

TITLE

PROCESSES TO MAKE 1,2-DIFLUOROETHYLENE FROM
TETRACHLOROETHYLENE AND COMPOSITIONS THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/541,333 filed September 29, 2023, the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Hydrofluoroolefins (HFOs) having low ozone depletion potential (ODP) and low global warming potential (GWP) have been replacing saturated CFCs (chlorofluorocarbons), HCFCs (hydrochlorofluorocarbons), and HFCs (hydrofluorocarbons) in a variety of applications for several years because saturated hydrohalocarbons tend to have high GWP values. For example, HFC-32 (CH_2F_2), HFC-125 (C_2HF_5), and HFC-134a (CH_2FCF_3) have GWPs of 675, 3500 and 1430, respectively. As a result, low ODP and GWP materials continue to be of interest for use as refrigerants, solvents, foam expansion agents, cleaning agents, aerosol propellants, dielectrics, fire extinguishants, and power cycle working fluids.

[0003] The 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.

[0004] 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.

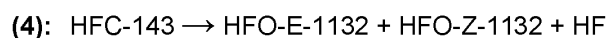
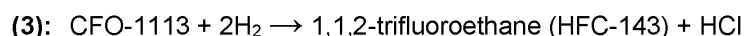
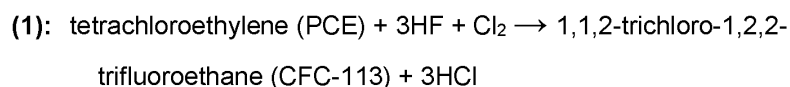
[0005] To meet these increasing demands, existing and new haloolefins continue to be developed, evaluated and produced with more efficient processes. One such candidate is the E- and/or Z-isomers of 1,2-difluoroethylene (HFO-1132) which are suitable as blending components given its environmentally friendly decomposition

profile in atmosphere. Current processing generally favors the production of the Z-isomer, which requires significant amounts to be isomerized to the E-isomer. Thus, the need for new processes to produce these new refrigerant candidate remains.

SUMMARY

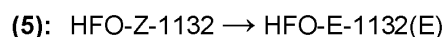
[0006] The present invention relates to processes for producing the E- and Z-isomers of 1,2-difluoroethylene (HFO-E-1132 and HFO-Z-1132) through intermediates, compositions thereof and methods of using the isomers.

[0007] Certain embodiments disclosed herein relate to integrated processes of making E- and Z-isomers of HFO-1132 using tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$, PCE) as the starting material according to the following reactions.



[0008] Certain embodiments disclosed herein relate to integrated processes involving a sequence of first, second, third, and fourth chemical reactions, stemming from conversion of PCE to a mixture of HFO-E-1132 and HFO-Z-1132.

[0009] Certain embodiments disclosed herein relate to an integrated process of making E- and Z-isomers of HFO-1132 using PCE as the starting material according to reactions (1), (2), (3) and (4) above, as well as the following isomerization reaction,



[0010] In certain embodiments disclosed herein, reactions (1), (2), (3), and (4) respectively produce first, second, third and fourth product mixture compositions which respectively form the reactant feeds for subsequent reactions (2), (3), (4) and (5).

[0011] In certain embodiments disclosed herein, reactions (1), (2), (3), and (4) are part of an integrated process, and each reaction is respectively conducted in a separate and discrete reactor.

[0012] In certain embodiments disclosed herein, reactions (2) and (3) are respectively conducted in discrete reactors/reactor systems in close proximity to one another because CFO-1113 is highly unstable, in the absence or presence of air. CFO-1113 should be treated as tetrafluoroethylene, and therefore it is desired the system for producing CFO-1113 is in close proximity to the system for hydrogenating CFO-1113. This can be achieved by integrating the two processes at the same location with minimum transportation either by directly coupling the two process steps together or building the hydrogenation process system at the location where CFO-1113 is produced, optionally at a common plant facility.

[0013] In certain embodiments disclosed herein, reactions (2) and (3) are combined in the same reactor and CFC-113 is converted directly to HFC-143 in a single process step.

[0014] In certain embodiments, reactions (1), (2), (3), (4) and (5) are part of an integrated process and each reaction is respectively conducted in a separate and discrete reactor, optionally at a common plant facility.

[0015] In certain embodiments, reactions (1), (2), (3), (4) and (5) are part of an integrated process and reactions (1), (4) and (5) are respectively conducted in a separate and discrete reactor, optionally at a common plant facility, whereas reactions (2) and (3) are combined in the same reactor and CFC-113 is converted directly to HFC-143 in a single process step.

[0016] In certain reactions embodiments, for reactions (1), (2), (3), and (4), the feed composition, respectively, includes,

- a. a PCE feed composition, preferably comprising PCE and one or more additional compounds selected from CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene, and 1,1,1,3-tetrachloropropane (HCC-250fb);
- b. a CFC-113 feed composition, preferably comprising CFC-113 and one or more additional compounds selected from CFC-113a, CFC-114a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFO-1317,

CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb. HCFC-122, CFC-112, CFC-112a, CFO-1112a, and PCE;

- c. a CFO-1113 feed composition, preferably comprising CFO-1113 and one or more additional compounds selected from 1,1,2-trifluoroethylene (HFO-1123), 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 1-chloro-2,2,2-trifluoroethane (HCFC-133a), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), and 1-chloro-1,2,2-trifluoroethane (HCFC-133); and
- d. an HFC-143 feed composition, preferably comprising HFC-143 and one or more additional compounds selected from: HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, HCFC-133, HCFC-133b, and HCO-1140.

[0017] In certain reaction embodiments, for reactions (1), (2), (3), and (4), the feed composition, respectively, includes,

- a. a PCE feed composition, preferably comprising PCE and one or more additional compounds selected from CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene, and 1,1,1,3-tetrachloropropane (HCC-250fb);
- b. a CFC-113 feed composition, preferably comprising CFC-113 and one or more additional compounds selected from CFC-113a, CFC-114a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb. HCFC-122, CFC-112, CFC-112a, CFO-1112a, and PCE;
- c. a CFO-1113 feed composition, preferably comprising CFO-1113 and one or more additional compounds selected from 1,1,2-trifluoroethylene (HFO-1123), 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 1-chloro-2,2,2-trifluoroethane (HCFC-133a), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), and 1-chloro-1,2,2-trifluoroethane (HCFC-133); and
- d. an HFC-143 feed composition, preferably comprising HFC-143 and one or more additional compounds selected from: HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, HCFC-133, HCFC-133b, and HCO-1140,

wherein the respective feed compositions of a), b), c), and d) are independently present an amount selected from one of >95% by weight, >96% by weight, >97% by

weight, >98% by weight, or >99% by weight, based on the total weight of the composition, and corresponding balances are respectively comprised of the total amount of the additional compounds of a), b), c), and d), after purification, for example by distillation.

[0018] In certain reaction embodiments, for reactions (1), (2), (3), and (4), the feed compositions respectively include PCE, CFC-113, CFO-1113, or HFC-143 components which are independently present an amount selected from between one of >50% by weight, >60% by weight, >70% by weight, >80% by weight or >90% by weight before purification, for example by distillation, and about <95% by weight, based on the total weight of the composition, and corresponding balances respectively are comprised of the total amount of the additional compounds of a), b), c), and d), after purification, for example by distillation.

[0019] In certain reaction embodiments, for reactions (1), (2), (3), and (4), the feed compositions respectively include PCE, CFC-113, CFO-1113, or HFC-143 components and additional compounds, wherein the amount of each PCE, CFC-113, CFO-1113, or HFC-143 component and corresponding additional compounds is independently selected from one of:

- >95 weight percent component and <5 weight percent additional compounds, based on the total weight of the composition,
- >96 weight percent component and <4 weight percent additional compounds, based on the total weight of the composition,
- >97 weight percent component and <3 weight percent additional compounds, based on the total weight of the composition,
- >98 weight percent component and <2 weight percent additional compounds, and
- >99 weight percent component and <1 weight percent additional compounds.

[0020] In certain embodiments, the CFC-113 feed composition preferably comprises CFC-113 and one or more additional compounds selected from CFC-113a, CFC-114a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, and CFO-1112a.

[0021] In certain embodiments, the relative molar amount of hydrogen to CFC-113 in reaction (3) is from about 1:1 to about 3:1.

[0022] In certain embodiments, the relative molar amount of hydrogen to CFC-113 in reaction (3) contacting is conducted a temperature of from about 80°C to about 250°C.

[0023] In certain embodiments, CFC-113 is contacted with hydrogen in the vapor phase in the presence of a catalyst to form an HFC-143 composition.

[0024] In certain embodiments, CFC-113 is contacted with hydrogen in the vapor phase in the presence of a catalyst which comprises a catalytic metal, selected from Pd, Pt, or a mixture thereof, preferably supported on Al₂O₃, fluorided alumina, AlF₃, or chromium oxide as disclosed in U.S. Patent Application 20080207962 and 20080207963, the disclosure of each of which is incorporated herein by reference.

[0025] In certain embodiments, CFC-113 is contacted with hydrogen in the vapor phase in the presence of a catalyst wherein the amount of catalytic metal on the support comprises from about 0.5 weight% to about 10 weight% of the catalyst composition.

[0026] In certain embodiments, the HFC-143 product comprises at least one compound selected from HCFC-123a, HCFC-132c, HCFC-133, HCFC-133b, C₂H₆, HFC-143a, HFC-134a, and HFC-152a.

[0027] In certain embodiments involving reaction (5), the HFO-1132 composition comprises at least one of HFO-E-1132 or HFO-Z-1132, and one or more additional compounds selected from acetylene, fluoroacetylene, difluoromethane (HFC-32), 1,1,1,2,2 pentafluoroethane (HFC-125), E-1-chloro-1,2-difluoroethylene (HCFO-E-1122a), Z-1-chloro-1,2-difluoroethylene (HCFO-Z-1122a), 1,1,2-trifluoroethylene (HFO-1123), fluoroethylene (HFO-1141), 1-chloro-1,2,2-trifluoroethane (HCFC-133), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1,2-difluoroethane (HFC-152), 1,1,2-trifluoroethane (HFC-143), fluoromethane (HFC-41), chlorodifluoromethane (HCFC-22), ethylene, 1-chloro-1,2-difluoroethane (HCFC-142a), 1,1-difluoroethylene (HFO-1132a), vinyl chloride (1140), 1-chloro-1-fluoroethene (HCFO-1131a), E-1-chloro-2-fluoroethene (HCFO-E-1131), Z-1-chloro-1-fluoroethene (HCFO-Z-1131), and 1-chloro-2,2-difluoroethylene

(HCFO-1122). Preferably, the amount of 1,2-difluoroethane (HFC-152) is selected from one of <100 ppm, <50 ppm, <10 ppm, <5 ppm, or <1 ppm.

[0028] In certain HFO-E-1132, HFO-Z-1132 or HFO-Z/E-1132 product mixture embodiments, the amount of fluoroethylene (HFO-1141), vinyl chloride (HCO-1140), acetylene and fluoroacetylene is selected from one of <2000 ppm, <1000 ppm, <500 ppm, <400 ppm, <300 ppm, <200 ppm, <100 ppm, <50 ppm, <10 ppm, <5 ppm, between ≥ 0.00001 ppm and <500 ppm, between ≥ 0.0001 ppm and <500 ppm, between ≥ 0.00001 ppm and <100 ppm, between ≥ 0.0001 ppm and <100 ppm, between ≥ 1 ppm and less than about 2000 ppm, between ≥ 1 ppm and less than about 1000 ppm, or ≥ 0 and <100 ppm, and all values and ranges between about 0.00001 ppm and 2000 ppm.

[0029] In certain embodiments, the HFO-E-1132, HFO-Z-1132 or HFO-Z/E-1132 product mixture contains at least two additional members selected from: one of HFO-Z-1132 or HFO-E-1132, and at least one of acetylene, fluoroacetylene, difluoromethane (HFC-32), 1,1,1,2,2 pentafluoroethane (HFC-125), E-1-chloro-1,2-difluoroethylene (HCFO-E-1122a), Z-1-chloro-1,2-difluoroethylene (HCFO-Z-1122a), 1,1,2-trifluoroethylene (CFO-1123), fluoroethylene (HFO-1141), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1-chloro-1,2,2-trifluoroethane (HCFC-133), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1,2-difluoroethane (HFC-152), 1,1,2-trifluoroethane (HFC-143), fluoromethane (HFC-41), chlorodifluoromethane (HCFC-22), ethylene, 1-chloro-1,2-difluoroethane (HCFC-142a), 1,1-difluoroethylene (HFO-1132a), vinyl chloride (HCO-1140), 1-chloro-1-fluoroethene (HCFO-1131a), E-1-chloro-2-fluoroethene (HCFO-E-1131), Z-1-chloro-2-fluoroethene (HCFO-Z-1131), vinylidene fluoride (HFO-1132a) and 1-chloro-2,2-difluoroethylene (HCFO-1122). Preferably the amount of 1,2-difluoroethane (HFC-152) is selected from one of <100 ppm, 50 ppm, 10 ppm, 5 ppm, or 1 ppm.

[0030] Embodiments disclosed herein relate to process of converting (chlorofluorinating) PCE to CFC-113, e.g., making or producing CFC-113, in either **(1)** the liquid phase which is catalyzed by a metal halide in the presence of HF and Cl_2 , at temperatures between 80°C-120°C, or **(2)** the gas phase in the presence of a partially fluorided metal catalyst wherein the metal comprises a Group 6 metal of the Periodic Table, at temperatures between 250°C and 400°C. In one embodiment

disclosed herein, the PCE composition comprises tetrachloroethylene and at least one or more compounds selected from CCl₄, CHCl₃, bromotrichloromethane, bromodichloroethylene isomer(s), bromotrichloroethylene, trichloroethylene, 1,1,3-trichloropropene, ethylene, and 1,1,1,3-tetrachloropropane.

[0031] Certain embodiments disclosed herein relate to a tetrachloroethylene (PCE) composition containing >99% by weight PCE based on the total amount of the composition, and one or more additional compounds selected from chloroform, carbon tetrachloride, bromotrichloromethane, bromodichloroethylene isomer(s), bromotrichloroethylene, 1,2-dichloroethane, ethylene, trichloroethylene, 1,1,3-trichloro-1-propene, and 1,1,1,3-tetrachloropropane. In one embodiment disclosed herein, the PCE composition comprises tetrachloroethylene and one or more compounds selected from CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene, and 1,1,1,3-tetrachloropropane, wherein the amount of said compounds is less than 1 weight% of the total composition.

[0032] In another embodiment disclosed herein, a PCE composition is converted to a CFC-113 composition comprising, two or more, three or more, or four or more additional compounds selected from CFC-113a, CFC-114a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, CFO-1112a, and PCE.

[0033] Certain embodiments disclosed herein relate to the process of reaction (2) which comprises contacting a CFC-113 composition and a reducing metal comprising zinc, magnesium, or cadmium in the liquid phase, to dechlorinate CFC-113 and produce CFO-1113.

[0034] In one embodiment, the CFC-113 composition comprises, consists essentially or, or consists of CFC-113 and less than about 1% by weight of two or more additional compounds selected from CFC-113a, CFC-114a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, CFO-1112a, and PCE, wherein the total amount of said additional compounds is less than 1 weight % of the total composition.

[0035] In another embodiment disclosed herein, the product mixture comprising CFO-1113 comprises, consists essentially of, or consists of at least one or more

compounds selected from: HCFC-123a, HCFC-133a, HCFC-133b, HCFC-133, and CFC-113.

[0036] Certain embodiments disclosed herein relate to a composition which comprises, consists essentially or, or consists of >99% by weight CFC-113 based on the total amount of the composition, and three or more additional compounds selected from CFC-113a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114a, CFC-114, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, CFO-1112a, and PCE, wherein the total amount of said additional compounds is less than 1 weight% of the total composition.

[0037] In certain embodiments disclosed herein, the second product mixture comprises CFO-1113 in an amount >99% by weight based on the total amount of the composition which also includes one or more additional compounds selected from selected from CFC-113a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFC-114a, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, CFO-1112a, HFO-1123, HCFC-133, HCFC-133a, HCFC-133b, and PCE, wherein the total amount of said additional compounds is less than 1 weight% of the total composition.

[0038] In certain embodiments disclosed herein, the second product mixture comprises CFO-1113 in an amount >99% by weight based on the total amount of the composition which also includes two or more additional compounds selected from CFC-113a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFC-114a, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, CFO-1112a, HFO-1123, HCFC-133, HCFC-133a, HCFC-133b, and PCE, wherein the total amount of said additional compounds is less than 1 weight% of the total composition.

[0039] Certain embodiments disclosed herein relate to the process of reaction (3) comprising contacting the CFO-1113 second product mixture and hydrogen, in the gas phase, optionally in the presence of a catalyst, to produce a third product mixture comprising HFC-143, e.g., making or producing HFC-143.

[0040] In one embodiment disclosed herein, the HFC-143 composition comprises HFC-143 and one or more additional compounds selected from HFO-1123, CFO-1113, HCFC-133, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a,

HCFO-1122, HCFO-1122a, and HCO-1140, and the amount of additional compounds is greater than 0 and less than 1% by weight based on the total amount of the HFC-143 composition.

[0041] Certain embodiments disclosed herein relate to processes comprising contacting CFO-1113 with hydrogen at a temperature of from about 50°C to about 150°C.

[0042] Certain embodiments disclosed herein relate to processes comprising contacting CFO-1113 with hydrogen at a temperature of from about 50°C to about 150°C and in the presence of a hydrogenation catalyst comprising a catalytic metal selected from the group Re, Ni, Pd, Pt, Ru, Rh, and Ir. Catalytic metals are preferably supported on carbon, aluminum oxide, fluorided alumina, or aluminum fluoride as disclosed, for example, in U.S. 5,068,473, the disclosure of which is incorporated herein by reference in its entirety.

[0043] Certain embodiments disclosed herein relate to the processes integrating steps (2) and (3) above in which CFC-113 is contacted with hydrogen in the vapor phase in a reaction zone to provide a mixture comprising HFC-143 at a temperature of from about 150°C to about 350°C, wherein said reaction zone contains a catalytic metal, selected from Pd, Pt, or a mixture thereof, preferably supported on Al₂O₃, fluorided alumina, AlF₃, or chromium oxide as disclosed in U.S. Patent Application 20080207962 and 20080207963, the disclosure of each of which is incorporated herein by reference in its entirety.

