

TITLE

COMPOSITIONS AND PROCESSES FOR SYNTHESIS OF 3,3,4,4,4-PENTAFLUORO-1-BUTENE

FIELD

[0001] The present application relates to compositions comprising fluorinated compounds, processes of preparing such compositions and their use, particularly 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf, $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$).

BACKGROUND

[0002] A growing public awareness of the environmental impacts from the extraction, transportation and use of fossil fuels are motivating a new environmental sustainability driver in the form of regulations and reduction in output of CO_2 equivalence in the atmosphere. In particular, new environmental regulations on refrigerants have forced the refrigeration and air-conditioning industry to look for new refrigerants with low global warming potential (GWP). Replacement refrigerants with low global warming potential (GWP) and ozone depletion potential (ODP) for both existing and new applications in thermal management segments will need to adhere to these new regulations.

[0003] Certain hydrofluoroolefins, such as 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf, $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$) and *E*-1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene (*E*- $\text{C}_2\text{F}_5\text{CH}=\text{CHC}_2\text{F}_5$, *E*-HFO-153-10mczz), meet both goals. In particular, 3,3,4,4,4-pentafluoro-1-butene maybe useful in heat transfer, etching gas, cleaning solvent and dielectric gas application, *E*-1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene may be useful in heat transfer fluid applications (e.g., immersion cooling systems, data-center cooling systems or thermal management solution for EV batteries), dielectric liquid and cleaning solvent. Accordingly, there is a need to develop new processes and intermediate compositions for preparing 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf, $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$) and *E*-1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene. In addition, the intermediates produced in the process making HFO-1345zf, such as chlorotetrafluorobutene isomers (HCFO-1344 isomers) are good low GWP

candidates for applications in heat transfer, dielectric liquid and cleaning solvents too.

SUMMARY

[0004] The present invention relates to compositions comprising 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf, $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$), processes of preparing such compositions and their use.

[0005] The present invention provides a process for preparing HFO-1345zf comprising contacting 2,2,4-trichloro-1,1,1-trifluorobutane (HCFC-353maf, $\text{CH}_2\text{ClCH}_2\text{CCl}_2\text{CF}_3$) with HF in a reactor in the presence of a fluorination catalyst to obtain a process mixture comprising HFO-1345zf.

[0006] In certain embodiments, the process is performed at a temperature of about 250-450°C, a pressure of about 0 to 200 psig. Preferably, the temperature is in the range of about 300 to about 380°C.

[0007] Preferably the pressure is in the range from about 30 to 180 psig or about 40 to 150 psig, or about 60-120 psig.

[0008] The present invention also provides a composition comprising HFO-1345zf, and at least one additional compound chosen from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd), dichlorotrifluorobutene isomers (HCFO-1343 isomers), chlorotetrafluorobutene isomers (HCFO-1344 isomers), chloropentafluorobutane isomers (HCFC-355 isomers), 1,1,1,4,4,4-hexafluorobutane (HFC-356mff), chlorotrifluorobutene isomers (HCFO-1353 isomers), 1,1,1-trifluoroethane (HFC-143a), trifluoromethane (HFC-23), chlorotrifluoromethane (CFC-13), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,3,3,3-tetrafluoropropene (HFO-1234ze), 2-chloro-1,1,1,3,3,3-hexafluoro-2-butene (HCFO-1326mxz), heptafluorobutene isomers (HFO-1327 isomers), 2,2,3,3,3-pentafluoropropanal and 2,2,4-trichloro-1,1,1-trifluorobutane (353maf). The composition may be prepared by the process disclosed herein.

[0009] The present invention also provides a composition comprising 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf, $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$) and 2,3,3,4,4,4-hexafluoro-1-butene (HFO-1336yf).

[0010] The present invention also provides a composition comprising 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf, $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$) and 1,3,3,4,4,4-hexafluoro-1-butene (HFO-1336ze).

BRIEF DESCRIPTION OF THE FIGURE

[0011] Figure 1 provides a flow diagram for a process useful to prepare 3,3,4,4,4-pentafluoro-1-butene according to an embodiment of this invention.

DETAILED DESCRIPTION

[0012] The present invention relates broadly to compositions comprising 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf, $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$), processes of preparing such compositions and their use.

GENERAL TERMS

[0013] Compounds may be referred to herein by the compound name (e.g., 3,3,4,4,4-pentafluoro-1-butene) or ASHRAE designation (e.g., 1345zf) or chemical formula (e.g., $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$) and optionally prefaced by “CFC”, “HCFC”, “HFC”, “CFO”, “HCFO”, or “HFO”, meaning “chlorofluorocarbon”, “hydrochlorofluorocarbon”, “hydrofluorocarbon”, “chlorofluoroolefin”, “hydrochlorofluoroolefins”, or “hydrofluoroolefin”. The absence of the preface does not change the meaning of the compound.

[0014] The term “isomers” is used to represent one or more compounds having the recited chemical formula that are identified using standard analytical techniques (GC and GC-mass spectrometry). The isomers may include one or more compounds having the recited chemical formula, such as linear, branched and cyclic compounds). Alternatively, isomers may include unsaturated compounds (having a double bond) or cyclic compounds having the same chemical formula or multiple unsaturations (two or more double bonds) or combinations with cyclic structures.

[0015] In addition, with respect to compounds having unsaturation (double bond), the compound may have “E-” and “Z-” isomers. If neither “E-” nor “Z-” are identified, the compound disclosed may contain one or both isomers. Specific isomers are identified as “E-” or “Z-”. For example, HFO-1336mzz may include one or both of E-

HFO-1336mzz and Z-HFO-1336mzz, whereas specific isomers are identified as “E-HFO-1336mzz” and “Z-HFO-1336mzz.”

[0016] 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 composition, 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 composition, 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 are true (or present).

[0017] 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.

[0018] 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”.

[0019] 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.”

[0020] 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.

[0021] 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.

[0022] 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.

[0023] As used herein, the term “fluorination catalyst”, refers to a substance that speeds up the chemical reaction, but is not consumed by the reaction; thus it can be recovered chemically unchanged at the end of the reaction.

[0024] 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.

[0025] 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.

PROCESS DESCRIPTION

[0026] The present invention describes processes for preparing a mixture or a composition comprising, consisting of, or consisting essentially of 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf, $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$) and one or more additional compounds.

[0027] In one embodiment, the present invention provides a process for preparing HFO-1345zf comprising HCFC-353maf with HF in the presence of a fluorination catalyst in a reactor.

[0028] The present invention provides a process for preparing HFO-1345zf comprising contacting HCFC-353maf with HF in a reactor in the presence of a fluorination catalyst, to obtain a process mixture comprising HFO-1345zf, wherein the process is performed at a temperature of about 250-450°C, a pressure of about 0 to 200 psig. Preferably, the temperature is in the range of about 300 to about 380°C, such as about 320°C. Preferably the pressure is in the range of from about 30 to 180 psig or about 40 to 150 psig, or about 60-120 psig, such as about 80 psig.

[0029] The process of the present invention is preferably performed in the presence of an oxygen-containing gas, which may be co-fed with the starting material 353maf and/or HF. The oxygen-containing gas may be, for example, air.

[0030] In the present invention, it has been found particularly advantageous to perform the process of contacting HCFC-353maf with HF in the presence of a fluorination catalyst at a temperature of about 250-450°C. At lower temperatures, 300°C the oxygen is less effective at removing carbon deposits from the catalyst resulting in faster deactivation. Higher temperatures increase the rate of fluorination of the catalyst also deactivating the catalyst.

[0031] In one embodiment, a composition comprising HFO-1345zf is produced in one step by fluorination of HCFC-353maf. More particularly, the process comprises fluorination of HCFC-353maf by reacting with HF, in the presence of a fluorination catalyst, preferably a fluorinated catalyst, to produce a process mixture comprising HFO-1345zf. The process mixture comprises, consists of, or consists essentially of HFO-1345zf, which is or can be used to produce other compounds, including, but not limited to, 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd,

CF₃CF₂CHClCH₂CCl₂CF₃) and subsequently *E*-1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene (*E*-HFO-153-10mczz, *E*-CF₃CF₂CH=CHCF₂CF₃).

FLUORINATION CATALYST

[0032] The fluorination catalyst used in the process of this invention comprises one or more metals, metal oxides, metal oxyfluorides or metal fluorides. A metal oxide catalyst preferably forms a metal (oxy)fluoride having Lewis acid character. Examples of metals suitable for use in the fluorination catalyst is chosen from one or more of metals selected from Al, Sc, Y, Ti, Zr, Hf, V Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, La and Ce.

[0033] In certain embodiments, the fluorination catalyst comprises one or more of Al, Zr, Cr, Co, Ni and Zn.

[0034] In one embodiment, the fluorination catalyst comprises chromium or aluminum. In one embodiment the fluorination catalyst comprises chromium or aluminum and one or more of Zn, Zr, Co, and Ni.

[0035] Certain metal oxide or metal fluoride fluorination catalysts may contain one or more additional metals selected from the group consisting of Li, Na, K, Ca, Mg, and Cs. The additional metal may be present in smaller amounts (such in an amount of less than 2000 or less than 1000 or less than 500 or less than 100 or less than 10 ppm).

[0036] In certain embodiments, the fluorination catalyst comprises aluminum. The aluminum may be present in the form of aluminum oxide, aluminum fluoride or aluminum oxyfluoride. In certain embodiments the fluorination catalyst comprises Al and further comprises one or more of Sc, Y, Ti, Zr, Hf, V Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, La and Ce. In certain embodiments the fluorination catalyst comprises Al and one or more of Zn, Zr, Cr, Co, and Ni.

[0037] In certain embodiments, the fluorination catalyst comprises chromium. The chromium may be present in the form of chromium oxide, chromium chloride, chromium fluoride or chromium oxyfluoride. Chromium may be in the form of Cr(III), such as Cr₂O₃. In certain embodiments the fluorination catalyst comprises Cr and further comprises one or more of Al, Sc, Y, Ti, Zr, Hf, V Nb, Ta, Mo, W, Mn, Re, Fe,

Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, La and Ce. In certain embodiments the fluorination catalyst comprises Cr and one or more of Zn, Zr, Co, and Ni.

