiments disclosed herein, HBFC-253dbB is converted to HFO-1252zc in the vapor phase with H<sub>2</sub> in the presence of a catalyst. In some embodiments, the catalyst for the conversion of HBFC-253dbB to HFO-1252zc comprises a metal selected from Ni, Cu, Au or combinations thereof, with or without a support, such as carbon, graphite (e.g., SiC) or a metal oxide (e.g., Al<sub>2</sub>O<sub>3</sub>). In some embodiments, the catalyst has been treated with hydrogen. In some embodiments, the catalyst is Au/C or Cu/C.

**[0152]** The amount of catalyst on the support can range from about 2 wt.% to about 10 wt.%, based on the total weight of the support and catalyst. In certain embodiments disclosed herein, the amount of catalyst on the support is up to and including 2.0 wt.%, 3.0 wt.%, 4.0 wt.%, 5.0 wt.%, 6.0 wt.%, 7.0 wt.%, 8.0 wt.%, 9.0 wt.%, 10 wt.% and all values and ranges therebetween, based on the total weight of the support and catalyst.

**[0153]** In some embodiments, the catalyst for the vapor phase conversion of HBFC-253dbB to HFO-1252zc is an Au/C catalyst, wherein the Au loading is in the range of about 2 wt.% to about 10 wt.%.

[0154] Hydrogenation catalysts supported on low ash carbon are described in U.S. Pat. No. 5,136,113, the disclosure of which is incorporated herein by reference in its entirety and may be used for the conversion of HBFC-253dbB to HFO-1252zc.

[0155] In certain embodiments disclosed herein, reaction of HBFC-253dbB with hydrogen to form HFO-1252zc is conducted at a temperature between about 200°C and about 500°C, preferably between about 300°C and about 450°C, in the presence of a catalyst preferably comprising a metal on a support, such as Au or Cu on a support, and preferably where the amount of catalyst on the support ranges from about 2 wt.% to about 10 wt.%, and optionally in the presence of nitrogen. Preferably, a molar ratio of hydrogen:HCFC-253db for the vapor phase conversion of HCFC-235db is in the range of about 5:1 to about 40:1, more preferably about 10:1 to about 30:1.

[0156] In certain embodiments, the present invention relates to conversion of HBFC-253dbB to HFO-1252zc by contacting the HCFC-253db with a metal, such as Zn, Mg or a combination thereof. More particularly, HBFC-253dbB is converted to HFO-1252zc by removal of the halogens on adjacent carbons to form a double bond. The removal of the adjacent halogens is considered dehalogenation.

[0157] In some embodiments, the HBFC-253dbB is an intermediate formed by step (1) of the above reaction scheme which converts HBFO-1233xfB to HBFC-253dbB, such that the present invention provides a multi-step integrated process to form HFO-1252zc from HBFO-1233xfB.

[0158] In certain embodiments, conversion of HBFC-253dbB to HFO-1252zc is conducted in the liquid phase by a metal, such as Zn or Mg or a combination thereof. In some embodiments, the metal is a reactive metal.

[0159] In some embodiments, reaction of HBFC-253dbB and the metal (e.g., zinc) occurs at temperatures of between about 40°C and about 120°C, preferably between about 50°C and 100°C.

[0160] In some embodiments, reaction of HBFC-253dbB and the metal (e.g., zinc) occurs at a temperature of about 40°C, about 45°C, about 50°C, about 55°C, about 60°C, about 65°C, about 70°C, about 75°C, about 80°C, about 85°C, about 90°C,

about 95°C, about 100°C, about 105°C, about 110°C, about 115°C, or about 120°C, and all values and ranges therebetween.

**[0161]** In certain embodiments, reaction of HBFC-253dbB and the metal (e.g., zinc) occurs under autogenous pressure.

**[0162]** In some embodiments, a molar ratio of metal:HBFC-253dbB for the liquid phase conversion of HBFC-253dbB is in the range of about 1:1 to about 5:1, preferably about 1.05:1 to about 3:1.

**[0163]** In some embodiments, the metal is activated by an acid, and more particularly is activated by contact with an acid before used for reaction with HBFC-253dbB.

**[0164]** In some embodiments, the metal is zinc, and more particularly zinc powder. In some embodiments, the zinc is activated by an acid, such as HCl. In certain embodiments disclosed herein, zinc powder is activated with HCl (e.g., aqueous or in an alcohol) and is then used to convert HBFC-253dbB to HFO-1252zc.

**[0165]** In some embodiments, the reaction of HBFC-253dbB and the metal (e.g., zinc) is conducted in the absence of a catalyst.

**[0166]** In some embodiments, the reaction of HBFC-253dbB and the metal (e.g., zinc) is conducted in the presence of a catalyst. In some embodiments, the catalyst is selected from zinc salt, ammonium salt and phosphonium salt. In some embodiments, the catalyst comprises a zinc salt selected from zinc acetate and ZnCl<sub>2</sub>. In some embodiments, the catalyst comprises an ammonium salt, such as tetrabutylammonium bromide.

**[0167]** In some embodiments, the reaction of HBFC-253dbB and the metal (e.g., zinc) is conducted in the presence of a solvent. In some embodiments, the solvent is solvent selected from alcohol, amide, pyridine and ether. In certain embodiments disclosed herein, the solvent comprises an alcohol selected from methanol, ethanol, propanol, isopropanol and ethylene glycol.

**[0168]** In some embodiments, the reaction of HBFC-253dbB and the metal (e.g., zinc) is conducted in the liquid phase in the presence of a catalyst and a solvent.

**[0169]** In other embodiments, the present invention relates to liquid phase reaction of HBFC-253dbB and zinc at a temperature between 40°C and about 120°C, preferably between about 50°C and 100°C, in the presence of a catalyst preferably selected from a zinc salt (e.g.,  $\text{ZnCl}_2$  or zinc acetate), ammonium salt (e.g., tetrabutylammonium bromide) or phosphonium salt, and in the presence of a solvent preferably selected from alcohol, amide, pyridine and ether, and more preferably an alcohol solvent selected from methanol, ethanol, propanol, isopropanol and ethylene glycol. In some embodiments, the zinc used for this reaction has been activated by an acid, for example zinc powder which has been activated with HCl (e.g., aqueous or in an alcohol). Preferably, a molar ratio of metal:HBFC-253dbB for the liquid phase conversion of HBFC-253dbB is in the range of about 1:1 to about 5:1, more preferably about 1.05:1 to about 3:1.

**[0170]** In one embodiment, the HBFO-1233xfB used in any of the above processes is formed from HFO-1243zf. More particularly, in some embodiments, HFO-1243zf is converted to dibromotrifluoropropane in the presence of  $\text{Br}_2$ , and the dibromotrifluoropropane is converted to HBFO-1233xfB in the presence of a caustic agent.

**[0171]** In some embodiments, the present invention relates to processes for producing HFO-1252zc from at least one compound selected from HCFC-253db, HBFC-253dbB, HCFO-1233xf and HBFO-1233xfB, in one or more reactors.

**[0172]** In some embodiments, the present invention relates a system for conducting multi-step processes, as shown in **Fig. 1**, in which a first feed **10** is converted to an intermediate in reactor **20** and discharged as a first product stream **30**. First product stream is transferred to and further reacted in reactor **40**, which can include one or more reactors. The final product mixture is discharged through line **50**. Reactor **20** and the one or more reactors **30** can be configured for liquid or vapor phase conversion. Intermediate product streams, such as first product stream **30**, can be treated and the intermediate/product recovered prior to downstream processing.

### Compositions

[0173] Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

[0174] Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc), wherein at least HFO-1252zc is present.

[0175] Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-

difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc), wherein at least HFO-1252zc and HFO-1243zf are present.

**[0176]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc), wherein at least HFO-1252zc and HFO-1261ze are present.

**[0177]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-

trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc), wherein at least HFO-1252zc and HFC-263fb are present.

**[0178]** Certain embodiments disclosed herein relate to compositions comprising, consisting essentially of, or consisting of one or more compounds selected from propane, 3,3,3-trifluoropropene (HFO-1243zf), 1,1,1-trifluoropropane (HFC-263fb), dichloromethane (HCC-30), 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), tetrafluorobutane (HFC-374), chlorofluoropropene (HCFO-1251), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3-difluoropropene (HBFO-1242xfB), dichlorotrifluoropropane isomers (HCFC-243), and dibromotrifluoropropane ( $C_3H_3Br_2F_3$ ), wherein at least HBFO-1233xfB is present.

**[0179]** In some embodiments, the present invention relates to compositions comprising HFC-263fb and HCFC-253db.

**[0180]** In some embodiments, the present invention relates to compositions comprising HFC-263fb, HCFO-1233xf and HCFC-253db.

**[0181]** In some embodiments, the present invention relates to compositions comprising HFO-1252zc, HFC-263fb, HCFO-1233xf and HCFC-253db.

**[0182]** In some embodiments, the present invention relates to compositions comprising up to 50 mole percent HFC-263fb and up to about 99 mole percent HCFC-253db, based on a total composition of 100 mole percent.

**[0183]** In some embodiments, the present invention relates to compositions comprising HFC-263fb and HCFC-253dbB.

**[0184]** In some embodiments, the present invention relates to compositions comprising HFC-263fb, HCFO-1233xfB and HCFC-253dbB.

**[0185]** In some embodiments, the present invention relates to compositions comprising HFO-1252zc, HFC-263fb, HCFO-1233xfB and HCFC-253dbB.

[0186] For all of the compositions disclosed herein, aside from HFO-1252zc, the total amount of the other compounds may be about 5 wt.% or less, about 4 wt.% or less, about 3 wt.% or less, about 2 wt.% or less, about 1 wt.% or less, about 0.9 wt.% or less, about 0.8 wt.% or less, about 0.7 wt.% or less, about 0.6 wt.% or less, about 0.5 wt.% or less, about 0.4 wt.% or less, about 0.3 wt.% or less, about 0.2 wt.% or less, about 0.1 wt.% or less, about 0.09 wt.% or less, about 0.08 wt.% or less, about 0.07 wt.% or less, about 0.06 wt.% or less, about 0.05 wt.% or less, about 0.04 wt.% or less, about 0.03 wt.% or less, about 0.02 wt.% or less, or about 0.01 wt.% or less, or about 10 ppm or less, or about 1 ppm or less.