[0044] In certain embodiments disclosed herein, the product mixture of reaction (3), the third product mixture comprises primarily HFC-143 and one or more of the following compounds HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-123a, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113. In certain embodiments disclosed herein, the dehydrofluorination of HFC-143 (4) is conducted in the gas phase or the liquid phase.

[0045] In certain embodiments disclosed herein, the dehydrofluorination reaction (4) is conducted in the gas phase.

[0046] In certain embodiments disclosed herein, the dehydrofluorination reaction (4) is conducted in the liquid phase.

[0047] In certain embodiments disclosed herein, the dehydrofluorination reaction (4) is conducted in the gas phase at a temperature between 150°C and 400°C.

[0048] In certain embodiments disclosed herein the dehydrofluorination reaction (4) is conducted in the liquid phase at a temperature between -20°C and 150°C.

[0049] In certain embodiments disclosed herein, reaction (4) is conducted in the gas phase, at a temperature between 150°C and 400°C and in the presence of a catalyst selected from the group consisting of aluminum fluoride, fluorided alumina, a metal supported on a trivalent aluminum compound containing fluoride anion (e.g., aluminum fluoride and/or fluorided alumina), lanthanum fluoride, fluorided lanthanum oxide, metal supported on a trivalent lanthanum compound containing fluoride anion (e.g., lanthanum fluoride and/or fluorided lanthanum oxide), trivalent chromium compounds (e.g., Cr₂O₃) wherein the said metal is selected from the group consisting of one or more of chromium, manganese, iron, cobalt, nickel, magnesium, and zinc. Other suitable catalysts comprise cobalt- or nickel-substituted chromium oxide catalysts prepared as disclosed in U.S. 7,217,678, the disclosure of which is incorporated herein by reference in its entirety.

[0050] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase at a temperature between -20°C and 150°C, in the presence of a strong base, a polar solvent, and optionally a phase transfer catalyst.

[0051] Certain embodiments disclosed herein relate to reaction (4), where the starting material comprises an HFC-143 composition containing at least two of the compounds selected from HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HCFO-E-1122a, HCFO-Z-1122a, HFO-1140, HCFC-133, HCFC-133b, HCFC-123a, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.

[0052] Certain embodiments disclosed herein relate to reaction (4), where the starting material comprises a HFC-143 composition containing at least two of the compounds selected from HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-133b, HCFC-133, HCFC-123a, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113

and the reaction is conducted in the liquid phase at a temperature between -20 °C and 150°C, in the presence of an alkaline metal hydroxide, including but not limited to LiOH, NaOH, or KOH, in water or a polar solvent, and optionally a phase transfer catalyst.

[0053] In certain embodiments disclosed herein, reaction (4) is conducted in the liquid phase at a temperature between -20 °C and 150°C in the presence of a strong base, a polar solvent, and optionally a phase transfer catalyst which comprises a material selected from quaternary ammonium salts of the formula [NR₁R₂R₃R₄]X and phosphonium salts of the formula [PR₁R₂R₃R₄]X wherein X = F, Cl, Br, I, OH, HCO₃, CO₃, HSO₄, or SO₄, and R₁, R₂, R₃, and R₄ are independently selected from the group consisting of alkyl group, an aryl group or an aralkyl group. Specific examples include tetramethylammonium chloride, tetramethylammonium bromide, benzyltriethylammonium chloride, methyltriethylammonium chloride, tetra-n-butylammonium chloride, tetra-n-butylammonium bromide, tetra-n-butylammonium hydrogen sulfate, tetra-n-butylphosphonium chloride, tetraphenylphosphonium bromide, tetraphenylphosphonium chloride, triphenylmethylphosphonium bromide and triphenylmethylphosphonium chloride.

[0054] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase at a temperature between -20°C and 100°C in the presence of a strong base and the presence or absence of a catalyst.

[0055] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of a strong base, a solvent and the presence or absence of a catalyst.

[0056] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of an alkali metal or alkaline earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline metal amide, and a solvent.

[0057] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or

an alkaline-earth metal amide, in the presence of an organic solvent comprising an acyclic or cyclic ether.

[0058] Certain embodiments disclosed herein relate to reaction **(4)** which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide in the presence of an organic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst.

[0059] Certain embodiments disclosed herein relate to reaction **(4)** which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of **(i)** an alkaline metal or alkaline earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, **(ii)** an organic solvent comprising an acyclic or cyclic ether, and **(iii)** the presence or absence of a catalyst comprising a Crown ether or cryptand.

[0060] Certain embodiments disclosed herein relate to reaction **(4)** which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an organic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst comprising a Crown ether or cryptand, wherein the alkaline metal is a Group 1A metal of the Periodic Table excluding hydrogen, and the alkaline-earth metal is a Group 2A metal of the Periodic Table excluding beryllium.

[0061] Certain embodiments disclosed herein relate to reaction **(4)** which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of an alkaline or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an organic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst comprising a Crown ether or cryptand, wherein the alkaline metal or alkaline-earth metal alkoxide comprises one of lithium methoxide, sodium methoxide, sodium ethoxide, potassium tert-butoxide,

sodium tert-butoxide, sodium isopropoxide, or magnesium ethoxide, the alkaline or alkaline-earth metal hydride comprises lithium hydride, sodium hydride, potassium hydride, or calcium hydride, the organometallic lithium compound comprises n-butyl lithium, methyl lithium, or isopropyl lithium, and the alkaline or an alkaline-earth metal amide, comprises lithium dimethylamide, lithium diethylamide, lithium diisopropylamide, or magnesium bis(diisopropylamide).

[0062] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of an alkaline or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an organic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst comprising a Crown ether or cryptand, wherein the alkaline metal or alkaline-earth metal alkoxide comprises one of lithium methoxide, sodium methoxide, sodium ethoxide, potassium tert-butoxide, sodium tert-butoxide, sodium isopropoxide, or magnesium ethoxide, the alkaline or alkaline-earth metal hydride comprises lithium hydride, sodium hydride, potassium hydride, or calcium hydride, the organometallic lithium compound comprises n-butyl lithium, methyl lithium, or isopropyl lithium, and the alkaline or an alkaline-earth metal amide, comprises lithium dimethylamide, lithium diethylamide, lithium diisopropylamide, or magnesium bis(diisopropylamide).

[0063] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of an alkaline or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an organic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst and the organic solvent comprises one of diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, tetrahydrofuran, or dioxane.

[0064] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C in the presence of an alkali or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-

earth metal amide, in the presence of an organic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst and the organic solvent comprises one of diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, tetrahydrofuran, or dioxane and a catalyst which comprises a crown ether selected from one of 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) or a cryptand comprising 4,7,13,16, 21,24-hexaoxa-1,10-diazabicyclo-(8.8.8)hexacosane (also known as 2,2,2-cryptand).

[0065] One embodiment disclosed herein relates a process involving reaction (5) and heating a mixture of HFO-Z-1132 and HFO-E-1132 at temperature $\geq 600^{\circ}\text{C}$ to isomerize at least a portion of HFO-Z-1132 into HFO-E-1132.

[0066] One embodiment disclosed herein relates to a process involving reaction (5) and catalytically isomerizing HFO-Z-1132 to HFO-E-1132 at temperature of about 250°C to about 500°C .

[0067] One embodiment disclosed herein relates a process involving reaction (5) and catalytically converting a portion of HFO-Z-1132 to HFO-E-1132 at temperature of about 300°C to about 450°C and the catalyst is selected from Cr_2O_3 , fluorided Cr_2O_3 , Al_2O_3 , fluorided Al_2O_3 , or AlF_3 , chromium supported on alumina, fluorided alumina, or AlF_3 , or cobalt- or nickel-substituted chromium oxide as disclosed in U.S. 7,217,678, the disclosure of which is incorporated herein by reference in its entirety.

[0068] One embodiment disclosed herein relates to a composition comprising PCE and at least two of the compounds/components selected from chloroform, carbon tetrachloride, bromotrichloromethane, bromodichloroethylene isomer(s), bromotrichloroethylene, 1,2-dichloroethane, ethylene, trichloroethylene, 1,1,3-trichloro-1-propene, and 1,1,1,3-tetrachloropropane.

[0069] One embodiment disclosed herein relates to a composition comprising PCE and at least two of the compounds/components selected from chloroform, carbon tetrachloride, bromotrichloromethane, bromotrichloroethylene, bromodichloroethylene isomer(s), 1,2-dichloroethane, ethylene, trichloroethylene, 1,1,3-trichloro-1-propene, and 1,1,1,3-tetrachloropropane and the amount of PCE is

>99 weight percent based on the total amount of the composition and where the amount of other components is less than 1 weight % of the total composition.

[0070] One embodiment disclosed herein relates to a composition comprising CFO-1113 and at least one or two of the compounds/components selected from HFO-1123, 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), and 1-chloro-1,2,2-trifluoroethane (HCFC-133).

[0071] One embodiment disclosed herein relates to a composition comprising HFC-143 and at least two of the compounds/components selected HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-123a, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.

[0072] One embodiment disclosed herein relates to a composition comprising HFC-143 and at least three of the compounds/components selected HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-123a, HCFC-133, HCFC-133b, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.

[0073] One embodiment disclosed herein relates to a composition comprising HFC-143 and at least four of the compounds/components selected HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-123a, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.

[0074] One embodiment disclosed herein relates to a composition comprising HFC-143 and at least five or more of the compounds/components selected HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-123a, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.

[0075] In one embodiment disclosed herein HFO-E-1132 and/or HFO-Z-1132 is blended with other HFC, HFO, e.g., HFO-E/Z1234, HFO-1234yf, HFO-1336, and HCFO compounds for use as refrigerants, solvents, foam expansion agents, cleaning agents, aerosol propellants, dielectrics, fire extinguishants, and power cycle working fluids.

[0076] 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.

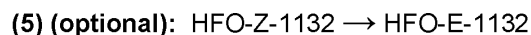
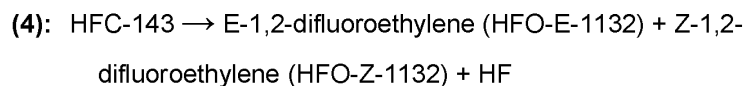
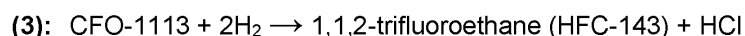
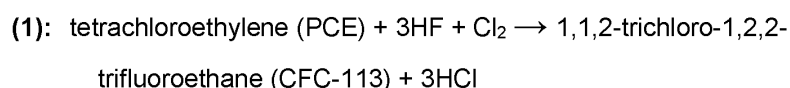
BRIEF DESCRIPTION OF THE DRAWING

[0077] Fig. 1 schematically illustrates a system for carrying out the integrated process, according to one embodiment of the present invention; and

[0078] Fig. 2 is a schematic flow scheme illustrating the use of a distillation column and optional recycle stream to obtain a composition having a low Z:E ratio of HFO-1132, according to some embodiments of the present invention.

DETAILED DESCRIPTION

[0079] The present invention relates to processes for producing E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132) according to the following reactions:



[0080] In some embodiments, the present invention relates to compositions from steps (1), (2), (3) and/or (4), and optionally also (5).

[0081] Referring to Fig. 1, the present invention also relates to a system comprising a series of reactors 10, 20, 30 and 40 for conducting reactions (1), (2), (3) and (4), respectively. Optionally, in one embodiment, the reactors 10, 20, 30, 40 are integrated such that each reactor 10, 20, 30, 40 is in flow communication with the immediately preceding/upstream reactor and/or the immediately following/downstream reactor. Reactors 10, 20, 30 and 40 are suitably configured as liquid phase or gas phase reactors, with or without catalysts or reactive metals, as required for each individual reaction step as discussed herein, for producing intermediate mixtures and HFO-E/Z-1132 mixtures from a starting feed of tetrachloroethylene (PCE or R-1110), HF and chlorine. The first, second, and the third reactors, 10, 20 and 30 respectively, produce intermediate product streams respectively comprising CFC-113, CFO-1113, and HFC-143.

[0082] More particularly, referring to Fig. 1, a starting feed composition comprising PCE is introduced into a first reactor 10, along with HF and Cl₂, to synthesize CFC-113. The first reactor 10 thus produces a first intermediate product mixture containing CFC-113, which is withdrawn from the first reactor 10 through line 12 and fed to the second reactor 20. Optionally, in one embodiment, the CFC-113 is separated from the first intermediate stream using conventional separation equipment (not shown), and then the purified CFC-113 stream is introduced into the liquid phase reactor 20, which contains a zinc suspension, to synthesize CFO-1113. The second reactor 20 thus produces a second intermediate product mixture containing CFO-1113, which is withdrawn from the second reactor through line 14 and fed to the third reactor 30. Optionally, in one embodiment, the CFO-1113 is separated from the second intermediate stream using conventional separation equipment (not shown), and then the purified CFO-1113 is introduced into the third reactor 30. Hydrogen is also fed to the third reactor 30 along with the CFO-1113, and the components are reacted to form HFC-143.

[0083] In another embodiment, the CFC-113 produced in the first reactor 10, optionally purified as described above, may be directly fed to the third reactor 30 via line 17.

[0084] The third reactor 30 thus produces a third intermediate product mixture containing HFC-143, which is withdrawn from the third reactor 30 through line 16 and

fed to the fourth reactor 40. Optionally, in one embodiment, the HFC-143 is separated from the third intermediate stream using conventional separation equipment (not shown), and then the purified HFC-143 is introduced into the fourth reactor 40 for conversion into a fourth product mixture comprising HFO-E-1132 + HFO-Z-1132.

[0085] For example, in one embodiment, the fourth product mixture may have a HFO-Z-1132 to HFO-E-1132 ratio of about 5:1 to about 100:1. In such cases, where the Z:E ratio is relatively high, it may be desirable to subject the product mixture to distillation to produce a low-boiling fraction rich in HFO-E-1132 and high-boiling fraction rich in HFO-Z-1132.

[0086] More particularly, as shown in Fig. 2, in one embodiment, the fourth product mixture, having a relatively high Z:E ratio of HFO-1132, is withdrawn from the fourth reactor 40 and fed to a separation system, such as distillation column 50, via line 18. Thus, in one embodiment, the present invention relates to a system of reactors 10, 20, 30 and 40, optionally integrated, along with transfer lines 12, 14, 16, and 17, as discussed above with respect to Fig. 1, and further comprising a further transfer line 18 and distillation column 50.

[0087] The separation system, which for example may comprise one or more distillation columns 50, is configured to separate the fourth product mixture into an overhead stream 22 comprising a low-boiling fraction rich in HFO-E-1132 and a bottoms stream 24 comprising a high-boiling fraction rich in HFO-Z-1132.

[0088] In certain embodiments, the overhead stream 22 comprises (i) HFO-E-1132; (ii) HFO-Z-1132; and (iii) at least one additional compound selected from acetylene, fluoroacetylene, HFC-32, HFC-125, HCFO-E-1122a, HCFO-Z-1122a, CFO-1123, HFO-1141, HCFC-133b, HCFC-133, HCFC-123, HFC-152, HFC-143, HFC-41, HCFC-22, ethylene, HCFC-142a, HFO-1132a, HCO-1140, HCFO-1131a, HCFO-E-1131, HCFO-Z-1131, HFO-1132a and HCFO-1122.

[0089] In one embodiment, the overhead stream 22 has a relatively low Z:E ratio of HFO-1132 isomers, for example a Z:E ratio of from about 0.01:1 to about 0.1:1, while the bottoms stream 24 has a relatively higher Z:E ratio of HFO-1132 isomers, for example a Z:E ratio of about 10:1 or greater. In one embodiment, either or both of the streams 22, 24 may be conveyed to an isomerization reactor (not shown) for

isomerization of the HFO-Z-1132 to HFO-E-1132. stream can be subjected to an isomerization reaction to increase the content of the E-isomer.

[0090] Additionally, or alternatively, in one embodiment, as shown in Fig. 2, the bottoms stream 24 may be recycled to the first reactor 10 for use in the synthesis of CFC-113. More particularly, in one embodiment, the high boiling fraction 24 comprised mainly of HFO-Z-1132 may be returned to the first reactor 10, where it undergoes chlorofluorination by a series of the following reactions to produce CFC-113.

1. $\text{HFO-Z-1132} + \text{Cl}_2 \rightarrow \text{CHClFCHClF}$ (HCFC-132)
2. $\text{HCFC-132} + \text{Cl}_2 \rightarrow \text{HCl} + \text{CHClFCCl}_2\text{F}$ (HCFC-122a)
3. $\text{HCFC-122a} + \text{Cl}_2 \rightarrow \text{HCl} + \text{CCl}_2\text{FCCl}_2\text{F}$ (CFC-112)
4. $\text{CFC-112} + \text{HF} \rightarrow \text{HCl} + \text{Cl}_2\text{FCClF}_2$ (CFC-113)

[0091] Before addressing details of embodiments described herein, some terms are defined or clarified as follows.

[0092] The term “compound” as used herein is meant to include all stereoisomers, geometric isomers, tautomers, and isotopes of the structures or chemical described. Compounds herein identified by name or structure as one particular tautomeric form are intended to include other tautomeric forms unless otherwise specified.

[0093] The term “hydrohaloalkane,” as used herein means a molecule containing hydrogen, carbon, fluorine (HFCs) and/or chlorine (HCFCs) and/or bromine and/or iodine, with no carbon-carbon double bond (halo = fluoro, chloro, bromo, iodo). Examples are described throughout the instant specification.

[0094] The term “hydrohaloalkene” is intended to mean a chemical compound selected from the classes of hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) which include a double bond between adjacent carbon atoms and can contain 1 to 8 carbon atoms.

[0095] The term “isomerization process,” as used herein, means a process for changing geometry of a molecule, e.g., from the cis- orientation to the trans- orientation in an olefin. As well known in the art, cis-isomers and trans-isomers are more accurately referred to as Z- or E-isomers depending on the exact substitution

pattern in the olefin. In an isomerization process, the relative ratio of Z and E isomers is changed.

[0096] The term “scrubbing” is meant using solid or liquid media to selectively remove certain components to achieve desired production quality.

