

TITLE OF THE INVENTION

PROCESS AND COMPOSITIONS TO REMOVE 1243ZF FROM 1252ZC USING A SOLUTION OF A METAL-HYDRIDE CATALYST IN A LIQUID HYDROSILANE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/527,217 filed July 17, 2023, and U.S. Provisional Application 63/565,036 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 relates to processes and compositions for removing 3,3,3-trifluoropropene (HFO-1243zf, $\text{CF}_3\text{CH}=\text{CH}_2$) from 1,1-difluoropropene (HFO-1252zc, $\text{CF}_2=\text{CHCH}_3$) product streams.

BACKGROUND OF THE INVENTION

[0003] The present invention is directed to processes for producing difluoroolefins, particularly difluoropropenes, intermediates, compositions and uses thereof.

BACKGROUND OF THE INVENTION

[0004] The fluorocarbon industry has been working for the past few decades to find replacement refrigerants for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being phased out as a result of the Montreal Protocol. The solution for many applications has been the commercialization of hydrofluorocarbon (HFC) compounds for use as refrigerants, solvents, fire extinguishing agents, blowing agents and propellants. These new compounds, such as HFC refrigerants, HFC-134a and HFC-125 being the most widely used at this time, have zero ozone depletion potential (ODP) and thus are not affected by the current regulatory phase-out as a result of the Montreal Protocol. In addition to ozone depleting concerns, global warming is another environmental concern in many of these applications. HFC refrigerants such as HFC-134a and HFC-125

respectively have global warming potentials (GWP) of 1,300 and 3,170 according to the UN's IPCC Fifth Assessment Report (AR5).

[0005] This regulatory landscape is continuously evolving, taking into consideration properties beyond just ODP and GWP. More particularly, there is a need for refrigerant compositions that not only meet low ODP standards and have low global warming potentials, but that also exhibit low or no flammability, provide superior performance in a variety of applications and which meet the standards of evolving regulations.

[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 HFO-1252zc, are such potential new refrigerants. There continues to be need for effective and efficient processes for preparing and purifying HFO-1252zc and compositions thereof.

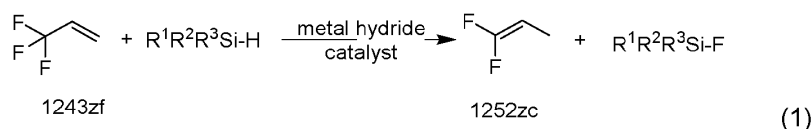
SUMMARY OF THE INVENTION

[0008] HFO-1252zc is a fluoroolefin compound and a candidate for use as a next generation refrigerant molecule possessing the desired low GWP and ODP properties. One route for making HFO-1252zc involves dehydrofluorinating 1,1,1-trifluoropropane (HFC-263fb, $\text{CF}_3\text{CH}_2\text{CH}_3$) which results in a product mixture which includes HFO-1252zc and at least HFO-1243zf. In some embodiments, HFO-1243zf is a byproduct present in amounts of between 1 and 10 mole percent with respect to HFO-1252zc. The boiling point of HFO-1243zf is relatively close to that of HFO-1252zc, and thus makes it difficult, if not impractical, to remove HFO-1243zf from HFO-1252zc using conventional separation techniques, such as distillation. In addition, various chemical processes to produce HFO-1252zc including the hydro-defluorination of HFO-1243zf can yield 1-fluoropropene(s) (HFO-1261ze) as a minor co-product having a similar boiling point. It may not be practical or possible to fully separate the HFO-1261ze from HFO-1252zc by conventional techniques including distillation.

[0009] One aspect of the invention disclosed herein relates to a process of increasing the HFO-1252zc content of a composition or product stream comprising

HFO-1252zc and at least HFO-1243zf present at a first level by contacting the composition or product stream with a solution of a metal-hydride catalyst. In some embodiments, the metal-hydride catalyst is selected from a copper hydride, silver hydride, or gold hydride. In some embodiments, the solution of the metal-hydride catalyst comprises a stabilizing ligand and >50% w/w of a liquid hydrosilane as a solvent component in a solvent system with respect to a co-solvent. The liquid hydrosilane is also a reactant in a catalytic reaction cycle with the metal-hydride catalyst.

[0010] In some embodiments, the liquid hydrosilane is a tetravalent silicon compound containing one or more Si-H bonds and may be defined by the formula $R^1R^2R^3SiH$, wherein R^1 , R^2 , R^3 , are each independently H, Alk(C_1 to C_6 alkyl group), Ar(aryl), SiR_3 (silyl), $OSiR_3$ (siloxo), OR (alkoxy), NR_2 (amino) or halogen. Specific examples of the liquid hydrosilane may include triethylsilane, dimethylphenylsilane, and 1,1,3,3-tetramethyldisiloxane. The metal-hydride catalyst in the presence of the liquid hydrosilane can selectively and catalytically convert HFO-1243zf to HFO-1252zc as outlined in Scheme 1 thereby reducing the amount of HFO-1243zf in the composition or product stream to a second level, with respect to the HFO-1252zc, that is lower than the first level, such as to less than or equal to about 0.1 mole percent, and concomitantly increasing the HFO-1252zc in the product stream.



[0011] A second aspect relates to the solution of a metal-hydride catalyst wherein the liquid hydrosilane is a solvent component in a solvent system for the metal-hydride catalyst and the solvent system comprises, consists essentially of, or consists of the liquid hydrosilane present in an amount that is >50% w/w, > 55% w/w, >60% w/w, >70% w/w, > 80% w/w, >90% w/w, >95% w/w, or 100% with respect to any co-solvent in the solvent system. The solution of the metal-hydride catalyst comprising more than 50% w/w of the liquid hydrosilane can catalytically convert HFO-1243zf to HFO-1252zc with a selectivity of at least 98% or at least 99%, and is more efficient, requiring a relatively smaller amount of the solution of the metal-hydride catalyst.