[0187] Certain embodiments of the invention disclosed herein relate to any of the foregoing compositions being 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).

[0188] 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).

[0189] In embodiments, Group A Fluorinated Substances include, but are not limited to, TFA.

[0190] 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  $\leq 5$  wt.%, or  $> 0$  wt.% and  $\leq 4$  wt.%, or  $> 0$  wt.% and  $\leq 3$  wt.%, or  $> 0$  wt.% and  $\leq 2$  wt.%, or  $> 0$  wt.% and  $\leq 1$  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.

**[0191]** 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.

[0192] In the present invention, reactors, distillation columns, and their associated feed lines, effluent lines, and associated units used in applying the processes of this invention should be constructed of materials resistant to hydrogen fluoride and hydrogen chloride. Typical materials of construction, well-known to the fluorination art, include stainless steels, in particular of the austenitic type, the well-known high nickel alloys, such as Monel™ nickel-copper alloys, Hastelloy™ nickel-based alloys and, Inconel™ nickel-chromium alloys, and copper-clad steel.

[0193] In the present invention, the series of reaction steps to produce HFO-1252zc is performed in one or more vapor phase reactor reactors, one or more liquid phase reactors, and combinations thereof.

[0194] In the present invention, the series of reaction steps to produce HFO-1252zc is performed in one or more vapor phase reactor reactors, one or more liquid phase reactors and combinations thereof, and the effluent from a reactor is optionally subjected to separation to recycle unreacted feed material and purify/concentrate intermediates for downstream conversion.

### **EXAMPLES**

[0195] **Example 1:** Hydrogenation of HCFO-1233xf to HCFC-253db in vapor phase with 0.02%Pd/Al<sub>2</sub>O<sub>3</sub>

[0196] In a 12-inch long ½" OD Monel reactor, 4ml 0.02% Pd/Al<sub>2</sub>O<sub>3</sub> was loaded. The catalyst was treated at 120°C by a flow of H<sub>2</sub> for 1 hour. Then, the reactor was cooled down to 30°C. H<sub>2</sub> and N<sub>2</sub> feeds were controlled by a mass flow controller and HCFO-1233xf was fed by a pump. The reaction test conditions are listed in Table 2 below. The reactor effluent was analyzed by online GC-MS-FID. The results of the analysis are listed in Table 2 below which shows complete high conversion of HCFO-1233xf and good selectivity to HCFC-253db.

**TABLE 2**

| Furnace | Pressure | 1233xf | N2    | H2   | GC-FID area% |       |        |        |
|---------|----------|--------|-------|------|--------------|-------|--------|--------|
| Temp °C | psig     | cc/hr  | sccm  | Scm  | others       | 263fb | 1233xf | 253db  |
| 30      | 10.0     | 0.99   | 10.32 | 7.05 | 0.03%        | 3.16% | 8.65%  | 88.16% |
| 30      | 10.0     | 0.99   | 10.32 | 7.02 | 0.04%        | 3.16% | 11.00% | 85.81% |
| 35      | 10.0     | 0.99   | 10.32 | 7.07 | 0.02%        | 3.85% | 2.52%  | 93.61% |
| 35      | 10.0     | 0.99   | 10.32 | 7.07 | 0.02%        | 3.69% | 0.63%  | 95.66% |

| Furnace | Pressure | 1233xf | N2    | H2   | GC-FID area% |       |        |        |
|---------|----------|--------|-------|------|--------------|-------|--------|--------|
| Temp °C | psig     | cc/hr  | sccm  | Scm  | others       | 263fb | 1233xf | 253db  |
| 40      | 10.0     | 0.99   | 10.32 | 7.03 | 0.02%        | 4.35% | 0.12%  | 95.51% |
| 40      | 10.0     | 0.99   | 10.32 | 7.03 | 0.02%        | 4.32% | 0.20%  | 95.47% |
| 45      | 10.0     | 0.99   | 10.32 | 7.06 | 0.01%        | 4.86% | 0.02%  | 95.11% |
| 45      | 10.0     | 0.99   | 10.32 | 7.07 | 0.01%        | 4.82% | 0.01%  | 95.15% |
| 50      | 10.0     | 0.99   | 10.32 | 7.07 | 0.01%        | 5.67% | 0.00%  | 94.32% |
| 50      | 10.0     | 0.99   | 10.32 | 7.07 | 0.01%        | 5.46% | 0.00%  | 94.53% |
| 60      | 10.0     | 0.99   | 10.32 | 7.07 | 0.01%        | 7.27% | 0.00%  | 92.72% |
| 60      | 10.0     | 0.99   | 10.32 | 7.07 | 0.01%        | 6.93% | 0.00%  | 93.06% |
| 30      | 10.0     | 0.99   | 10.32 | 6.06 | 0.03%        | 2.46% | 30.90% | 66.61% |
| 30      | 10.0     | 0.99   | 10.32 | 6.06 | 0.04%        | 2.22% | 39.41% | 58.32% |
| 30      | 10.0     | 0.99   | 10.32 | 6.06 | 0.04%        | 2.22% | 38.97% | 58.76% |
| 35      | 10.0     | 0.99   | 10.32 | 6.11 | 0.03%        | 3.21% | 24.66% | 72.10% |
| 35      | 10.0     | 0.99   | 10.32 | 6.11 | 0.03%        | 3.29% | 17.96% | 78.72% |
| 40      | 10.0     | 0.99   | 10.32 | 6.11 | 0.02%        | 4.54% | 8.30%  | 87.14% |
| 40      | 10.0     | 0.99   | 10.32 | 6.07 | 0.02%        | 4.33% | 13.96% | 81.68% |
| 45      | 10.0     | 0.99   | 10.32 | 6.07 | 0.01%        | 5.32% | 4.28%  | 90.39% |
| 45      | 10.0     | 0.99   | 10.32 | 6.07 | 0.01%        | 5.41% | 4.84%  | 89.74% |
| 50      | 10.0     | 0.99   | 10.32 | 6.07 | 0.01%        | 6.41% | 1.32%  | 92.26% |
| 50      | 10.0     | 0.99   | 10.32 | 6.07 | 0.01%        | 6.50% | 1.94%  | 91.55% |
| 55      | 10.0     | 0.99   | 10.32 | 6.07 | 0.00%        | 7.43% | 0.24%  | 92.33% |
| 55      | 10.0     | 0.99   | 10.32 | 6.07 | 0.00%        | 7.71% | 0.47%  | 91.82% |
| 60      | 10.1     | 0.99   | 10.32 | 6.07 | 0.00%        | 9.02% | 0.11%  | 90.87% |
| 60      | 10.0     | 0.99   | 10.32 | 6.07 | 0.00%        | 9.19% | 0.15%  | 90.66% |

**[0197] Example 2:** Hydrogenation of HCFO-1233xf to HCFC-253db in vapor phase with 0.04%Pd/A<sub>l</sub><sub>2</sub>O<sub>3</sub>

**[0198]** In a 12-inch long ½" OD Monel reactor, 4ml 0.04% Pd/AI<sub>2</sub>O<sub>3</sub> was loaded. The catalyst was treated at 120°C by a flow of H<sub>2</sub> for 1 hour. Then, the reactor was cooled down to 30°C. H<sub>2</sub> and N<sub>2</sub> feeds were controlled by a mass flow controller and HCFO-1233xf was fed by a pump. The reaction test conditions are listed on Table 3 below. The reactor effluent was analyzed by online GC-MS-FID. The results of the analysis are listed in Table 3 below which shows complete high conversion of HCFO-1233xf and good selectivity to HCFC-253db.

TABLE 3

| Furnace | Pressure | 1233xf | N2    | H2   | GC-FID area% |       |        |        |
|---------|----------|--------|-------|------|--------------|-------|--------|--------|
| Temp °C | psig     | cc/hr  | sccm  | Scm  | Others       | 263fb | 1233xf | 253db  |
| 29      | 10.0     | 0.99   | 10.00 | 7.08 | 0.02%        | 6.12% | 0.00%  | 93.85% |
| 29      | 10.0     | 0.99   | 10.30 | 7.08 | 0.02%        | 4.90% | 0.00%  | 95.08% |
| 35      | 10.0     | 0.99   | 10.00 | 7.08 | 0.05%        | 4.77% | 0.00%  | 95.18% |
| 35      | 10.0     | 0.99   | 10.00 | 7.07 | 0.05%        | 4.42% | 0.00%  | 95.53% |
| 40      | 10.0     | 0.99   | 10.00 | 7.07 | 0.05%        | 5.10% | 0.00%  | 94.85% |
| 40      | 10.0     | 0.99   | 10.00 | 7.07 | 0.05%        | 5.19% | 0.00%  | 94.76% |