[0097] The term “chlorofluorination” as used herein is meant to include a liquid or vapor phase process in which a suitable substrate (e.g., PCE) is contacted with a mixture of hydrogen fluoride (HF) and chlorine (Cl₂) in a reaction zone to increase the fluorine content of said substrate. In addition to the reactors disclosed herein, heat exchangers, effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, and feed and material transfer lines associated with reactors, heat exchangers, vessels, columns, and units that are used in the processes of embodiments disclosed herein should be constructed of materials resistant to corrosion. Preferably, the reactors and components are made of an acid resistant alloy, e.g., nickel, nickel-based alloys (e.g., Hastelloy® available from Special Metals Corp), nickel-chromium alloys commercially available under the trade name of Inconel® (hereafter “Inconel®”), or nickel-copper alloys marketed under the trade name Monel®. Alternatively, containers, piping, or reactors fabricated from less corrosive-resistant metals such as stainless steel or carbon steel may be lined with a fluoropolymer such as poly(tetrafluoroethylene). In addition to the reactors disclosed herein, preheaters and vaporizers, heat exchangers, feed and effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, and valving associated with reactors, heat exchangers, vessels, columns, and units that are used in the processes of various embodiments disclosed herein should be constructed of materials resistant to corrosion.

[0098] 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).

[0099] 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.

[0100] 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.’

[0101] 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.”

[0102] 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.

[0103] 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. It is not intended that the scope of the invention be limited to the specific values recited when defining a range. Moreover, all ranges set forth herein are intended to include not only the particular ranges specifically described, but also any combination of values therein, including the minimum and maximum values recited.

[0104] 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.

[0105] As used herein GC/FID peak area correlates to the amount of a compound present as a proportion of the total area of all detected peaks. FID area% can be converted to mol% using a response factor either calculated or measured

[0106] As used herein, the term “substantially free” means that less than about 0.0001 percent by weight is present (1 ppm).

[0107] As used herein the term “about” in certain embodiments can be quantified to mean $\pm 1\%$, $\pm 2\%$, $\pm 3\%$ up to and including $\pm 10\%$ of the stated value, and all whole numbers and fractions therebetween.

TABLE OF COMPOUNDS

[0108] By way of example, mention is made of the following compounds:

TABLE 1

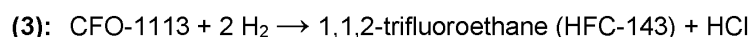
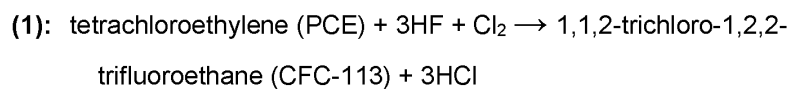
Name	Chemical Name	Formula
HC	acetylene	$\text{CH}\equiv\text{CH}$
HCC-170	ethane	CH_3CH_3
DCM	dichloromethane, methylene chloride	CH_2Cl_2
HCC-10	carbon tetrachloride	CCl_4
CFC-12	dichlorodifluoromethane	CCl_2F_2
HCFC-21	dichlorofluoromethane	CHCl_2F
HCFC-22	chlorodifluoromethane	CHClF_2
HFC-23	trifluoromethane	CHF_3
TCE	trichloroethylene	$\text{CCl}_2=\text{CHCl}$
PCE	tetrachloroethylene	$\text{CCl}_2=\text{CCl}_2$
CFC-112	1,1,2,2-tetrachloro-1,2-difluoroethane	$\text{CCl}_2\text{FCCl}_2\text{F}$

Name	Chemical Name	Formula
CFC-112a	1,1,1,2-tetrachloro-2,2-difluoroethane	$\text{CCl}_3\text{CCIF}_2$
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane	$\text{CCl}_2\text{FCCIF}_2$
CFC-113a	1,1,1-trichloro-2,2,2-trifluoroethane	CCl_3CF_3
CFC-114	1,2-dichloro-1,1,2,2-tetrafluoroethane	$\text{CCIF}_2\text{CCIF}_2$
CFC-114a	1,1-dichloro-1,2,2,2-tetrafluoroethane	CCl_2FCF_3
CFC-115	1-chloro-1,1,2,2,2-pentafluoroethane	CCIF_2CF_3
HCFC-122	1,1,2-trichloro-2,2-difluoroethane	$\text{CHCl}_2\text{CCIF}_2$
HCFC-123	1,1-dichloro-2,2,2-trifluoroethane	CHCl_2CF_3
HCFC-123a	1,2-dichloro-1,1,2-trifluoroethane	$\text{CCIF}_2\text{CHCIF}$
HCFC-124	1-chloro-1,2,2,2-tetrafluoroethane	CHCIFCF_3
HCFC-124a	1-chloro-1,1,2,2-tetrafluoroethane	$\text{CCIF}_2\text{CHF}_2$
HCFC-133	1-chloro-1,2,2-trifluoroethane	CHCIFCHF_2
HCFC-133a	1-chloro-2,2,2-trifluoroethane	CH_2CICF_3
HCFC-133b	1-chloro-1,1,2-trifluoroethane	$\text{CCIF}_2\text{CH}_2\text{F}$
HFC-134	1,1,2,2-tetrafluoroethane	CHF_2CHF_2
HFC-134a	1,1,1,2-tetrafluoroethane	CH_2FCF_3
HCFC-141	1,2-dichloro-1-fluoroethane	$\text{CH}_2\text{CICHCIF}$
HCFC-142	1-chloro-2,2-difluoroethane	$\text{CH}_2\text{CICHF}_2$
HCFC-142a	1-chloro-1,2-difluoroethane	CH_2FCHCIF
HFC-143	1,1,2-trifluoroethane	CH_2FCHF_2
HFC-143a	1,1,1-trifluoroethane	CH_3CF_3
HCFC-151a	1-chloro-1-fluoroethane	CHCIFCH_3
HFC-152	1,2-difluoroethane	$\text{CH}_2\text{FCH}_2\text{F}$
HFC-152a	1,1-difluoroethane	CH_3CHF_2
HCC-160	chloroethane	CH_2ClCH_3
HFC-161	fluoroethane	CH_2FCH_3
CFC-214cb	1,1,1,3-tetrachloro-2,2,3,3-tetrafluoropropane	$\text{CCIF}_2\text{CF}_2\text{CCl}_3$
CFC-215cb	1,1,1-trichloro-2,2,3,3,3-pentafluoropropane	$\text{CF}_3\text{CF}_2\text{CCl}_3$
CFC-216	dichlorohexafluoropropane	$\text{C}_3\text{Cl}_2\text{F}_6$
HFC-236fa	1,1,1,3,3,3-hexafluoropropane	$\text{CF}_3\text{CH}_2\text{CF}_3$
CFC-316	tetrachlorohexafluorobutane	$\text{C}_4\text{Cl}_4\text{F}_6$
CFC-318	dichlorooctafluorobutane	$\text{C}_4\text{Cl}_2\text{F}_8$
CFO-E-1112	E-1,2-dichloro-1,2-difluoroethylene	E-CCIF=CCIF
CFO-Z-1112	Z-1,2-dichloro-1,2-difluoroethylene	Z-CCIF=CCIF
CFO-1112a	1,1-dichloro-2,2-difluoroethylene	$\text{CCl}_2=\text{CF}_2$

Name	Chemical Name	Formula
CFO-1113	chlorotrifluoroethylene	$\text{CClF}=\text{CCF}_2$
HCFO-1122	1-chloro-2,2-difluoroethylene	$\text{CHCl}=\text{CF}_2$
HCFO-E-1122a	E-1-chloro-1,2-difluoroethylene	$\text{E-CClF}=\text{CHF}$
HCFO-Z-1122a	Z-1-chloro-1,2-difluoroethylene	$\text{Z-CClF}=\text{CHF}$
HFO-1123	1,1,2-trifluoroethylene	$\text{CF}_2=\text{CHF}$
HCFO-E-1131	E-1-chloro-2-fluoroethylene	$\text{E-CHCl}=\text{CHF}$
HCFO-Z-1131	Z-1-chloro-2-fluoroethylene	$\text{Z-CHCl}=\text{CHF}$
HCFO-1131a	1-chloro-1-fluoroethylene	$\text{CH}_2=\text{CClF}$
HFO-E-1132	E-1,2-difluoroethylene	$\text{E-CHF}=\text{CHF}$
HFO-Z-1132	Z-1,2-difluoroethylene	$\text{Z-CHF}=\text{CHF}$
HFO-1132a	1,1-difluoroethylene	$\text{CH}_2=\text{CF}_2$
HCO-1140	vinyl chloride	$\text{CH}_2=\text{CHCl}$
HFO-1141	fluoroethylene	$\text{CHF}=\text{CH}_2$
HCO-1150	ethylene	$\text{CH}_2=\text{CH}_2$
CFO-1317	chloroheptafluorobutene	C_4ClF_7

[0109] Some of the compounds present in the compositions of the present invention identified in Table 1 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. For instance, 1,2-difluoroethylene (HFO-1132) is meant to represent the cis-isomer (Z), trans-isomer (E), or any combination or mixture of both isomers in any ratio. Similarly, 1-chloro-1,2-difluoroethylene (HFO-1122a) exists as the Z-isomer, E-isomer, or any combination or mixture of both isomers in any ratio. Single isomers or multiple isomers of the same compound may be used in any proportion.

[0110] One embodiment disclosed herein relates to an integrated process of making E- and Z-isomers of 1,2-difluoroethylene using PCE as the starting material according to the following reaction steps.



(4): $\text{HFC-143} \rightarrow \text{E-1,2-difluoroethylene (HFO-E-1132)} + \text{Z-1,2-difluoroethylene (HFO-Z-1132)} + \text{HF}$

[0111] Another embodiment disclosed herein relates to an integrated process includes reaction steps (1), (2), (3), (4) and

(5): $\text{HFO-Z-1132} \rightarrow \text{HFO-E-1132}$

[0112] One embodiment disclosed herein relates to a process of converting a mixture comprising tetrachloroethylene (PCE), hydrogen fluoride, and chlorine in the liquid phase to a mixture comprising CFC-113, in the presence of a metal halide catalyst at temperatures between 80°C and 120°C.

[0113] In certain embodiments involving the liquid phase chlorofluorination of PCE using a metal halide, the metal halide catalyst includes, but is not limited to, SbCl_5 , SbCl_3 , SbF_5 , SnCl_4 , TiCl_4 , FeCl_3 , TaCl_5 and combinations of two or more. The extent of conversion of PCE to 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) is between 20-100%, and selectivity to 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) is greater than 90%. Preferably the catalyst is SbCl_5 and the conversion is conducted at a temperature of between about 80°C and about 120°C, including but not limited to 80°C, 90°C, 100°C, 110°C, or 120°C, and all values and ranges between 80°C and about 120°C.

[0114] Another embodiment disclosed herein relates to a process of catalytically converting a mixture comprising tetrachloroethylene (PCE), hydrogen fluoride, and chlorine in the gas phase to a mixture comprising CFC-113, at temperatures between 250°C and 400°C.

[0115] In certain embodiments involving the gas phase conversion of PCE the catalyst comprises a chromium-based fluorination catalyst selected from chromium oxide (Cr_2O_3), fluorided chromium oxide, chromium fluoride, chromium chloride, or chromium oxide, chloride, or fluoride supported on carbon or alumina, fluorided alumina, or AlF_3 . Of note are chromium oxide-based catalysts containing about 1 to 10 mole % of a transition metal selected from group Mn, Fe, Co, Ni, Zn, Pd, and Ag. Said catalyst may be prepared by co-precipitating mixtures of chromium and transition metal salts from aqueous solutions at pH greater than about 8 followed by

evaporation of the mixture and calcination at temperatures of from about 300°C to 900°C.

[0116] In certain embodiments disclosed herein the gas phase catalytic conversion of PCE is conducted at a temperature of between about 250°C and about 400°C, including but not limited to 250°C, 260°C, 270°C, 280°C, 290°C, 300°C, 310°C, 320°C, 330°C, 340°C, 350°C, 360°C, 370°C, 380°C, 390°C, or 400°C, and all values and ranges between 250°C and 400°C, including but not limited to 250°C to 375°C, 250°C to 350°C, 250°C to 325°C, 250°C to 300°C, 275°C to 375°C, 275°C to 350°C, 275°C to 325°C, 275°C to 300°C, 300°C to 400°C, 300°C to 375°C.

[0117] In certain embodiment disclosed herein the PCE to be converted to 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) comprises >99 percent PCE, and one of more compound compounds selected from CCl₄, CHCl₃, trichloroethylene, bromotrichloromethane, bromodichloroethylene isomer(s), bromotrichloroethylene, 1,1,3-trichloropropene, ethylene, and 1,1,1,3-tetrachloropropane where the total amount of other compounds is less than 1 weight % of the total composition.

[0118] In certain embodiments disclosed herein the conversion of tetrachloroethylene (PCE) produces a composition which comprises 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) and one or more additional compounds comprising 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a), 1,1,1,2-tetrachloro-2,2-difluoroethane (CFC-112a), 1,1,2,2-tetrachloro-1,2-difluoroethane (CFC-112), 1,1-dichloro-1,2,2,2-tetrafluoroethane (CFC-114a), 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114), 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), and 2-chloro-1,1,1,2-tetrafluoroethane (HCFC- 124).

[0119] In certain embodiments disclosed a CFC-113 feed composition, preferably comprises CFC-113 and one or more additional compounds selected from CFC-113a, CFC-114a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, CFO-1112a, and PCE. In one embodiment disclosed herein chlorotrifluoroethylene (CFO-1113) is made by contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) or the first product mixture with a reducing metal in the liquid phase. The liquid phase conversion of CFC-113 is between 50-100%, and selectivity to CFO-1113 is greater than 90%.

[0120] In certain embodiments disclosed herein the liquid phase conversion of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) is conducted at a temperature between about 20°C and about 120°C, optionally in the presence of a solvent selected from polar aprotic solvents such as dimethylsulfoxide, N,N-dimethylformamide, N-methylpyrrolidinone or ethereal solvents such as diethyl ether, tetrahydrofuran, dioxane, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, or dimethyl carbonate.

[0121] In certain embodiments disclosed herein the liquid phase conversion of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) is conducted at a temperature between about 20°C and about 120°C, optionally in the presence of a solvent selected from dimethylsulfoxide, N,N-dimethylformamide, N-methylpyrrolidinone, diethyl ether, tetrahydrofuran, dioxane, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, or dimethyl carbonate and in the presence of a reducing metal selected from magnesium, zinc, or cadmium. Optionally, said reducing metal may be promoted with metal chloride such as ZnCl₂, MgCl₂, or CdCl₂. Said reducing metal is preferably activated. Said activation of the reducing metal may be carried out by washing the reducing metal with aqueous hydrochloric acid having a concentration of 1M to about 5M followed by washing with water and acetone and vacuum drying. Other activators suitable for the process of the invention include bromine (Br₂), iodine (I₂), bromoalkanes (e.g., bromoethane), iodoalkanes (e.g., iodomethane), vicinal dibromoalkanes (e.g., 1,2-dibromoethane), vicinal diiodoalkanes (e.g., 1,2-diiodoethane), or vicinal dibromochlorocarbons (e.g., 1,2-dibromotetrachloroethane). Said reducing metal may be generated by reaction of a metal chloride with an alkali metal such as sodium or potassium as generally described by R. D. Rieke in *Topics in Current Chemistry*, Volume 59, pages 1-31 (1975).

[0122] In certain embodiments disclosed herein the amount of CFO-1113 is >99% by weight and includes one or more compounds selected from and one of the following components CFO-1112, CFO-1112a, HCFC-123a, HCFC-133, HCFC-133a, and HCFC-133b where the total amount of other compounds is less than 1 weight % of the total composition.

[0123] In one embodiment disclosed herein the HFC-143 composition, produced in reaction (3) and converted in reaction (4) comprises (>99% by weight of HFC-143)

and one the following components HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-123a, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113 where the total amount of other compounds is less than 1 weight % of the total composition.

[0124] In certain embodiments disclosed herein reaction (4), involving the dehydrofluorination of HFC-143 is conducted in the gas phase or the liquid phase.

[0125] In certain embodiments disclosed herein reaction (4) is conducted in the gas phase.

[0126] In certain embodiments disclosed herein reaction (4) conducted in the liquid phase.

[0127] In certain embodiments disclosed herein reaction (4) conducted in the gas phase at a temperature between 150°C and 400°C, including but not limited to 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, 260°C, 270°C, 280°C, 290°C, 300°C, 310°C, 320°C, 330°C, 340°C, 350°C, 360°C, 370°C, 380°C, 390°C, or 400°C or and ranges between 250°C and 400°C, including but not limited to 250°C to 375°C, 250°C to 350°C, 250°C to 325°C, 250°C to 300°C, 275°C to 375°C, 275°C to 350°C, 275°C to 325°C, 275°C to 300°C, 300°C to 400°C, 300°C to 375°C.

[0128] In certain embodiments disclosed herein reaction (4) is conducted in the liquid phase at a temperature between -20 °C and 150°C, including but not limited to -20°C, -10°C, 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140°C, or 150°C, and all ranges between -20 °C and 150°C.

[0129] In certain embodiments disclosed herein reaction (4) is conducted in the gas phase, at a temperature between 150°C and 400°C, a temperature between 150°C and 400°C, including but not limited to 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, 260°C, 270°C, 280°C, 290°C, 300°C, 310°C, 320°C, 330°C, 340°C, 350°C, 360°C, 370°C, 380°C, 390°C, or 400°C, and in the presence of a catalyst selected from the group consisting of aluminum fluoride, fluorided alumina, a metal supported on a trivalent aluminum compound containing fluoride anion (e.g., aluminum fluoride and/or fluorided alumina), lanthanum fluoride,

fluorided lanthanum oxide, metal supported on a trivalent lanthanum compound containing fluoride anion (e.g., lanthanum fluoride and/or fluorided lanthanum oxide), trivalent chromium compounds (e.g., Cr_2O_3) wherein the said metal is selected from the group consisting of one or more of chromium, manganese, iron, cobalt, nickel, magnesium and zinc.

[0130] Certain embodiments disclosed herein relate to reaction (4) is conducted in the liquid phase at a temperature between -20°C and 150°C in the presence of a strong base, a polar solvent, and optionally a phase transfer catalyst.

[0131] Certain embodiments disclosed herein relate to reaction (4), where the starting material comprises an HFC-143 composition containing at least two of the compounds selected HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-123a, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.

[0132] Certain embodiments disclosed herein relate to reaction (4) where the starting material comprises a HFC-143 composition containing at least two of the compounds selected HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-123a, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113 and the reaction is conducted in the liquid phase at a temperature between -20°C and 150°C , in the presence of a strong base, a polar solvent, and optionally a phase transfer catalyst. Said strong base comprises one or more of lithium hydroxide, sodium hydroxide, and potassium hydroxide, said polar solvent comprises one of more of water, dimethyl sulfoxide, sulfolane, N,N-dimethyl formamide, formamide, N,N-dimethylacetamide, N-methylpyrrolidinone, diethyl ether, tetrahydrofuran, dioxane, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, or dimethyl carbonate.