[0012] Embodiments of the second aspect include a solution of a copper-hydride catalyst wherein the liquid hydrosilane is a solvent component in a solvent system for the copper-hydride catalyst and the solvent system comprises, consists essentially of, or consists of a liquid hydrosilane present in an amount that is >50% w/w, > 55% w/w, >60% w/w, >70% w/w, > 80% w/w, >90% w/w, >95% w/w, or 100% with respect to any co-solvent in the solvent system.

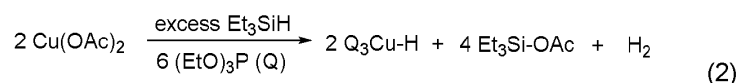
[0013] In some embodiments, the co-solvent may be excluded and the liquid hydrosilane may be 100% of the solvent system.

[0014] The solution of the copper-hydride catalyst having more than 50% w/w of the liquid hydrosilane can catalytically convert HFO-1243zf to HFO-1252zc with a selectivity of at least 98%, or at least 99% and is more efficient, requiring a relatively smaller amount of the solution of the copper-hydride catalyst.

[0015] A third aspect relates to a process of making a solution of a metal-hydride catalyst and comprises, consists essentially of, or consists of: (1) providing a liquid hydrosilane as a solvent component in an amount of >50% w/w, > 55% w/w, >60% w/w, >70% w/w, > 80% w/w, >90% w/w, >95% w/w, or 100% with respect to any co-solvent in a solvent system; (2) contacting a metal-hydride or a metal-hydride catalyst precursor with a stabilizing ligand and the liquid hydrosilane; (3a) dissolution of the metal-hydride in the solvent system or (3b) reaction of the metal-hydride catalyst precursor with the liquid hydrosilane and dissolution in the solvent to form the solution of the metal-hydride catalyst of general formula Q_xM-H_y , where Q is the stabilizing ligand, M-H_y is the metal-hydride, x and y are independent integers of 1 to 3, and M is selected from copper (Cu), silver (Ag), or gold (Au).

[0016] Embodiments of the third aspect include: (1) contacting Stryker's Reagent (a copper hydride) or a metal acetate (a metal-hydride catalyst precursor) selected from copper acetate, silver acetate, or gold acetate with the stabilizing ligand (Q) and the liquid hydrosilane as a solvent component in an amount of >50% w/w, > 55% w/w, >60% w/w, >70% w/w, > 80% w/w, >95%w/w, or 100% with respect to any co-solvent in a solvent system, (2) contacting Stryker's Reagent or the metal acetate with a stabilizing ligand and the liquid hydrosilane, (3a) dissolution of the Stryker's reagent in the solvent system or (3b) reaction of the metal acetate with the liquid hydrosilane and dissolution in the solvent system to form the solution of the metal-

hydride catalyst at temperatures between about 25°C and 80°C, preferably between greater than 25°C and 60°C. An example of the process for making/producing the solution of the metal-hydride catalyst using copper (II) acetate as the metal-hydride catalysts precursor, triethyl phosphite ((EtO)₃P) as the stabilizing ligand (Q), and an excess of triethyl silane (Et₃SiH) as the liquid hydrosilane (as both a reactant with the metal-acetate and a solvent component) may be represented by the reaction shown in Scheme (2).



[0017] In certain embodiments disclosed herein, the metal-hydride catalyst comprises, consists essentially of, or consists of the general formula Q_xM-H_y, where Q is the stabilizing ligand having one or more binding sites that can comprise phosphorous, nitrogen, oxygen, sulfur, a stabilized carbene or combinations thereof. The stabilizing ligand may be selected from PR₃, R₃PO, NR₃, SR₂, OR₂, or :CR₂ where each R is independently: H, a C₁-C₈ alkyl, aryl, silyl, C₁-C₈ alkoxy, amino, or halogen selected from F, Cl, Br or I, and the metal M selected from one of Cu, Au or Ag, and x and y are independently integers from about 1 to 3. Specific examples of a stabilizing ligand can include a trialkyl phosphite including triethyl phosphite.

[0018] In certain embodiments, the solution of the metal-hydride catalyst contains less than 50 weight percent, less than 25 weight percent, or less than 5 weight percent, and may contain 0 weight percent of a co-solvent with respect to the liquid hydrosilane in the solvent system. The co-solvent can include an aromatic compound such as benzene, toluene, xylenes, a silane such as hexamethyldisiloxane, or an excess of the stabilizing ligand (Q). The co-solvent may help to form a homogenous solution of the metal-hydride catalyst.

[0019] A fourth aspect disclosed herein relate to compositions comprising HFO-1252zc, HFC-263fb, HFO-1243zf, the metal-hydride catalyst (Q_xM-H_y), and the liquid hydrosilane or hydrosiloxane. Certain embodiments include compositions wherein the metal M can be copper, the stabilizing ligand can be triethyl phosphite, the hydrosiloxane can be tetramethyldisiloxane, and HFO-1243zf can be present in an amount of less than 0.1 mole percent or 0.1 to 10 mole percent with respect to HFO-1252zc.

[0020] Other aspects disclosed herein relate to a mixture/composition containing HFO-1252zc and approximately 0.26% (GC-FID area %) of HFO-1261ze (cis and trans isomers), wherein the composition is not acutely toxic by inhalation.

[0021] Other aspects disclosed herein relate to compositions which comprises, consists essentially of or consists of HFO-1252zc and HFO-1261ze, preferably less than about 50 wt% HFO-1261ze, more preferably less than about 1 wt% HFO-1261ze.

[0022] Other aspects disclosed herein relate to compositions to a refrigerant composition which comprises, consists essentially of or consists of HFO-1252zc and HFO-1261ze in amount < about 5% by weight, preferably < about 3 % by weight, more preferably less than about 1% by weight.