| Furnace | Pressure | 1233xf | N2    | H2   | GC-FID area% |        |        |        |
|---------|----------|--------|-------|------|--------------|--------|--------|--------|
| Temp °C | psig     | cc/hr  | sccm  | Sccm | Others       | 263fb  | 1233xf | 253db  |
| 45      | 10.0     | 0.99   | 10.00 | 7.07 | 0.05%        | 6.16%  | 0.00%  | 93.80% |
| 45      | 10.0     | 0.99   | 10.00 | 7.07 | 0.05%        | 5.91%  | 0.00%  | 94.04% |
| 50      | 10.0     | 0.99   | 10.03 | 7.07 | 0.05%        | 7.59%  | 0.00%  | 92.36% |
| 50      | 10.0     | 0.99   | 10.01 | 7.07 | 0.05%        | 7.14%  | 0.00%  | 92.82% |
| 60      | 10.0     | 0.99   | 10.15 | 7.07 | 0.04%        | 12.42% | 0.00%  | 87.54% |
| 60      | 10.0     | 0.99   | 23.01 | 7.07 | 0.02%        | 15.93% | 0.00%  | 84.05% |
| 32      | 10.0     | 0.99   | 22.98 | 7.07 | 0.02%        | 4.28%  | 0.00%  | 95.71% |
| 30      | 10.0     | 0.99   | 23.01 | 7.07 | 0.02%        | 3.95%  | 0.00%  | 96.03% |
| 30      | 10.0     | 0.99   | 23.41 | 7.07 | 0.02%        | 3.80%  | 0.00%  | 96.18% |
| 35      | 10.0     | 0.99   | 25.23 | 7.07 | 0.00%        | 4.61%  | 0.00%  | 95.39% |
| 35      | 10.0     | 0.99   | 22.98 | 7.03 | 0.02%        | 4.74%  | 0.00%  | 95.24% |
| 40      | 10.0     | 0.99   | 22.98 | 7.03 | 0.02%        | 5.76%  | 0.00%  | 94.22% |
| 40      | 10.0     | 0.99   | 22.98 | 7.03 | 0.00%        | 5.69%  | 0.00%  | 94.31% |
| 45      | 10.0     | 0.99   | 22.98 | 7.03 | 0.00%        | 7.22%  | 0.00%  | 92.78% |
| 45      | 10.0     | 0.99   | 22.98 | 7.03 | 0.02%        | 7.18%  | 0.00%  | 92.80% |
| 50      | 10.0     | 0.99   | 22.98 | 7.03 | 0.02%        | 9.35%  | 0.00%  | 90.64% |
| 50      | 10.0     | 0.99   | 22.98 | 7.03 | 0.00%        | 9.53%  | 0.00%  | 90.47% |
| 60      | 10.0     | 0.99   | 22.98 | 7.03 | 0.02%        | 14.79% | 0.00%  | 85.19% |
| 60      | 10.0     | 0.99   | 22.98 | 7.03 | 0.02%        | 15.82% | 0.00%  | 84.16% |
| 32      | 10.0     | 0.99   | 10.00 | 6.08 | 0.02%        | 4.69%  | 0.00%  | 95.29% |
| 31      | 10.0     | 0.99   | 10.00 | 6.08 | 0.02%        | 4.44%  | 0.00%  | 95.54% |
| 31      | 10.0     | 0.99   | 10.00 | 6.08 | 0.02%        | 4.52%  | 0.00%  | 95.47% |
| 36      | 10.0     | 0.99   | 10.01 | 6.08 | 0.02%        | 5.59%  | 0.00%  | 94.39% |
| 35      | 10.0     | 0.99   | 10.01 | 6.08 | 0.02%        | 5.41%  | 0.00%  | 94.57% |
| 40      | 10.0     | 0.99   | 10.01 | 6.08 | 0.02%        | 6.72%  | 0.00%  | 93.27% |
| 40      | 10.0     | 0.99   | 10.01 | 6.08 | 0.02%        | 6.97%  | 0.00%  | 93.01% |
| 45      | 10.0     | 0.99   | 10.01 | 6.08 | 0.02%        | 8.25%  | 0.00%  | 91.74% |
| 45      | 10.0     | 0.99   | 10.01 | 6.08 | 0.02%        | 8.27%  | 0.00%  | 91.71% |
| 50      | 10.0     | 0.99   | 10.01 | 6.08 | 0.02%        | 10.57% | 0.00%  | 89.41% |
| 50      | 10.0     | 0.99   | 10.01 | 6.06 | 0.02%        | 10.95% | 0.00%  | 89.03% |
| 55      | 10.0     | 0.99   | 10.01 | 6.06 | 0.02%        | 13.79% | 0.00%  | 86.19% |
| 55      | 10.0     | 0.99   | 10.00 | 6.06 | 0.02%        | 14.14% | 0.00%  | 85.84% |
| 60      | 10.0     | 0.99   | 10.00 | 6.07 | 0.02%        | 18.63% | 0.00%  | 81.36% |
| 60      | 10.0     | 0.99   | 10.03 | 6.08 | 0.02%        | 19.66% | 0.00%  | 80.32% |
| 30      | 10.0     | 1.19   | 10.03 | 6.06 | 0.02%        | 5.18%  | 0.00%  | 94.80% |
| 30      | 10.0     | 1.19   | 10.07 | 6.06 | 0.02%        | 5.11%  | 0.00%  | 94.87% |
| 30      | 10.0     | 1.19   | 10.07 | 6.06 | 0.02%        | 5.04%  | 0.00%  | 94.94% |
| 35      | 10.0     | 1.19   | 10.00 | 6.07 | 0.02%        | 5.92%  | 0.00%  | 94.06% |
| 35      | 10.0     | 1.19   | 10.00 | 6.07 | 0.02%        | 5.98%  | 0.00%  | 94.01% |
| 40      | 10.0     | 1.19   | 10.00 | 6.05 | 0.02%        | 6.80%  | 0.00%  | 93.19% |
| 40      | 10.0     | 1.19   | 10.00 | 6.05 | 0.01%        | 7.14%  | 0.00%  | 92.85% |
| 45      | 10.0     | 1.19   | 10.00 | 6.06 | 0.01%        | 8.51%  | 0.00%  | 91.48% |
| 45      | 10.0     | 1.19   | 10.00 | 6.06 | 0.01%        | 8.20%  | 0.00%  | 91.78% |
| 50      | 10.0     | 1.19   | 10.00 | 6.06 | 0.01%        | 9.92%  | 0.00%  | 90.06% |
| 50      | 10.0     | 1.19   | 10.00 | 6.06 | 0.01%        | 10.42% | 0.00%  | 89.57% |
| 55      | 10.0     | 1.19   | 10.00 | 6.06 | 0.01%        | 13.33% | 0.00%  | 86.66% |
| 55      | 10.0     | 1.19   | 10.02 | 6.06 | 0.01%        | 13.72% | 0.00%  | 86.27% |
| 60      | 10.0     | 1.19   | 10.02 | 6.06 | 0.01%        | 18.23% | 0.00%  | 81.76% |
| 60      | 10.0     | 1.19   | 10.02 | 6.06 | 0.01%        | 18.60% | 0.00%  | 81.39% |

**[0199] Example 3:** Hydrogenation of HCFO-1233xf to HCFC-253db in liquid phase with 0.5%Pd/C

**[0200]** 8g 0.5%Pd/C was loaded into a 400ml Hastelloy C shaker tube. Then the shaker tube was chilled to -30°C and vacuumed. 200g of HCFO-1233xf was charged into shaker, and the tube was heated back to 100°C. At 100°C, H<sub>2</sub> was added slowly to 250 psig pressure. The pressure drop quickly indicated the reaction happened at this condition. The H<sub>2</sub> was further added until the pressure of reactor does not drop anymore. About 3g of H<sub>2</sub> were added at end of the test. The product of the reaction was analyzed by GC-MS-FID and is shown in Table 4 below.

**TABLE 4**

| Compounds | GC-FID area% |
|-----------|--------------|
| 263fb     | 7.95%        |
| 1233xf    | 55.66%       |
| 253db     | 36.39%       |

**[0201] Example 4:** Hydrogenation of HCFO-1233xf to HCFC-253db in liquid phase with 5%Pd/C

**[0202]** 8g 5%Pd/C was loaded into a 400ml Hastelloy C shaker tube. The tube was pressure purged with H<sub>2</sub> three times, then shaker tube was pressured with H<sub>2</sub> to 250 psig and heated to 60°C for 3hr. After that, the H<sub>2</sub> was vented off and shaker tube was chilled to -30°C and vacuumed. 200g of HCFO-1233xf was charged into shaker, and the tube was heated back to 40°C. At 40°C, H<sub>2</sub> was added slowly to 250 psig pressure. The pressure drop quickly indicated the reaction happened at this condition. The H<sub>2</sub> was further added until the pressure of reactor does not drop anymore. There was about 3g of H<sub>2</sub> added at end of the test. The product of the reaction was analyzed by GC-MS-FID and is shown in Table 5 below.

**TABLE 5: GC analysis of product with 5% Pd/C as catalyst.**

| Compounds | GC FID area% |
|-----------|--------------|
| 263fb     | 3.2421%      |
| 244bb     | 0.3751%      |
| 1233xf    | 1.2550%      |
| 253db     | 95.1277%     |

**[0203] Example 5:** Hydrogenation of HCFC-253db to HFO-1252zc in vapor phase with 4% Au/Carbon

**[0204]** In a 12-inch long ½" OD Monel reactor, 4ml 4%/Au/C is loaded. The catalyst is treated at 200°C by a flow of H<sub>2</sub> for 1 hour. Then, the reactor is heated to 260°C. 10 sccm H<sub>2</sub> is fed and controlled by a mass flow controller and HCFC-253db is fed by a pump at 0.5ml/hr rate. The reactor effluent is analyzed by online GC-MS-FID. The results of the analysis show about 20 mol% of HFO-1252zc is formed in the reaction mixture and the main byproduct is HFC-263fb.

**[0205] Example 6:** Converting HCFC-253db to HFO-1252zc in liquid phase by zinc powder

**[0206]** 20 g preactivated zinc powder (activated by 2% HCl) and 50 g ethanol are added into a 400ml Hastelloy C autoclave. After it is heated to 70°C, 20 g HCFC-253db is added into the reactor. The increase of reactor pressure is an indication that the reaction has occurred. After stirring at 70°C for 30 minutes, the reactor temperature is further increased to 90°C and the contents are stirred at 90°C for 2 hrs. After the reactor is cooled down to room temperature, the product from the reactor is analyzed by GC-MS-FID, which shows about 30% HFO-1252zc is formed. The main byproduct is HFC-263fb.