[0038] In one embodiment, the fluorination catalyst comprises Cr_2O_3 . In one embodiment, the fluorination catalyst comprises Cr_2O_3 and one or more of Zn, Zr, Co, K, Na and Ni. In one embodiment, the fluorination catalyst comprises Cr_2O_3 and Zn. In one embodiment, the fluorination catalyst comprises Cr_2O_3 and Co. In one embodiment, the fluorination catalyst comprises Cr_2O_3 and Ni. In one embodiment, the fluorination catalyst comprises Cr_2O_3 and Zr.

[0039] In one embodiment, the fluorination catalyst comprises Cr_2O_3 and at least one of Zn, Zr, Co, and Ni, wherein the amount of Zn, Zr, Co, and/or Ni ranges from about 100 ppm to about 10% by weight, based on weight of Cr_2O_3 . In one embodiment the fluorination catalyst comprises Cr_2O_3 and Zn wherein the amount of Zn is in the range of from about 100 ppm to about 10% by weight, based on weight of Cr_2O_3 . In one embodiment the fluorination catalyst comprises Cr_2O_3 and Zr wherein the amount of Zr is in the range of from about 100 ppm to about 10% by weight, based on weight of Cr_2O_3 . In one embodiment the fluorination catalyst comprises Cr_2O_3 and Co wherein the amount of Co is in the range of from about 100 ppm to about 10% by weight, based on weight of Cr_2O_3 . In one embodiment the fluorination catalyst comprises Cr_2O_3 and Ni, wherein the amount of Ni is in the range of from about 100 ppm to about 10% by weight, based on weight of Cr_2O_3 .

[0040] In one embodiment, the fluorination catalyst comprises Al_2O_3 . In one embodiment, the fluorination catalyst comprises Al_2O_3 and one or more of Zn, Zr, Cr, Co, and Ni. In one embodiment, the fluorination catalyst comprises Al_2O_3 and Zn. In one embodiment, the fluorination catalyst comprises Al_2O_3 and Zr. In one embodiment, the fluorination catalyst comprises Al_2O_3 and Cr. In one embodiment, the fluorination catalyst comprises Al_2O_3 and Co. In one embodiment, the fluorination catalyst comprises Al_2O_3 and Ni.

[0041] In one embodiment, the fluorination catalyst comprises Al_2O_3 and at least one of Zn, Zr, Cr, Co, and Ni, wherein the amount of Zn, Zr, Cr, Co, and/or Ni ranges from about 100 ppm to about 10% by weight, based on weight of Al_2O_3 . In one embodiment the fluorination catalyst comprises Al_2O_3 and Zn wherein the amount of Zn is in the range of from about 100 ppm to about 10% by weight, based on weight

of Al_2O_3 . In one embodiment the fluorination catalyst comprises Al_2O_3 and Zr wherein the amount of Zr is in the range of from about 100 ppm to about 10% by weight, based on weight of Al_2O_3 . In one embodiment the fluorination catalyst comprises Al_2O_3 and Cr wherein the amount of Cr is in the range of from about 100 ppm to about 10% by weight, based on weight of Al_2O_3 . In one embodiment the fluorination catalyst comprises Al_2O_3 and Co wherein the amount of Co is in the range of from about 100 ppm to about 10% by weight, based on weight of Al_2O_3 . In one embodiment the fluorination catalyst comprises Al_2O_3 and Ni, wherein the amount of Ni is in the range of from about 100 ppm to about 10% by weight, based on weight of Al_2O_3 .

[0042] The fluorination catalyst may be on a support ("supported") or unsupported or a mixture of a support with the fluorination catalyst. If a support is present, suitable supports include AlF_3 , alumina, fluorinated alumina or activated carbon. In one embodiment, the fluorination catalyst comprises chromium oxide and alumina.

[0043] The fluorination catalyst may comprise a metal oxide or metal oxyhalides supported on chromia or alumina, for example oxides of zinc, iron, magnesium or nickel. The fluorination catalyst may comprise a metal oxides/halides/oxyhalides, or mixed metal oxides/halides/oxyhalides supported on carbon, wherein the metal is chosen from one or more of Al, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, La and Ce.

[0044] In one embodiment, the fluorination catalyst is a chromium-based catalyst, such as chromium oxide (Cr_2O_3) or fluorinated chromium oxide, or chromium chloride, or chromium fluoride, which catalyst may either be unsupported, or supported on a support such as activated carbon, graphite, fluoride graphite, or alumina fluoride. The chromium fluorination catalyst may either be used alone, or in the presence of a co-catalyst selected from nickel, cobalt, manganese, potassium, sodium or zinc. In one embodiment, optionally a chromium fluorination catalyst is high surface area chromium oxide, or chromium/nickel on alumina fluoride (Cr/Ni/AlF_3), or chromium halide on carbon, the preparation of which is reported in European Patent EP486333. In another embodiment, the fluorination catalyst is fluorinated Guignet's green catalyst.

[0045] In one embodiment, the fluorination catalyst comprises Al_2O_3 . In one embodiment, the fluorination catalyst comprises Al_2O_3 and one or more of Zn, Zr, Cr, Co, and Ni. In one embodiment, the fluorination catalyst comprises Al_2O_3 and Zn, or Al_2O_3 and Cr, or Al_2O_3 and Co, or Al_2O_3 and Ni, or Al_2O_3 and Zr.

[0046] In one embodiment, the fluorination catalyst comprises chromium supported on AlF_3 , alumina, fluorinated alumina or activated carbon. In one embodiment, the fluorination catalyst comprises chromium supported on alumina.

[0047] In one embodiment, the fluorination catalyst comprises zinc supported on AlF_3 , alumina, fluorinated alumina or activated carbon. In one embodiment, the fluorination catalyst comprises zinc supported on alumina.

[0048] The physical shape of the fluorination catalyst is not critical and may, for example, include pellets, extrudates, powders, or granules.

[0049] In one embodiment, the fluorination catalyst is shaped into a form, such as Al, Zr, Cr, Co as granulated, or pressed into pellets. A variety of methods generally known in the art, may be used that are suitable to provide, for example, a packed bed of catalyst in a flow reactor.

[0050] In one embodiment, the process comprises activating the fluorination catalyst in a prefluorination treatment prior to contacting HCFC-353maf with HF in the presence of the catalyst. Activation of the fluorination catalyst is preferably carried out on the final shape of the catalyst, in the event the catalyst is shaped into a form. It should be understood that while the term "fluorination catalyst" is used to refer to metal oxides, including Cr_2O_3 and Al_2O_3 , metal halide, including CrCl_3 , CrF_3 herein, the metal oxide may undergo a prefluorination step to generate the active catalyst in situ.

[0051] In one embodiment, the catalyst undergoes a prefluorination treatment by passing HF, with or without an inert diluent such as nitrogen, over the catalyst at a temperature within the range of about 250 to 450°C prior to use.

[0052] In a particular embodiment, the fluorination catalyst comprises chromium and the fluorination catalyst is activated before use, by a procedure comprising heating the fluorination catalyst to a temperature of from 350°C to 400°C under a flow of nitrogen for a period of time, then heating the fluorination catalyst under a

flow of HF and nitrogen or air for an additional period of time in one embodiment of a prefluorination treatment.

[0053] After use for a period of time, the activity of the fluorination catalyst may decrease. When this occurs, the fluorination catalyst may be regenerated, wherein a regenerating step comprises treating the catalyst with oxygen or air at elevated temperature. The regenerating step is performed purging the majority of the organic components from the process mixture.

REACTION CONDITIONS

[0054] In one embodiment, suitable temperatures for the process of the reaction of HCFC-353maf with HF are from about 250°C to about 450°C, preferably from about 300°C to about 380°C. Temperature ranges are set to advantageously protect the catalyst from deactivation. It has been found that operating at temperatures outside of the recited ranges results in faster deactivation of the catalyst. For example, it is believed at lower temperatures, carbon-containing compounds deposits remain on the surface of the catalyst. In addition, at higher temperatures, the catalyst is more susceptible to becoming fluorinated in a way that also results in catalyst deactivation. Thus, a balance must be found to address fluorination catalyst deactivation from both carbon containing compounds deposits as well as fluorination of the fluorination catalyst.

[0055] In one embodiment, suitable pressures for the process of the reaction of HCFC-353maf with HF are from about 0 to 200 psig, preferably from about 30 to 180 psig or about 40 to 150 psig, or about 60-120 psig. Pressure ranges are set to achieve desired conversion and product selectivity as well as to enhance separation and recovery of HCl component of the process mixture. At lower pressures, the recovery of HCl is more complex or more expensive. In addition, at pressures, the catalyst is found the rate of catalyst deactivation increases. Furthermore, pressure also impacts reaction rate, product selectivity and productivity.

[0056] In the process of this invention, it is preferred to have a molar ratio of HF to HCFC-353maf from about 3:1 to about 50:1, preferably from about 10:1 to about 45:1, more preferred, 15:1 to 40:1. Higher ratios are undesired for overall efficiency

of the process, and also impact temperature, pressure and contact time. Lower ratios impact productivity (conversion, selectivity and yield).

[0057] In the process of this invention, comprising contacting HCFC-353maf ($\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$) with hydrogen fluoride (HF) in a reactor, in the presence of a fluorination catalyst, a process mixture comprising HFO-1345zf and HCl is produced. In the process, an amount of oxygen is optionally added. The oxygen amount added ranges from about 0 to about 10 mole % based on the amount of organic feed to the contacting step. The organic feed comprises 353maf. Optionally, the organic feed further comprises intermediates recycled from separation processes.

[0058] Preferably the amount of oxygen added in the process of this invention is greater than 0% and less than 10 mole %, such as from about 0.2 mole % to about 5 mole %, or about 1 mole %. An amount of oxygen added in the process such as in the range of about 0.2 mole % to about 5 mole %, improves life of the fluorination catalyst. In the absence of added oxygen the rate of catalyst deactivation increases. It is also important to avoid adding too much oxygen in the process. A higher concentration of oxygen, particularly greater than 15 mole % oxygen results in lower yield as there is an increase in the formation of oxygenated byproducts. In addition, a higher concentration of oxygen presents a flammability risk.