[0023] Other aspects disclosed herein relate to compositions to refrigerant blends which comprise, consist essentially of or consist of C₃ or C₄ fluoroolefins, HFO-1252zc, and HFO-1261ze in amount < about 5% by weight, preferably < about 3 % by weight, more preferably less than < about 1% by weight.

[0024] Other aspects disclosed herein relate to compositions of HFO-1252zc and HFO-1261ze (cis and trans isomers)

[0025] Other aspects disclosed herein relate to compositions which comprise, consist of or consist essentially of HFO-1252zc and less than 50 wt% HFO-1261ze based on a total weight of the composition.

[0026] Other aspects disclosed herein relate to compositions which comprise, consist of or consist essentially of HFO-1252zc and less than about 1 wt% HFO-1261ze based on a total weight of the composition.

[0027] Other aspects disclosed herein relate to compositions which comprise, consist of or consist essentially of HFO-1252zc and HFO-1261ze in amount between greater than 0 and less than about 5% by weight.

[0028] Other aspects disclosed herein relate to compositions which comprise, consist of or consist essentially of at least one C₃ or C₄ fluoroolefin, HFO-1252zc, and HFO-1261ze in amounts less than about 1% by weight.

[0029] Other aspects disclosed herein relate to compositions which comprise, consist of or consist essentially of HFO-1252zc and at least one additional compound selected from E-1-fluoropropene (trans-HFO-1261ze), Z-1-fluoropropene (cis-HFO-1261ze), 1,1,1-trifluoropropane (HFC-263fb), 3,3,3-trifluoropropene (HFO-1243zf) and propylene, wherein the amount of E/Z-HFO-1261ze is less than about 1% by weight.

[0030] Other aspects disclosed herein relate to compositions wherein the amount of E/Z-HFO-1261ze is selected from one of between > about 0 and < about 0.5 wt%, between > about 0 and < about 0.25 wt%, between > about 0 and < about 0.1 wt%.

[0031] This summary of the invention has introduced the aspects and some of the embodiments of the invention and is not intended to be limiting. As used herein, an aspect is a defining characteristic of the invention as may be recited in an independent claim and further disclosed in the detailed description. An embodiment may be viewed as a variation, or one implementation of an aspect as may be recited in a dependent claim and further disclosed in the detailed description. Certain exemplary embodiments are described herein and are only for purposes of illustrating the invention and should not be interpreted as limiting the scope of the invention. Alternate embodiments, including certain modifications, combinations, and improvements of the exemplary embodiments will occur to those skilled in the art and all such alternate embodiments are within the scope of the invention.

DETAILED DESCRIPTION

[0032] 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.

[0033] As disclosed herein, in the pursuit of improving the manufacturing yield of HFO-1252zc, applicants have unexpectedly found that a solution of a metal-hydride

catalyst (Q_xM-H_y), wherein Q is a ligand having one or more binding sites, wherein x and y are independently integers of 1-3, wherein the solution of the metal-hydride catalyst substantially comprises a liquid hydrosilane as a solvent component and having reduced amounts of co-solvent, is capable of selectively converting HFO-1243zf to HFO-1252zc, whether the HFO-1243zf is present as a neat compound or as a component of a composition or reaction product mixture containing substantial amounts of HFO-1252zc. The method of the present invention concomitantly reduces the amount of HFO-1243zf to levels of about 0.1 mole percent, and increases the amount of HFO-1252zc in the composition or product stream.

[0034] Before addressing details of embodiments described herein, certain terms are defined or clarified as follows.

[0035] 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.

[0036] 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.

[0037] 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).

[0038] 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.”

[0039] 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.

[0040] 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.”

[0041] 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.

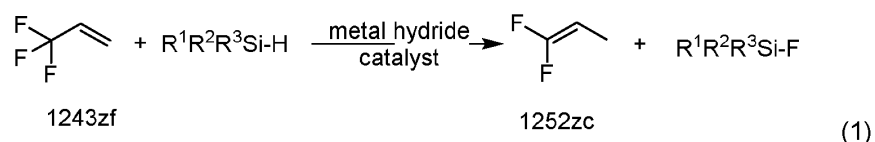
[0042] When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and/or lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred 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.

[0043] As used herein, the term “about” is meant to account for variations due to experimental error (e.g., plus or minus approximately 10% of the indicated value. $\pm 1\%$, $\pm 2\%$, ± 3 , ... $\pm 10\%$). 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.

[0044] Some of the compounds present in the compositions of the present invention may exist as different configurational isomers or stereoisomers. The present invention is intended to include all single configurational isomers, single stereoisomers or any combination or mixture thereof. Single isomers or multiple isomers of the same compound may be used in any proportion.

[0045] In one aspect, the applicants have unexpectedly found that a solution of a metal hydride catalyst selected from a copper hydride, silver hydride, or gold hydride, and > 50% w/w of liquid hydrosilane as a solvent with respect to a co-solvent catalytically converts HFO-1243zf to HFO-1252zc with a selectivity of at least 98%, preferably at least 99%. The liquid hydrosilane is a reactant in a catalytic reaction cycle with the metal-hydride catalyst and is a tetravalent silicon compound containing one or more Si-H bonds and may be defined by the formula $R^1R^2R^3SiH$, wherein R^1 , R^2 , R^3 are each independently H, Alk(C1 to C6 alkyl group), Ar(aryl), SiR_3 (silyl), $OSiR_3$ (siloxy), OR (alkoxy), NR_2 (amino) or a halogen. Specific examples of the liquid hydrosilane can include triethylsilane, dimethylphenylsilane, and tetramethyldisiloxane. The metal-hydride catalyst in the presence of the liquid hydrosilane can selectively and catalytically convert HFO-1243zf to HFO-1252zc as outlined in Scheme 1, thereby reducing the amount of HFO-1243zf in a composition or product stream to levels less than or equal to about 0.1 mole percent, and concomitantly increasing the HFO-1252zc in the composition or product stream.