**[0207] Example 7:** Converting HCFC-253db to HFO-1252zc in liquid phase by zinc powder with TBAB at 140°C.

**[0208]** 0.8g preactivated zinc powder (activated by 2% HCl), 0.13g TBAB, 1.25 g 253db, and 4g methanol were added into a 10ml Hastelloy C autoclave. Then, the autoclave was chilled to -40°C and was evacuated. After that, it was heated to 140°C and maintained at 140°C for 16 hours with agitation. The reactor pressure increased to about 820 psig. Then, the reactor was cooled down to room temperature. The vapor portion of the product from reactor was analyzed by GC-MS-FID and the results are listed in Table 6 below.

TABLE 6

| Compounds | GC area% |
|-----------|----------|
| E-1132    | 0.0629%  |
| Z-1132    | 0.0040%  |

| Compounds         | GC area% |
|-------------------|----------|
| 1243zf            | 0.1467%  |
| propylene         | 0.1326%  |
| propane           | 0.2002%  |
| 263fb             | 2.6636%  |
| 1252zc            | 67.2581% |
| 1345              | 0.0027%  |
| 1261ze            | 0.0256%  |
| 1252 isomer       | 0.0057%  |
| methanol          | 6.4856%  |
| 2-butene          | 0.0250%  |
| butane            | 0.0063%  |
| 1233xf            | 0.0422%  |
| 253db             | 22.7905% |
| acetone           | 0.0886%  |
| 2-methoxy-Propane | 0.0031%  |
| 2-chloropropane   | 0.0443%  |
| Others            | 0.0123%  |

**[0209] Example 8:** Converting HCFC-253db to HFO-1252zc in liquid phase by zinc powder with TBAB at 120°C.

**[0210]** 1g preactivated zinc powder (activated by 2% HCl), 0.25g TBAB, 1 g 253db, and 4g methanol were added into a 10ml Hastelloy C autoclave. Then, the autoclave was chilled to -40°C and was evacuated. After that, it was heated to 120°C and maintained at 120°C for 16 hours with agitation. The reactor pressure increased to about 1040 psig. Then, the reactor was cooled down to room temperature. The vapor portion of the product from reactor was analyzed by GC-MS-FID and the results are listed in Table 7 below.

TABLE 7

| Compounds  | GC area% |
|------------|----------|
| E-1132     | 0.0367%  |
| 1243zf     | 0.0207%  |
| Propylene  | 0.0393%  |
| 1252zc     | 29.6063% |
| 1261ze     | 0.0115%  |
| 1252isomer | 0.0243%  |
| methanol   | 58.3130% |
| 1233xf     | 0.0421%  |
| 253db      | 11.2606% |
| acetone    | 0.5328%  |

| Compounds          | GC area% |
|--------------------|----------|
| 2-methoxy- Propane | 0.0424%  |
| 2-chloropropane    | 0.0245%  |
| Others             | 0.0459%  |

**[0211] Example 9:** Converting HCFC-253db to HFO-1252zc in liquid phase by zinc powder with  $\text{ZnCl}_2$  at 120°C.

**[0212]** 1 g preactivated zinc powder (activated by 2% HCl), 0.25g  $\text{ZnCl}_2$ , 1 g 253db, and 4g methanol were added into a 10ml Hastelloy C autoclave. Then, the autoclave was chilled to -40°C and was evacuated. After that, it was heated to 120°C and maintained at 120°C for 16 hours with agitation. The reactor pressure increased to about 1040 psig. Then, the reactor was cooled down to room temperature. The vapor portion of the product from the reactor was analyzed by GC-MS-FID and the results are listed in Table 8 below.

TABLE 8

| Compounds         | GC FID area% |
|-------------------|--------------|
| E-1132            | 0.0064%      |
| Z-1132            | 0.0008%      |
| 1243zf            | 0.0111%      |
| Propylene         | 0.0674%      |
| Propane           | 0.0229%      |
| 263fb             | 1.6448%      |
| 1252zc            | 33.7686%     |
| 1261ze            | 0.0109%      |
| 1252 isomer       | 0.0049%      |
| Methanol          | 17.6571%     |
| 253db             | 46.5525%     |
| 1242zf            | 0.0054%      |
| Acetone           | 0.0151%      |
| 2-methoxy-propane | 0.0792%      |
| 2-chloropropane   | 0.0067%      |
| 1232xf            | 0.1017%      |
| 252dc             | 0.0352%      |
| Others            | 0.0093%      |

**[0213] Example 10:** Hydrogenation of HBFO-1233xfB to HBFC-253dbB in vapor phase with 0.5%Pd/ $\text{Al}_2\text{O}_3$

**[0214]** In a 12-inch long ½" OD Monel reactor, 8ml 0.5% Pd/ $\text{Al}_2\text{O}_3$  was loaded. The catalyst was treated at 120°C by a flow of  $\text{H}_2$  for 1 hour. Then, the reactor was

cooled down to 30°C. H<sub>2</sub> and N<sub>2</sub> feeds were controlled by a mass flow controller and HBFO-1233xfB was fed by a pump. The reaction test conditions are listed in Table 9 below. The reactor effluent was analyzed by online GC-MS-FID at time indicated in Table 10 below. The results of the analysis are listed in Table 10 below which shows complete high conversion of HBFO-1233xfB and good selectivity to HBFC-253dbB.

TABLE 9

| Temp<br>°C | P<br>psig | 1233xfB<br>cc/hr | N2<br>sccm | H2<br>sccm | product GC FID area% |        |         |          |        |
|------------|-----------|------------------|------------|------------|----------------------|--------|---------|----------|--------|
|            |           |                  |            |            | 1243zf               | 263fb  | 1233xfB | 253db-Br | Others |
| 70         | 10        | 0.8              | 10.41      | 7.02       | 0.00%                | 63.84% | 0.00%   | 34.55%   | 1.61%  |
| 70         | 10        | 0.8              | 10.41      | 7.06       | 0.71%                | 31.37% | 0.00%   | 64.50%   | 3.42%  |
| 70         | 10        | 0.8              | 10.37      | 7.07       | 4.93%                | 18.04% | 30.69%  | 44.20%   | 2.13%  |
| 40         | 5.1       | 0.8              | 10.37      | 7.04       | 1.39%                | 1.22%  | 89.94%  | 7.27%    | 0.18%  |
| 40         | 5.1       | 0.8              | 10.34      | 7.04       | 1.45%                | 1.32%  | 88.77%  | 8.30%    | 0.17%  |
| 45         | 4.9       | 0.8              | 10.34      | 7.07       | 1.97%                | 1.97%  | 84.96%  | 10.91%   | 0.19%  |
| 45         | 5.2       | 0.8              | 10.34      | 7.07       | 1.90%                | 1.85%  | 85.64%  | 10.43%   | 0.19%  |
| 50         | 5.1       | 0.8              | 10.36      | 7.07       | 2.38%                | 2.37%  | 83.33%  | 11.70%   | 0.21%  |
| 50         | 5.1       | 0.8              | 10.36      | 7.02       | 2.27%                | 2.23%  | 84.06%  | 11.23%   | 0.21%  |
| 55         | 5.1       | 0.8              | 10.34      | 7.06       | 2.83%                | 2.82%  | 81.48%  | 12.35%   | 0.52%  |
| 55         | 5.1       | 0.8              | 10.33      | 7.08       | 2.69%                | 2.62%  | 82.44%  | 11.77%   | 0.48%  |
| 60         | 5.2       | 0.8              | 10.33      | 7.08       | 3.16%                | 2.96%  | 81.64%  | 11.67%   | 0.56%  |
| 60         | 5         | 0.8              | 10.34      | 7.02       | 3.17%                | 2.95%  | 81.57%  | 11.75%   | 0.57%  |
| 65         | 10        | 0.8              | 10.34      | 7.08       | 3.83%                | 3.98%  | 75.28%  | 16.16%   | 0.74%  |
| 65         | 10        | 0.8              | 10.34      | 7.08       | 3.32%                | 2.97%  | 80.76%  | 12.23%   | 0.72%  |
| 65         | 10        | 0.8              | 10.34      | 7.09       | 3.18%                | 2.73%  | 82.05%  | 11.37%   | 0.68%  |
| 70         | 10        | 0.8              | 10.36      | 7.08       | 3.71%                | 3.13%  | 80.78%  | 11.64%   | 0.74%  |
| 70         | 10        | 0.8              | 10.35      | 7.08       | 3.66%                | 3.05%  | 81.14%  | 11.41%   | 0.74%  |
| 75         | 10        | 0.8              | 10.35      | 7.05       | 4.31%                | 3.55%  | 79.58%  | 11.71%   | 0.86%  |
| 75         | 10        | 0.8              | 10.34      | 7.05       | 4.23%                | 3.42%  | 80.01%  | 11.50%   | 0.84%  |
| 80         | 10        | 0.8              | 5          | 7.07       | 5.52%                | 6.17%  | 66.33%  | 20.58%   | 1.40%  |
| 80         | 10        | 0.8              | 5          | 7.04       | 4.27%                | 3.48%  | 77.90%  | 13.27%   | 1.07%  |
| 90         | 10        | 0.8              | 5          | 7.07       | 7.09%                | 7.11%  | 66.16%  | 17.73%   | 1.91%  |
| 90         | 10        | 0.8              | 5          | 7.07       | 6.80%                | 6.55%  | 67.40%  | 17.43%   | 1.82%  |
| 100        | 10        | 0.8              | 5          | 7.07       | 9.04%                | 8.77%  | 63.44%  | 16.34%   | 2.42%  |
| 100        | 10        | 0.8              | 5          | 7.07       | 9.05%                | 8.99%  | 62.63%  | 17.09%   | 2.24%  |
| 80         | 10        | 0.5              | 0          | 12.03      | 4.05%                | 20.28% | 17.50%  | 56.42%   | 1.74%  |
| 80         | 10        | 0.5              | 0          | 12.03      | 4.20%                | 19.59% | 19.21%  | 55.28%   | 1.73%  |
| 90         | 10        | 0.5              | 0          | 12.03      | 3.75%                | 27.73% | 9.24%   | 56.74%   | 2.54%  |
| 90         | 10        | 0.5              | 0          | 12.03      | 3.94%                | 27.28% | 10.31%  | 56.03%   | 2.44%  |
| 100        | 10        | 0.5              | 0          | 12.03      | 3.05%                | 34.79% | 4.81%   | 53.53%   | 3.83%  |
| 100        | 10        | 0.5              | 0          | 12.03      | 2.30%                | 36.05% | 3.06%   | 54.86%   | 3.73%  |
| 110        | 10        | 0.5              | 0          | 12.03      | 1.08%                | 43.66% | 0.00%   | 49.96%   | 5.30%  |