[0059] In the process of this invention, comprising contacting HCFC-353maf ($\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$) with hydrogen fluoride (HF), in the presence of a fluorination catalyst, to produce a process mixture comprising HFO-1345zf and HCl, the contact time can be chosen from a range of contact times, such as from as low as about 1 second to 180 seconds. In one embodiment, contact time is from 5 seconds to 120 seconds or from 5 to 60 seconds, or from 10 to 25 seconds, such as about 15 seconds. It should be appreciated that shorter contact times reduces conversion of the starting material HCFC-353maf. However longer contact times may be undesirable as they may increase formation of byproducts (lower yield, selectivity) for a given set of reaction conditions.

[0060] Preferably, the fluorination reaction is carried out in the vapor phase. However, it will be understood by those skilled in the art that the fluorination of HCFC-353maf may, alternatively, be performed in the liquid phase.

[0061] In one embodiment, the HCFC-353maf starting material may be pre-mixed with the HF, and then introduced into the reactor to form a process mixture comprising HFO-1345zf and HCl. In another embodiment, the HF may not be contacted with the HCFC-353maf until both have been introduced into the reactor. In another embodiment, HCFC-353maf may be mixed with recycled organic stream before introduced into the reactor.

[0062] In some embodiments, the reaction of HCFC-353maf produces an effluent stream comprising process mixture or composition comprising HFO-1345zf and HCl.

[0063] In some embodiments, this step may be conducted in a reactor or reaction zone which is operating in batch, semi-batch, semi-continuous, or continuous modes, to produce a reaction mixture comprising 1345zf. An effluent stream of the reactor or reaction zone comprises the reaction mixture comprising HFO-1345zf and HCl.

[0064] For the reaction of HCFC-353maf with HF, the process mixture comprises HFO-1345zf and HCl, and may further contain excess HF, as well as optionally, reaction byproducts and intermediates. The reaction byproducts and intermediates may include one or more of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd), dichlorotrifluorobutene isomers (HCFO-1343 isomers), chlorotetrafluorobutene isomers (HCFO-1344 isomers), chloropentafluorobutene isomers (HCFO-1335 isomers), chloropentafluorobutane isomers (HCFC-355 isomers), 1,1,1,4,4,4-hexafluorobutane (HFC-356mff), chlorotrifluorobutene isomers (HCFO-1353 isomers), pentafluorobutene isomers (HFO-1345 isomers), 1,1,1-trifluoroethane (HFC-143a), trifluoromethane (HFC-23), chlorotrifluoromethane (CFC-13), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,3,3,3-tetrafluoropropene (HFO-1234ze), 2-chloro-1,1,1,3,3,3-hexafluoro-2-butene (HCFO-1326mxz), heptafluorobutene isomers (HFO-1327 isomers), hexafluorobutene isomers (HFO-1336 isomers), 2,2,3,3,3-pentafluoropropanal and HCFC-353maf.

[0065] The process mixture may comprise additional components such as unreacted starting material, HCFC-353maf ($\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$), reaction intermediates and reaction byproducts. In one embodiment, the reaction intermediates comprise HCFO-1343 isomers, HFO-1344 isomers, or mixtures of two or more thereof.

[0066] In one embodiment, the reaction intermediates comprise HCFO-1343 isomers.

[0067] In one embodiment, the reaction intermediates comprise HCFO-1344 isomers.

[0068] In one embodiment, the reaction intermediates comprise a mixture of HCFO-1343 isomers and HCFO-1344 isomers.

[0069] In any embodiment in which the reaction intermediates comprise HCFO-1343 isomers, the HCFO-1343 isomers comprise one or more of *E*-2,4-dichloro-1,1,1-trifluoro-2-butene (*E*-HCFO-1343mxz), 3,3-dichloro-4,4,4-trifluoro-1-butene (HCFO-1343maz), and *Z*-2,4-dichloro-1,1,1-trifluoro-2-butene (*Z*-HCFO-1343mxz).

[0070] In any embodiment in which the reaction intermediates comprise HCFO-1344 isomers, the HCFO-1344 isomers comprise one or more of *Z*-4-chloro-1,1,1,2-tetrafluoro-2-butene (*Z*-HCFO-1344myz), *E*-4-chloro-1,1,1,2-tetrafluoro-2-butene (*E*-HCFO-1344myz), *Z*-2-chloro-1,1,1,4-tetrafluoro-2-butene (*Z*-HCFO-1344mxz), *E*-2-chloro-1,1,1,4-tetrafluoro-2-butene (*E*-HCFO-1344mxz), 3-chloro-3,4,4,4-tetrafluoro-1-butene (HCFO-1344fzb), *E*-2-chloro-1,1,1,3-tetrafluoro-2-butene (*E*-HCFO-1344mxy), and *Z*-2-chloro-1,1,1,3-tetrafluoro-2-butene (*Z*-HCFO-1344mxy).

[0071] In one embodiment, the reaction byproducts and intermediates comprise HCFO-1335 isomers. In certain embodiments in which the reaction byproducts and intermediates comprise HCFO-1335 isomers, the HCFO-1335 isomers comprise one or more of *E*-1-chloro-3,3,4,4,4-pentafluoro-1-butene (*E*-HCFO-1335dz), *E*-1-chloro-1,1,4,4,4-pentafluoro-2-butene (*E*-HCFO-1335lzz), *Z*-1-chloro-1,1,4,4,4-pentafluoro-2-butene, (*Z*-HCFO-1335lzz), and *E*-2-chloro-1,1,1,4,4-pentafluoro-2-butene (*E*-HCFO-1335mxz).

[0072] In one embodiment, the reaction byproducts and intermediates comprise HCFC-335 isomers. In certain embodiments in which the reaction byproducts and intermediates comprise HCFC-355 isomers, the HCFC-355 isomers comprise 4-chloro-1,1,1,2,2-pentafluorobutane (HCFC-355of).

[0073] In one embodiment, the reaction byproducts and intermediates comprise HCFO-1353 isomers. In certain embodiments in which the reaction byproducts and

intermediates comprise HCFO-1353 isomers, the HCFO-1353 isomers comprise 3-chloro-4,4,4-trifluoro-2-butene (HCFO-1353mxz).

[0074] In one embodiment, the reaction byproducts and intermediates comprise HCFO-1345 isomers). In certain embodiments, in which the reaction byproducts and intermediates comprise HCFO-1345 isomers, the HCFO-1345 isomers comprise 1,1,4,4,4-pentafluoro-2-butene (HFO-1345mzz).

[0075] In one embodiment, the reaction byproducts and intermediates comprise HFO-1336 isomers. In certain embodiments in which the reaction byproducts and intermediates comprise HFO-1336 isomers, the HFO-1336 isomers comprise one or more of *E*-1,1,1,4,4,4-hexafluoro-2-butene (*E*-HFO-1336mzz), *Z*-1,1,1,4,4,4-hexafluoro-2-butene (*Z*-HFO-1336mzz), 2,3,3,4,4,4-hexafluoro-1-butene (HFO-1336yf), and 1,3,3,4,4,4-hexafluoro-1-butene (HFO-1336ze).

[0076] Any reaction byproducts, additional components of the process mixture other than HFO-1336ze and HFO-1336yf, may be, optionally removed from recycled stream back to the reaction vessel. Advantageously, when the process mixture comprises any of HF, HCFC-353maf, and intermediates (HCFO-1343 and/or HCFO-1344), the process comprises separating the HF, HCFC-353maf, and intermediates from the process mixture and recycling each of these to the process for contacting with the fluorination catalyst.

[0077] In one embodiment, the process of this invention involves reacting 353maf with an excess of HF (HF to 353maf of about 3:1 to about 50:1, preferably from about 10:1 to about 45:1, more preferred, 15:1 to 40:1). In one embodiment, the catalyst comprises chrome oxide (Cr₂O₃) and the catalyst is dried and partially fluorinated with HF before use. The operating temperature is about 300°C to about 380°C and the operating pressure is about 0 to about 200 psig. The process further comprising adding about 0.2 mole % to about 5 mole % or 0.5 to 2 mole % oxygen in the feed (based on the feed of 353maf) to maintain / increase catalyst life. In one embodiment, in a continuous process, the reactor is shut down periodically to regenerate the catalyst. Shut down may occur once every year, 6 months, 30 days or once every 20 days or once every 15 days, such as once every 18 days. The reactor has a heat transfer system to achieve and maintain a target operating temperature.

[0078] Specific conditions of temperature, pressure, HF:organic ratio, oxygen concentration and contact time are provided, wherein the organic is 353maf. It has been found that the recited conditions provide limit disadvantages of operating outside of the recited conditions. Disadvantages include one or more of catalyst deactivation, increased difficulties to recover product, increased byproducts (loss of yield, loss of selectivity), lower conversion, need for larger reactor.

[0079] After exiting the reactor, the process mixture comprising HFO-1345zf and HCl undergoes distillation to remove HCl. The process mixture further comprises unreacted HF as the process uses an excess of HF. The unreacted HF in the process mixture is preferably then recovered and recycled back to the reactor. The process mixture may further comprise intermediates. The intermediates may comprise HCFO-1343 isomers, HCFO-1344 isomers, or mixtures thereof. In one embodiment, the intermediates comprise HCFO-1343 isomers. In one embodiment, the intermediates comprise HCFO-1344 isomers. In one embodiment, the intermediates comprise a mixture of HCFO-1343 isomers and HCFO-1344 isomers. The intermediates and unreacted HCFC-353maf may be recovered and recycled back to reactor.

[0080] In one embodiment, HF may be recovered. The recovery of HF may comprise a combination of distillation and/or liquid-liquid phase separation. When the process mixture comprises residual acids, residual acids may be removed from the process mixture by distillation, absorbing by Al_2O_3 or absorbing into an aqueous medium, which optionally contains base, and neutralizing with base (such as alkali metal hydroxide, including, but not limited to KOH), providing a neutralized stream. Following removal of acids from the process mixture, the neutralized stream may be dried, if needed, for example, using molecular sieves. The dried HFO-1345zf may undergo a final distillation to provide a purified product comprising HFO-1345zf, available for use.

[0081] Equipment used in the process of this invention includes feed systems, storage tanks, reactor, distillation columns and the like. Carbon steel may be acceptable for ambient temperature feed systems and storage tanks. The reactor and high temperature portions of the equipment, including the HCl column are

preferably constructed of an alloy such as Inconel or Hastelloy. Certain equipment may be lined with PTFE.