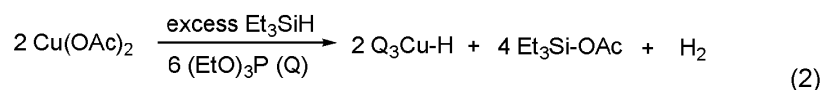
[0046] A second aspect relates to the solution of a metal-hydride catalyst, wherein the liquid hydrosilane is a solvent component for the metal-hydride catalyst and the solvent comprises, consists essentially of, or consists of the liquid hydrosilane present in an amount that is > 50% w/w, > 55% w/w, > 60% w/w, > 70% w/w, > 80% w/w, > 90% w/w, or > 95% w/w and 100% w/w, or between > 90% w/w and up to and including 100% w/w with respect to a co-solvent. The solution of the metal-hydride catalyst having > 50% w/w of the liquid hydrosilane can catalytically convert HFO-1243zf to HFO-1252zc with a selectivity of at least 98% or at least 99% and is more efficient, requiring a relatively smaller amount of the solution of the metal-hydride catalyst.

[0047] Embodiments of the second aspect include a solution of a copper-hydride catalyst wherein the liquid hydrosilane is a solvent component for the copper-hydride catalyst and the solvent comprises, consists essentially of, or consists of a liquid hydrosilane present in an amount that is > 50% w/w, > 55% w/w, > 60% w/w, > 70% w/w, > 80% w/w, > 90% w/w, or > 95% w/w and 100% w/w, or between > 90% w/w and up to and including 100% w/w with respect to a co-solvent. The solution of the copper-hydride catalyst having > 50% w/w of the liquid hydrosilane can catalytically convert HFO-1243zf to HFO-1252zc with a selectivity of at least 98%, or at least 99% and is more efficient, requiring a relatively smaller amount of the solution of the copper-hydride catalyst.

[0048] A third aspect relates to a process of making a solution of a metal-hydride catalyst and comprises, consists essentially of, or consists of: (1) providing an excess of the liquid hydrosilane as a solvent component in an amount of > 50% w/w, > 55% w/w, > 60% w/w, > 70% w/w, > 80% w/w, > 90% w/w, or > 95% w/w, or between > 90% w/w and up to and including 100% w/w with respect to a co-solvent, (2) contacting a metal-hydride or a metal-hydride catalyst precursor with a stabilizing ligand and the liquid hydrosilane, and (3a) dissolution of the metal-hydride in the solvent or (3b) reaction of the metal-hydride catalyst precursor with the liquid hydrosilane and dissolution in the solvent to form the solution of the metal-hydride catalyst of general formula Q_xM-H_y , where Q is the stabilizing ligand, $M-H_y$ is the metal-hydride, x and y are independent integers of 1 to 3, and M is selected from copper (Cu), silver (Ag), or gold (Au).

[0049] Embodiments of the third aspect include: (1) contacting Stryker's Reagent (a copper hydride) or a metal acetate (a metal-hydride catalyst precursor) selected from copper acetate, silver acetate, or gold acetate with the stabilizing ligand (Q) and an excess of the liquid hydrosilane as a solvent component in an amount of > 50% w/w, > 55% w/w, > 60% w/w, > 70% w/w, > 80% w/w, > 90% w/w, or > 95% w/w, or between > 90% w/w and up to and including 100% w/w with respect to a co-solvent, (2) contacting Stryker's Reagent or the metal acetate with a stabilizing ligand and the liquid hydrosilane, and (3a) dissolution of the Stryker's reagent in the solvent, or (3b) reaction of the metal acetate with the liquid hydrosilane and dissolution in the solvent to form the solution of the metal-hydride catalyst at temperatures between about 25°C and 80°C, preferably between greater than 25°C and 60°C.

[0050] An example of the process for making/producing the solution of the metal-hydride catalyst using copper (II) acetate as the metal-hydride catalysts precursor, triethyl phosphite ((EtO)₃P) as the stabilizing ligand (Q), and an excess of triethyl silane (Et₃SiH) as the liquid hydrosilane (as both a reactant with the metal-acetate and the solvent) may be represented by the reaction shown in Scheme (2).



[0051] In certain embodiments disclosed herein the metal-hydride catalyst comprises, consists essentially of, or consists of the general formula Q_xM-H_y where Q is the stabilizing ligand having one or more binding sites that can comprise phosphorous, nitrogen, oxygen, sulfur, a stabilized carbene or combinations thereof. The stabilizing ligand may be selected from PR₃, R₃PO, NR₃, SR₂, OR₂, or :CR₂ where each R is independently: H, a C₁-C₈ alkyl, aryl, silyl, C₁-C₈ alkoxy, amino, or halogen selected from F, Cl, Br or I, and the metal M selected from one of Cu, Au or Ag, and x and y are independently integers from about 1 to 3. Specific examples of a stabilizing ligand can include a trialkyl phosphite including, but not limited to, triethyl phosphite.

[0052] In certain embodiments, the solution of the metal-hydride catalyst contains less than about 50 weight percent, less than about 25 weight percent, or less than about 5 weight percent, and may contain 0 weight percent of a co-solvent with respect to the liquid hydrosilane as the solvent. The co-solvent can include an

aromatic compound such as benzene, toluene, xylenes, a silane such as hexamethyldisiloxane, or an excess less than about 50 weight percent of the stabilizing ligand (Q). The co-solvent may help to form a homogenous solution.

[0053] A fourth aspect disclosed herein relates to compositions comprising HFO-1252zc, HFC-263fb, HFO-1243zf, the metal-hydride catalyst (Q_xM-H_y), and the liquid hydrosilane or hydrosiloxane. Certain embodiments include compositions wherein the metal M can be copper, the stabilizing ligand can be triethyl phosphite, the hydrosiloxane can be tetramethyldisiloxane, and HFO-1243zf can be present in an amount of less than about 0.1 mole percent or about 0.1 to about 10 mole percent with respect to HFO-1252zc.