[0133] Certain embodiments disclosed herein relate to reaction (4) is conducted in the liquid phase at a temperature between -20°C and 150°C , including but not limited to, -20°C , -10°C , 0°C , 10°C , 20°C , 30°C , 40°C , 50°C , 60°C , 70°C , 80°C , 90°C , 100°C , 110°C , 120°C , 130°C , 140°C , or 150°C or all ranges between -20°C and 150°C , in the presence of a strong base, a polar solvent, and optionally a phase

transfer catalyst which comprises a material selected from quaternary ammonium salts of the formula $[NR_1R_2R_3R_4]X$ and phosphonium salts of the formula $[PR_1R_2R_3R_4]X$ wherein $X = F, Cl, Br, I, OH, HCO_3, CO_3, HSO_4, \text{ or } SO_4$, and $R_1, R_2, R_3, \text{ and } R_4$ are independently selected from the group consisting of alkyl group, an aryl group or an aralkyl group. Specific examples include tetramethylammonium chloride, tetramethylammonium bromide, benzyltriethylammonium chloride, methyltrioctylammonium chloride, tetra-n-butylammonium chloride, tetra-n-butylammonium bromide, tetra-n-butylammonium hydrogen sulfate, tetra-n-butylphosphonium chloride, tetraphenylphosphonium bromide, tetraphenylphosphonium chloride, triphenylmethylphosphonium bromide and triphenylmethylphosphonium chloride.

[0134] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase at a temperature between -20°C and 100°C in the presence of a strong base in an aprotic solvent in the presence or absence of a catalyst.

[0135] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C , including but not limited to $-20^\circ\text{C}, -10^\circ\text{C}, 0^\circ\text{C}, 10^\circ\text{C}, 20^\circ\text{C}, 30^\circ\text{C}, 40^\circ\text{C}, 50^\circ\text{C}, 60^\circ\text{C}, 70^\circ\text{C}, 80^\circ\text{C}, 90^\circ\text{C}$, or 100°C , or all ranges therebetween, in the presence of a strong base in an aprotic solvent in the presence or absence of a catalyst.

[0136] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C including but not limited to $-20^\circ\text{C}, -10^\circ\text{C}, 0^\circ\text{C}, 10^\circ\text{C}, 20^\circ\text{C}, 30^\circ\text{C}, 40^\circ\text{C}, 50^\circ\text{C}, 60^\circ\text{C}, 70^\circ\text{C}, 80^\circ\text{C}, 90^\circ\text{C}$, or 100°C , or all ranges therebetween, in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide in the presence of an aprotic solvent.

[0137] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C , including but not limited to $-20^\circ\text{C}, -10^\circ\text{C}, 0^\circ\text{C}, 10^\circ\text{C}, 20^\circ\text{C}, 30^\circ\text{C}, 40^\circ\text{C}, 50^\circ\text{C}, 60^\circ\text{C}, 70^\circ\text{C}, 80^\circ\text{C}, 90^\circ\text{C}$, or 100°C , or all ranges therebetween, in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an

organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an aprotic solvent comprising an acyclic or cyclic ether.

[0138] Certain embodiments disclosed herein relate to reaction **(4)** which is conducted in the liquid phase, at a temperature between -20°C and 100°C, including but not limited to -20°C, -10°C, 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, or 100°C, or all ranges therebetween, in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide in the presence of an aprotic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst.

[0139] Certain embodiments disclosed herein relate to reaction **(4)** which is conducted in the liquid phase, at a temperature between -20°C and 100°C, including but not limited to -20°C, -10°C, 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, or 100°C, or all ranges therebetween, in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an aprotic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst comprising a Crown ether or cryptand.

[0140] Certain embodiments disclosed herein relate to reaction **(4)** which is conducted in the liquid phase, at a temperature between -20°C and 100°C, including but not limited to -20°C, -10°C, 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, or 100°C, in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an aprotic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst comprising a Crown ether or cryptand, wherein the alkaline metal or alkaline-earth metal is a Group 1A metal of the Periodic Table excluding hydrogen, and the alkaline-earth metal is a Group 2A metal of the Periodic Table excluding beryllium.

[0141] Certain embodiments disclosed herein relate to reaction **(4)** which is conducted in the liquid phase, at a temperature between -20°C and 100°C, including but not limited to -20°C, -10°C, 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C,

80°C, 90°C, or 100°C, or all ranges therebetween, in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an aprotic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst comprising a Crown ether or cryptand, wherein the alkaline metal or alkaline-earth metal alkoxide comprises one of lithium methoxide, sodium methoxide, sodium ethoxide, potassium tert-butoxide, sodium tert-butoxide, sodium isopropoxide, or magnesium ethoxide, the alkaline or alkaline-earth metal hydride comprises lithium hydride, sodium hydride, potassium hydride, or calcium hydride, the organometallic lithium compound comprises n-butyl lithium, methyl lithium, or isopropyl lithium, and the alkaline or an alkaline-earth metal amide, comprises lithium dimethylamide, lithium diethylamide, lithium diisopropylamide, or magnesium bis(diisopropylamide).

[0142] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C, including but not limited to -20°C, -10°C, 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, or 100°C, or all ranges therebetween, in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an aprotic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst comprising a Crown ether or cryptand, wherein the alkaline metal or alkaline-earth metal alkoxide comprises one of lithium methoxide, sodium methoxide, sodium ethoxide, potassium tert-butoxide, sodium tert-butoxide, sodium isopropoxide, magnesium ethoxide, the alkaline or alkaline-earth metal hydride comprises lithium hydride, sodium hydride, potassium hydride, or calcium hydride, the organometallic lithium compound comprises n-butyl lithium, methyl lithium, or isopropyl lithium, and the alkaline or an alkaline-earth metal amide, comprises lithium dimethylamide, lithium diethylamide, lithium diisopropylamide, or magnesium bis(diisopropylamide).

[0143] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C, including but not limited to -20°C, -10°C, 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, or 100°C, or all ranges therebetween, in the presence of an alkaline

metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an aprotic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst and the aprotic solvent comprises one of diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, tetrahydrofuran, or dioxane.

[0144] Certain embodiments disclosed herein relate to reaction (4) which is conducted in the liquid phase, at a temperature between -20°C and 100°C, or all ranges therebetween, in the presence of an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide, in the presence of an aprotic solvent comprising an acyclic or cyclic ether, in the presence or absence of a catalyst and the aprotic solvent comprises one of diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, tetrahydrofuran, or dioxane and a catalyst which comprises a crown ether selected from one of 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) or a cryptand comprising 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-(8.8.8)hexacosane (also known as 2,2,2-cryptand).

[0145] In certain embodiments disclosed herein dehydrofluorination of HFC-143, which is present in an amount of at least 99 weight percent and at least two or more compounds selected from HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HFO-1141, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113, wherein the total amount of other compounds is less than 1 weight % of the total composition, is conducted in the gas phase at a temperature between 150°C and 400°C. in the presence of a catalyst selected from the group consisting of aluminum fluoride, fluorided alumina, a metal supported on a trivalent aluminum compound containing fluoride anion (e.g., aluminum fluoride and/or fluorided alumina), lanthanum fluoride, fluorided lanthanum oxide, metal supported on a trivalent lanthanum compound containing fluoride anion (e.g., lanthanum fluoride and/or fluorided lanthanum oxide), trivalent chromium compounds (e.g., Cr₂O₃) wherein the

said metal is selected from the group consisting of one or more of chromium, manganese, iron, cobalt, nickel, magnesium, and zinc.

[0146] In certain embodiments disclosed herein conversion of HFC-143 and at least two of the compounds selected from HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HFO-1141, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113 in the liquid phase is conducted at a temperature between -20 °C and 150°C in the presence of a strong base in a polar solvent, and optionally a phase transfer catalyst selected from quaternary ammonium salts of the formula $[NR_1R_2R_3R_4]X$ and phosphonium salts of the formula $[PR_1R_2R_3R_4]X$ wherein $X = F, Cl, Br, I, OH, HCO_3, CO_3, HSO_4, \text{ or } SO_4$, and $R_1, R_2, R_3, \text{ and } R_4$ are independently selected from the group consisting of alkyl group, an aryl group or an aralkyl group. Specific examples include tetramethylammonium chloride, tetramethylammonium bromide, benzyltriethylammonium chloride, methyltrioctylammonium chloride, tetra-n-butylammonium chloride, tetra-n-butylammonium bromide, tetra-n-butylammonium hydrogen sulfate, tetra-n-butylphosphonium chloride, tetraphenylphosphonium bromide, tetraphenylphosphonium chloride, triphenylmethylphosphonium bromide and triphenylmethylphosphonium chloride.

[0147] In certain embodiments disclosed herein HFC-143 is converted using a composition which comprises HFC-143 and **(1)** at least two of the compounds selected from HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HFO-1141, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113, or **(2)** at least two or more compounds selected from 1,1-difluoroethylene (HFO-1132a), 1,1,1-trifluoroethane (HFC-143a), 1-chloro-1,2,2-trifluoroethylene (CFO-1113), 1-chloro-1-fluoroethylene (HCFO-1131a), 1,2-difluoroethane (HFC-152), fluoroethane (HFC-161), 1,2-dichloro-1-fluoroethane (HCFC-141), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1-chloro-2,2-difluoroethane (HCFC-142), 1-chloro-1,2-difluoroethane (HCFC-142a), 1-chloro-2,2-difluoroethylene (HCFO-1122), 1-chloro-1,2-difluoroethylene (HCFO-1122a), fluoroethylene (HFO-1141), dichlorofluoromethane (HCFC-21), chlorodifluoromethane (HCFC-22), trifluoromethane (HFC-23), ethylene, and acetylene, or **(3)** at least two of the compounds selected from HFC-1123, CFO-

1113, HFC-134, HFC-134a, HFCO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140, in the liquid phase, conducted under anhydrous conditions at a temperature between 20°C and 100°C in the presence of a strong base such as an alkaline metal or alkaline-earth metal alkoxide, an alkaline or alkaline-earth metal hydride, an organometallic lithium compound, or an alkaline or an alkaline-earth metal amide where the alkaline metal is a Group 1A metal of the Periodic Table excluding hydrogen and the alkaline-earth metal is a Group 2A metal of the Periodic Table excluding beryllium and wherein the alkaline metal or alkaline-earth metal alkoxide comprises one of lithium methoxide, sodium methoxide, sodium ethoxide, potassium tert-butoxide, sodium tert-butoxide, sodium isopropoxide, or magnesium ethoxide, the alkaline or alkaline-earth metal hydride comprises lithium hydride, sodium hydride, potassium hydride, or calcium hydride, the organometallic lithium compound comprises n-butyl lithium, methyl lithium, or isopropyl lithium, and the alkaline or an alkaline-earth metal amide, comprises lithium dimethylamide, lithium diethylamide, lithium diisopropylamide, or magnesium bis(diisopropylamide). in an aprotic solvent selected from an ether (e.g., diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether) or a cyclic ether (e.g., tetrahydrofuran, dioxane). Reaction with a strong base may be conducted with or without a catalyst such as a Crown ether or cryptand. Specific examples of crown ether include 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). A well-known example of a cryptand is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-(8.8.8)hexacosane (also known as 2,2,2-cryptand).

[0148] Certain embodiments disclosed herein relate to a composition which comprises, consists essentially of, or consists of HFC-143, and one or more compounds selected from 1,1-difluoroethylene (HFO-1132a), 1,1,1-trifluoroethane (HFC-143a), 1-chloro-1,2,2-trifluoroethylene (1113), 1-chloro-1-fluoroethylene (HCFO-1131a), 1,2-difluoroethane (HFC-152), fluoroethane (HFC-161), 1,2-dichloro-1-fluoroethane (HCFC-141), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1-chloro-2,2-difluoroethane (HCFC-142), 1-chloro-1,2-difluoroethane (HCFC-142a), 1-chloro-2,2-difluoroethylene (HCFO-1122), 1-chloro-1,2-difluoroethylene (HCFO-1122a), fluoroethylene (HFO-1141), dichlorofluoromethane (HCFC-21),

chlorodifluoromethane (HCFC-22), trifluoromethane (HFC-23), ethylene, and acetylene.

[0149] Certain embodiments disclosed herein relate to a HFC-143 feed composition which comprises, consists essentially of, or consists of HFC-143, and one or more compounds selected from 1,1-difluoroethylene (HFO-1132a), 1,1,1-trifluoroethane (HFC-143a), 1-chloro-1,2,2-trifluoroethylene (1113), 1-chloro-1-fluoroethylene (HCFO-1131a), 1,2-difluoroethane (HFC-152), fluoroethane (HFC-161), 1,2-dichloro-1-fluoroethane (HCFC-141), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1-chloro-2,2-difluoroethane (HCFC-142), 1-chloro-1,2-difluoroethane (HCFC-142a), 1-chloro-2,2-difluoroethylene (HCFO-1122), 1-chloro-1,2-difluoroethylene (HCFO-1122a), fluoroethylene (HFO-1141), dichlorofluoromethane (HCFC-21), chlorodifluoromethane (HCFC-22), trifluoromethane (HFC-23), ethylene, and acetylene.

[0150] Certain embodiments disclosed herein relate to a composition which comprises, consists essentially of, or consists of HFC-143, and two or more compounds selected from 1,1-difluoroethylene (HFO-1132a), 1,1,1-trifluoroethane (HFC-143a), 1-chloro-1,2,2-trifluoroethylene (1113), 1-chloro-1-fluoroethylene (HCFO-1131a), 1,2-difluoroethane (HFC-152), fluoroethane (HFC-161), 1,2-dichloro-1-fluoroethane (HCFC-141), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1-chloro-2,2-difluoroethane (HCFC-142), 1-chloro-1,2-difluoroethane (HCFC-142a), 1-chloro-2,2-difluoroethylene (HCFO-1122), 1-chloro-1,2-difluoroethylene (HCFO-1122a), fluoroethylene (HFO-1141), dichlorofluoromethane (HCFC-21), chlorodifluoromethane (HCFC-22), trifluoromethane (HFC-23), ethylene, and acetylene.

[0151] Certain embodiments disclosed herein relate to a HFC-143 feed composition which comprises, consists essentially of, or consists of HFC-143, and two or more compounds selected from 1,1-difluoroethylene (HFO-1132a), 1,1,1-trifluoroethane (HFC-143a), 1-chloro-1,2,2-trifluoroethylene (1113), 1-chloro-1-fluoroethylene (HCFO-1131a), 1,2-difluoroethane (HFC-152), fluoroethane (HFC-161), 1,2-dichloro-1-fluoroethane (HCFC-141), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1-chloro-2,2-difluoroethane (HCFC-142), 1-chloro-1,2-difluoroethane (HCFC-142a), 1-chloro-2,2-difluoroethylene (HCFO-1122), 1-chloro-1,2-

difluoroethylene (HCFO-1122a), fluoroethylene (HFO-1141), dichlorofluoromethane (HCFC-21), chlorodifluoromethane (HCFC-22), trifluoromethane (HFC-23), ethylene, and acetylene.

[0152] Certain embodiments disclosed herein relate to a process comprising contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with hydrogen in the vapor phase in the presence of a catalyst to form 1,1,2-trifluoroethane (HFC-143).

[0153] Certain embodiments disclosed herein relate to a process comprising contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with hydrogen in the vapor phase in the presence of a catalyst to form 1,1,2-trifluoroethane (HFC-143) wherein relative molar amounts of hydrogen to CFC-113 in from about 1:1 to about 3:1.

[0154] Certain embodiments disclosed herein relate to a process comprising contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with hydrogen in the vapor phase in the presence of a catalyst to form 1,1,2-trifluoroethane (HFC-143) wherein the contacting is conducted a temperature of from about 80°C to about 250°C.

[0155] Certain embodiments disclosed herein relate to a process comprising contacting CFC-113 with hydrogen in the vapor phase in the presence of a catalyst which comprises a catalytic metal, selected from Pd, Pt, or a mixture thereof, preferably supported on Al₂O₃, fluorided alumina, AlF₃, or chromium oxide as disclosed in U.S. Patent Application 20080207962 and 20080207963.

[0156] Certain embodiments disclosed herein relate to a process comprising contacting CFC-113 with hydrogen in the vapor phase in the presence of a catalyst to form an HFC-143 composition wherein the amount of catalytic metal on the support comprises from about 0.5 weight % to about 10 weight % of the catalyst composition.

[0157] In certain embodiment the content of HFO-E-1132 in a mixture of HFO-Z-1132 and HFO-E-1132 is increased in step (5) by isomerization in the presence or absence of a catalyst. In certain embodiments disclosed herein isomerization is conducted at temperature between 600°C and 800°C, from one of 600°C, 610°C, 620°C, 630°C, 640°C, 650°C, 660°C, 670°C, 680°C, 690°C to one of 700°C, 710°C, 720°C, 730°C, 740°C, 750°C, 760°C, 770°C, 780°C, 790°C or 800°C, and all values and ranges therebetween including 600°C to 690°C, 610°C to 690°C, 600°C to

680°C, 600°C to 670°C, 600°C to 660°C, 700°C to 800°C, 710°C to 790°C or 800°C, 720°C to 780°C, 790°C or 800°C, or 730°C to 750°C, 760°C, 770°C, 780°C, 790°C or 800°C.

[0158] In certain embodiment disclosed herein isomerization is conducted at temperatures between 600°C and 800°C including but not limited to 600°C, 610°C, 620°C, 630°C, 640°C, 650°C, 660°C, 670°C, 680°C, 690°C, 700°C, 710°C, 720°C, 730°C, 740°C, 750°C, 760°C, 770°C, 780°C, 790°C or 800°C.

[0159] In certain embodiments disclosed herein the molar ratio of HFO-E-1132 to HFO-Z-1132 is increased in step (5) by isomerization in the vapor phase in the presence a catalyst selected from Cr₂O₃, fluorided Cr₂O₃, Al₂O₃, fluorided Al₂O₃, or AlF₃, chromium supported on alumina, fluorided alumina, or AlF₃, or cobalt- or nickel-substituted chromium oxide at a temperature between from about 300°C to about 450°C.