[0082] In one embodiment of the process of this invention, there is provided a reaction system comprising a reactor and a purification system. The reaction system includes feeds to introduce reactants to the reactor. The feeds include a fresh reactant 353maf feed, recycled intermediates, recycled 353maf, a fresh reactant HF feed, and a recycled HF feed. The fresh reactant HF feed and recycled HF feed may be combined in a single feed for HF to be introduced to the reactor. There is also a fluorination catalyst feed to introduce the fluorination catalyst to the reactor, such as from a catalyst bed.

[0083] A reactor process stream, the process mixture, exits the reactor. The process mixture may proceed through a mechanism to separate catalyst from the reaction product in a reaction process mixture. The reaction process mixture proceeds through heat exchangers prior to entering the purification system.

[0084] In one embodiment, the present invention provides a composition comprising HFO-1345zf, and one or more additional compounds chosen from HCFO-1233xf, HCFO-1233zd, HCFO-1343 isomers, HCFO-1344 isomers, HCFO-1335 isomers, HCFO-1353 isomers, HFO-1345 isomers, HFO-1336 isomers, HCFC-355 isomers, HFC-356mff, HFC-143a, HFC-23, CFC-13, HFO-1234yf, HFO-1234ze, HCFO-1326mxz, HFO-1327 isomers, 2,2,3,3,3-pentafluoropropanal and HFC-353maf. In certain embodiments, the HCFO-1343 isomers includes one or more of *E*-HCFO-1343mxz, HCFO-1343maz, and *Z*-HCFO-1343mxz. In certain embodiments, the HCFO-1344 isomers includes one or more of *Z*-HCFO-1344myz, *E*-HCFO-1344myz, *Z*-HCFO-1344mxz, *E*-HCFO-1344mxz, HCFO-1344fzb, *E*-HCFO-1344mxy, and *Z*-HCFO-1344mxy. In certain embodiments, the HCFO-1335 isomers includes one or more of *E*-HCFO-1335dz, *E*-HCFO-1335lzz, *Z*-HCFO-1335lzz), and *E*-HCFO-1335mxz. In certain embodiments, the HCFC-355 isomers comprises HCFC-355of. In certain embodiments, the HCFO-1353 isomers comprises HCFO-1353mxz. In certain embodiments, the HFO-1345 isomers comprises HFO-1345mzz. In certain embodiments the HFO-1336 isomers includes one or more of *E*-HFO-1336mzz, *Z*-HFO-1336mzz, HFO-1336yf, and HFO-1336ze.

[0085] The purification system comprises distillation columns, absorbers, scrubbers and dryers.

[0086] The products from the reaction of the process of this invention may be purified in a series of additional steps.

[0087] In one embodiment of the process of this invention, the process mixture is cooled, such as through heat exchangers and is then treated in distillation columns to remove HCl (a product of the reaction) to provide a process stream with reduced HCl. The process stream with reduced HCl further comprises unreacted HF as the process uses an excess of HF.

[0088] Following removal of HCl, HF may be removed in a distillation column or a phase separation. Since HF is a reactant in the process, the removed HF is recycled to the contacting step of the process as recycled HF feed. HF removal for recycling may comprise a combination of distillation and liquid-liquid phase separation.

[0089] In addition to HCl and HF, the process mixture may comprise residual acids. Residual acids may be removed from the process mixture after removing HCl and HF, by absorbing with Al_2O_3 , or absorbing into an aqueous medium in an absorber, which optionally contains base (such as alkali metal hydroxide, including, but not limited to KOH). Following removal of residual acids, a scrubbed process mixture is provided.

[0090] The scrubbed process mixture may comprise intermediates, wherein the intermediates may comprise HCFO-1343 isomers, HCFO-1344 isomers, or mixtures thereof. The intermediates comprising HCFO-1343 isomers, HCFO-1344 isomers or mixtures thereof can be also removed, such as by distillation and recycled back to the reactor.

[0091] Following removal of residual acids and intermediates, a scrubbed and distilled process mixture is provided. The scrubbed and distilled process mixture is then dried by passing through a drying agent. The drying agent may be, for example, molecular sieves, providing a dried process mixture. The dried process mixture is distilled using one or more distillation columns to provide a purified product comprising 1345zf. The purified product may comprise greater than 95% or greater

than 98% or greater than 99% or greater than 99.5% 1345zf. The purified product is available for storage or use.

[0092] The purified product is useful in manufacture of other fluorochemicals, including, for example, 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd) and *E*-1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene (HFO-153-10mczz).

Compositions

[0093] The present invention further provides compositions comprising HFO-1345zf, and one or more additional compounds chosen from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd), dichlorotrifluorobutene isomers (HCFO-1343 isomers), chlorotetrafluorobutene isomers (HCFO-1344 isomers), chloropentafluorobutene isomers (HCFO-1335 isomers), hexafluorobutene isomers (HFO-1336 isomers), pentafluorobutene isomers (HFO-1345 isomers), chloropentafluorobutane isomers (HCFC-355 isomers), chlorotrifluorobutene isomers (HCFO-1353 isomers), 1,1,1,4,4,4-hexafluorobutane (HFC-356mff), 1,1,1-trifluoroethane (HFC-143a), trifluoromethane (HFC-23), chlorotrifluoromethane (CFC-13), heptafluorobutane isomers (HFC-347 isomers), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,3,3,3-tetrafluoropropene (HFO-1234ze), 2-chloro-1,1,1,3,3,3-hexafluoro-2-butene (HCFO-1326mxz), heptafluorobutene isomers (HFO-1327 isomers), 2,2,3,3,3-pentafluoropropanal and 2,2,4-trichloro-1,1,1-trifluorobutane (353maf).

[0094] In certain embodiments, the HCFO-1343 isomers is one or more of *E*-2,4-dichloro-1,1,1-trifluoro-2-butene (*E*-HCFO-1343mxz), 3,3-dichloro-4,4,4-trifluoro-1-butene (HCFO-1343maz), and *Z*-2,4-dichloro-1,1,1-trifluoro-2-butene (*Z*-HCFO-1343mxz).

[0095] In certain embodiments, the HCFO-1344 isomers is one or more of *Z*-4-chloro-1,1,1,2-tetrafluoro-2-butene (*Z*-HCFO-1344myz), *E*-4-chloro-1,1,1,2-tetrafluoro-2-butene (*E*-HCFO-1344myz), *Z*-2-chloro-1,1,1,4-tetrafluoro-2-butene (*Z*-HCFO-1344mxz), *E*-2-chloro-1,1,1,4-tetrafluoro-2-butene (*E*-HCFO-1344mxz), 3-chloro-3,4,4,4-tetrafluoro-1-butene (HCFO-1344fzb), *E*-2-chloro-1,1,1,3-tetrafluoro-2-butene (*E*-HCFO-1344mxy), and *Z*-2-chloro-1,1,1,3-tetrafluoro-2-butene (*Z*-HCFO-1344mxy).

[0096] In certain embodiments, the HCFO-1335 isomers is one or more of *E*-1-chloro-3,3,4,4,4-pentafluoro-1-butene (*E*-HCFO-1335dz), *E*-1-chloro-1,1,4,4,4-pentafluoro-2-butene (*E*-HCFO-1335lzz), *Z*-1-chloro-1,1,4,4,4-pentafluoro-2-butene, (*Z*-HCFO-1335lzz), and *E*-2-chloro-1,1,1,4,4-pentafluoro-2-butene (*E*-HCFO-1335mxz).

[0097] In certain embodiments, the HFO-1336 isomers is one or more of *E*-1,1,1,4,4,4-hexafluoro-2-butene (*E*-HFO-1336mzz), *Z*-1,1,1,4,4,4-hexafluoro-2-butene (*Z*-HFO-1336mzz), 2,3,3,4,4,4-hexafluoro-1-butene (HFO-1336yf), and 1,3,3,4,4,4-hexafluoro-1-butene (HFO-1336ze).

[0098] In certain embodiments, the HFO-1345 isomers comprises 1,1,4,4,4-pentafluoro-2-butene.

[0099] In certain embodiments, the HCFC-355 isomers comprises 4-chloro-1,1,1,2,2-pentafluorobutane (HCFC-355of).

[0100] In certain embodiments, the HCFO-1353 isomers comprises 3-chloro-4,4,4-trifluoro-2-butene (HCFO-1353mxz),

[0101] The structures of such compounds are provided in Table 1.

TABLE 1

Name	Formula	Compound
2,2,4-trichloro-1,1,1-trifluorobutane	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$	HCFC-353maf
3,3,4,4,4-pentafluoro-1-butene	$\text{CH}_2=\text{CHCF}_2\text{CF}_3$	HFO-1345zf
chlorotrifluoromethane	CClF_3	CFC-13
trifluoromethane	CHF_3	HFC-23
chloropentafluoroethane	CF_3CClF_2	CFC-115
1,1,1-trifluoroethane	CF_3CH_3	HFC-143a
chlorotetrafluoropropane isomers	$\text{C}_3\text{H}_3\text{F}_4\text{Cl}$	HCFC-244 isomers
1,1,1,2,2-pentafluoropropane	$\text{CF}_3\text{CF}_2\text{CH}_3$	HFC-245cb
dichloropentafluorobutane isomers	$\text{C}_4\text{H}_3\text{Cl}_2\text{F}_5$	HCFC-345 isomers
heptafluorobutane isomers	$\text{C}_4\text{H}_3\text{F}_7$	HFC-347 isomers
chloropentafluorobutane isomers	$\text{C}_4\text{H}_4\text{ClF}_5$	HCFC-355 isomers