| Temp<br>°C | P<br>psig | 1233xfB<br>cc/hr | N2<br>sccm | H2<br>sccm | product GC FID area% |        |         |          |        |
|------------|-----------|------------------|------------|------------|----------------------|--------|---------|----------|--------|
|            |           |                  |            |            | 1243zf               | 263fb  | 1233xfB | 253db-Br | Others |
| 110        | 10        | 0.5              | 0          | 12.03      | 0.12%                | 47.92% | 0.00%   | 47.57%   | 4.38%  |
| 100        | 10        | 0.78             | 0          | 14.97      | 0.00%                | 55.29% | 0.00%   | 43.07%   | 1.65%  |
| 100        | 10.1      | 0.78             | 0          | 14.97      | 0.00%                | 43.63% | 0.00%   | 54.38%   | 1.99%  |
| 100        | 10        | 0.78             | 0          | 14.93      | 0.00%                | 68.90% | 0.00%   | 29.33%   | 1.76%  |
| 105        | 10        | 0.78             | 0          | 14.93      | 0.00%                | 47.67% | 0.00%   | 49.49%   | 2.84%  |
| 105        | 10        | 0.78             | 0          | 14.98      | 0.00%                | 72.24% | 0.00%   | 24.98%   | 2.78%  |
| 110        | 10        | 0.78             | 0          | 14.98      | 2.49%                | 39.67% | 0.00%   | 49.07%   | 8.77%  |
| 110        | 10        | 0.78             | 0          | 14.98      | 3.99%                | 38.79% | 5.88%   | 46.68%   | 4.66%  |
| 100        | 10        | 0.78             | 0          | 15.01      | 5.54%                | 27.41% | 15.19%  | 49.02%   | 2.84%  |
| 100        | 10        | 0.78             | 0          | 15.01      | 6.18%                | 25.55% | 19.02%  | 46.67%   | 2.57%  |
| 100        | 10        | 0.78             | 0          | 14.98      | 3.14%                | 37.69% | 4.06%   | 52.72%   | 2.39%  |
| 105        | 10        | 0.78             | 0          | 14.98      | 0.30%                | 45.07% | 0.00%   | 52.00%   | 2.63%  |
| 105        | 10        | 0.78             | 0          | 14.97      | 7.08%                | 6.73%  | 65.73%  | 18.95%   | 1.51%  |
| 110        | 10        | 0.78             | 0          | 14.97      | 8.62%                | 26.55% | 22.48%  | 39.05%   | 3.31%  |
| 110        | 10.1      | 0.78             | 0          | 14.97      | 7.29%                | 30.66% | 16.31%  | 42.27%   | 3.47%  |

**TABLE 10:** Detailed GC analysis of reaction  
product at condition 80°C, 1233xfB feed at 0.5ml/hr rate

| Compounds                                                    | GC FID area% |
|--------------------------------------------------------------|--------------|
| Propane                                                      | 0.2828%      |
| 1243zf                                                       | 3.9716%      |
| 263fb                                                        | 22.9652%     |
| HCC-30                                                       | 0.0206%      |
| 1233xf/HFC-374                                               | 0.3123%      |
| 1251                                                         | 0.0032%      |
| 1233xfB                                                      | 16.3881%     |
| 253dbB                                                       | 55.1736%     |
| 1242xfB                                                      | 0.3312%      |
| 243 isomer                                                   | 0.0476%      |
| C <sub>3</sub> H <sub>3</sub> Br <sub>2</sub> F <sub>3</sub> | 0.4622%      |
| Others                                                       | 0.0416%      |

**[0215] Example 11:** Converting HBFC-253dbB to HFO-1252zc in liquid phase by zinc powder with TBAB at 60°C.

**[0216]** 73  $\mu$ L CF<sub>3</sub>CHBrCH<sub>3</sub> was mixed with 50 mg Zn and 40 mg TBAB in 2.5 mL MeOH in an NMR tube. The mixture rested at ambient temperature for a few hours, during which time about half of the reaction occurred. The second half test was done at 60°C and recorded by NMR. The results of the NMR analysis during reaction at 60°C are shown in Fig. 2. The reaction was clean and only had ~ 0.5% byproduct.

**Other Embodiments**

**[0217]** Embodiment 1. A process of making a compound of formula (II), the process comprising contacting a compound of formula (I) with hydrogen in the presence of a catalyst,  $\text{CF}_3\text{CX}=\text{CH}_2$  (I);  $\text{CF}_3\text{CHXCH}_3$  (II), wherein X is selected from the group consisting of Cl, Br and I.

**[0218]** Embodiment 2. A process of making HFO-1252zc ( $\text{CF}_2=\text{CHCH}_3$ ), the process comprising contacting a compound of formula (II) with a metal or with hydrogen,  $\text{CF}_3\text{CHXCH}_3$  (II), wherein X is selected from the group consisting of Cl, Br and I.

**[0219]** Embodiment 3. A process of making HFO-1252zc ( $\text{CF}_2=\text{CHCH}_3$ ), the process comprising: (i) converting a precursor compound of formula (I) to an intermediate compound of formula (II) by reaction of the precursor compound with hydrogen in the presence of a catalyst, and (ii) converting the intermediate compound of formula (II) to HFO-1252zc by reaction of the intermediate compound with a metal or with hydrogen,  $\text{CF}_3\text{CX}=\text{CH}_2$  (I);  $\text{CF}_3\text{CHXCH}_3$  (II), wherein X is selected from the group consisting of Cl, Br and I.

**[0220]** Embodiment 4. The process of any of Embodiments 1 or 3, wherein the formula (I) compound is 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf,  $\text{CF}_3\text{CCl}=\text{CH}_2$ ) and the formula (II) compound is 2-chloro-1,1,1-trifluoropropane (HCFC-253db,  $\text{CF}_3\text{CHClCH}_3$ ).

**[0221]** Embodiment 5. The process of any of Embodiments 1 or 3 to 4, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase or the liquid phase.

**[0222]** Embodiment 6. The process of any of Embodiments 1 or 3 to 5, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the presence of a catalyst comprising a metal.

**[0223]** Embodiment 7. The process of Embodiment 6, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support.

[0224] Embodiment 8. The process of Embodiment 7, wherein the support is selected from the group consisting of carbon, graphite and a metal oxide.

[0225] Embodiment 9. The process of any of Embodiments 6 to 8, wherein the catalyst is Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C.

[0226] Embodiment 10. The process of any of Embodiments 1 or 3 to 9, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase in the presence of a catalyst, wherein preferably the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.01 wt.% to about 0.1 wt.%, preferably from about 0.02 wt.% to about 0.05 wt.%, based on the total weight of the support and catalyst.

[0227] Embodiment 11. The process of Embodiment 10, wherein the catalyst is a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, and wherein preferably the Pd loading is in the range of 0.01 wt.% to 0.05 wt.%.

[0228] Embodiment 12. The process of any of Embodiments 1 or 3 to 11, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase at a temperature between about 20°C to about 80°C, preferably about 20°C and about 60°C.

[0229] Embodiment 13. The process of any of Embodiments 1 or 3 to 12, wherein a molar ratio of hydrogen to the formula (I) compound for vapor phase conversion of the formula (I) compound to the formula (II) compound is in the range of from about 0.5:1 to about 3:1, preferably from about 1:1 to about 2:1.

[0230] Embodiment 14. The process of any of Embodiments 1 or 3 to 9, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the liquid phase in the presence of a catalyst, wherein preferably the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.01 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst.

**[0231]** Embodiment 15. The process of Embodiment 14, wherein the catalyst is a Pd/C catalyst, and wherein preferably the Pd loading is in the range of 0.1 wt.% to 10 wt.%.

**[0232]** Embodiment 16. The process of any of Embodiments 1, 3 to 9 or 14 to 15, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the liquid phase at a temperature between about 20°C to about 120°C, preferably about 30°C and about 110°C.

**[0233]** Embodiment 17. The process of any of Embodiments 1, 3 to 9 or 14 to 16, wherein a molar ratio of hydrogen to the formula (I) compound for liquid phase conversion of the formula (I) compound to the formula (II) compound is in the range of from about 0.5:1 to about 2:1, preferably from about 0.8:1 to about 1.2:1.

**[0234]** Embodiment 18. The process of any of Embodiments 1 or 3, wherein the formula (I) compound is 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB,  $\text{CF}_3\text{CBr}=\text{CH}_2$ ) and the formula (II) compound is 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB,  $\text{CF}_3\text{CHBrCH}_3$ ).

**[0235]** Embodiment 19. The process of any of Embodiments 1, 3 or 18, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase or the liquid phase.

**[0236]** Embodiment 20. The process of any of Embodiments 1, 3 or 18 to 19, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the presence of a catalyst comprising a metal.

**[0237]** Embodiment 21. The process of any of Embodiments 1, 3 or 18 to 20, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, the support preferably being selected from the group consisting of carbon, graphite and a metal oxide.

**[0238]** Embodiment 22. The process of Embodiment 21, wherein the catalyst is Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C.

**[0239]** Embodiment 23. The process of any of Embodiments 1, 3 or 18 to 22, wherein conversion of the formula (I) compound to the formula (II) compound is

conducted in the vapor phase in the presence of a catalyst, wherein preferably the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.1 wt.% to about 1.0 wt.%, preferably from about 0.2 wt.% to about 0.8 wt.%, based on the total weight of the support and catalyst.

**[0240]** Embodiment 24. The process of Embodiment 23, wherein the catalyst is a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, and wherein preferably the Pd loading is in the range of 0.1 wt.% to 1.0 wt.%.