[0160] Certain embodiments disclosed herein relate to a composition which comprises, consists essentially of or, consists of (i) HFO-E-1132 and at least one of HFO-1141, HFO-1123, acetylene, HFO-Z-1132, HCFO-E-1131, HCFO-Z-1131, HFC-125, HFC-32, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140, or (ii) HFO-Z-1132 and at least one of HFO-1141, HFO-1123, acetylene, HFC-134, HFO-E-1132, HCFO-E-1131, HCFO-Z-1131, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140.

[0161] In certain embodiments disclosed herein relate to a composition which comprises, consists essentially or, consists of (i) HFO-E-1132 and at least two of HFO-1141, HFO-1123, acetylene, HFO-Z-1132, HCFO-E-1131, HCFO-Z-1131, HFC-125, HFC-32, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140, or (ii) HFO-Z-1132 and at least two of HFO-1141, HFO-1123, acetylene, HFC-134, HFO-E-1132, HCFO-E-1131, HCFO-Z-1131, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140.

[0162] In certain embodiments disclosed herein relate to a composition which comprises, consists essentially or, consists of (i) HFO-E-1132 and at least three of HFO-1141, HFO-1123, acetylene, HFO-Z-1132, HCFO-E-1131, HCFO-Z-1131, HFC-125, HFC-32, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122,

and HCO-1140, or (ii) HFO-Z-1132 and at least three of HFO-1141, HFO-1123, acetylene, HFC-134, HFO-E-1132, HCFO-E-1131, HCFO-Z-1131, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140.

[0163] In certain embodiments disclosed herein relate to a composition which comprises, consists essentially or, consists of (i) HFO-E-1132 and four or more of HFO-1141, HFO-1123, acetylene, HFO-Z-1132, HCFO-E-1131, HFC-125, HFC-32, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140, or (ii) HFO-Z-1132 and four or more of HFO-1141, HFO-1123, acetylene, HFC-134, HFO-E-1132, HCFO-E-1131, HCFO-Z-1131, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140.

EXAMPLES

Example 1 – Preparation of 98%Chromium/2% Palladium Catalyst

[0164] A solution of 760.28 g $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (1.90 moles) and 10.1 g $\text{Pd}(\text{NO}_3)_2[2(\text{H}_2\text{O})]$ (0.038 mole) is prepared in 2000 mL of deionized water. The pH of the solution is adjusted to 8.5 by treatment with 7.4M aqueous ammonium hydroxide. The resulting slurry is stirred at room temperature overnight and then dried at 110-120°C in air for 48 hours. The dried solid is crushed to a powder and the calcined in air at 400°C for 24 hours. The calcined powder is pressed into disks, broken up, and sieved to provide a 10 to +20 mesh (1.68 to 0.84 mm) fraction used for catalyst evaluation.

Preparation of 97%Chromium/3% Iron Catalyst

[0165] A beaker containing 500 mL of 2M aqueous $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (1.00 mole) is treated with a solution of 7.64 g of $\text{Fe}(\text{NO}_3)_3(\text{H}_2\text{O})_9$ (0.0189 mole) dissolved in 500 mL deionized water. The pH of the solution is adjusted to 8.50 by treatment with 7.4M aqueous ammonium hydroxide. The resulting slurry is stirred at room temperature overnight and then dried at 110-120°C in air for 48 hours. The dried solid is crushed to a powder and calcined in air at 400°C for 24 hours. The calcined powder is pressed into disks, broken up and sieved to provide a –12 to +20 mesh (1.68 to 0.84 mm) fraction that was used in catalyst evaluation.

Preparation of 98%Chromium/2% Silver Catalyst

[0166] A solution of 784.30 g $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (1.96 moles) and 6.79 g AgNO_3 (0.04 moles) is prepared in 2000 mL deionized water. The pH of the solution is adjusted to 8.50 by treatment with 7.4M aqueous ammonium hydroxide. The resulting slurry is stirred at room temperature overnight and then dried at 110-120°C in air for 48 hours. The dried solid is crushed to a powder and calcined in air at 900°C for 24 hours. The calcined powder is pressed into disks, broken up and sieved to provide a -12 to +20 mesh (1.68 to 0.84 mm) fraction used in catalyst evaluation.

Chlorofluorination of Tetrachloroethene over Cr/Ag (98/2)

[0167] The pelletized Cr/Ag (98/2) catalyst (15 mL, 31.64 g) is placed in a 5/8-inch (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The tube is heated from 67°C to 174° C in a flow of nitrogen (50 cc/min; $8.3(10)^{-7}\text{m}^3/\text{sec}$) over the course of about 0.5 hour. HF is then admitted to the reactor at a flow rate of 50 cc/min ($8.3(10)^{-7}\text{m}^3/\text{sec}$). After about 10 minutes, the nitrogen flow is decreased to 20 cc/min ($3.3(10)^{-7}\text{m}^3/\text{sec}$) and the HF flow is increased to 80 cc/min ($1.3(10)^{-6}\text{m}^3/\text{sec}$); this flow is maintained for about 0.5 hour. The reactor temperature is then gradually increased to 400°C over 3 hours. The nitrogen flow is decreased to 10 cc/min ($1.7(10)^{-7}\text{m}^3/\text{sec}$) and fluorination continued at 400°C for 2 hours. At the end of this period, the HF flow is ceased and the reactor cooled under 20 sccm ($3.3(10)^{-7}\text{m}^3/\text{sec}$) nitrogen flow. Mixtures of HF, C_2Cl_4 , and Cl_2 are then passed over the catalyst in various ratios and temperatures of 325-400°C. At 350°C with a HF/ C_2Cl_4 / Cl_2 ratio of 5/1/1 and a contact time of 15 seconds, the reactor effluent is primarily $\text{CCl}_3\text{CClF}_2$ (56.6%) and $\text{CClF}_2\text{CCl}_2\text{F}$ (37.2%) (with small amounts of $\text{CClF}_2\text{CClF}_2$ (0.29%), $\text{CF}_3\text{CCl}_2\text{F}$ (0.99%), $\text{CCl}_2=\text{CF}_2$ (0.37%), $\text{CHCl}_2\text{CClF}_2$ (0.12%), $\text{CCl}_2=\text{CClF}$ (0.73%), and $\text{CCl}_3\text{CCl}_2\text{F}$ (1.9%). The conversion is 100%.

Chlorofluorination of Tetrachloroethene over Cr/Fe (97/3)

[0168] The pelletized Cr/Fe (97/3) catalyst (20 mL, 28.8 g) is placed in a 5/8-inch (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The tube is heated from 67°C to 176° C in a flow of nitrogen (50 cc/min;

$8.3(10)^{-7} \text{ m}^3/\text{sec}$ over night. HF is then co-fed to the reactor at a flow rate of 50 cc/min ($8.3(10)^{-7} \text{ m}^3/\text{sec}$) for about 45 minutes. The HF flow is then increased to 80 cc/min ($1.3(10)^{-6} \text{ m}^3/\text{sec}$) and the nitrogen flow decreased to 20 cc/min ($3.3(10)^{-7} \text{ m}^3/\text{sec}$) as the temperature is raised from 175°C to 402°C over the course of about 5.5 hours. The HF flow is ceased and the reactor cooled under 20 sccm ($3.3(10)^{-7} \text{ m}^3/\text{sec}$) nitrogen flow. Mixtures of HF, C_2Cl_4 , and Cl_2 are then passed over the catalyst in various ratios and temperatures of 250-375°C. At 350°C with a HF/ C_2Cl_4 / Cl_2 ratio of 6/1/1 and a contact time of 15 seconds, the reactor effluent is primarily $\text{C}_2\text{Cl}_4\text{F}_2$ isomers (4.9%), $\text{CClF}_2\text{CCl}_2\text{F}$ (81.5%), $\text{CClF}_2\text{CClF}_2$ (7.2%), and $\text{CF}_3\text{CCl}_2\text{F}$ (4.6%) with small amounts of CF_3CCl_3 (0.94%), CClF_2CF_3 (0.07%), C_2HClF_4 isomers (0.03%), $\text{CHCl}_2\text{CClF}_2$ (0.01%), $\text{CHCl}=\text{CClF}$ (0.02%), $\text{CCl}_2=\text{CClF}$ (0.06%), $\text{CCl}_2=\text{CF}_2$ (0.6%), and $\text{CCl}_3\text{CCl}_2\text{F}$ (0.02%). The conversion is 100%.

Chlorofluorination of PCE

[0169] Gas phase: An Inconel tube® (0.5-inch OD, 15-inch length, 0.34 in wall thickness) is filled with 12 cc (6.45 g) of 15% chrome chloride on carbon catalyst. The catalyst is activated with anhydrous HF at 300°C. The reactor is heated in a Lindberg furnace to 300°C and tetrachloroethylene and one more additional compound selected from chloroform, carbon tetrachloride, bromotrichloromethane, bromotrichloroethylene, 1,2-dichloroethane, ethylene, trichloroethylene, 1,1,3-trichloro-1-propene, and 1,1,1,3-tetrachloropropane are fed at 4 ml/hour and HF gas at 22.2 sccm (standard cubic centimeters per minute) and Cl_2 gas at 5.4 sccm through a vaporizer controlled at 150°C. All of the experiments were carried out at 1-2 psig. The effluent of the reactor is analyzed online using an Agilent® 6890 GC/5973 MS and a Restek® PC2618 5% Krytox® CBK-D/60/80 6-meter x 2mm ID 1/8" OD packed column purged with helium at 30 sccm. The reaction has 55% conversion with 90% 113 selectivity.

[0170] In one embodiment the chlorofluorination of PCE produces a CFC-113 composition which, after purification, comprises about 99% by weight CFC-113 based on the total amount of the composition, and two or more additional compounds selected from CFC-113a, CFC-114a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFO-1317, CFC-216, CFC-318, CFC-316,

CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, CFO-1112a, and PCE where the total amount of additional compounds is less than 1 weight % of the total composition.

[0171] Liquid phase: SbCl_5 (10.5 g) is added to a 210 mL Hastelloy C reactor, followed by HF (49 g) and Cl_2 (42 g). The reaction mixture is heated at 100°C for 1 hour and then cooled to 0°C. Tetrachloroethylene (19 g) and one or more additional compounds selected from chloroform, carbon tetrachloride, bromotrichloromethane, bromotrichloroethylene, 1,2-dichloroethane, ethylene, trichloroethylene, 1,1,3-trichloro-1-propene, and 1,1,1,3-tetrachloropropane are added to the reactor and the reaction mixture is heated to 100°C. The reaction rate is indicated by the pressure increase and stabilization of the pressure indicating completion of the reaction. Similar reactions are also performed using TaCl_5 or NbCl_5 as catalysts. The reaction has 100% conversion with 95% 113 selectivity.

Step 2: CFC-113 + Zn $\rightarrow$ CFO-1113 + ZnCl_2

Dechlorination of CFC-113

[0172] A 500 mL three-neck round bottom flask is equipped with a large stirring bar, a thermocouple well, an addition funnel, and a condenser connected in series to two traps resting in a dry ice/acetone bath followed by a nitrogen bubbler. Each trap contains 100 mg of d-limonene as a polymerization inhibitor. The flask is charged with magnesium powder (9.0 g, 0.37 mole) and tetrahydrofuran (222.2 g) followed by a crystal of iodine as a magnesium activator. The addition funnel is charged with 1,1,2-trichloro-1,2,2-trifluoroethane (58.0 g, 0.31 mole). The 1,1,2-trichloro-1,2,2-trifluoroethane is added dropwise to the magnesium/THF mixture initially at room temperature. As the temperature rises, the exotherm is regulated to 40-50°C using an ice-water bath. The volatile reaction products are collected in the cylinders. Analysis of the product by gas chromatography indicates that it consists of chlorotrifluoroethene. Other low-level impurities are 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 1-chloro-2,2,2-trifluoroethane (HCFC-133a), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1-chloro-1,2,2-trifluoroethane (HCFC-133), 1,1-dichloro-2,2-difluoroethylene, and E/Z-1,2-dichloro-1,2-difluoroethene. In one embodiment the isolated chlorotrifluoroethylene (CFO-1113) comprises 1,2-dichloro-

1,1,2-trifluoroethane (HCFC-123a), 1-chloro-2,2,2-trifluoroethane (HCFC-133a), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1-chloro-1,2,2-trifluoroethane (HCFC-133), 1,1-dichloro-2,2-difluoroethylene, and E/Z-1,2-dichloro-1,2-difluoroethene.

Hydrodechlorination of CFC-113

[0173] A 15 mL portion (19 g) of the granulated Cr/Pd (98/2) catalyst is placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst is dried in a stream of nitrogen (20 cc/min) over the course of 1.5 h as the temperature is raised from 34°C to 150°C. The nitrogen flow is then replaced with hydrogen (20 cc). The catalyst is reduced for 3 h at 150°C and for 3 h at 200°C. The performance of the catalyst for hydrodechlorination of CFC-113 is then tested at 87°C to 156°C at various ratios of H₂ to CClF₂CCl₂F. At a H₂/CClF₂CCl₂F ratio of 2/1, at a reaction temperature of 95°C and a contact time of 15 seconds, the reactor effluent is primarily CHF₂CH₂F (84.5%) and CClF₂CH₂F (6.8%) with small amounts of C₂H₆ (0.2%), CH₃CF₃ (0.2%), CH₂FCF₃ (0.2%), and CH₃CHF₂ (0.5%) as determined by GC-MS. The conversion is 100%.

Step 3: CFO-1113 + H₂ → HFC-143 + HCl

[0174] A Hastelloy tube reactor 80" long with a 1" O.D. (outside diameter) and 0.074" wall thickness is filled with 30 g of 0.5% Pd on carbon catalyst. The catalyst is conditioned with a flow of nitrogen (1000 sccm) and hydrogen (1000 sccm) for one hour at 200°C. A mixture of CFO-1113, hydrogen and N₂ are then flowed into the reactor with a back pressure of 10 psig. The reaction is run at 50% conversion with 90% HFC-143 selectivity.

[0175] In one embodiment contacting chlorotrifluoroethylene (CFO-1113) with hydrogen is conducted at a temperature between one of (i) 50°C to about 150°C, including but not limited to 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140°C, or 150°C in the presence of a hydrogenation catalyst comprising a catalytic metal selected from the group Re, Ni, Pd, Pt, Ru, Rh, and Ir, or (ii) 150°C to about 350°C, including but not limited to 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, 260°C, 270°C, 280°C, 290°C, 300°C, 310°C, 320°C, 330°C, 340°C, 350°C.

Step 4: HFC-143 → HFO-Z-1132 + HFO-E-1132 + HF**Gas phase:**

[0176] An Inconel® pipe (0.5-inch OD, 10-inch length, 0.35 in wall thickness) is filled with 2 cc of chromium oxide catalyst. The reactor is heated to 375°C, optionally with an oxygen containing gas. HFC-143 generated in step (3), includes HFC-143 and at least one or more compounds selected from (i) HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HFO-1141, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113 or (ii) at least one or more compounds selected from 1,1-difluoroethylene (HFO-1132a), 1,1,1-trifluoroethane (HFC-143a), 1-chloro-1,2,2-trifluoroethylene (1113), 1-chloro-1-fluoroethylene (HCFO-1131a), 1,2-difluoroethane (HFC-152), fluoroethane (HFC-161), 1,2-dichloro-1-fluoroethane (HCFC-141), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1-chloro-2,2-difluoroethane (HCFC-142), 1-chloro-1,2-difluoroethane (HCFC-142a), 1-chloro-2,2-difluoroethylene (HCFO-1122), 1-chloro-1,2-difluoroethylene (HCFO-1122a), fluoroethylene (HFO-1141), dichlorofluoromethane (HCFC-21), chlorodifluoromethane (HCFC-22), trifluoromethane (HFC-23), ethylene, and acetylene or (iii) at least one or more compounds selected from HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140, is fed at 4.23 mL/hr via an ISCO pump via a vaporizer controlled at 20°C. The pressure of the reaction is varied from 0 to 50 psig. The effluent of the reactor is analyzed online using an Agilent® 7890 GC/5971 MS. The HFC-143 conversion is 53% with 90% HFO-1132 selectivity. The molar ratio of Z-1132 to E-1132 ratio is about 4 to 1.

Liquid phase:

[0177] A mixture of HFC-143 (84 g, 1 mol) and (i) one or more compounds selected from HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HFO-1141, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113 or (ii) 1,1-difluoroethylene (HFO-1132a), 1,1,1-trifluoroethane (HFC-143a), 1-chloro-1,2,2-trifluoroethylene (1113), 1-chloro-1-fluoroethylene (HCFO-1131a), 1,2-difluoroethane (HFC-152), fluoroethane (HFC-161), 1,2-dichloro-1-fluoroethane (HCFC-141), 1,1-

dichloro-2,2,2-trifluoroethane (HCFC-123), 1-chloro-2,2-difluoroethane (HCFC-142), 1-chloro-1,2-difluoroethane (HCFC-142a), 1-chloro-2,2-difluoroethylene (HCFO-1122), 1-chloro-1,2-difluoroethylene (HCFO-1122a), fluoroethylene (HFO-1141), dichlorofluoromethane (HCFC-21), chlorodifluoromethane (HCFC-22), trifluoromethane (HFC-23), ethylene, and acetylene, or (iii) at least two of the compounds selected from HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140, and t-BuOK (80 g, 1 mmol) in anhydrous DMF (200 ml) is stirred in a 400 mL autoclave at 0°C. Gas chromatography is used to monitor the reaction. After 3 hours, the product is collected in a dry ice trap connected to the autoclave. The HFO-1132 is formed with about 70% conversion of HFC-143 with a selectivity of 96%. The molar ratio of HFO-Z-1132 to HFO-E-1132 is about 9 to 1.

Step 5: HFO-Z-1132 → HFO-E-1132

[0178] In certain embodiment the content of HFO-E-1132 in a mixture of HFO-Z-1132 and HFO-E-1132 is increased in step (5) by isomerization in the presence or absence of a catalyst. In the absence of a catalyst isomerization is conducted at temperature between 600°C and 800°C, and all values and ranges therebetween.

[0179] In certain embodiment disclosed herein isomerization reaction (5) is in the vapor phase in the presence a catalyst selected from Cr₂O₃, fluorided Cr₂O₃, Al₂O₃, fluorided Al₂O₃, or AlF₃, chromium supported on alumina, fluorided alumina, or AlF₃, or cobalt- or nickel-substituted chromium oxide at a temperature between from about 300°C to about 450°C.