Name	Formula	Compound
4-chloro-1,1,1,2,2-pentafluorobutane	$\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{Cl}$	HCFC-355of
1,1,1,4,4,4-hexafluorobutane	$\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$	HFC-356mff
2-chloro-3,3,3-trifluoropropene	$\text{CF}_3\text{CCl}=\text{CH}_2$	HCFO-1233xf
1-chloro-3,3,3-trifluoropropene	$\text{CF}_3\text{CH}=\text{CHCl}$	HCFO-1233zd
2,3,3,3-tetrafluoropropene	$\text{CF}_3\text{CF}=\text{CH}_2$	HFO-1234yf
1,3,3,3-tetrafluoropropene	$\text{CF}_3\text{CH}=\text{CHF}$	HFO-1234ze
dichloropentafluorobutene isomers	$\text{C}_4\text{HCl}_2\text{F}_5$	HCFO-1325 isomers
1,1,1,4,4,4-hexafluoro-2-chloro-2-butene	$\text{CF}_3\text{CCl}=\text{CHCF}_3$	HCFO-1326mxz
heptafluorobutene isomers	C_4HF_7	HFO-1327 isomers
chloropentafluorobutene isomers	$\text{C}_4\text{H}_2\text{ClF}_5$	HCFO-1335 isomers
1-chloro-3,3,4,4,4-pentafluoro-1-butene	$\text{CF}_3\text{CF}_2\text{CH}=\text{CHCl}$	HCFO-1335dz
<i>E</i> -1-chloro-1,1,4,4,4-pentafluoro-2-butene	$\text{CF}_2\text{ClCH}=\text{CHCF}_3$	<i>E</i> -HCFO-1335lzz
<i>Z</i> -1-chloro-1,1,4,4,4-pentafluoro-2-butene	$\text{CF}_2\text{ClCH}=\text{CHCF}_3$	<i>Z</i> -HCFO-1335lzz
1,1,1,4,4-pentafluoro-2-chloro-2-butene	$\text{CF}_3\text{CCl}=\text{CHCF}_2\text{H}$	HCFO-1335mxz
<i>E</i> -2-chloro-1,1,1,4,4-pentafluoro-2-butene	<i>E</i> - $\text{CF}_3\text{CCl}=\text{CHCF}_2\text{H}$	<i>E</i> -HCFO-1335mxz
hexafluorobutene isomers	$\text{C}_4\text{H}_2\text{F}_6$	HFO-1336 isomers
<i>E</i> -1,1,1,4,4,4-hexafluoro-2-butene	$\text{CF}_3\text{CH}=\text{CHCF}_3$	<i>E</i> -HFO-1336mzz
<i>Z</i> -1,1,1,4,4,4-hexafluoro-2-butene	$\text{CF}_3\text{CH}=\text{CHCF}_3$	<i>Z</i> -HFO-1336mzz
2,3,3,4,4,4-hexafluoro-1-butene	$\text{CF}_3\text{CF}_2\text{CF}=\text{CH}_2$	HFO-1336yf
1,3,3,4,4,4-hexafluoro-1-butene	$\text{CF}_3\text{CF}_2\text{CH}=\text{CHF}$	HFO-1336ze
dichlorotrifluorobutene isomers	$\text{C}_4\text{H}_3\text{Cl}_2\text{F}_3$	HCFO-1343 isomers
3,3-dichloro-4,4,4-trifluoro-1-butene	$\text{CF}_3\text{CCl}_2\text{CH}=\text{CH}_2$	HCFO-1343maz
1,3-dichloro-4,4,4-trifluoro-2-butene	$\text{CF}_3\text{CCl}=\text{CHCH}_2\text{Cl}$	HCFO-1343mxz
<i>E</i> -1,3-dichloro-4,4,4-trifluoro-2-butene	$\text{CF}_3\text{CCl}=\text{CHCH}_2\text{Cl}$	<i>E</i> -HCFO-1343mxz
<i>Z</i> -1,3-dichloro-4,4,4-trifluoro-2-butene	$\text{CF}_3\text{CCl}=\text{CHCH}_2\text{Cl}$	<i>Z</i> -HCFO-1343mxz

Name	Formula	Compound
chlorotetrafluorobutene isomers	$C_4H_3ClF_4$	HCFO-1344 isomers
3-chloro-3,4,4,4-tetrafluoro-1-butene	$CF_3CClFCH=CH_2$	HCFO-1344fzb
2-chloro-1,1,1,3-tetrafluoro-2-butene	$CF_3CCl=CFCH_3$	HCFO-1344mxy
2-chloro-1,1,1,4-tetrafluoro-2-butene	$CF_3CCl=CHCH_2F$	HCFO-1344mxz
4-chloro-1,1,1,2-tetrafluoro-2-butene	$CF_3CF=CHCH_2Cl$	HCFO-1344myz
<i>E</i> -2-chloro-1,1,1,3-tetrafluoro-2-butene	<i>E</i> - $CF_3CCl=CFCH_3$	<i>E</i> -HCFO-1344mxy
<i>E</i> -2-chloro-1,1,1,4-tetrafluoro-2-butene	<i>E</i> - $CF_3CCl=CHCH_2F$	<i>E</i> -HCFO-1344mxz
<i>E</i> -4-chloro-1,1,1,2-tetrafluoro-2-butene	<i>E</i> - $CF_3CF=CHCH_2Cl$	<i>E</i> -HCFO-1344myz
<i>Z</i> -2-chloro-1,1,1,3-tetrafluoro-2-butene	<i>Z</i> - $CF_3CCl=CFCH_3$	<i>Z</i> -HCFO-1344mxy
<i>Z</i> -2-chloro-1,1,1,4-tetrafluoro-2-butene	<i>Z</i> - $CF_3CCl=CHCH_2F$	<i>Z</i> -HCFO-1344mxz
<i>Z</i> -4-chloro-1,1,1,2-tetrafluoro-2-butene	<i>Z</i> - $CF_3CF=CHCH_2Cl$	<i>Z</i> -HCFO-1344myz
1,1,4,4,4-pentafluoro-2-butene	$CF_3CH=CHCHF_2$	HFO-1345mzz
<i>E</i> -1,1,4,4,4-pentafluoro-2-butene	<i>E</i> - $CF_3CH=CHCHF_2$	<i>E</i> -HFO-1345mzz
<i>Z</i> -1,1,4,4,4-pentafluoro-2-butene	<i>Z</i> - $CF_3CH=CHCHF_2$	<i>Z</i> -HFO-1345mzz
3-chloro-4,4,4-trifluoro-2-butene	$CF_3CCl=CHCH_3$	HCFO-1353mxz
chlorotrifluorobutene isomers	$C_4H_4ClF_3$	HCFO-1353 isomers
	$C_7H_5F_7$	$C_7H_5F_7$ isomers

[0102] In one embodiment, the composition comprises HFO-1345zf and one or more of chlorotetrafluorobutene isomers, dichlorotrifluorobutene isomers and chloropentafluorobutene isomers. In one embodiment, the composition comprises HFO-1345zf and chlorotetrafluorobutene isomers, trichlorotrifluorobutene isomers and chloropentafluorobutene isomers. In one embodiment, the composition comprises HFO-1345zf and chlorotetrafluorobutene isomers and dichlorotrifluorobutene isomers. In one embodiment, the composition comprises HFO-1345zf and chlorotetrafluorobutene isomers and chloropentafluorobutene isomers.

[0103] The composition comprising 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf) and one or more additional compounds as defined herein may be purified, such as by distillation, absorption and scrubbing to remove undesired compounds. The purified product can be used, such as an intermediate to produce 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd).

DESCRIPTION OF THE FIGURE

[0104] Figure 1 provides a flow diagram for a process useful to prepare 3,3,4,4,4-pentafluoro-1-butene according to an embodiment of this invention. In Figure 1, there is provided a process system 100 which includes reactor system 101 and purification system 102. In reactor system 101, reactant 353maf feed 103, fresh reactant HF feed 104 and recycled HF feed stream 105 are mixed into a single feed stream 106 and fed through a series of heat exchangers (107a, 107b and 107c) and introduced to reactor 109 in feed stream 108. Heat exchanger 107a vaporizes feed stream 106. Heat exchanger 107b is a process-to-process heat exchanger in which stream from heat exchanger 107a is heated using the heat from reactor process stream 110. The heated feed stream from heat exchanger 107b proceeds through preheater heat exchanger 107c to provide reactor feed stream 108.

[0105] Reactor feed stream 108 enters tubular reactor 109, which contains solid fluorination catalyst (not shown). Feed stream 108 reacts in reactor 109 in the presence of solid fluorination catalyst in a vapor phase reaction to produce reactor process stream 110.

[0106] Reactor process stream 110 passes through heat exchanger 107b, thus cooling stream 110 and providing process stream 111. Process stream 111 is further cooled by passing through heat exchanger 112, providing process stream 113, which enters purification system 102.

[0107] Purification system 102 comprises distillation columns, absorbers, scrubbers and dryers.

[0108] Process feed stream 113 is distilled in HCl distillation column 114 to remove HCl generated in reactor 109. HCl is removed overhead in stream 115. Distilled stream 116 then enters HF distillation column 117, in which HF is removed. A recycle stream comprising HF 118 is removed from column 117. A portion of

stream **118** is mixed with reactant HCFC-353maf feed **103** and fresh reactant HF feed **104** as recycled HF feed stream **105**. A purge stream comprising HF **119** is removed from stream **118**.

[0109] After HCl and HF distillation columns, process stream **120** enters absorber **121**. Water is fed to absorber **121** as stream **122**. A solution of HF in water is removed from absorber **121** in stream **123**. Treated stream **124** from absorber **121** is circulated through column **125** in a process step for scrubbing stream **124** with base through scrubber **126**, such as, for example, using an aqueous solution of KOH. Spent KOH solution **127** is removed from scrubber **126** and column **125**. The process stream following scrubbing is removed from column **125** in stream **128**, which is then dried by passing through drying agent column **129**. The drying agent may be, for example, molecular sieves. Dried process stream **130** exits drying agent column **129** for further purification.

[0110] Dried process stream **130** enters low boiler distillation column **131** in which low boilers are removed overhead and pass through a condenser in stream **132**. From low boiler distillation column **131**, the process stream **133** passes to distillation column **134**, from which high boilers are purged in stream **136** and product stream **135** comprising 1345zf is provided. Product stream **135** comprising 1345zf may be stored in tank **137** for future or immediate use in manufacture of other fluorochemicals, including, for example, 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd) and *E*-1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene (HFO-153-10mczz).

[0111] Pumps such as illustrated with feed streams **103**, **104** and **105** are used to introduce and/or circulate materials (reactants, intermediates, products) through reaction system **100**. Heat exchangers such as illustrated at **107a-d** are used to manage temperature through reaction system **100**.

[0112] Additional components not shown in Figure 1 may include purge lines, heat exchangers, pumps, and vacuum equipment for distillation columns.

[0113] 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.

[0114] The following Examples are provided to illustrate certain aspects of the invention and shall not limit the scope of the appended claims.