[0054] In some embodiments of the present invention, HFC-263fb can be converted to HFO-1252zc in the liquid and or vapor phase, and the HFO-1243zf byproduct of the conversion can be selectively converted to additional HFO-1252zc in a liquid phase reactor using a metal-hydride catalyst solution. The reactors for the HFC-263fb conversion or for the selective HFO-1243zf removal can be operated in batch, semi-batch and continuous modes, and integrated for continuous operation. The reactors disclosed herein can contain preheaters, coolers, vaporizers, heat exchangers, feed and effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, and valving associated with the reactors, heat exchangers, vessels, columns, and units that are used in the processes of various embodiments disclosed herein should be constructed of materials resistant to corrosion.

[0055] Aspects of the present invention will now be described with reference to the following Examples.

EXAMPLES

Example 1 – Making a solution of a metal-hydride catalyst in a liquid hydrosilane

[0056] A 0.20 M copper-hydride catalyst solution in 4.9-M 1,1,3,3-tetramethyldisiloxane (TMDS) was prepared in a dry 500-mL 3-neck RB flask fitted with a heating mantle, magnetic stirring, condenser connected to a nitrogen manifold, and a thermocouple. 10 g of copper (II) acetate monohydrate (50.1 mmol)

was added to the flask with 24.9-g of triethyl phosphite (150 mmol) and 150 g of TMDS. The mixture was heated to between about 50°C and about 70°C with magnetic stirring and the bluish-green copper (II) acetate solid slowly dissolved over a period of approximately 12 hours to form the copper-hydride catalyst solution having a red color. The copper-hydride catalyst solution was cooled to ambient room temperature and then transferred to a 250 mL volumetric flask. An additional approximately 14g of TMDS in two portions was used to rinse the RB flask and added to the volumetric flask to adjust the volume to the mark.

Example 2 – NMR-scale reaction of HFO-1243zf with a solution of a metal-hydride catalyst in a liquid hydrosilane

[0057] 0.4 mL of the metal-hydride catalyst solution in TMDS of Example 1 was added to a 5 mm NMR tube, which was then chilled in liquid nitrogen. The NMR tube was evacuated then backfilled with approximately 0.15 mmol of 3,3,3-trifluoropropene (HFO-1243zf). The NMR tube was then flame sealed and warmed to ambient temperature (about 25°C), and then placed in a 600-MHz NMR spectrometer at the same ambient temperature. ¹⁹F NMR spectra were periodically collected and showed at least 99.9% conversion of the HFO-1243zf at 10 hours with 98.4% selectivity to HFO-1252zc and 1.4% HFC-263fb.

Example 3 – Preparation of a copper (I) hydride catalyst solution

[0058] A solution of a copper (I) hydride catalyst in 1,1,3,3-tetramethyldisiloxane (TMDS) was prepared by a reduction reaction of copper (II) acetate with the TMDS in the presence of a stabilizing ligand. 20.0 g (0.100 moles) of copper (II) acetate monohydrate was placed in a 1 L 3-neck RB flask under nitrogen and fitted with a condenser (15°C), thermocouple well, and heating mantle. 500 mL (~2.83 moles) of TMDS and 50 mL of triethyl phosphite (~0.29 moles) were added to the flask. With magnetic stirring, the reaction mixture was heated to between about 50°C and about 70°C and the solid and bluish-green copper (II) acetate slowly dissolved over approximately 3 hours with the evolution of hydrogen gas to form a reddish-brown solution of the copper (I) hydride catalyst.

Example 4 – Hydrodefluorination of HFO-1243zf to produce HFO-1252zc and an HFO-1261ze coproduct

[0059] 250 mL of the catalyst solution of Example 3 was charged to an evacuated 600 mL Hastelloy Parr reactor. The reactor contents were heated to about 60°C with stirring and then 206 g (~2.15 moles) of HFO-1243zf was added over 1 to 2 hours such that the reactor cooling loop was able to maintain a 60°C reaction temperature. The reaction mixture was stirred at 60°C for 21 hours. At that time, a gas sample from the headspace of the Parr reactor was analyzed by gas chromatography (GC) with mass spectral (MS) and flame ionization (FID) detection and showed that the remaining HFO-1243zf was less than 500 ppm. The crude HFO-1252zc product (177g) at 60°C was then vapor transferred into an evacuated 300 mL Hoke cylinder that was chilled in dry ice. On warming to ambient room temperature, a liquid sample from the Hoke cylinder was analyzed by gas chromatography. Table 1 below shows that the composition of the reactor headspace and the liquid sample in the Hoke cylinder both contain HFO-1252zc and HFO-1261ze.

Table 1

Component	Sampling Location	Uncalibrated GC-FID area %
1,1-difluoropropene (HFO-1252zc)	Headspace Hoke cylinder	98.089 82.267
1-fluoropropene (trans and cis HFO-1261ze)	Headspace Hoke cylinder	0.260 0.303
3,3,3-trifluoropropene (HFO-1243zf)	Headspace Hoke cylinder	0.025 0.048
Difluorodimethylsilane	Headspace Hoke cylinder	0.386 1.347
1,1,3,3-tetramethyldisiloxane (TMDS)	Headspace Hoke cylinder	0.039 Not identified
1,3-difluoro-TMDS	Headspace Hoke cylinder	1.201 15.589
Unknowns at long retention time	Hoke cylinder	0.445

Example 5 – Distillation purification of crude HFO-1252zc.

[0060] The crude HFO-1252zc product from Example 4 was transferred to an insulated glass distillation apparatus including an 18-inch jacketed distillation column containing stainless steel Pro-Pak® distillation packing, and a still head incorporating

a dry ice condenser and needle valve to adjust the takeoff rate. A major distillate fraction boiling at -29°C was collected in a nitrogen purged Hoke cylinder that was chilled with dry ice. On warming to ambient room temperature, a liquid sample from the Hoke cylinder was analyzed by gas chromatography. Table 2 below shows that the purified HFO-1252zc contains 0.26% of HFO-1261ze isomers.