[0180] In certain embodiment the content of HFO-Z-1132 in HFO-E/Z-can be increased by isomerization of HFO-E-1132 in the presence or absence of a catalyst in gas phase.

[0181] The E to Z molar ratio of a mixture of HFO-Z-1132 and HFO-E-1132 is increased by thermal isomerization between 600°C to 800°C with a contact time of about 0.1 to 60 seconds.

[0182] Certain embodiments disclosed herein relate to a system and process, wherein the system comprises a series of reactors including first, second and third

reactors configured for respectively synthesizing a first CFC-113 intermediate product mixture, a second CFO-1113 intermediate product mixture, a third HFC-143 intermediate product mixture, a fourth reactor configured for synthesizing a mixture of HFO-E-1132 and HFO-Z-1132 isomers, wherein the system further comprises a conversion system in fluid communicated with the fourth reactor for changing the HFO-1132 E/Z, wherein the conversion system includes one of a distillation column, a catalyst free thermal converter or a catalyst reactor suitable for changing the HFO-E-1132 to HFO-Z-1132 ratio

[0183] Certain embodiments disclosed herein relate to process of providing and contacting a starting feed contacting tetrachloroethylene (PCE), HF and chlorine thereby synthesizing 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) from the starting feed, contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) as part of a product mixture with a reducing metal in the liquid phase to form chlorotrifluoroethylene (CFO-1113), contacting the chlorotrifluoroethylene (CFO-1113) as part of a product mixture and hydrogen in one of the gas or liquid phase to form 1,1,2-trifluoroethane (HFC-143), and then converting the 1,1,2-trifluoroethane (HFC-143) as part of a product mixture from step (d) in the liquid or gas phase to form a mixture of E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0184] Certain embodiments disclosed herein relate to process of providing and contacting a starting feed contacting tetrachloroethylene (PCE), HF and chlorine thereby synthesizing 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) from the starting feed, contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) as part of a product mixture with hydrogen in one of the gas or liquid phase to form 1,1,2-trifluoroethane (HFC-143), and then converting the 1,1,2-trifluoroethane (HFC-143) as part of a product mixture from step (d) in the liquid or gas phase to form a mixture of E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0185] Certain embodiments disclosed herein relate to processes further comprising conducting steps (a), (b), (c), (d) and (e) in separate and discrete reactors.

[0186] Certain embodiments disclosed herein relate to processes further comprising purifying one of CFC-113, CFO-113 or HFC-143 is first separated from its product mixture prior to the next step.

[0187] A system comprising a contained source of refrigerant, a refrigerant circuit comprising an evaporator, a compressor, a condenser, a charging valve and a charging line for temporarily connecting said contained source and said charging valve, wherein said contained source comprises a refrigerant including at least (E)-1,2-difluoroethylene (HFO-E-1132) and (Z)-1,2-difluoroethylene (HFO-Z-1132).

[0188] A system comprising a contained source of refrigerant, a refrigerant circuit comprising an evaporator, a compressor, a condenser, a charging valve and a charging line for temporarily connecting said contained source and said charging valve, wherein said contained source comprises a refrigerant including at least (E)-1,2-difluoroethylene (HFO-E-1132) and (Z)-1,2-difluoroethylene (HFO-Z-1132), wherein the system is part of a heat transfer system selected from one of refrigeration systems, refrigerators, air conditioning systems, heat pumps, chillers, and mobile air conditioning systems.

CLAIM EMBODIMENTS

[0189] Embodiment 1. A process comprising:

- (a) contacting tetrachloroethylene (PCE) with HF and chlorine to form 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113),
- (b) contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with a reducing metal in the liquid phase to form chlorotrifluoroethylene (CFO-1113),
- (c) contacting chlorotrifluoroethylene (CFO-1113) and hydrogen in one of the gas or liquid phase to form 1,1,2-trifluoroethane (HFC-143), and
- (d) converting 1,1,2-trifluoroethane (HFC-143) in the liquid or gas phase to form a mixture of E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0190] Embodiment 2. The process of Embodiment 1, further comprising (e) isomerizing a portion of the Z-1,2-difluoroethylene (HFO-Z-1132) in the mixture of E- and Z-1,2-difluoroethylene to E-1,2-difluoroethylene (HFO-E-1132).

[0191] Embodiment 3. The process of Embodiment 1, wherein (a), (b), and (c) are part of an integrated process, and each reaction is respectively conducted in a separate and discrete reactor.

[0192] Embodiment 4. The process of Embodiment 1, wherein (a), (b), (c) and (d) are part of an integrated process and each reaction is respectively conducted in a separate and discrete reactor.

[0193] Embodiment 5. The process of Embodiment 2, wherein (a), (b), (c), (d) and (e) are part of an integrated process each reaction is respectively conducted in a separate and discrete reactor.

[0194] Embodiment 6. The process of any of Embodiments 1 or 2, wherein (a) comprises chlorofluorination, (b) comprises dechlorination, (c) comprises hydrogenation, and (d) comprises dehydrofluorination.

[0195] Embodiment 7. The process of Embodiment 6, wherein the chlorofluorination of PCE produces a first product mixture, wherein the dechlorination of CFC-113 produces a second product mixture, wherein the hydrogenation of CFO-1113 produces a third product mixture, and wherein the dehydrofluorination of HFC-143 produces a fourth product mixture.

[0196] Embodiment 8. The process of any of Embodiments 1 or 2, wherein PCE conversion is conducted in the presence of hydrogen fluoride and chlorine in one of: (1) the liquid phase catalyzed by a metal halide catalyst at temperatures between 80 and 120°C, or (2) the gas phase in the presence of a chromium-based fluorination catalyst, and at temperatures between 250°C and 400°C.

[0197] Embodiment 9. The process of any of Embodiments 1 or 2, wherein the PCE is a feed composition comprising >99% by weight PCE based on the total amount of the composition, and one or more additional compounds selected from the group consisting of 1,1,1-trichloroethane, carbon tetrachloride, dichloromethane and trichloroethylene.

[0198] Embodiment 10. The process of Embodiment 9, wherein the amount of additional compounds is greater than 0 and less than 1% by weight based on the total amount of the feed composition.

[0199] Embodiment 11. The process of any of Embodiments 1 or 2, wherein the PCE conversion produces a first product mixture comprising 1,1,2-trichloro-1,2,2-trifluoroethane (CFO-113) and one or more additional compounds selected from the

group consisting of 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), CFC-113a, CFC-114, CFC-114a, HCFC-124, and HCFC-123, and PCE.

[0200] Embodiment 12. The process of Embodiment 11, wherein the amount of CFC-113 in the first product mixture is >95% by weight, based on the total weight of the composition.

[0201] Embodiment 13. The process of Embodiment 12, where the amount of additional compounds in the first product composition comprises greater than 0 and less than 1% by weight by weight based on the total amount of the first product composition.

[0202] Embodiment 14. The process of Embodiment 11, wherein the 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) comprises a part of the first product mixture.

[0203] Embodiment 15. The process of 14, wherein the first product mixture is used to prepare the second product mixture.

[0204] Embodiment 16. The process of any of Embodiments 1 or 2, wherein the reducing metal comprises zinc, magnesium, or cadmium in a solvent as the liquid phase.

[0205] Embodiment 17. The process of any of Embodiments 1 or 2, wherein the solvent comprises a polar aprotic solvent.

[0206] Embodiment 18. The process of 15, wherein contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with the reducing metal in the liquid phase is conducted at a temperature between about 20°C and about 120°C.

[0207] Embodiment 19. The process of any of Embodiments 1 or 2, wherein contacting chlorotrifluoroethylene (CFO-1113) with hydrogen is conducted at a temperature between one of (i) 50°C to about 150°C and in the presence of a hydrogenation catalyst comprising a catalytic metal selected from the group consisting of Re, Ni, Pd, Pt, Ru, Rh, and Ir, or (ii) 150°C to about 350°C in the presence of a hydrogenation catalyst comprising a catalytic metal selected from the group consisting of Re, Ni, Pd, Pt, Ru, Rh, and Ir.

[0208] Embodiment 20. The process of any of Embodiments 1 or 2, wherein contacting chlorotrifluoroethylene (CFO-1113) with hydrogen is conducted presence of a hydrogenation catalyst selected from the group consisting of Pd and Pt.

[0209] Embodiment 21. The process of Embodiment 11 wherein the hydrogenation of chlorotrifluoroethylene (CFO-1113) produces the third product mixture which comprises primarily HFC-143 and one or more additional compounds selected from the group consisting of HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-133b, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.

[0210] Embodiment 22. The process of Embodiment 11, wherein the third product mixture is converted in the gas phase or the liquid phase to fourth product mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0211] Embodiment 23. The process of Embodiment 20, wherein the conversion is conducted in the gas phase at a temperature between 150°C and 400°C.

[0212] Embodiment 24. The process of Embodiment 20, wherein the conversion is conducted in the liquid phase at a temperature between -20°C and 150°C.

[0213] Embodiment 25. A composition comprising one of:

- (a) tetrachloroethylene (PCE) and at least one additional compound selected from the group consisting of CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene or 1,1,1,3-tetrachloropropane;
- (b) 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) and at least one additional compound selected from the group consisting of CFC-113a, CFC-114, CFC-114a, HCFC-124, HCFC-123, and PCE;
- (c) chlorotrifluoroethylene (CFO-1113) and at least one additional compound selected from the group consisting of HCFC-123a, HCFC-133, HCFC-133a, HCFC-133b and CFC-113;
- (d) 1,1,2-trifluoroethane (HFC-143) at least one additional compound selected from the group consisting of HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140;

- (e) E-1,2-difluoroethylene (HFO-E-1132) and at least one additional compound selected from the group consisting of HFO-1141, HFO-1123, acetylene, HFO-Z-1132, HCFO-E-1131, HFC-125, HFC-32, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140; or
- (f) Z-1,2-difluoroethylene (HFO-Z-1132) and at least one additional compound selected from the group consisting of HFO-1141, HFO-1123, acetylene, HFC-134, HFO-E-1132, HCFO-E-1131, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140.

[0214] Embodiment 26. A composition comprising at least one of:

- (a) HFO-E-1132 and at least one additional compound selected from the group consisting of HFO-1141, HCFO-1140, acetylene and fluoroacetylene in an amount of <500 ppm,
- (b) HFO-Z-1132 and at least one additional compound selected from the group consisting of HFO-1141, HCFO-1140, acetylene and fluoroacetylene in an amount of <500 ppm,
- (c) at least one of HFO-E-1132 and HFO-Z-1132, and at least two additional compounds selected from the group consisting of acetylene, fluoroacetylene, difluoromethane (HFC-32), 1,1,1,2,2 pentafluoroethane (HFC-125), E-1-chloro-1,2-difluoroethylene (HCFO-E-1122a), Z-1-chloro-1,2-difluoroethylene (HCFO-Z-1122a), 1,1,2-trifluoroethylene (HFO-1123), fluoroethylene (HFO-1141), 1-chloro-1,1,2-trifluoroethane (HCFC-133), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1,2-difluoroethane (HFC-152), 1,1,2-trifluoroethane (HFC-143), fluoromethane (HFC-41), chlorodifluoromethane (HCFC-22), ethylene (HCO-1150), 1-chloro-1,2-difluoroethane (HCFC-142a), 1,1-difluoroethylene (HFO-1132a), vinyl chloride (1140), 1-chloro-1-fluoroethene (HCFO-E-1131a), E-1-chloro-2-fluoroethene (HCFO-E-1131), Z-1-chloro-2-fluoroethene (HCFO-Z-1131), and 1-chloro-2,2-difluoroethylene (HCFO-1122).

[0215] Embodiment 27. A composition comprising at least one of HFO-E-1132 and HFO-Z-1132, and at least two additional compounds selected from the group consisting of acetylene, fluoroacetylene, difluoromethane (HFC-32), 1,1,1,2,2

pentafluoroethane (HFC-125), E-1-chloro-1,2-difluoroethylene (HCFO-E-1122a), Z-1-chloro-1,2-difluoroethylene (HCFO-Z-1122a), 1,1,2-trifluoroethylene (HFO-1123), fluoroethylene (HFO-1141), 1-chloro-1,1,2-trifluoroethane (HCFC-133), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1,2-difluoroethane (HFC-152), 1,1,2-trifluoroethane (HFC-143), fluoromethane (HFC-41), chlorodifluoromethane (HCFC-22), ethylene, 1-chloro-1,2-difluoroethane (HCFC-142a), 1,1-difluoroethylene (HFO-1132a), vinyl chloride (1140), 1-chloro-1-fluoroethene (HCFO-E-1131a), , E-1-chloro-2-fluoroethene (HCFO-E-1131), Z-1-chloro-2-fluoroethene (HCFO-Z-1131), and 1-chloro-2,2-difluoroethylene (HCFO-1122), wherein the total amount of HFO-1141, HCFO-1140, acetylene and fluoroacetylene is selected from one of: <2000 ppm, <1000 ppm, <500 ppm, <2000 ppm, <1000 ppm, <500 ppm, 400 ppm, <300 ppm, <200 ppm, <100 ppm, <50 ppm, <10 ppm, <5 ppm, or between ≥ 0.00001 ppm and <500 ppm, between ≥ 0.0001 ppm and <500 ppm, between ≥ 0.0001 ppm and <100 ppm, between ≥ 1 ppm and less than about 2000 ppm, between ≥ 1 ppm and less than about 1000 ppm, or ≥ 0 and <100 ppm and all values an ranges between about 0.00001 ppm and 2000 ppm.

[0216] Embodiment 28. A composition comprising tetrachloroethylene (PCE) and at least two additional compounds selected from the group consisting of 1,1,1-trichloroethane, carbon tetrachloride, dichloromethane, and trichloroethylene (TCE).

[0217] Embodiment 29. A composition comprising 1-chloro-1,2,2-trifluoroethylene (CFO-1113) and one or more additional compounds selected from the group consisting of 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), and 1-chloro-1,2,2-trifluoroethane (HCFC-133).

[0218] Embodiment 30. The composition of Embodiment 29, wherein the amount of 1-chloro-2-fluoroethylene (HCFC-1113) is 99 weight percent or greater based on the total amount of the composition.

[0219] Embodiment 31. A composition comprising 1,1,2-trifluoroethane (HFC-143) and at least two additional members selected from the group consisting of HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-E-1132, HFO-Z-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.

[0220] Embodiment 32. The composition of Embodiment 31, wherein the amount of 1,1,2-trifluoroethane (HFC-143) is 99 weight percent or greater based on the total amount of the composition.

[0221] Embodiment 33. The composition of Embodiment 31, wherein the total amount of additional compounds is greater than 0 and less than 1 weight percent based on the total amount of the composition.

[0222] Embodiment 34. A process comprising blending HFO-E-1132 and/or HFO-Z-1132 formed in any one of Embodiments 1 or 2 with one or more other compounds selected from the group consisting of:

- (i) one or more HFC compounds selected from the group consisting of HFC-32, HFC-134, HFC-134a, HFC-125, HFC-152a, HFC-227ea and HFC-1123, and
- (ii) one or more HFO compounds selected from the group consisting of HFO-E-1234ze, HFO-Z-1234ze, HFO-1234yf, HFO-Z-1224yd and HFO-E-1336mzz.

[0223] Embodiment 35. A blend composition comprising HFO-E-1132 and/or HFO-Z-1132, and one or more HFC and/or HFO compounds selected from at least one of:

- (i) one or more HFC compounds selected from the group consisting of HFC-32, HFC-134, HFC-134a, HFC-125, HFC-152a, HFC-227ea and HFC-1123, and
- (ii) one or more HFO compounds selected from the group consisting of HFO-E-1234ze, HFO-Z-1234ze, HFO-1234yf, HFO-Z-1224yd and HFO-E-1336mzz.

[0224] Embodiment 36. A process of using the blend composition of Embodiment 35 as refrigerants, solvents, foam expansion agents, cleaning agents, aerosol propellants, dielectrics, fire extinguishants, or power cycle working fluids.

[0225] Embodiment 37. A process comprising:

- (a) contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with a reducing metal in the liquid phase to dehydrochlorinate the CFC-113 and forming chlorotrifluoroethylene (CFO-1113), and
- (b) contacting the CFO-1113 and hydrogen in one of the gas or liquid phase and forming 1,1,2-trifluoroethane (HFC-143).

[0226] Embodiment 38. The process of Embodiment 38, further comprising converting the HFC-143 in the liquid or gas phase to form a mixture of E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0227] Embodiment 39. The process of Embodiment 38, further comprising isomerizing a portion of the HFO-Z-1132 in the mixture of E- and Z-1,2-difluoroethylene to HFO-E-1132.

[0228] Embodiment 40. The process of Embodiment 37, wherein steps (a) and (b) are conducted in one of separate reactors or the same reactor.

[0229] Embodiment 41. The process of Embodiment 1, further comprising isomerizing the HFO-E-1132 to HFO-Z-1132.

[0230] Embodiment 42. A process comprising contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with hydrogen in the vapor phase in the presence of a catalyst to form 1,1,2-trifluoroethane (HFC-143).

[0231] Embodiment 43. The process of Embodiment 42, wherein relative molar amounts of hydrogen to CFC-113 are from about 1:1 to about 3:1.

[0232] Embodiment 44. The process of Embodiment 42 or 43, wherein the contacting is conducted a temperature of from about 80°C to about 250°C.

[0233] Embodiment 45. A process comprising contacting PCE with hydrogen in the vapor phase in the presence of a catalyst to form an HFC-143 composition.

[0234] Embodiment 46. The process of Embodiment 45, wherein the PCE is contacted with hydrogen in the vapor phase in the presence of a catalyst which comprises a catalytic metal selected from the group consisting of Pd, Pt, and a mixture thereof, preferably supported on Al₂O₃, fluorided alumina, AlF₃, or chromium oxide.

[0235] Embodiment 47. The process of Embodiment 46, wherein the amount of catalytic metal on the support comprises from about 0.5 weight % to about 10 weight% of the catalyst composition.

[0236] Embodiment 48. The process of Embodiment 1, further comprising isomerizing the HFO-E-1132 to HFO-Z-1132.

[0237] Embodiment 49. A system comprising:

a first reactor configured to synthesize a first mixture comprising 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) from a feed composition comprising tetrachloroethylene (PCE) and at least one additional compound selected from the group consisting of CCl_4 , CHCl_3 , trichloroethylene, 1,1,3-trichloropropene, ethylene and 1,1,1,3-tetrachloropropane;

a second reactor configured to convert the CFC-113 of the first mixture to a second mixture comprising chlorotrifluoroethylene (CFO-1113);

a third reactor configured to convert the CFO-1113 of the second mixture to a third mixture comprising 1,1,2-trifluoroethane (HFC-143); and

a fourth reactor configured to convert the HFC-143 of the third mixture to a fourth mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0238] Embodiment 50. The system of Embodiment 49, wherein the first, second, third and fourth reactors are in flow communication with each other.