EXAMPLES

[0115] In the following Examples, the letter "T" designates temperature; the letter "P" designates pressures. All temperatures are provided in degrees Celsius (°C).

[0116] Unless otherwise stated, all analyses for products in the following Examples were performed using GC/MS FID and results are reported in GC FID Area%.

EXAMPLE 1

[0117] Into an Into an Inconel (0.5 inch OD) tube reactor was added 4 cc of chromium oxide catalyst (12/20 mesh). The reaction was run by feeding liquid 353maf into a heated chamber where it vaporized and mixed with HF and N₂. The process mixture was then allowed to pass through the reactor. Part of the reactor effluent was passed through a series of valves and analyzed by GC-FID-MS. Part of the reactor effluent was also be passed through a caustic scrubber, dried over a desiccant and trap in a dry ice acetone trap. The trapped material was then analyzed by NMR to give HFO-1345zf composition listed in Table 2.

TABLE 2

Compound	Chemical Formula	mole %
1345zf	$\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$	43.11%
E-1335dz	$\text{CF}_3\text{CF}_2\text{CH}=\text{CHCl}$	12.50%
Z-1335mxz	$\text{CF}_2\text{HCH}=\text{CClCF}_3$	11.60%
356mff	$\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$	10.21%
1353mxz	$\text{CH}_3\text{CH}=\text{CClCF}_3$	7.93%
1343mxz	$\text{CH}_2\text{ClCH}=\text{CClCF}_3$	7.52%
1345mzz	$\text{CF}_2\text{HCH}=\text{CHCF}_3$	7.13%
353maf	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$	0.00%

EXAMPLE 2

[0118] Into an Inconel (0.5 inch OD) tube reactor was added 6 cc of 2.5 wt% zinc-impregnated alumina oxide catalyst (12/20 mesh). The reaction was run by feeding liquid HCFC-353maf ("feed") into a heated chamber where it vaporized and mixed with HF and N₂. The process mixture was then allowed to pass through the reactor heated at 285°C to 325°C. A portion of the reactor effluent was passed through a series of valves and analyzed by GCMS. The conditions are provided in Table 3. For each set of conditions in Table 3, 5 GC analyses were taken. These results (averaged 5 GC analyses, area %) are provided in Table 4.

TABLE 3

Condition	Temperature, °C	Contact time (seconds)	Molar ratio of N ₂ :HF:feed
1	310	15.3	0 : 25.3 : 1
2	310	10.9	9.3 : 25.3 : 1
3	325	10.7	9.3 : 25.3 : 1
4	285	16.1	0 : 25.3 : 1

TABLE 4

Condition	1345zf	353maf	1344 isomers	1343 isomers	1336 isomers	Other compounds
GC Area %						
1	95.8794%	0.0000%	1.6406%	0.0000%	0.4761%	2.4473%
2	86.7588%	0.0000%	6.6134%	0.6027%	0.4098%	5.6592%
3	84.8460%	0.0000%	7.5002%	0.6299%	0.5418%	6.5610%
4	75.4958%	0.9959%	13.3079%	3.5538%	0.0000%	6.5053%

EXAMPLE 3

[0119] Into an Inconel (0.5 inch OD) tube reactor was added 6 cc of 12-20 mesh 20% CrCl₃/C catalyst. The catalyst was activated with HF starting from 150°C and raising the temperature to end at 450°C. HCFC-353maf was fed by a pump and was passed through a vaporizer at 150°C with 4.6 sccm N₂ and then mixed with HF. Reaction test conditions are provided in Table 5 below. The process mixture flowed through the reactor containing the catalyst. Part of the reactor effluent was passed through a GC sample loop and analyzed by GC-MS-FID. The GC (FID) results (area %) are provided in Table 6.

[0120]

TABLE 5

Temperature, °C	353maf feed, ml/hr	HF feed, sccm	N ₂ feed, sccm	Air feed, sccm	P, psig
260	0.1	8	4.6	0	0
270	0.1	8	4.6	0	0

TABLE 6

Compound	GC Area%	
	260°C	270°C
HFO-1345zf	75.8183%	45.0412%
CFC-13	0.0046%	0.0026%
HFC-23	0.0039%	0.0023%
HFC-347 isomers	1.1466%	0.4112%
HCFC-353maf	0.6403%	4.5976%
HCFC-355 isomers	0.9913%	0.0000%
HCFC-355 isomers	0.1361%	0.0837%
HCFO-1335 isomers	1.6212%	0.568%
HCFO-1335 isomers	2.3968%	1.5776%
HFO-1336 isomers	0.2212%	0.1410%
<i>E</i> -HCFO-1343mxz	0.3658%	0.7115%
<i>Z</i> -HCFO-1343mxz	6.6028%	31.7556%
HCFO-1344 isomers	0.7042%	5.8206%
HCFO-1344 isomers	0.0118%	0.0069%
HCFO-1344 isomers	3.1490%	11.1224%
<i>E</i> -HFO-1345mzz	1.4294%	0.5950%
<i>Z</i> -HFO-1345mzz	0.1610%	0.0520%
HCFO-1353 isomers	4.2904%	2.0901%
HCFO-1353 isomers	0.2476%	0.3187%
Other compounds	0.7736%	0.9292%

EXAMPLE 3a

[0121] In the course of Example 3, the amount of HFO-1345zf formed was found to decrease over time at 270°C as shown in Table 7, below. After 10 hr operation at 270°C, the organic feed was stopped. The catalyst was regenerated using air at the conditions shown in Table 8, below. After air regeneration, the test was resumed at 315°C and 335°C with co-feeding air. The GC (FID, area %) results at 315°C and 335°C are provided in Table 9. As seen from the results in Table 10, the activity of catalyst was maintained well at 335°C with co-feed of air.

TABLE 7

Time	Temp	GC Area%			
		1345zf	1343 isomers	353maf	Other compounds
1.25	260	70.4%	9.04%	1.20%	19.3%
2.50	260	60.2%	8.29%	1.24%	30.2%
3.75	260	47.2%	7.13%	1.09%	44.6%
5.00	260	75.3%	11.6%	1.82%	11.2%
6.25	260	75.4%	9.83%	1.62%	13.2%
7.50	260	74.4%	8.55%	1.40%	15.7%
8.75	260	75.5%	6.42%	1.01%	17.1%
10.00	260	75.0%	5.71%	0.95%	18.3%
11.25	260	74.9%	5.84%	0.83%	18.4%
12.50	260	74.6%	7.39%	0.70%	17.3%
13.75	260	65.4%	14.1%	0.87%	19.6%
15.00	260	59.7%	20.4%	1.38%	18.5%
16.25	270	52.4%	27.0%	2.59%	18.0%
17.50	270	45.4%	33.0%	3.53%	18.1%
18.75	270	38.7%	37.7%	4.92%	18.7%
20.00	270	31.8%	42.1%	6.99%	19.1%
21.25	270	25.9%	44.6%	9.80%	19.7%
22.50	270	22.4%	45.6%	12.3%	19.7%

Time	Temp	GC Area%			
hr	°C	1345zf	1343 isomers	353maf	Other compounds
23.75	270	16.6%	47.1%	15.5%	20.8%
25.00	270	14.4%	46.3%	18.5%	20.8%
26.25	270	12.6%	44.9%	21.4%	21.2%
27.50	270	8.33%	44.3%	25.1%	22.3%
28.75	270	6.49%	43.6%	28.2%	21.6%
30.00	270	4.67%	42.6%	31.2%	21.6%

TABLE 8

T	353maf	HF	N ₂	Air	P
°C	ml/hr	sccm	sccm	sccm	psig
350	0	0	12	12	0
350	0	24	12	0	0
400	0	24	12	0	0
450	0	24	12	0	0
450	0	24	0	0	0
315	0	0	25	0	0
315	0.15	12	4.6	4.5	0
335	0.15	12	4.6	4.5	0

TABLE 9

Compound	GC Area %	
	315°C	335°C
HFO-1345zf	64.3685%	58.9238%
CFC-13	0.6518%	0.8209%
HFC-23	0.5313%	0.4178%
CFC-115	0.1143%	0.1910%
HFC-143a	0.2906%	0.3096%
HFO-1234yf/HFC-245cb	0.3293%	0.4085%
HFO-1234ze	0.5549%	0.4595%
HCFC-345 isomers	0.1719%	0.1495%
HFC-347 isomers	3.0946%	2.3971%
HCFC-353maf	1.2326%	1.4726%
HCFC-355 isomers	1.2235%	5.2454%
HCFO-1325 isomers	0.8718%	1.0074%
HCFO-1326mxz	0.7700%	0.7696%
HCFO-1335 isomers	4.5721%	3.8533%
HCFO-1335mxz	7.5839%	7.0669%
HFO-1336	1.3753%	0.9901%
<i>E</i> -HCFO-1343mxz	0.2443%	1.0106%
<i>Z</i> -HCFO-1343mxz	5.3337%	10.9610%
HCFO-1344 isomers	3.5150%	0.0663%
HCFO-1344 isomers	0.7195%	1.4394%
<i>E</i> -HFO-1345mzz	0.4762%	0.3120%
<i>Z</i> -HFO-1345mzz	0.1805%	0.1278%
HCFO-1353 isomers	0.6349%	0.6124%
C ₇ H ₅ F ₇ isomers	0.0404%	0.0498%
Other compounds	1.1191%	0.9377%

TABLE 10

Time	Temp	GC Area%			
hr	°C	1345zf	1343 isomers	353maf	Other compounds
1.25	315	38.68%	1.33%	1.69%	58.29%
2.50	315	63.00%	1.56%	0.41%	35.03%
3.75	315	61.20%	2.51%	0.39%	35.90%
5.00	315	59.40%	4.33%	0.81%	35.46%
6.25	315	59.38%	6.67%	1.34%	32.61%
7.50	315	51.95%	12.19%	3.70%	32.16%
8.75	315	47.52%	15.50%	5.26%	31.72%
10.00	315	69.28%	10.06%	3.62%	17.04%
11.25	315	44.23%	19.40%	6.99%	29.38%
12.50	315	41.57%	21.63%	7.96%	28.83%
13.75	315	31.83%	26.67%	12.70%	28.80%
15.00	315	40.24%	22.65%	8.67%	28.45%
16.25	335	56.59%	11.16%	1.51%	30.73%
17.50	335	54.94%	12.48%	1.72%	30.86%
18.75	335	58.32%	11.64%	1.61%	28.44%
20.00	335	66.35%	8.32%	0.89%	24.45%
21.25	335	64.90%	9.21%	1.10%	24.79%
22.50	335	52.63%	15.29%	2.84%	29.24%
23.75	335	51.44%	16.06%	3.24%	29.26%
25.00	335	50.48%	15.84%	3.05%	30.63%
26.25	335	52.38%	15.58%	3.07%	28.97%
27.50	335	55.31%	13.53%	2.33%	28.83%
28.75	335	54.21%	14.62%	2.84%	28.34%
30.00	335	52.67%	15.84%	3.22%	28.27%

EXAMPLE 4

[0122] Into an Inconel (0.5 inch OD) tube reactor was added 6 cc of 12-20 mesh 6% zinc doped chromium oxide (Cr_2O_3). The catalyst was activated by treating HF starting from 150°C and ending at 450°C. 353maf was fed by a pump and went through a vaporizer at 150°C with 4.6 sccm N_2 and then mixed with HF. The molar ratio of HF to 353maf was 28.91:1. Reaction test conditions are provided in Table 11 below. The process mixture flowed through the reactor containing the catalyst. Part of the reactor effluent was passed through a GC sample loop and analyzed by GC/MS(FID). The GC results are provided in Table 12. The product from this Example was collected and the GC analysis is in Table 13.