Table 2

Component	CAS #	Uncalibrated GC-FID area %
1,1-difluoropropene (HFO1252zc)	430-63-7	99.675
1-fluoropropene (trans HFO-1261ze)	20327-65-5	0.223
1-fluoropropene (cis HFO-1261ze)	19184-10-2	0.036
1,1,1-trifluoropropane (HFC-263fb)	421-07-8	0.034
3,3,3-trifluoropropene (HFO-1243zf)	677-21-4	0.021
Propylene	115-07-1	0.005
Difluorodimethylsilane	353-66-2	0.003
Unknown	n/a	0.003

Example 6 – Inhalation acute toxicity of 1252zc containing a 1261ze coproduct.

[0061] A sample of the purified HFO-1252zc mixture of Example 4 was used for a 1 hour acute inhalation study at 50,000 ppm in a rat model. There were no deaths reported post inhalation at the end of the prescribed observation period.

Example 7 – Treatment of a product stream comprising 1252zc and a 1243zf byproduct

[0062] A 600 mL pressure reactor constructed from Hastelloy® C276 and comprising a pressure vessel and a reactor head with a magnetic-mechanical stirring drive is assembled, leak tested with 125 psig nitrogen, then evacuated. 100 mL of the copper-hydride catalyst solution in TMDS of Example 1 is transferred into the pressure reactor. The reactor vessel is chilled with dry ice and approximately 44 liters (STP) of a product stream comprising HFO-1252zc and 5 mole percent of a HFO-1243zf byproduct from a vapor-phase dehydrofluorination of HFC-263fb is condensed into the pressure reactor. With stirring, the contents of the pressure reactor are heated and maintained at 45°C. The vapor space is sampled at 8 hours and analyzed by gas chromatography with mass spectral detection (GC-MS). The

concentration of HFO-1243zf remaining in the product stream is less than 0.1 mole-percent.

Example 8 – Preparation of a copper (I) hydride catalyst solution in a solvent system comprising a co-solvent

[0063] A solution of a copper (I) hydride catalyst in a solvent system comprising 60% (v/v) 1,1,3,3-tetramethyldisiloxane (TMDS) and 40% (v/v) benzene is prepared by a reduction reaction of copper (II) acetate with the TMDS in the presence of a stabilizing ligand. 12.0g (0.0600 moles) of copper (II) acetate monohydrate is placed in a 1 L 3-neck RB flask under nitrogen and fitted with a condenser (15°C), thermocouple well, and heating mantle. 228 g (~1.70 moles) of TMDS, 176 g (~200mL) of benzene, and 31 mL of triethyl phosphite (~0.18 moles) are added to the flask. With magnetic stirring, the reaction mixture was heated to between 50°C and 70°C and the solid and bluish-green copper (II) acetate slowly dissolved over approximately 3 hours with the evolution of hydrogen gas to form a reddish-brown copper (I) hydride catalyst solution.

OTHER EMBODIMENTS

[0064] Embodiment 1. A process comprising, a) contacting a composition or product stream comprising and 3,3,3-trifluoropropene (HFO-1243zf, $\text{CF}_3\text{CH}=\text{CH}_2$) with a solution of a metal-hydride catalyst including a stabilizing ligand and a liquid hydrosilane as a solvent component in a solvent system, wherein the amount of HFO-1243zf is present at a first level, and wherein the composition or product stream optionally further comprises 1,1-difluoropropene (HFO-1252zc, $\text{CF}_2=\text{CHCH}_3$); and b) selectively converting the HFO-1243zf to HFO-1252zc with the solution of the metal-hydride catalyst to reduce the amount of HFO-1243zf in the composition or product stream to a second level lower than the first level, wherein the level of HFO-1243zf is with respect to the HFO-1252zc in the product stream, and wherein the solution of the metal-hydride catalyst contains greater than 50% w/w of the liquid hydrosilane as a solvent component in the solvent system with respect to any co-solvent.

[0065] Embodiment 2. The process of claim 1, wherein the stabilizing ligand is triethyl phosphite, and wherein the liquid hydrosilane is selected from the group consisting of triethylsilane, dimethylphenylsilane, and 1,1,3,3-tetramethyldisiloxane.

[0066] Embodiment 3. The process of any of claims 1 and 2, wherein any co-solvent is excluded and the liquid hydrosilane is 100% of the solvent system.

[0067] Embodiment 4. The process of any of claims 1 to 3, wherein the stabilizing ligand has one or more binding sites.

[0068] Embodiment 5. The process of any of claims 1 to 4, wherein a metal hydride in the solution of the metal hydride catalyst is selected from the group consisting of a copper hydride, a silver hydride, and a gold hydride.

[0069] Embodiment 6. The process of any of claims 1 to 5, wherein the product stream additionally comprises 1,1,1-trifluoropropane (HFC-263fb, $\text{CF}_3\text{CH}_2\text{CH}_3$).

[0070] Embodiment 7. A process for producing a solution of a metal-hydride catalyst comprising: a) providing a liquid hydrosilane as a solvent component in an amount > 50% w/w in a solvent system with respect to any co-solvent, b) contacting a metal hydride or a metal-hydride catalyst precursor with a stabilizing ligand and the liquid hydrosilane, c) dissolution of the metal-hydride in the solvent system to form the solution of the metal-hydride catalyst or reaction of the metal-hydride catalyst precursor with the liquid hydrosilane and dissolution in the solvent system to form the solution of the metal-hydride catalyst.

[0071] Embodiment 8. The process of claim 7, wherein the metal hydride is Stryker's reagent and the metal-hydride catalyst precursor is selected from the group consisting of a copper acetate, silver acetate, and a gold acetate.