[0239] Embodiment 51. The system of Embodiment 50, wherein the system is an integrated system comprised of the first, second, third and fourth reactors.

[0240] Embodiment 52. The system of any of Embodiments 49 to 51, the system further comprising a conversion system in fluid communication with the fourth reactor, the conversion system being configured to adjust the HFO-1132 E/Z ratio of the fourth mixture.

[0241] Embodiment 53. The system of Embodiment 52, wherein the conversion system is selected from the group consisting of a distillation column, a catalyst free thermal converter, and a catalytic reactor.

[0242] Embodiment 54. A process comprising:

(a) providing a starting feed comprising tetrachloroethylene (PCE), HF and chlorine,

(b) synthesizing 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) as part of a first product mixture from the starting feed,

- (c) contacting the CFC-113 with a reducing metal in the liquid phase to form chlorotrifluoroethylene (CFO-1113) as part of a second product mixture,
- (d) contacting the CFO-1113 and hydrogen in the gas phase or liquid phase to form 1,1,2-trifluoroethane (HFC-143) as part of a third product mixture, and
- (e) converting the HFC-143 in the liquid phase or gas phase to a fourth product mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0243] Embodiment 55. The process of Embodiment 54, wherein at least one of CFC-113, CFO-1113 or HFC-143 is first separated from its respective product mixture prior to the next step.

[0244] Embodiment 56. The process of Embodiment 54 or Embodiment 55, the process further comprising processing the fourth product mixture to form a composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the fourth product mixture.

[0245] Embodiment 57. The process of Embodiment 56, wherein the processing comprises distillation of the fourth product mixture to form a first stream comprising the composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the fourth product mixture, and a second stream having a HFO-Z-1132:HFO-E-1132 ratio which is higher than the HFO-Z-1132:HFO-E-1132 ratio of the first stream.

[0246] Embodiment 58. The process of Embodiment 57, the process further comprising recycling the second stream to step (b).

[0247] Embodiment 59. A process comprising:

- (a) providing a starting feed comprising tetrachloroethylene (PCE), HF and chlorine,
- (b) synthesizing 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) as part of a first product mixture from the starting feed,
- (c) contacting the CFC-113 with hydrogen in the gas phase or liquid phase to form 1,1,2-trifluoroethane (HFC-143) as part of a second product mixture, and

- (d) converting the HFC-143 in the liquid phase or gas phase to a third product mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0248] Embodiment 60. The process of Embodiment 59, wherein at least one of CFC-113 or HFC-143 is separated from its respective product mixture prior to the next step.

[0249] Embodiment 61. The process of Embodiment 59 or Embodiment 60, the process further comprising processing the third product mixture to form a composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the third product mixture.

[0250] Embodiment 62. The process of Embodiment 61, wherein the processing comprises distillation of the third product mixture to form a first stream comprising the composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the third product mixture, and a second stream having a HFO-Z-1132:HFO-E-1132 ratio which is higher than the HFO-Z-1132:HFO-E-1132 ratio of the first stream.

[0251] Embodiment 63. The process of Embodiment 62, the process further comprising recycling the second stream to step (b).

OTHER EMBODIMENTS

[0252] OE1. A PCE feed mixture comprising one or more additional compounds selected from PCE, CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene, 1,1,1,3-tetrachloropropane.

[0253] OE2. A PCE conversion product mixture comprising one or more additional compounds selected from CFC-113, CFC-113a, CFC-114, CFC-114a, HCFC-124, HCFC-123, and PCE.

[0254] OE3. A CFC-113 product mixture comprising one or more additional compounds selected from CFC-113a, CFC-114, CFC-114a, HCFC-124, HCFC-123, and PCE.

[0255] OE4. A CFO-1113 product mixture comprising one or more additional compounds selected from HCFC-123a, HCFC-133b, HCFC-133a, HCFC-133, and CFC-113.

[0256] OE5. An HFC-143 feed mixture comprising HFC-143 and one or more additional compounds selected from HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140.

[0257] OE6. An HFC-143 product mixture comprising one or more additional compounds selected from HFO-1123, CFO-1113, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140

[0258] OE7. An HFO-E-1132 and/or HFO-Z-1132 product mixture which comprises HFO-1141, HCO-1140, and acetylene in an amount selected from one of <2000 ppm, <1000 ppm, <500 ppm, <400 ppm, <300 ppm, <200 ppm, <100 ppm, <50 ppm, <10 ppm, <5 ppm, between ≥ 0.00001 ppm and <500 ppm, between ≥ 0.0001 ppm and <500 ppm, between ≥ 0.00001 ppm and <100 ppm, between ≥ 0.0001 ppm and <100 ppm, between ≥ 1 ppm and less than about 2000 ppm, between ≥ 1 ppm and less than about 1000 ppm, or ≥ 0 and <100 ppm and all values an ranges between about 0.00001 ppm and 2000 ppm.

[0259] OE8. An HFO-E-1132 (or HFO-Z-1132) product mixture which comprises HFO-1141, HCO-1140, and acetylene in an amount selected from one of <100 ppm, <50 ppm, <10 ppm, <5 ppm.

[0260] OE9. An HFO-E-1132 and/or HFO-Z-1132 product mixture which comprises HFO-1141, HCO-1140, and acetylene in an amount selected from one of <100 ppm, <50 ppm, <10 ppm, or <5 ppm.

[0261] OE10. In certain HFO-E-1132 and/or HFO-Z-1132 product mixture embodiments, the amount of fluoroethylene (HFO-1141), vinyl chloride (HCO-1140), acetylene and fluoroacetylene is selected from one of <2000 ppm, <1000 ppm, <500 ppm, <2000 ppm, <1000 ppm, <500 ppm, <400 ppm, <300 ppm, <200 ppm, <100 ppm, <50 ppm, <10 ppm, <5 ppm, between ≥ 0.00001 and <500 ppm, between ≥ 0.0001 and <500 ppm, between ≥ 0.00001 and <100 ppm, between ≥ 0.0001 and <100 ppm, or ≥ 0 and <100 ppm.

[0262] OE11. An HFO-E-1132 and/or HFO-Z-1132 product mixture embodiment wherein the total amount of fluoroethylene (HFO-1141), vinyl chloride (HCO-1140), and acetylene and fluoroacetylene is selected from one of <100 ppm, <50 ppm, <10 ppm, <5 ppm, between ≥ 0.00001 and <100 ppm, between ≥ 0.0001 and <100 ppm, or ≥ 0 and <100 ppm.

[0263] OE12. An HFO-E-1132 and/or HFO-Z-1132 product mixture embodiment optionally containing at least one of fluoroethylene (HFO-1141), vinyl chloride (HCO-1140), acetylene, and fluoroacetylene is selected from one of <100 ppm, <50 ppm, <10 ppm, <5 ppm, between ≥ 0.00001 and <100 ppm, between ≥ 0.0001 and <100 ppm, or ≥ 0 and <100 ppm, preferably free of at least one of fluoroethylene (HFO-1141), vinyl chloride (HCO-1140),.

[0264] OE13. An HFO-E-1132 and/or HFO-Z-1132 product mixture which comprises at least two of the following components: HFO-Z-1132 (or HFO-E-1132), acetylene, fluoroacetylene, difluoromethane (HFC-32), 1,1,1,2,2 pentafluoroethane (HFC-125), E-1-chloro-1,2-difluoroethylene (HCFO-E-1122a), Z-1-chloro-1,2-difluoroethylene (HCFO-Z-1122a), 1,1,2-trifluoroethylene (HFO-1123), fluoroethylene (HFO-1141), 1-chloro-1,1,2-trifluoroethane (HCFC-133), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1,2-difluoroethane (HFC-152), 1,1,2-trifluoroethane (HFC-143), fluoromethane (HFC-41), chlorodifluoromethane (HCFC-22), ethylene (HCO-1150), 1-chloro-1,2-difluoroethane (HCFC-142a), 1,1-difluoroethylene (HFO-1132a), vinyl chloride (1140), 1-chloro-1-fluoroethene (HCFO-1131a), E-1-chloro-2-fluoroethene (HCFO-E-1131), Z-1-chloro-2-fluoroethene (HCFO-Z-1131), and 1-chloro-2,2-difluoroethylene (HCFO-1122) where the total amount of other components is less than 1 weight % of the total composition.

[0265] OE14. A process of converting a PCE feed mixture comprising one or more additional compounds selected from PCE, CCl_4 , CHCl_3 , trichloroethylene, 1,1,3-trichloropropene, ethylene, 1,1,1,3-tetrachloropropane to a CFC-113 product mixture.

[0266] OE15. A process of converting a PCE product mixture (also a CFC-113 feed) comprising one or more additional compounds selected from CFC-113, CFC-113a, CFC-114, CFC-114a, HCFC-124, HCFC-123, and PCE.

[0267] OE16. A process of converting a CFC-113 mixture comprising CFC-113 and one or more additional compounds selected from CFC-113a, CFC-114, CFC-114a, HCFC-124, HCFC-123, and PCE to a product mixture comprising CFO-1113.

[0268] OE17. A process of converting a CFO-1113 mixture comprising one or more additional compounds selected from HCFC-123a, HCFC-133, HCFC-133a, HCFC-133b, and CFC-113 to a product mixture comprising HFC-143.

[0269] OE18. A process of converting an HFC-143 mixture comprising one or more additional compounds selected from HFC-143, HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140 to an HFO-E-1132 and HFO-Z-1132 product mixture

[0270] OE19. An HFC-143 product mixture comprising one or more additional compounds selected from HFO-1123, CFO-1113, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140 to an HFO-E-1132 (or HFO-Z-1132) product mixture.

[0271] OE20. A process of converting a PCE feed mixture also comprising one or more additional compounds selected from PCE, CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene, 1,1,1,3-tetrachloropropane by chlorofluorination to a CFC-113 product mixture.

[0272] OE21. A process of converting CFC-113 in a product mixture also comprising one or more additional compounds selected from CFC-113a, CFC-114, CFC-114a, HCFC-124, HCFC-123, and PCE by dechlorination to a product mixture comprising CFO-1113

[0273] OE22. A process of converting CFO-1113 in a product mixture also comprising one or more additional compounds selected from HCFC-123a, HCFC-133, HCFC-133a, HCFC-133b, and CFC-113 to a product mixture comprising HFC-143 by hydrogenation.

[0274] OE23. A process of converting HFC-143 in a product mixture also comprising one or more additional compounds selected from HFC-143, HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140 by dehydrofluorination to an HFO-E-1132 and HFO-Z-1132 product mixture.

[0275] OE24. A process of converting a PCE feed mixture also comprising one or more additional compounds selected from PCE, CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene, 1,1,1,3-tetrachloropropane by chlorofluorination to a CFC-113 product mixture wherein the chlorofluorination is conducted at temperatures selected from between 80-120°C, or between 250°C and 400°C.

[0276] OE25. A process of converting CFC-113 in a product mixture also comprising one or more additional compounds selected from CFC-113a, CFC-114, CFC-114a, HCFC-124, HCFC-123, and PCE by dechlorination to a product mixture comprising CFO-1113 wherein the CFC-113 is hydrodechlorinated or dechlorinated to CFO-1113.

[0277] OE26. A process of converting CFO-1113 in a product mixture also comprising one or more additional compounds selected from HCFC-123a, HCFC-133, HCFC-133a, HCFC-133b, and CFC-113 to a product mixture comprising HFC-143 by hydrogenation.

[0278] OE27. A process of converting HFC-143 in a product mixture also comprising one or more additional compounds selected from HFC-143, HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140 by dehydrofluorination to an HFO-E-1132 and HFO-Z-1132 product mixture.

[0279] OE28. Any of OE7-OE12 wherein the total amount of additional compounds is greater than 0 and less than 1 % by weight based on the total amount of the composition.

[0280] OE29. Any of OE7-OE12 wherein the total amount of additional compounds is greater than 0 and less than 0.5 % by weight based on the total amount of the composition.

[0281] OE30. A process comprising blending any of the HFO-E-1132 and/or HFO-Z-1132 compositions of OE7-OE12 with at least one of:

- one or more HFC compounds selected from HFC-32, HFC-134, HFC-134a, HFC-125, HFC-152a, HFC-227ea and HFC-1123,
- one or more HFO compounds selected from and HFO-E-1234ze, HFO-Z-1234ze, HFO-1234yf, HFO-Z-1224yd and HFO-E-1336mzz.

[0282] OE31. In certain embodiments disclosed herein HFO-E-1132 and/or HFO-Z-1132 blends containing one or more HFC and/or HFO compounds are used as refrigerants, solvents, foam expansion agents, cleaning agents, aerosol propellants, dielectrics, fire extinguishants, and power cycle working fluids.

[0283] OE32. A process comprising using a blend of the HFO-E-1132 and/or HFO-Z-1132 compositions of OE7-OE12 with other HFC, HFO and HCFO compounds as a refrigerant, solvent, foam expansion agent, cleaning agent, aerosol propellant, dielectric, fire extinguishant, or power cycle working fluids.

[0284] OE33. A process comprising:

- (a) contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with a reducing metal in the liquid phase to dehydrochlorinate CFC-113 and form chlorotrifluoroethylene (CFO-1113),
- (b) contacting chlorotrifluoroethylene (CFO-1113) and hydrogen in one of the gas or liquid phase and form 1,1,2-trifluoroethane (HFC-143), and
- (c) converting 1,1,2-trifluoroethane (HFC-143) in the liquid or gas phase to form E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0285] OE34. OE33 further comprising isomerizing Z-1,2-difluoroethylene (HFO-Z-1132) to E-1,2-difluoroethylene (HFO-E-1132)

[0286] OE35. The process of OE 32-34 wherein steps "a" and "b" are conducted in one of separate reactors or the same reactor.

[0287] OE36. The process of OE 32-34 wherein steps "a" and "b" are conducted in the same reactor.

[0288] OE37. The process of OE 32-34 wherein steps "a" and "b" are conducted in separate and different reactors.

[0289] OE38. A process embodiment wherein a CFC-113 feed composition, preferably comprises CFC-113 and one or more additional compounds selected from CFC-113a, CFC-114a, HCFC-123, HCFC-123a, CFC-115, CFC-12, HCFC-124, CFC-114, CFO-1317, CFC-216, CFC-318, CFC-316, CFC-215cb, CFC-214cb, HCFC-122, CFC-112, CFC-112a, and CFO-1112a.

[0290] OE39. Process embodiment OE37 wherein CFC-113 and hydrogen are contacted and the relative molar amount of hydrogen to CFC-113 in reaction is from about 1:1 to about 3:1.

[0291] OE40. Process embodiment OE37 wherein contacting is conducted a temperature of from about 80°C to about 250°C.

[0292] OE41. Process embodiment wherein CFC-113 is contacted with hydrogen in the vapor phase in the presence of a catalyst to form an HFC-143 composition.

[0293] OE42. Process embodiment OE40 wherein CFC-113 is contacted with hydrogen in the vapor phase in the presence of a catalyst which comprises a catalytic metal, selected from Pd, Pt, or a mixture thereof, preferably supported on Al₂O₃, fluorided alumina, AlF₃, or chromium oxide as disclosed in U.S. Patent Application 20080207962 and 20080207963.

[0294] OE43. Process embodiment OE41 wherein CFC-113 is contacted with hydrogen in the vapor phase in the presence of a catalyst wherein the amount of catalytic metal on the support comprises from about 0.5 weight % to about 10 weight % of the catalyst composition.

[0295] OE44. Composition embodiment derived from OE40-OE-42 wherein the HFC-143 product comprises at least one compounds selected from HCFC-123a, HCFC-132c, HCFC-133, HCFC-133b, C₂H₆, HFC-143a, HFC-134a, and HFC-152a.

[0296] OE45. The process of OE32 further comprising isomerizing E-1,2-difluoroethylene (HFO-E- 1132) to Z-1,2-difluoroethylene (HFO-Z-1132).

[0297] OE46. In each OE process the feed for any of reactions (1)-(4) is independently selected from one of >50% by weight, >60% by weight, >70% by weight, <80% by weight or <90% by weight before purification, for example by distillation and about >95% or >99% by weight, based on the total weight of the composition after distillation.

[0298] OE47. A system comprising:

a first reactor configured to synthesize a first mixture comprising 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) from a feed composition comprising tetrachloroethylene (PCE) and at least one additional compound selected from

CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene or 1,1,1,3-tetrachloropropane;

a second reactor configured to convert the CFC-113 of the first mixture to a second mixture comprising chlorotrifluoroethylene (CFO-1113);

a third reactor configured to convert the CFO-1113 of the second mixture to a third mixture comprising 1,1,2-trifluoroethane (HFC-143); and

a fourth reactor configured to convert the HFC-143 of the third mixture to a fourth mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0299] **OE48.** The system of **OE47**, wherein the first, second, third and fourth reactors are in flow communication with each other.

[0300] **OE49.** The system of **OE48**, wherein the system is an integrated system comprised of the first, second, third and fourth reactors.

[0301] **OE50.** The system of any of **OE47** to **OE49**, the system further comprising a conversion system in fluid communication with the fourth reactor, the conversion system being configured to adjust the HFO-1132 E/Z ratio of the fourth mixture.

[0302] **OE51.** The system of **OE50**, wherein the conversion system is selected from the group consisting of a distillation column, a catalyst free thermal converter, and a catalytic reactor.

[0303] **OE52.** A process comprising:

- a. providing a starting feed comprising tetrachloroethylene (PCE), HF and chlorine,
- b. synthesizing 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) as part of a first product mixture from the starting feed,
- c. contacting the CFC-113 with a reducing metal in the liquid phase to form chlorotrifluoroethylene (CFO-1113) as part of a second product mixture,
- d. contacting the CFO-1113 and hydrogen in the gas phase or liquid phase to form 1,1,2-trifluoroethane (HFC-143) as part of a third product mixture, and

- e. converting the HFC-143 in the liquid phase or gas phase to a fourth product mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

[0304] OE53. The process of **OE52**, wherein at least one of CFC-113, CFO-1113 or HFC-143 is first separated from its respective product mixture prior to the next step.