**[0241]** Embodiment 25. The process of any of Embodiments 1, 3 or 18 to 24, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase at a temperature between about 30°C to about 130°C, preferably about 60°C and about 110°C.

**[0242]** Embodiment 26. The process of any of Embodiments 1, 3 or 18 to 25, wherein a molar ratio of hydrogen to the formula (I) compound for vapor phase conversion of the formula (I) compound to the formula (II) compound is in the range of from about 1:1 to about 10:1, preferably from about 2:1 to about 8:1.

**[0243]** Embodiment 27. The process of any of Embodiments 1, 3 or 18 to 22, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the liquid phase in the presence of a catalyst, wherein preferably the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.1 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst.

**[0244]** Embodiment 28. The process of Embodiment 27, wherein the catalyst is a Pd/C catalyst, and wherein preferably the Pd loading is in the range of 0.1 wt.% to 10 wt.%.

**[0245]** Embodiment 29. The process of any of Embodiments 1, 3, 18 to 22 or 27 to 28, wherein conversion of the formula (I) compound to the formula (II) compound

is conducted in the liquid phase at a temperature between about 40°C to about 120°C, preferably about 60°C and about 100°C.

**[0246]** Embodiment 30. The process of any of Embodiments 1, 3, 18 to 22 or 27 to 29, wherein a molar ratio of hydrogen to the formula (I) compound for liquid phase conversion of the formula (I) compound to the formula (II) compound is in the range of from about 0.5:1 to about 3:1, preferably from about 0.8:1 to about 2:1.

**[0247]** Embodiment 31. The process of any of Embodiments 2 or 3, wherein the formula (II) compound is 2-chloro-1,1,1-trifluoropropane (HCFC-253db,  $\text{CF}_3\text{CHClCH}_3$ ) or 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB,  $\text{CF}_3\text{CHBrCH}_3$ ).

**[0248]** Embodiment 32. The process of any of Embodiments 2, 3 or 31, wherein the formula (II) compound is contacted with hydrogen in the presence of a catalyst, preferably in the vapor phase.

**[0249]** Embodiment 33. The process of Embodiment 32, wherein the catalyst comprises a metal catalyst, preferably the catalyst comprises a metal selected from the group consisting of Ni, Cu, Au and combinations thereof, with or without a support, wherein preferably the support is selected from the group consisting of carbon, graphite and a metal oxide.

**[0250]** Embodiment 34. The process of any of Embodiments 32 to 33, wherein the catalyst is Au/C or Cu/C.

**[0251]** Embodiment 35. The process of any of Embodiments 32 to 34, wherein the amount of catalyst on the support ranges from about 2 wt.% to about 10 wt.%, based on the total weight of the support and catalyst.

**[0252]** Embodiment 36. The process of any of Embodiments 2, 3, or 31 to 35, wherein conversion of the formula (II) compound to HFO-1252zc is conducted in the vapor phase at a temperature between about 200°C to about 500°C, preferably about 300°C and about 450°C.

**[0253]** Embodiment 37. The process of any of Embodiments 2, 3, or 31 to 36, wherein a molar ratio of hydrogen to the formula (II) compound is in the range of from about 5:1 to about 40:1, preferably from about 10:1 to about 30:1.

**[0254]** Embodiment 38. The process of any of Embodiments 2, 3 or 31, wherein the formula (II) compound is contacted with a metal in the absence or presence of a catalyst, preferably in the liquid phase.

**[0255]** Embodiment 39. The process of any of Embodiments 2, 3, 31 or 38, wherein the metal is selected from the group consisting of zinc, magnesium and a combination thereof.

**[0256]** Embodiment 40. The process of any of Embodiments 38 to 39, wherein the metal is activated by an acid before being contacted with the formula (II) compound.

**[0257]** Embodiment 41. The process of any of Embodiments 38 to 40, wherein the metal comprises zinc that has been activated by HCl.

**[0258]** Embodiment 42. The process of any of Embodiments 2, 3, 31 or 38 to 41, wherein the reaction is conducted in the presence of a catalyst, preferably the catalyst is selected from the group consisting of zinc salt, ammonium salt and phosphonium salt.

**[0259]** Embodiment 43. The process of Embodiment 42, wherein the catalyst is selected from the group consisting of zinc acetate,  $\text{ZnCl}_2$  and tetrabutylammonium bromide.

**[0260]** Embodiment 44. The process of any of Embodiments 2, 3, 31 or 38 to 43, wherein the reaction is conducted in the presence of a solvent, preferably a solvent selected from the group consisting of alcohol, amide, pyridine and ether, more preferably a solvent comprising an alcohol selected from the group consisting of methanol, ethanol, propanol, isopropanol and ethylene glycol.

**[0261]** Embodiment 45. The process of any of Embodiments 2, 3, 31 or 38 to 44, wherein the formula (II) compound is HCFC-253db and wherein conversion of the formula (II) compound to HFO-1252zc is conducted in the liquid phase at a temperature between about 50°C to about 180°C, preferably about 80°C and about 150°C.

**[0262]** Embodiment 46. The process of any of Embodiments 2, 3, 31 or 38 to 45, wherein the formula (II) compound is HBFC-253dbB and wherein conversion of the

formula (II) compound to HFO-1252zc is conducted in the liquid phase at a temperature between about 40°C to about 120°C, preferably about 50°C and about 100°C.

**[0263]** Embodiment 47. The process of any of Embodiments 2, 3, 31 or 38 to 46, wherein a molar ratio of the metal to the formula (II) compound is in the range of from about 1:1 to about 5:1, preferably from about 1.05:1 to about 3:1.

**[0264]** Embodiment 48. A process of making HCFC-253db, the process comprising contacting HCFO-1233xf with hydrogen in the presence of a catalyst.

**[0265]** Embodiment 49. The process of Embodiment 48, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.01 wt.% to about 0.1 wt.%, preferably from about 0.02 wt.% to about 0.05 wt.%, based on the total weight of the support and catalyst.

**[0266]** Embodiment 50. The process of Embodiment 48, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.01 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst.

**[0267]** Embodiment 51. A process of making HBFC-253dbB, the process comprising contacting HBFO-1233xfB with hydrogen in the presence of a catalyst.

**[0268]** Embodiment 52. The process of Embodiment 51, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.1 wt.% to about 1.0 wt.%, preferably from about 0.2 wt.% to about 0.8 wt.%, based on the total weight of the support and catalyst.

**[0269]** Embodiment 53. The process of Embodiment 51, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount

of catalyst on the support ranges from about 0.1 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst.

**[0270]** Embodiment 54. A process of making HFO-1252zc, the process comprising contacting HCFC-253db or HBFC-253dbB with a metal in the absence or presence of a catalyst and/or a solvent, wherein the metal is selected from the group consisting of zinc, magnesium and a combination thereof.

**[0271]** Embodiment 55. The process of Embodiment 54, wherein the metal is activated by an acid before being contacted with the formula (II) compound.

**[0272]** Embodiment 56. The process of any of Embodiments 54 to 55, wherein the metal comprises zinc that has been activated by HCl.

**[0273]** Embodiment 57. The process of any of Embodiments 54 to 56, wherein the reaction is conducted in the presence of a catalyst, preferably the catalyst is selected from the group consisting of zinc salt, ammonium salt and phosphonium salt, and more preferably the catalyst is selected from the group consisting of zinc acetate,  $\text{ZnCl}_2$  and tetrabutylammonium bromide.

**[0274]** Embodiment 58. The process of any of Embodiments 54 to 57, wherein the reaction is conducted in the presence of a solvent, preferably a solvent selected from the group consisting of alcohol, amide, pyridine and ether, more preferably a solvent comprising an alcohol selected from the group consisting of methanol, ethanol, propanol, isopropanol and ethylene glycol.

**[0275]** Embodiment 59. A process of making HFO-1252zc, the process comprising contacting HCFC-253db or HBFC-253dbB with hydrogen in the presence of a catalyst.

**[0276]** Embodiment 60. The process of Embodiment 59, wherein the catalyst comprises a metal catalyst, preferably the catalyst comprises a metal selected from the group consisting of Ni, Cu, Au and combinations thereof, with or without a support, wherein preferably the support is selected from the group consisting of carbon, graphite and a metal oxide.

**[0277]** Embodiment 61. The process of any of Embodiments 59 to 60, wherein the catalyst is Au/C or Cu/C.

**[0278]** Embodiment 62. The process of any of Embodiments 59 to 61, wherein the amount of catalyst on the support ranges from about 2 wt. % to about 10 wt. %, based on the total weight of the support and catalyst.

**[0279]** Embodiment 63. A process of making HFO-1252zc, the process comprising: (i) converting HCFO-1233xf to HCFC-253db by reaction of the HCFO-1233xf with hydrogen in the presence of a catalyst, and (ii) converting the HCFC-253db to HFO-1252zc by reaction of the HCFC-253db with a metal in the absence or presence of a catalyst and/or a solvent, wherein the metal is selected from the group consisting of zinc, magnesium and a combination thereof, or with hydrogen in the presence of a catalyst.

**[0280]** Embodiment 64. A process of making HFO-1252zc, the process comprising: (i) converting HBFO-1233xfB to HBFC-253dbB by reaction of the HBFO-1233xfB with hydrogen in the presence of a catalyst, and (ii) converting the HBFC-253dbB to HFO-1252zc by reaction of the HBFC-253dbB with a metal in the absence or presence of a catalyst and/or a solvent, wherein the metal is selected from the group consisting of zinc, magnesium and a combination thereof, or with hydrogen in the presence of a catalyst.

**[0281]** Embodiment 65. A system comprising sources of HCFO-1233xf and hydrogen or of HBFO-1233xfB and hydrogen, first and second reactors for respectively conducting different reactions, optionally at least one mixer connected to the first reactor for premixing reactants comprising hydrogen and HCFO-1233xf or hydrogen and HBFO-1233xfB, the second reactor arranged downstream of the first reactor, wherein said first reactor produces a first intermediate product mixture and the second reactor converts the intermediate product produced in said first reactor, wherein the first reactor is configured to operate in the vapor or liquid phase and said second reactor is configured to operate in the vapor or liquid phase.