TABLE 11

Time	353maf	HF	N_2	Air	T	P
hr	ml/hr	sccm	sccm	sccm	°C	psig
1.25	0.1	8	4.6	0	260	0
2.50	0.1	8	4.6	0	260	0
3.75	0.1	8	4.6	0	260	0
5.00	0.1	8	4.6	0	260	0
6.25	0.1	8	4.6	0	260	0
7.50	0.1	8	4.6	0	260	0
8.75	0.1	8	4.6	0	260	0
10.00	0.1	8	4.6	0	260	0
11.25	0.1	8	4.6	0	260	0
12.50	0.1	8	4.6	0	260	0
13.75	0.1	8	4.6	0	260	0
15.00	0.1	8	4.6	0	260	0
16.25	0.1	8	4.6	0	260	0
17.50	0.1	8	4.6	0	260	0
18.75	0.1	8	4.6	0	260	0
20.00	0.1	8	4.6	0	260	0
21.25	0.1	8	4.6	0	260	0
22.50	0.1	8	4.6	0	260	0

TABLE 12

Time	GC Area%			
hr	1345zf	1343 isomers	353maf	Other compounds
1.25	73.58%	4.54%	10.72%	11.15%
2.50	70.59%	9.97%	5.90%	13.54%
3.75	70.55%	9.51%	6.04%	13.91%
5.00	73.93%	7.26%	6.52%	12.29%
6.25	78.56%	6.16%	5.21%	10.07%
7.50	74.24%	9.96%	3.13%	12.68%
8.75	82.26%	3.51%	6.58%	7.65%
10.00	76.57%	7.37%	3.90%	12.16%
11.25	77.62%	6.57%	4.55%	11.25%
12.50	78.93%	5.18%	5.42%	10.46%
13.75	76.29%	6.35%	6.45%	10.91%
15.00	76.88%	6.18%	6.00%	10.94%
16.25	73.72%	9.70%	4.56%	12.03%
17.50	77.16%	5.97%	5.99%	10.87%
18.75	83.93%	3.32%	4.87%	7.87%
20.00	75.52%	8.39%	4.52%	11.57%
21.25	72.95%	11.06%	3.58%	12.41%
22.50	77.25%	7.34%	4.31%	11.09%

TABLE 13

Compound	GC Area%
HFO-1345zf	77.6898%
CFC-13	0.0009%
HFC-23	0.0011%
HFC-143a	0.0067%
HCFC-345	0.0976%
HFC-347 isomers	0.2222%
HCFC-355 isomers	1.4824%
HCFC-353maf	4.3658%
HFO-1325 isomers	0.0440%
HCFO-1335 isomers	0.5600%
HCFO-1335 isomers	0.5302%
Z-HCFO-1343mxz	10.7833%
<i>E</i> -HCFO-1343mxz	0.1585%
HCFO-1344 isomers	0.5065%
HCFO-1344 isomers	2.1625%
HCFO-1344 isomers	0.1511%
<i>E</i> -HFO-1345mzz	0.4129%
Z-HFO-1345mzz	0.0466%
HCFO-1353 isomers	0.4932%
Other compounds	0.2843%

EXAMPLE 5

[0123] The process of Example 4 was repeated at 315°C, 325°C and 335°C with air co-feed. The conditions are provided in Table 14. GC (FID, area%) analysis results in Table 15 show catalyst activity is stable with air co-feed.

TABLE 14

TIME	353MAF	HF	N ₂	AIR	T	P
HR	ML/HR	SCCM	SCCM	SCCM	°C	PSIG
2.5	0.1	8	4.6	3	315	0
5	0.1	8	4.6	3	315	0
7.5	0.1	8	4.6	3	315	0
10	0.1	8	4.6	3	315	0
12.5	0.1	8	4.6	3	315	0
15	0.1	8	4.6	3	315	0
17.5	0.1	8	4.6	3	315	0
20	0.1	8	4.6	3	315	0
22.5	0.1	8	4.6	3	315	0
25	0.1	8	4.6	3	315	0
27.5	0.1	8	4.6	3	315	0
30	0.1	8	4.6	3	315	0
32.5	0.1	8	4.6	3	315	0
35	0.1	8	4.6	3	315	0
37.5	0.1	8	4.6	3	315	0
40	0.1	8	4.6	3	315	0
42.5	0.1	8	4.6	3	325	0
45	0.1	8	4.6	3	325	0
47.5	0.1	8	4.6	3	325	0
50	0.1	8	4.6	3	325	0
52.5	0.1	8	4.6	3	325	0
55	0.1	8	4.6	3	325	0
57.5	0.1	8	4.6	3	335	0
60	0.1	8	4.6	3	335	0
62.5	0.1	8	4.6	3	335	0

TIME	353MAF	HF	N ₂	AIR	T	P
HR	ML/HR	SCCM	SCCM	SCCM	°C	PSIG
65	0.1	8	4.6	3	335	0
67.5	0.1	8	4.6	3	335	0
70	0.1	8	4.6	3	335	0
72.5	0.1	8	4.6	3	335	0

TABLE 15

Time	GC Area%			
hr	1345zf	1343 isomers	353maf	Other compounds
2.5	71.47%	7.19%	8.23%	13.12%
5	75.85%	4.66%	11.62%	7.87%
7.5	73.49%	8.20%	6.44%	11.88%
10	75.12%	7.93%	5.98%	10.97%
12.5	79.11%	6.46%	5.22%	9.21%
15	77.01%	8.48%	4.46%	10.04%
17.5	79.18%	7.79%	3.85%	9.18%
20	78.74%	8.26%	3.84%	9.16%
22.5	78.19%	8.87%	3.36%	9.58%
25	80.60%	7.52%	3.63%	8.25%
27.5	76.32%	10.47%	3.07%	10.14%
30	75.42%	11.69%	2.64%	10.25%
32.5	75.62%	11.51%	2.52%	10.35%
35	78.52%	10.02%	2.62%	8.84%
37.5	77.65%	10.80%	2.32%	9.23%
40	78.01%	10.87%	2.10%	9.02%
42.5	86.32%	2.93%	7.71%	3.04%

Time	GC Area%			
hr	1345zf	1343 isomers	353maf	Other compounds
45	79.00%	9.26%	1.83%	9.91%
47.5	79.50%	9.23%	1.71%	9.56%
50	78.20%	10.12%	1.59%	10.09%
52.5	74.44%	12.89%	1.46%	11.21%
55	78.73%	9.83%	1.55%	9.90%
57.5	78.05%	9.08%	1.50%	11.37%
60	81.86%	6.91%	1.68%	9.54%
62.5	77.14%	9.86%	1.46%	11.53%
65	81.13%	7.50%	1.58%	9.79%
67.5	79.27%	8.67%	1.41%	10.65%
70	79.27%	8.67%	1.41%	10.65%
72.5	78.99%	9.06%	1.24%	10.70%

EXAMPLE 6

[0124] The process of Examples 4 and 5 was repeated with lower HCFC-353maf mol ratio at 20:1. Deactivation of catalyst was observed faster than the previous test when HCFC-353maf mol ratio was at 29:1. The conditions are provided in Table 16. GC analysis results in Table 17 show deactivation of catalyst was observed faster than the previous test when HCFC-353maf mol ratio was at 29:1.

TABLE 16

Time	353maf	HF	N ₂	Air	T	P
hr	ml/hr	sccm	sccm	sccm	°C	psig
1.25	0.22	12	4.6	4.5	335	0
2.5	0.22	12	4.6	4.5	335	0
3.75	0.22	12	4.6	4.5	335	0
5	0.22	12	4.6	4.5	335	0
6.25	0.22	12	4.6	4.5	335	0
7.5	0.22	12	4.6	4.5	335	0

Time	353maf	HF	N ₂	Air	T	P
hr	ml/hr	sccm	sccm	sccm	°C	psig
8.75	0.22	12	4.6	4.5	335	0
10	0.22	12	4.6	4.5	335	0
11.25	0.22	12	4.6	4.5	335	0
12.5	0.22	12	4.6	4.5	335	0
13.75	0.22	12	4.6	4.5	335	0
15	0.22	12	4.6	4.5	335	0
16.25	0.22	12	4.6	4.5	335	0
17.5	0.22	12	4.6	4.5	335	0

TABLE 17

Time	GC Area %			
hr	1345zf	1343 isomers	353maf	Other compounds
1.25	70.89%	12.02%	0.00%	17.09%
2.5	76.04%	8.65%	0.00%	15.31%
3.75	63.95%	13.86%	0.00%	22.20%
5	65.06%	16.44%	0.00%	18.50%
6.25	61.49%	16.54%	0.00%	21.97%
7.5	64.99%	17.68%	0.00%	17.33%
8.75	61.95%	19.62%	0.00%	18.43%
10	58.51%	20.20%	0.00%	21.29%
11.25	56.67%	23.99%	0.00%	19.35%
12.5	54.51%	24.96%	0.00%	20.53%
13.75	51.45%	26.17%	0.00%	22.38%
15	50.60%	26.89%	0.00%	22.51%
16.25	46.26%	30.08%	0.00%	23.67%
17.5	44.03%	28.48%	0.00%	27.49%

EXAMPLE 7

[0125] The catalyst from Example 6 was treated with air for regeneration and then testing was resumed at 335°C with HCFC-353maf mol ratio at 29:1. The conditions

are provided in Table 18. GC (FID, area %) analysis results in Table 19 show activity of catalyst resumed and the catalyst stayed stable.