[0305] OE54. The process of **OE52** or **OE53**, the process further comprising processing fourth product mixture to form a composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the fourth product mixture.

[0306] OE55: The process of **OE54**, wherein the processing comprises distillation of the fourth product mixture to form a first stream comprising the composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the fourth product mixture, and a second stream having a HFO-Z-1132:HFO-E-1132 ratio which is higher than the HFO-Z-1132:HFO-E-1132 ratio of the first stream.

[0307] OE56: The process of **OE55**, the process further comprising recycling the second stream to step (b).

[0308] 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 comprising:
 - (a) contacting tetrachloroethylene (PCE) with HF and chlorine to form 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113),
 - (b) contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with a reducing metal in the liquid phase to form chlorotrifluoroethylene (CFO-1113),
 - (c) contacting chlorotrifluoroethylene (CFO-1113) and hydrogen in one of the gas or liquid phase to form 1,1,2-trifluoroethane (HFC-143), and
 - (d) converting 1,1,2-trifluoroethane (HFC-143) in the liquid or gas phase to form a mixture of E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).
2. The process of claim 1, further comprising (e) isomerizing a portion of the Z-1,2-difluoroethylene (HFO-Z-1132) in the mixture of E- and Z-1,2-difluoroethylene to E-1,2-difluoroethylene (HFO-E-1132).
3. The process of claim 1, wherein (a), (b), and (c) are part of an integrated process, and each reaction is respectively conducted in a separate and discrete reactor.
4. The process of claim 1, wherein (a), (b), (c) and (d) are part of an integrated process and each reaction is respectively conducted in a separate and discrete reactor.
5. The process of claim 2, wherein (a), (b), (c), (d) and (e) are part of an integrated process each reaction is respectively conducted in a separate and discrete reactor.
6. The process of any of claims 1 or 2, wherein (a) comprises chlorofluorination, (b) comprises dechlorination, (c) comprises hydrogenation, and (d) comprises dehydrofluorination.
7. The process of claim 6, wherein the chlorofluorination of PCE produces a first product mixture, wherein the dechlorination of CFC-113 produces a second product mixture, wherein the hydrogenation of CFO-1113 produces a third

product mixture, and wherein the dehydrofluorination of HFC-143 produces a fourth product mixture.

8. The process of any of claims 1 or 2, wherein PCE conversion is conducted in the presence of hydrogen fluoride and chlorine in one of: **(1)** the liquid phase catalyzed by a metal halide catalyst at temperatures between 80 and 120°C, or **(2)** the gas phase in the presence of a chromium-based fluorination catalyst, and at temperatures between 250°C and 400°C.
9. The process of any of claims 1 or 2, wherein the PCE is a feed composition comprising >99% by weight PCE based on the total amount of the composition, and one or more additional compounds selected from the group consisting of 1,1,1-trichloroethane, carbon tetrachloride, dichloromethane and trichloroethylene.
10. The process of claim 9, wherein the amount of additional compounds is greater than 0 and less than 1% by weight based on the total amount of the feed composition.
11. The process of any of claims 1 or 2, wherein the PCE conversion produces a first product mixture comprising 1,1,2-trichloro-1,2,2-trifluoroethane (CFO-113) and one or more additional compounds selected from the group consisting of 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), CFC-113a, CFC-114, CFC-114a, HCFC-124, and HCFC-123, and PCE.
12. The process of claim 11, wherein the amount of CFC-113 in the first product mixture is >95% by weight, based on the total weight of the composition
13. The process of claim 12, where the amount of additional compounds in the first product composition comprises greater than 0 and less than 1% by weight by weight based on the total amount of the first product composition.
14. The process of claim 11, wherein the 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) comprises a part of the first product mixture.
15. The process of 14, wherein the first product mixture is used to prepare the second product mixture.

16. The process of any of claims 1 or 2, wherein the reducing metal comprises zinc, magnesium, or cadmium in a solvent as the liquid phase.
17. The process of any of claims 1 or 2, wherein the solvent comprises a polar aprotic solvent.
18. The process of 15, wherein contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with the reducing metal in the liquid phase is conducted at a temperature between about 20°C and about 120°C.
19. The process of any of claims 1 or 2, wherein contacting chlorotrifluoroethylene (CFO-1113) with hydrogen is conducted at a temperature between one of (i) 50°C to about 150°C and in the presence of a hydrogenation catalyst comprising a catalytic metal selected from the group consisting of Re, Ni, Pd, Pt, Ru, Rh, and Ir, or (ii) 150°C to about 350°C in the presence of a hydrogenation catalyst comprising a catalytic metal selected from the group consisting of Re, Ni, Pd, Pt, Ru, Rh, and Ir.
20. The process of any of claims 1 or 2, wherein contacting chlorotrifluoroethylene (CFO-1113) with hydrogen is conducted presence of a hydrogenation catalyst selected from the group consisting of Pd and Pt.
21. The process of claim 11 wherein the hydrogenation of chlorotrifluoroethylene (CFO-1113) produces the third product mixture which comprises primarily HFC-143 and one or more additional compounds selected from the group consisting of HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-Z-1132, HFO-E-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-133b, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.
22. The process of claim 11, wherein the third product mixture is converted in the gas phase or the liquid phase to fourth product mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).
23. The process of claim 20, wherein the conversion is conducted in the gas phase at a temperature between 150°C and 400°C.
24. The process of claim 20, wherein the conversion is conducted in the liquid phase at a temperature between -20°C and 150°C.

25. A composition comprising one of:

- (a) tetrachloroethylene (PCE) and at least one additional compound selected from the group consisting of CCl_4 , CHCl_3 , trichloroethylene, 1,1,3-trichloropropene, ethylene or 1,1,1,3-tetrachloropropane;
- (b) 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) and at least one additional compound selected from the group consisting of CFC-113a, CFC-114, CFC-114a, HCFC-124, HCFC-123, and PCE;
- (c) chlorotrifluoroethylene (CFO-1113) and at least one additional compound selected from the group consisting of HCFC-123a, HCFC-133, HCFC-133a, HCFC-133b and CFC-113;
- (d) 1,1,2-trifluoroethane (HFC-143) at least one additional compound selected from the group consisting of HFO-1123, CFO-1113, HFC-134, HFC-134a, HCFO-1131a, HCFC-142, HCFC-142a, HCFO-1122, HCFO-1122a, and HCO-1140;
- (e) E-1,2-difluoroethylene (HFO-E-1132) and at least one additional compound selected from the group consisting of HFO-1141, HFO-1123, acetylene, HFO-Z-1132, HCFO-E-1131, HFC-125, HFC-32, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140;
or
- (f) Z-1,2-difluoroethylene (HFO-Z-1132) and at least one additional compound selected from the group consisting of HFO-1141, HFO-1123, acetylene, HFC-134, HFO-E-1132, HCFO-E-1131, HCFO-1131a, HCFO-Z-1122a, HCFO-E-1122a, HCFO-1122, and HCO-1140.

26. A composition comprising at least one of:

- (a) HFO-E-1132 and at least one additional compound selected from the group consisting of HFO-1141, HCFO-1140, acetylene and fluoroacetylene in an amount of <500 ppm,
- (b) HFO-Z-1132 and at least one additional compound selected from the group consisting of HFO-1141, HCFO-1140, acetylene and fluoroacetylene in an amount of <500 ppm,

- (c) at least one of HFO-E-1132 and HFO-Z-1132, and at least two additional compounds selected from the group consisting of acetylene, fluoroacetylene, difluoromethane (HFC-32), 1,1,1,2,2 pentafluoroethane (HFC-125), E-1-chloro-1,2-difluoroethylene (HCFO-E-1122a), Z-1-chloro-1,2-difluoroethylene (HCFO-Z-1122a), 1,1,2-trifluoroethylene (HFO-1123), fluoroethylene (HFO-1141), 1-chloro-1,1,2-trifluoroethane (HCFC-133), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1,2-difluoroethane (HFC-152), 1,1,2-trifluoroethane (HFC-143), fluoromethane (HFC-41), chlorodifluoromethane (HCFC-22), ethylene (HCO-1150), 1-chloro-1,2-difluoroethane (HCFC-142a), 1,1-difluoroethylene (HFO-1132a), vinyl chloride (1140), 1-chloro-1-fluoroethene (HCFO-E-1131a), E-1-chloro-2-fluoroethene (HCFO-E-1131), Z-1-chloro-2-fluoroethene (HCFO-Z-1131), and 1-chloro-2,2-difluoroethylene (HCFO-1122).
27. A composition comprising at least one of HFO-E-1132 and HFO-Z-1132, and at least two additional compounds selected from the group consisting of acetylene, fluoroacetylene, difluoromethane (HFC-32), 1,1,1,2,2 pentafluoroethane (HFC-125), E-1-chloro-1,2-difluoroethylene (HCFO-E-1122a), Z-1-chloro-1,2-difluoroethylene (HCFO-Z-1122a), 1,1,2-trifluoroethylene (HFO-1123), fluoroethylene (HFO-1141), 1-chloro-1,1,2-trifluoroethane (HCFC-133), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), 1,2-difluoroethane (HFC-152), 1,1,2-trifluoroethane (HFC-143), fluoromethane (HFC-41), chlorodifluoromethane (HCFC-22), ethylene, 1-chloro-1,2-difluoroethane (HCFC-142a), 1,1-difluoroethylene (HFO-1132a), vinyl chloride (1140), 1-chloro-1-fluoroethene (HCFO-E-1131a), , E-1-chloro-2-fluoroethene (HCFO-E-1131), Z-1-chloro-2-fluoroethene (HCFO-Z-1131), and 1-chloro-2,2-difluoroethylene (HCFO-1122), wherein the total amount of HFO-1141, HCFO-1140, acetylene and fluoroacetylene is selected from one of: <2000 ppm, <1000 ppm, <500 ppm, <2000 ppm, <1000 ppm, <500 ppm, 400 ppm, <300 ppm, <200 ppm, <100 ppm, <50 ppm, <10 ppm, <5 ppm, or between ≥ 0.00001 ppm and <500 ppm, between ≥ 0.0001 ppm and <500 ppm, between ≥ 0.00001 ppm and <100 ppm, between ≥ 0.0001 ppm and <100 ppm, between ≥ 1 ppm and less than about

2000 ppm, between ≥ 1 ppm and less than about 1000 ppm, or ≥ 0 and < 100 ppm and all values an ranges between about 0.00001 ppm and 2000 ppm.

28. A composition comprising tetrachloroethylene (PCE) and at least two additional compounds selected from the group consisting of 1,1,1-trichloroethane, carbon tetrachloride, dichloromethane, and trichloroethylene (TCE).
29. A composition comprising 1-chloro-1,2,2-trifluoroethylene (CFO-1113) and one or more additional compounds selected from the group consisting of 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 1-chloro-1,1,2-trifluoroethane (HCFC-133b), and 1-chloro-1,2,2-trifluoroethane (HCFC-133).
30. The composition of claim 29, wherein the amount of 1-chloro-2-fluoroethylene (HCFC-1113) is 99 weight percent or greater based on the total amount of the composition.
31. A composition comprising 1,1,2-trifluoroethane (HFC-143) and at least two additional members selected from the group consisting of HFO-1123, HFC-134a, HFC-152a, HFC-236fa, HFO-E-1132, HFO-Z-1132, HCFO-E-1122a, HCFO-Z-1122a, HCFO-1140, HCFC-133b, HCFC-133, HCFO-Z-1131, HCFO-E-1131, HCFC-151a, HCC-160, and CFC-113.
32. The composition of claim 31, wherein the amount of 1,1,2-trifluoroethane (HFC-143) is 99 weight percent or greater based on the total amount of the composition.
33. The composition of claim 31, wherein the total amount of additional compounds if greater than 0 and less than 1 weight percent based on the total amount of the composition.
34. A process comprising blending HFO-E-1132 and/or HFO-Z-1132 formed in any one of claims 1 or 2 with one or more other compounds selected from the group consisting of:
 - (i) one or more HFC compounds selected from the group consisting of HFC-32, HFC-134, HFC-134a, HFC-125, HFC-152a, HFC-227ea and HFC-1123, and

- (ii) one or more HFO compounds selected from the group consisting of HFO-E-1234ze, HFO-Z-1234ze, HFO-1234yf, HFO-Z-1224yd and HFO-E-1336mzz.
- 35. A blend composition comprising HFO-E-1132 and/or HFO-Z-1132, and one or more HFC and/or HFO compounds selected from at least one of:
 - (i) one or more HFC compounds selected from the group consisting of HFC-32, HFC-134, HFC-134a, HFC-125, HFC-152a, HFC-227ea and HFC-1123, and
 - (ii) one or more HFO compounds selected from the group consisting of HFO-E-1234ze, HFO-Z-1234ze, HFO-1234yf, HFO-Z-1224yd and HFO-E-1336mzz.
- 36. A process of using the blend composition of claim 35 as refrigerants, solvents, foam expansion agents, cleaning agents, aerosol propellants, dielectrics, fire extinguishants, or power cycle working fluids.
- 37. A process comprising:
 - (a) contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with a reducing metal in the liquid phase to dehydrochlorinate the CFC-113 and forming chlorotrifluoroethylene (CFO-1113), and
 - (b) contacting the CFO-1113 and hydrogen in one of the gas or liquid phase and forming 1,1,2-trifluoroethane (HFC-143).
- 38. The process of claim 37, further comprising converting the HFC-143 in the liquid or gas phase to form a mixture of E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).
- 39. The process of claim 38, further comprising isomerizing a portion of the HFO-Z-1132 in the mixture of E- and Z-1,2-difluoroethylene to HFO-E-1132.
- 40. The process of claim 37, wherein steps (a) and (b) are conducted in one of separate reactors or the same reactor.
- 41. The process of claim 1, further comprising isomerizing the HFO-E-1132 to HFO-Z-1132.

42. A process comprising contacting 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) with hydrogen in the vapor phase in the presence of a catalyst to form 1,1,2-trifluoroethane (HFC-143).
43. The process of claim 42, wherein relative molar amounts of hydrogen to CFC-113 are from about 1:1 to about 3:1.
44. The process of claim 42 or 43, wherein the contacting is conducted at a temperature of from about 80°C to about 250°C.
45. A process comprising contacting PCE with hydrogen in the vapor phase in the presence of a catalyst to form an HFC-143 composition.
46. The process of claim 45, wherein the PCE is contacted with hydrogen in the vapor phase in the presence of a catalyst which comprises a catalytic metal selected from the group consisting of Pd, Pt, and a mixture thereof, preferably supported on Al₂O₃, fluorided alumina, AlF₃, or chromium oxide.
47. The process of claim 46, wherein the amount of catalytic metal on the support comprises from about 0.5 weight % to about 10 weight% of the catalyst composition.
48. The process of claim 1, further comprising isomerizing the HFO-E-1132 to HFO-Z-1132.
49. A system comprising:
 - a first reactor configured to synthesize a first mixture comprising 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) from a feed composition comprising tetrachloroethylene (PCE) and at least one additional compound selected from the group consisting of CCl₄, CHCl₃, trichloroethylene, 1,1,3-trichloropropene, ethylene and 1,1,1,3-tetrachloropropane;
 - a second reactor configured to convert the CFC-113 of the first mixture to a second mixture comprising chlorotrifluoroethylene (CFO-1113);
 - a third reactor configured to convert the CFO-1113 of the second mixture to a third mixture comprising 1,1,2-trifluoroethane (HFC-143); and

a fourth reactor configured to convert the HFC-143 of the third mixture to a fourth mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).

50. The system of claim 49, wherein the first, second, third and fourth reactors are in flow communication with each other.
51. The system of claim 50, wherein the system is an integrated system comprised of the first, second, third and fourth reactors.
52. The system of any of claims 49 to 51, the system further comprising a conversion system in fluid communication with the fourth reactor, the conversion system being configured to adjust the HFO-1132 E/Z ratio of the fourth mixture.
53. The system of claim 52, wherein the conversion system is selected from the group consisting of a distillation column, a catalyst free thermal converter, and a catalytic reactor.
54. A process comprising:
 - (a) providing a starting feed comprising tetrachloroethylene (PCE), HF and chlorine,
 - (b) synthesizing 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) as part of a first product mixture from the starting feed,
 - (c) contacting the CFC-113 with a reducing metal in the liquid phase to form chlorotrifluoroethylene (CFO-1113) as part of a second product mixture,
 - (d) contacting the CFO-1113 and hydrogen in the gas phase or liquid phase to form 1,1,2-trifluoroethane (HFC-143) as part of a third product mixture, and
 - (e) converting the HFC-143 in the liquid phase or gas phase to a fourth product mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).
55. The process of claim 54, wherein at least one of CFC-113, CFO-1113 or HFC-143 is first separated from its respective product mixture prior to the next step.

56. The process of claim 54 or claim 55, the process further comprising processing the fourth product mixture to form a composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the fourth product mixture.
57. The process of claim 56, wherein the processing comprises distillation of the fourth product mixture to form a first stream comprising the composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the fourth product mixture, and a second stream having a HFO-Z-1132:HFO-E-1132 ratio which is higher than the HFO-Z-1132:HFO-E-1132 ratio of the first stream.
58. The process of claim 57, the process further comprising recycling the second stream to step (b).
59. A process comprising:
- (a) providing a starting feed comprising tetrachloroethylene (PCE), HF and chlorine,
 - (b) synthesizing 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) as part of a first product mixture from the starting feed,
 - (c) contacting the CFC-113 with hydrogen in the gas phase or liquid phase to form 1,1,2-trifluoroethane (HFC-143) as part of a second product mixture, and
 - (d) converting the HFC-143 in the liquid phase or gas phase to a third product mixture comprising E-1,2-difluoroethylene (HFO-E-1132) and Z-1,2-difluoroethylene (HFO-Z-1132).
60. The process of claim 59, wherein at least one of CFC-113 or HFC-143 is separated from its respective product mixture prior to the next step.
61. The process of claim 59 or claim 60, the process further comprising processing the third product mixture to form a composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the third product mixture.

62. The process of claim 61, wherein the processing comprises distillation of the third product mixture to form a first stream comprising the composition having a HFO-Z-1132:HFO-E-1132 ratio which is lower than a HFO-Z-1132:HFO-E-1132 ratio of the third product mixture, and a second stream having a HFO-Z-1132:HFO-E-1132 ratio which is higher than the HFO-Z-1132:HFO-E-1132 ratio of the first stream.
63. The process of claim 62, the process further comprising recycling the second stream to step (b).