**[0282]** Embodiment 66. The system of Embodiment 65, wherein unreacted HCFO-1233xf or HBFO-1233xfB from the first reactor is recycled.

**[0283]** Embodiment 67. A process for converting HCFO-1233xf or HBFO-1233xfB to HFO-1252zc using the system of any of Embodiments 65 to 66.

**[0284]** Embodiment 68. A composition comprising, consisting essentially of, or consisting of one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

**[0285]** Embodiment 69. The composition of Embodiment 68, wherein the composition comprises HFC-263fb and HCFC-253db.

**[0286]** Embodiment 70. The composition of Embodiment 68, wherein the composition comprises HCFO-1233xf, HFC-263fb and HCFC-253db.

**[0287]** Embodiment 71. The composition of Embodiment 68, wherein the composition comprises HFC-263fb, HCFO-1233xf and HCFC-253db.

**[0288]** Embodiment 72. The composition of Embodiment 68, wherein the composition comprises HFO-1252zc, HFC-263fb, HCFO-1233xf and HCFC-253db.

**[0289]** Embodiment 73. The composition of Embodiment 68, wherein the composition comprises HFC-263fb and HBFC-253dbB.

**[0290]** Embodiment 74. The composition of Embodiment 68, wherein the composition comprises HFC-263fb, HBFO-1233xfB and HBFC-253dbB.

**[0291]** Embodiment 75. The composition of Embodiment 68, wherein the composition comprises HFO-1252zc, HFC-263fb, HBFO-1233xfB and HBFC-253dbB.

**[0292]** Embodiment 76. The composition of Embodiment 68, wherein the composition comprises HCFO-1233xf, HFC-263fb, HFC-244bb and HFC-253db.

**[0293]** Embodiment 77. A composition comprising, consisting essentially of, or consisting of HFO-1252zc and one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

**[0294]** Embodiment 78. A composition comprising, consisting essentially of, or consisting of HFO-1252zc, HFO-1243zf, and one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), difluoropropene isomers (HFO-1252), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

**[0295]** Embodiment 79. A composition comprising, consisting essentially of, or consisting of HFO-1252zc, HFO-1261ze and one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-

263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

**[0296]** Embodiment 80. A composition comprising, consisting essentially of, or consisting of HFO-1252zc, HFC-263fb and one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

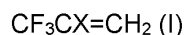
**[0297]** Embodiment 81. A composition comprising, consisting essentially of, or consisting of HBFO-1233xfB and one or more compounds selected from the group consisting of propane, 3,3,3-trifluoropropene (HFO-1243zf), 1,1,1-trifluoropropane (HFC-263fb), dichloromethane (HCC-30), 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), tetrafluorobutane (HFC-374), chlorofluoropropene (HCFO-1251), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3-difluoropropene (HBFO-1242xfB), dichlorotrifluoropropane isomers (HCFC-243), and dibromotrifluoropropane (C<sub>3</sub>H<sub>3</sub>Br<sub>2</sub>F<sub>3</sub>).

**[0298]** 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 compound of formula (II), the process comprising contacting a compound of formula (I) with hydrogen in the presence of a catalyst,



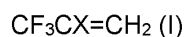
wherein X is selected from the group consisting of Cl, Br and I.

2. A process of making HFO-1252zc ( $\text{CF}_2=\text{CHCH}_3$ ), the process comprising contacting a compound of formula (II) with a metal or with hydrogen,



wherein X is selected from the group consisting of Cl, Br and I.

3. A process of making HFO-1252zc ( $\text{CF}_2=\text{CHCH}_3$ ), the process comprising:
  - (i) converting a precursor compound of formula (I) to an intermediate compound of formula (II) by reaction of the precursor compound with hydrogen in the presence of a catalyst, and
  - (ii) converting the intermediate compound of formula (II) to HFO-1252zc by reaction of the intermediate compound with a metal or with hydrogen,



wherein X is selected from the group consisting of Cl, Br and I.

4. The process of any of claims 1 or 3, wherein the formula (I) compound is 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf,  $\text{CF}_3\text{CCl}=\text{CH}_2$ ) and the formula (II) compound is 2-chloro-1,1,1-trifluoropropane (HCFC-253db,  $\text{CF}_3\text{CHClCH}_3$ ).
5. The process of any of claims 1 or 3 to 4, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase or the liquid phase.

6. The process of any of claims 1 or 3 to 5, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the presence of a catalyst comprising a metal.
7. The process of claim 6, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support.
8. The process of claim 7, wherein the support is selected from the group consisting of carbon, graphite and a metal oxide.
9. The process of any of claims 6 to 8, wherein the catalyst is Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C.
10. The process of any of claims 1 or 3 to 9, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase in the presence of a catalyst, wherein preferably the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.01 wt.% to about 0.1 wt.%, preferably from about 0.02 wt.% to about 0.05 wt.%, based on the total weight of the support and catalyst.
11. The process of claim 10, wherein the catalyst is a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, and wherein preferably the Pd loading is in the range of 0.01 wt.% to 0.05 wt.%.
12. The process of any of claims 1 or 3 to 11, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase at a temperature between about 20°C to about 80°C, preferably about 20°C and about 60°C.
13. The process of any of claims 1 or 3 to 12, wherein a molar ratio of hydrogen to the formula (I) compound for vapor phase conversion of the formula (I) compound to the formula (II) compound is in the range of from about 0.5:1 to about 3:1, preferably from about 1:1 to about 2:1.
14. The process of any of claims 1 or 3 to 9, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the liquid phase in the presence of a catalyst, wherein preferably the catalyst comprises a metal

selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.01 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst.

15. The process of claim 14, wherein the catalyst is a Pd/C catalyst, and wherein preferably the Pd loading is in the range of 0.1 wt.% to 10 wt.%.
16. The process of any of claims 1, 3 to 9 or 14 to 15, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the liquid phase at a temperature between about 20°C to about 120°C, preferably about 30°C and about 110°C.
17. The process of any of claims 1, 3 to 9 or 14 to 16, wherein a molar ratio of hydrogen to the formula (I) compound for liquid phase conversion of the formula (I) compound to the formula (II) compound is in the range of from about 0.5:1 to about 2:1, preferably from about 0.8:1 to about 1.2:1.
18. The process of any of claims 1 or 3, wherein the formula (I) compound is 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB,  $\text{CF}_3\text{CBr}=\text{CH}_2$ ) and the formula (II) compound is 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB,  $\text{CF}_3\text{CHBrCH}_3$ ).
19. The process of any of claims 1, 3 or 18, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase or the liquid phase.
20. The process of any of claims 1, 3 or 18 to 19, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the presence of a catalyst comprising a metal.
21. The process of any of claims 1, 3 or 18 to 20, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, the support preferably being selected from the group consisting of carbon, graphite and a metal oxide.
22. The process of claim 21, wherein the catalyst is Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C.

23. The process of any of claims 1, 3 or 18 to 22, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase in the presence of a catalyst, wherein preferably the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.1 wt.% to about 1.0 wt.%, preferably from about 0.2 wt.% to about 0.8 wt.%, based on the total weight of the support and catalyst.
24. The process of claim 23, wherein the catalyst is a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, and wherein preferably the Pd loading is in the range of 0.1 wt.% to 1.0 wt.%.
25. The process of any of claims 1, 3 or 18 to 24, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the vapor phase at a temperature between about 30°C to about 130°C, preferably about 60°C and about 110°C.
26. The process of any of claims 1, 3 or 18 to 25, wherein a molar ratio of hydrogen to the formula (I) compound for vapor phase conversion of the formula (I) compound to the formula (II) compound is in the range of from about 1:1 to about 10:1, preferably from about 2:1 to about 8:1.
27. The process of any of claims 1, 3 or 18 to 22, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the liquid phase in the presence of a catalyst, wherein preferably the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.1 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst.
28. The process of claim 27, wherein the catalyst is a Pd/C catalyst, and wherein preferably the Pd loading is in the range of 0.1 wt.% to 10 wt.%.
29. The process of any of claims 1, 3, 18 to 22 or 27 to 28, wherein conversion of the formula (I) compound to the formula (II) compound is conducted in the liquid

phase at a temperature between about 40°C to about 120°C, preferably about 60°C and about 100°C.

30. The process of any of claims 1, 3, 18 to 22 or 27 to 29, wherein a molar ratio of hydrogen to the formula (I) compound for liquid phase conversion of the formula (I) compound to the formula (II) compound is in the range of from about 0.5:1 to about 3:1, preferably from about 0.8:1 to about 2:1.
31. The process of any of claims 2 or 3, wherein the formula (II) compound is 2-chloro-1,1,1-trifluoropropane (HCFC-253db,  $\text{CF}_3\text{CHClCH}_3$ ) or 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB,  $\text{CF}_3\text{CHBrCH}_3$ ).
32. The process of any of claims 2, 3 or 31, wherein the formula (II) compound is contacted with hydrogen in the presence of a catalyst, preferably in the vapor phase.
33. The process of claim 32, wherein the catalyst comprises a metal catalyst, preferably the catalyst comprises a metal selected from the group consisting of Ni, Cu, Au and combinations thereof, with or without a support, wherein preferably the support is selected from the group consisting of carbon, graphite and a metal oxide.
34. The process of any of claims 32 to 33, wherein the catalyst is Au/C or Cu/C.
35. The process of any of claims 32 to 34, wherein the amount of catalyst on the support ranges from about 2 wt.% to about 10 wt.%, based on the total weight of the support and catalyst.
36. The process of any of claims 2, 3, or 31 to 35, wherein conversion of the formula (II) compound to HFO-1252zc is conducted in the vapor phase at a temperature between about 200°C to about 500°C, preferably about 300°C and about 450°C.
37. The process of any of claims 2, 3, or 31 to 36, wherein a molar ratio of hydrogen to the formula (II) compound is in the range of from about 5:1 to about 40:1, preferably from about 10:1 to about 30:1.