[0072] Embodiment 9. The process of any of claims 7 to 8, wherein the liquid hydrosilane is a tetravalent silicon compound containing one or more Si-H bonds and is defined by the formula $\text{R}^1\text{R}^2\text{R}^3\text{SiH}$, wherein R^1 , R^2 and R^3 are each independently selected from the group consisting of H, Alk(C_1 to C_6 alkyl group), Ar(aryl), SiR_3 (silyl), OSiR_3 (siloxo), OR (alkoxy), NR_2 (amino) and halogen.

[0073] Embodiment 10. The process of any of claims 7 to 9, wherein the stabilizing ligand comprises triethyl phosphite.

[0074] Embodiment 11. The process of any of claims 7 to 10, wherein any co-solvent is excluded and the liquid hydrosilane as a solvent component is 100% of the solvent system.

[0075] Embodiment 12. The process of any of claims 7 to 11, wherein any co-solvent is selected from the group consisting of benzene, toluene, xylenes, a silane, or an excess of the stabilizing ligand.

[0076] Embodiment 13. A solution of a metal-hydride catalyst comprising a stabilizing ligand and > 50% of a liquid hydrosilane as a solvent component in a solvent system with respect to any co-solvent.

[0077] Embodiment 14. The solution of claim 13, wherein the metal-hydride catalyst is of a general formula Q_xM-H_y , where Q is the stabilizing ligand, M-Hy is a metal-hydride, x and y are independent integers of 1 to 3, and M is selected from the group consisting of copper (Cu), silver (Ag), and gold (Au).

[0078] Embodiment 15. The solution of any of claims 13 to 14, wherein the stabilizing ligand comprise phosphorous, nitrogen, oxygen, sulfur, a stabilized carbene, or combinations thereof, and wherein the stabilizing ligand is selected from the group consisting of PR^3 , R^3PO , NR^3 , SR^2 , OR^2 , or $:CR^2$, where each R^2 and R^3 is each independently selected from the group consisting of H, a C_1 - C_8 alkyl, aryl, silyl, C_1 - C_8 alkoxy, amino, and a halogen selected from the group consisting of F, Cl, Br and I.

[0079] Embodiment 16. The solution of any of claims 13 to 15, wherein the stabilizing ligand comprises triethyl phosphite.

[0080] Embodiment 17. The solution of any of claims 13 to 16, wherein the liquid hydrosilane is a tetravalent silicon compound containing one or more Si-H bonds and is defined by the formula $R^1R^2R^3SiH$, wherein R^1 , R^2 , R^3 , are each independently selected from the group consisting of H, Alk(C_1 to C_6 alkyl group), Ar(aryl), SiR_3 (silyl), $OSiR_3$ (siloxyl), OR (alkoxy), NR_2 (amino) and halogen.

[0081] Embodiment 18. The solution of any of claims 13 to 17, wherein the liquid hydrosilane is selected from the group consisting of triethylsilane, dimethylphenylsilane, or 1,1,3,3-tetramethyldisiloxane.

[0082] Embodiment 19. The solution of any of claims 13 to 18, further comprising HFC-263fb, HFO-1252zc, and HFO-1243zf.

[0083] Embodiment 20. The solution of any of claims 13 to 19, wherein any co-solvent is excluded and the liquid hydrosilane as a solvent component is 100% of the solvent system.

[0084] Embodiment 21. A composition comprising HFO-1252zc and E/Z-1-fluoropropene (E/Z-HFO-1261ze).

[0085] Embodiment 22. The composition of claim 21, wherein the composition comprises less than about 50 wt.% E/Z-HFO-1261ze.

[0086] Embodiment 23. The composition of any of claims 21 to 22, wherein the composition comprises less than about 1 wt.% E/Z-HFO-1261ze.

[0087] Embodiment 24. A refrigerant composition comprising HFO-1252zc and E/Z-HFO-1261ze in amount between greater than 0 wt.% and less than about 5 wt.%.

[0088] Embodiment 25. A refrigerant comprising at least a C₃ or C₄ fluoroolefin, HFO-1252zc, and E/Z-HFO-1261ze in an amount of less than about 1 wt.%.

[0089] Embodiment 26. A composition comprising 1,1-difluoropropene (HFO-1252zc) and at least one additional compound selected from the group consisting of E-1-fluoropropene (trans-HFO-1261ze), Z-1-fluoropropene (cis-HFO-1261ze), 1,1,1-trifluoropropane (HFC-263fb) 3,3,3-trifluoropropene (HFO-1243zf) and propylene, wherein the amount of E/Z-1-fluoropropene is less than about 1% by weight.

[0090] Embodiment 27. The composition of claim 26, wherein the amount of E/Z-1-fluoropropene is selected from one of between > about 0 and < about 0.5 % by weight, between > about 0 and < about 0.25 % by weight, and between > about 0 and < about 0.1 % by weight.

[0091] Although certain aspects, embodiments and principals have been described above, it is understood that this description is made only by way of example and not as a 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 comprising,
 - a) contacting a composition or product stream comprising and 3,3,3-trifluoropropene (HFO-1243zf, $\text{CF}_3\text{CH}=\text{CH}_2$) with a solution of a metal-hydride catalyst including a stabilizing ligand and a liquid hydrosilane as a solvent component in a solvent system, wherein the amount of HFO-1243zf is present at a first level, and wherein the composition or product stream optionally further comprises 1,1-difluoropropene (HFO-1252zc, $\text{CF}_2=\text{CHCH}_3$); and
 - b) selectively converting the HFO-1243zf to HFO-1252zc with the solution of the metal-hydride catalyst to reduce the amount of HFO-1243zf in the composition or product stream to a second level lower than the first level,wherein the level of HFO-1243zf is with respect to the HFO-1252zc in the product stream, and wherein the solution of the metal-hydride catalyst contains greater than 50% w/w of the liquid hydrosilane as a solvent component in the solvent system with respect to any co-solvent.
2. The process of claim 1, wherein the stabilizing ligand is triethyl phosphite, and wherein the liquid hydrosilane is selected from the group consisting of triethylsilane, dimethylphenylsilane, and 1,1,3,3-tetramethyldisiloxane.
3. The process of any of claims 1 and 2, wherein any co-solvent is excluded and the liquid hydrosilane is 100% of the solvent system.
4. The process of any of claims 1 to 3, wherein the stabilizing ligand has one or more binding sites.
5. The process of any of claims 1 to 4, wherein a metal hydride in the solution of the metal hydride catalyst is selected from the group consisting of a copper hydride, a silver hydride, and a gold hydride.
6. The process of any of claims 1 to 5, wherein the product stream additionally comprises 1,1,1-trifluoropropane (HFC-263fb, $\text{CF}_3\text{CH}_2\text{CH}_3$).