38. The process of any of claims 2, 3 or 31, wherein the formula (II) compound is contacted with a metal in the absence or presence of a catalyst, preferably in the liquid phase.
39. The process of any of claims 2, 3, 31 or 38, wherein the metal is selected from the group consisting of zinc, magnesium and a combination thereof.
40. The process of any of claims 38 to 39, wherein the metal is activated by an acid before being contacted with the formula (II) compound.
41. The process of any of claims 38 to 40, wherein the metal comprises zinc that has been activated by HCl.
42. The process of any of claims 2, 3, 31 or 38 to 41, wherein the reaction is conducted in the presence of a catalyst, preferably the catalyst is selected from the group consisting of zinc salt, ammonium salt and phosphonium salt.
43. The process of claim 42, wherein the catalyst is selected from the group consisting of zinc acetate,  $\text{ZnCl}_2$  and tetrabutylammonium bromide.
44. The process of any of claims 2, 3, 31 or 38 to 43, wherein the reaction is conducted in the presence of a solvent, preferably a solvent selected from the group consisting of alcohol, amide, pyridine and ether, more preferably a solvent comprising an alcohol selected from the group consisting of methanol, ethanol, propanol, isopropanol and ethylene glycol.
45. The process of any of claims 2, 3, 31 or 38 to 44, wherein the formula (II) compound is HCFC-253db and wherein conversion of the formula (II) compound to HFO-1252zc is conducted in the liquid phase at a temperature between about 50°C to about 180°C, preferably about 80°C and about 150°C.
46. The process of any of claims 2, 3, 31 or 38 to 45, wherein the formula (II) compound is HBFC-253dbB and wherein conversion of the formula (II) compound to HFO-1252zc is conducted in the liquid phase at a temperature between about 40°C to about 120°C, preferably about 50°C and about 100°C.
47. The process of any of claims 2, 3, 31 or 38 to 46, wherein a molar ratio of the metal to the formula (II) compound is in the range of from about 1:1 to about 5:1, preferably from about 1.05:1 to about 3:1.

48. A process of making HCFC-253db, the process comprising contacting HCFO-1233xf with hydrogen in the presence of a catalyst.
49. The process of claim 48, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.01 wt.% to about 0.1 wt.%, preferably from about 0.02 wt.% to about 0.05 wt.%, based on the total weight of the support and catalyst.
50. The process of claim 48, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.01 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst.
51. A process of making HBFC-253dbB, the process comprising contacting HBFO-1233xfB with hydrogen in the presence of a catalyst.
52. The process of claim 51, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.1 wt.% to about 1.0 wt.%, preferably from about 0.2 wt.% to about 0.8 wt.%, based on the total weight of the support and catalyst.
53. The process of claim 51, wherein the catalyst comprises a metal selected from the group consisting of Pd, Pt, Ni, Cu, Au and combinations thereof, with or without a support, and wherein preferably the amount of catalyst on the support ranges from about 0.1 wt.% to about 10 wt.%, preferably from about 0.4 wt.% to about 6 wt.%, based on the total weight of the support and catalyst.
54. A process of making HFO-1252zc, the process comprising contacting HCFC-253db or HBFC-253dbB with a metal in the absence or presence of a catalyst and/or a solvent, wherein the metal is selected from the group consisting of zinc, magnesium and a combination thereof.
55. The process of claim 54, wherein the metal is activated by an acid before being contacted with the formula (II) compound.

56. The process of any of claims 54 to 55, wherein the metal comprises zinc that has been activated by HCl.
57. The process of any of claims 54 to 56, wherein the reaction is conducted in the presence of a catalyst, preferably the catalyst is selected from the group consisting of zinc salt, ammonium salt and phosphonium salt, and more preferably the catalyst is selected from the group consisting of zinc acetate,  $\text{ZnCl}_2$  and tetrabutylammonium bromide.
58. The process of any of claims 54 to 57, wherein the reaction is conducted in the presence of a solvent, preferably a solvent selected from the group consisting of alcohol, amide, pyridine and ether, more preferably a solvent comprising an alcohol selected from the group consisting of methanol, ethanol, propanol, isopropanol and ethylene glycol.
59. A process of making HFO-1252zc, the process comprising contacting HCFC-253db or HBFC-253dbB with hydrogen in the presence of a catalyst.
60. The process of claim 59, wherein the catalyst comprises a metal catalyst, preferably the catalyst comprises a metal selected from the group consisting of Ni, Cu, Au and combinations thereof, with or without a support, wherein preferably the support is selected from the group consisting of carbon, graphite and a metal oxide.
61. The process of any of claims 59 to 60, wherein the catalyst is Au/C or Cu/C.
62. The process of any of claims 59 to 61, wherein the amount of catalyst on the support ranges from about 2 wt.% to about 10 wt.%, based on the total weight of the support and catalyst.
63. A process of making HFO-1252zc, the process comprising:
- (i) converting HCFO-1233xf to HCFC-253db by reaction of the HCFO-1233xf with hydrogen in the presence of a catalyst, and
  - (ii) converting the HCFC-253db to HFO-1252zc by reaction of the HCFC-253db with a metal in the absence or presence of a catalyst and/or a solvent, wherein the metal is selected from the group consisting of zinc,

magnesium and a combination thereof, or with hydrogen in the presence of a catalyst.

64. A process of making HFO-1252zc, the process comprising:
- (i) converting HBFO-1233xfB to HBFC-253dbB by reaction of the HBFO-1233xfB with hydrogen in the presence of a catalyst, and
  - (ii) converting the HBFC-253dbB to HFO-1252zc by reaction of the HBFC-253dbB with a metal in the absence or presence of a catalyst and/or a solvent, wherein the metal is selected from the group consisting of zinc, magnesium and a combination thereof, or with hydrogen in the presence of a catalyst.
65. A system comprising sources of HCFO-1233xf and hydrogen or of HBFO-1233xfB and hydrogen, first and second reactors for respectively conducting different reactions, optionally at least one mixer connected to the first reactor for premixing reactants comprising hydrogen and HCFO-1233xf or hydrogen and HBFO-1233xfB, the second reactor arranged downstream of the first reactor, wherein said first reactor produces a first intermediate product mixture and the second reactor converts the intermediate product produced in said first reactor, wherein the first reactor is configured to operate in the vapor or liquid phase and said second reactor is configured to operate in the vapor or liquid phase.
66. The system of claim 65, wherein unreacted HCFO-1233xf or HBFO-1233xfB from the first reactor is recycled.
67. A process for converting HCFO-1233xf or HBFO-1233xfB to HFO-1252zc using the system of any of claims 65 to 66.
68. A composition comprising, consisting essentially of, or consisting of one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1,1-difluoropropene (HFO-1252zc), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-

bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

69. The composition of claim 68, wherein the composition comprises HFC-263fb and HCFC-253db.
70. The composition of claim 68, wherein the composition comprises HCFO-1233xf, HFC-263fb and HCFC-253db.
71. The composition of claim 68, wherein the composition comprises HFC-263fb, HCFO-1233xf and HCFC-253db.
72. The composition of claim 68, wherein the composition comprises HFO-1252zc, HFC-263fb, HCFO-1233xf and HCFC-253db.
73. The composition of claim 68, wherein the composition comprises HFC-263fb and HBFC-253dbB.
74. The composition of claim 68, wherein the composition comprises HFC-263fb, HBFO-1233xfB and HBFC-253dbB.
75. The composition of claim 68, wherein the composition comprises HFO-1252zc, HFC-263fb, HBFO-1233xfB and HBFC-253dbB.
76. The composition of claim 68, wherein the composition comprises HCFO-1233xf, HFC-263fb, HFC-244bb and HFC-253db.
77. A composition comprising, consisting essentially of, or consisting of HFO-1252zc and one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-

1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

78. A composition comprising, consisting essentially of, or consisting of HFO-1252zc, HFO-1243zf, and one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), difluoropropene isomers (HFO-1252), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).
79. A composition comprising, consisting essentially of, or consisting of HFO-1252zc, HFO-1261ze and one or more compounds selected from the group consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), 1,1,1-trifluoropropane (HFC-263fb), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).
80. A composition comprising, consisting essentially of, or consisting of HFO-1252zc, HFC-263fb and one or more compounds selected from the group

consisting of propylene, propane, dichlorotrifluoropropane isomers (HCFC-243), 2-chloro-1,1,1-trifluoropropane (HCFC-253db), E-1,2-difluoroethene (E-HFO-1132), Z-1,2-difluoroethene (Z-HFO-1132), 3,3,3-trifluoropropene (HFO-1243zf), difluoropropene isomers (HFO-1252), 1-fluoropropene (HFO-1261ze), pentafluorobutene isomers (HFO-1345), 2-butene, butane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), methanol, acetone, propane, propylene, 2-methoxy-propane, 2-chloropropane, 2-bromo-1,1-difluoropropene (HBFO-1242xfB), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 2,3-dichloro-3,3-difluoropropene (HCFO-1232xf), and 1,2-dichloro-1,1-difluoropropane (HCFC-252dc).

81. A composition comprising, consisting essentially of, or consisting of HBFO-1233xfB and one or more compounds selected from the group consisting of propane, 3,3,3-trifluoropropene (HFO-1243zf), 1,1,1-trifluoropropane (HFC-263fb), dichloromethane (HCC-30), 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), tetrafluorobutane (HFC-374), chlorofluoropropene (HCFO-1251), 2-bromo-3,3,3-trifluoropropene (HBFO-1233xfB), 2-bromo-1,1,1-trifluoropropane (HBFC-253dbB), 2-bromo-3,3-difluoropropene (HBFO-1242xfB), dichlorotrifluoropropane isomers (HCFC-243), and dibromotrifluoropropane (C<sub>3</sub>H<sub>3</sub>Br<sub>2</sub>F<sub>3</sub>).