7. A process for producing a solution of a metal-hydride catalyst comprising
 - a) providing a liquid hydrosilane as a solvent component in an amount > 50% w/w in a solvent system with respect to any co-solvent,
 - b) contacting a metal hydride or a metal-hydride catalyst precursor with a stabilizing ligand and the liquid hydrosilane,
 - c) dissolution of the metal-hydride in the solvent system to form the solution of the metal-hydride catalyst or reaction of the metal-hydride catalyst precursor with the liquid hydrosilane and dissolution in the solvent system to form the solution of the metal-hydride catalyst.
8. The process of claim 7, wherein the metal hydride is Stryker's reagent and the metal-hydride catalyst precursor is selected from the group consisting of a copper acetate, silver acetate, and a gold acetate.
9. The process of any of claims 7 to 8, wherein the liquid hydrosilane is a tetravalent silicon compound containing one or more Si-H bonds and is defined by the formula $R^1R^2R^3SiH$, wherein R^1 , R^2 and R^3 are each independently selected from the group consisting of H, Alk(C_1 to C_6 alkyl group), Ar(aryl), SiR₃ (silyl), OSiR₃ (siloxyl), OR (alkoxy), NR₂ (amino) and halogen.
10. The process of any of claims 7 to 9, wherein the stabilizing ligand comprises triethyl phosphite.
11. The process of any of claims 7 to 10, wherein any co-solvent is excluded and the liquid hydrosilane as a solvent component is 100% of the solvent system.
12. The process of any of claims 7 to 11, wherein any co-solvent is selected from the group consisting of benzene, toluene, xylenes, a silane, or an excess of the stabilizing ligand.
13. A solution of a metal-hydride catalyst comprising a stabilizing ligand and > 50% of a liquid hydrosilane as a solvent component in a solvent system with respect to any co-solvent.
14. The solution of claim 13, wherein the metal-hydride catalyst is of a general formula $QxM-Hy$, where Q is the stabilizing ligand, M-Hy is a metal-hydride, x

and y are independent integers of 1 to 3, and M is selected from the group consisting of copper (Cu), silver (Ag), and gold (Au).

15. The solution of any of claims 13 to 14, wherein the stabilizing ligand comprise phosphorous, nitrogen, oxygen, sulfur, a stabilized carbene, or combinations thereof, and wherein the stabilizing ligand is selected from the group consisting of PR^3 , R^3PO , NR^3 , SR^2 , OR^2 , or $:CR^2$, where each R^2 and R^3 is each independently selected from the group consisting of H, a C_1 - C_8 alkyl, aryl, silyl, C_1 - C_8 alkoxy, amino, and a halogen selected from the group consisting of F, Cl, Br and I.
16. The solution of any of claims 13 to 15, wherein the stabilizing ligand comprises triethyl phosphite.
17. The solution of any of claims 13 to 16, wherein the liquid hydrosilane is a tetravalent silicon compound containing one or more Si-H bonds and is defined by the formula $R^1R^2R^3SiH$, wherein R^1 , R^2 , R^3 , are each independently selected from the group consisting of H, Alk(C_1 to C_6 alkyl group), Ar(aryl), SiR3 (silyl), OSiR3 (siloxyl), OR (alkoxy), NR2 (amino) and halogen.
18. The solution of any of claims 13 to 17, wherein the liquid hydrosilane is selected from the group consisting of triethylsilane, dimethylphenylsilane, or 1,1,3,3-tetramethyldisiloxane.
19. The solution of any of claims 13 to 18, further comprising HFC-263fb, HFO-1252zc, and HFO-1243zf.
20. The solution of any of claims 13 to 19, wherein any co-solvent is excluded and the liquid hydrosilane as a solvent component is 100% of the solvent system.
21. A composition comprising HFO-1252zc and E/Z-1-fluoropropene (E/Z-HFO-1261ze).
22. The composition of claim 21, wherein the composition comprises less than about 50 wt.% E/Z-HFO-1261ze.
23. The composition of any of claims 21 to 22, wherein the composition comprises less than about 1 wt.% E/Z-HFO-1261ze.

24. A refrigerant composition comprising HFO-1252zc and E/Z-HFO-1261ze in amount between greater than 0 wt.% and less than about 5 wt.%.
25. A refrigerant comprising at least a C₃ or C₄ fluoroolefin, HFO-1252zc, and E/Z-HFO-1261ze in an amount of less than about 1 wt.%.
26. A composition comprising 1,1-difluoropropene (HFO-1252zc) and at least one additional compound selected from the group consisting of E-1-fluoropropene (trans-HFO-1261ze), Z-1-fluoropropene (cis-HFO-1261ze), 1,1,1-trifluoropropane (HFC-263fb) 3,3,3-trifluoropropene (HFO-1243zf) and propylene, wherein the amount of E/Z-1-fluoropropene is less than about 1% by weight.
27. The composition of claim 26, wherein the amount of E/Z-1-fluoropropene is selected from one of between > about 0 and < about 0.5 % by weight, between > about 0 and < about 0.25 % by weight, and between > about 0 and < about 0.1 % by weight.