TABLE 18

Time	353maf	HF	N ₂	Air	T	P
hr	ml/hr	sccm	sccm	sccm	°C	psig
2.5	0	0	12	12	350	0
1	0	24	12	0	350	0
1	0	24	12	0	400	0
1	0	24	12	0	450	0
1	0	24	0	0	450	0
1.5	0	0	25	0	335	0
2.75	0.15	12	4.6	4.5	335	0
4	0.15	12	4.6	4.5	335	0
5.25	0.15	12	4.6	4.5	335	0
6.5	0.15	12	4.6	4.5	335	0
7.75	0.15	12	4.6	4.5	335	0
9	0.15	12	4.6	4.5	335	0
10.25	0.15	12	4.6	4.5	335	0
11.5	0.15	12	4.6	4.5	335	0
12.75	0.15	12	4.6	4.5	335	0
14	0.15	12	4.6	4.5	335	0
15.25	0.15	12	4.6	4.5	335	0
16.5	0.15	12	4.6	4.5	335	0
17.75	0.15	12	4.6	4.5	335	0
19	0.15	12	4.6	4.5	335	0
20.25	0.15	12	4.6	4.5	335	0
21.5	0.15	12	4.6	4.5	335	0
22.75	0.15	12	4.6	4.5	335	0
24	0.15	12	4.6	4.5	335	0

TABLE 19

Time	GC Area%		
hr	1345zf	1343 isomers	353maf
2.75	87.88%	4.98%	0.06%
4	87.50%	4.96%	0.03%
5.25	88.02%	4.65%	0.06%
6.5	88.74%	4.36%	0.02%
7.75	86.70%	5.31%	0.02%
9	86.08%	5.54%	0.02%
10.25	91.44%	0.14%	0.00%
11.5	87.11%	5.10%	0.03%
12.75	87.25%	4.98%	0.03%
14	86.43%	5.44%	0.01%
15.25	90.36%	4.97%	0.03%
16.5	86.51%	5.49%	0.01%
17.75	87.03%	5.35%	0.09%
19	87.35%	5.06%	0.12%
20.25	85.77%	5.67%	0.02%
21.5	75.84%	4.24%	0.00%
22.75	87.77%	4.70%	0.00%
24	87.91%	4.72%	0.04%

EXAMPLE 8

[0126] In a 1" Hastelloy C tube reactor chromium oxide catalyst was loaded and activated by HF treatment. Then 353maf and HF were fed at mol ratio of 1:20 at 80 psig pressure with co-fed of 0.2-0.4mol% O₂ in the temp range 340-350°C with contact time around 22 seconds. The product was scrubbed by a caustic solution and then collected and analyzed by GC. The result of GC analysis is provided in Table 20.

TABLE 20

Compound	GC Area %
HFO-1345zf	43.2%
HFO-1345 isomers	0.574%
HCFO-1233xf	0.117%
<i>E</i> - HCFO-1335dz	0.623%
<i>E</i> - HCFO-1344fzb	4.79%
<i>E</i> - HCFO-1335mxz	1.45%
HCFO-1335 isomers	0.159%
HCFC-355 isomers	0.403%
<i>Z</i> - HCFO-1344mxz	4.99%
<i>Z</i> - HCFO-1344myz	4.58%
HCFO-1344 isomers	0.120%
HCFO-1343 isomers	0.210%
HCFO-1343 isomers	0.187%
<i>Z</i> - HCFO-1343mxz	33.7%
HCFO-1343 isomers	2.26%
HCFO-1343 isomers	2.04%
Other compounds	0.611%

[0127] This product was further distilled and a purified product was analyzed by GC-MS-TCD which revealed additional byproducts as showed in Table 21.

TABLE 21

Compound	GC TCD area%
HFO-1234yf	0.0023%
HCFO-1327 isomers	0.0009%
CF ₃ CF ₂ CHO	0.0045%
<i>E</i> -HFO-1336mzz	0.0742%
HFO-1336yf	0.2657%
HFO-1336ze	0.0418%
HFO-1345zf	99.4085%
<i>Z</i> -HFO-1336mzz	0.0189%
HCFC-244 isomers	0.0121%
HCFO-1233xf	0.1550%
HCFO-1233zd	0.0073%
Other compounds	0.0087%

[0128] A distillation cut collected at 65°C was analyzed by NMR to further identify the structure of intermediate compounds. The result of analysis and structure of intermediates identified are provided in Table 22.

TABLE 22

Compound	Name	Mole percent (mole %)
Z-HCFO-1344mxz	Z-2-chloro-1,1,1,4-tetrafluoro-2-butene	47.21
Z-HCFO-1344myz	Z-4-chloro-1,1,1,2-tetrafluoro-2-butene	43.10
E-HCFO-1344mxz	E-2-chloro-1,1,1,4-tetrafluoro-2-butene	3.92
E-HCFO-1344myz	E-4-chloro-1,1,1,2-tetrafluoro-2-butene	3.59
HCFC-355of	4-chloro-1,1,1,2,2-pentafluorobutane	0.58
HCFO-1343maz	3,3-dichloro-4,4,4-trifluoro-1-butene	0.44
E-HCFO-1344mxy	E-2-chloro-1,1,1,3-tetrafluoro-2-butene	0.100
Z-HCFO-1344mxy	Z-2-chloro-1,1,1,3-tetrafluoro-2-butene	0.010
Other compounds		1.07

CLAIMS

What is claimed is:

1. A process for preparing 3,3,4,4,4-pentafluoro-1-butene comprising contacting 2,2,4-trichloro-1,1,1-trifluorobutane with an excess of HF in the presence of a fluorination catalyst to obtain a process mixture comprising 3,3,4,4,4-pentafluoro-1-butene, wherein the process is performed at a temperature of about 250-450°C, a pressure of about 0 to 200 psig.
2. The process of claim 1 wherein the temperature is in the range of about 300 to about 380°C.
3. The process of claim 1 or claim 2 wherein the pressure is in the range of about 30 to about 180 psig or about 40 to 150 psig, or about 60-120 psig.
4. The process of any of claims 1-3, wherein the fluorination catalyst comprises one or more metals, metal oxides, metal oxyfluorides, metal chloride or metal fluorides.
5. The process of claim 4 wherein the fluorination catalyst is a metal oxide, which is converted to a metal (oxy)fluoride in an activation and the metal (oxy)fluoride has Lewis acid character.
6. The process of claim 1 wherein the metal oxide comprises chromium or aluminum or cobalt or zinc.
7. The process of claim 1 wherein the fluorination catalyst comprises one or more of metals selected from Al, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, La and Ce.
8. The process of claim 7 wherein the fluorination catalyst comprises one or more of Al, Zr, Cr, Co, Ni and Zn.
9. The process of claim 8 wherein the fluorination catalyst comprises chromium or aluminum.
10. The process of claim 8 wherein the fluorination catalyst comprises chromium or aluminum and one or more of Zn, Zr, Co, and Ni.

11. The process of claim 4, wherein the fluorination catalyst comprises a metal oxide or metal fluoride and contains one or more additional metals selected from the group consisting of Li, Na, K, Ca, Mg, and Cs.
12. The process of claim 11, wherein the additional metal is present in an amount of less than 2000 or less than 1000 or less than 500 or less than 100 or less than 10 ppm.
13. The process of claim 9, wherein the fluorination catalyst comprises aluminum.
14. The process of claim 13, wherein aluminum is present in the form of aluminum oxide, aluminum fluoride or aluminum oxyfluoride.
15. The process of claim 13, wherein the fluorination catalyst further comprises one or more of Sc, Y, Ti, Zr, Hf, V Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, La and Ce.
16. The process of claim 15, wherein the fluorination catalyst comprises one or more of Zn, Zr, Cr, Co, and Ni.
17. The process of claim 13, wherein the fluorination catalyst comprises Al_2O_3 .
18. The process of claim 17, wherein the fluorination catalyst comprises Al_2O_3 and one or more of Zn, Zr, Cr, Co, and Ni.
19. The process of claim 18, wherein the fluorination catalyst comprises Al_2O_3 and Zn, or Al_2O_3 and Cr, or Al_2O_3 and Co, or Al_2O_3 and Ni, or Al_2O_3 and Zr.
20. The process of claim 9, wherein the fluorination catalyst comprises chromium.
21. The process of claim 20, wherein chromium is present in the form of chromium oxide, chromium chloride, chromium fluoride or chromium oxyfluoride.
22. The process of claim 21, wherein the fluorination catalyst further comprises one or more of Al, Sc, Y, Ti, Zr, Hf, V Nb, Ta, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, La and Ce.
23. The process of claim 20, wherein the fluorination catalyst comprises Cr_2O_3 .
24. The process of claim 20, wherein the fluorination catalyst comprises Cr_2O_3 and one or more of Zn, Zr, Co, and Ni.

25. The process of claim 24, wherein the fluorination catalyst comprises Cr_2O_3 and Zn, or Cr_2O_3 and Co, or Cr_2O_3 and Ni, or Cr_2O_3 and Zr.
26. The process of claim 20 wherein, the catalyst comprises chromium supported on AlF_3 , alumina, fluorinated alumina or activated carbon.
27. The process of claim 26 wherein the catalyst comprises chromium supported on alumina.
28. The process of claim 8 wherein, the catalyst comprises zinc supported on AlF_3 , alumina, fluorinated alumina or activated carbon.
29. The process of claim 28 wherein the catalyst comprises zinc supported on alumina.
30. The process of any of claims 1-29 further comprising, a prefluorination treatment prior to contacting HCFC-353maf with HF in the presence of the fluorination catalyst in a reactor, wherein the prefluorination treatment comprises passing HF, with or without an inert diluent such as nitrogen, over the catalyst at a temperature within the range of about 250 to 450°C.
31. The process of any of claims 1-30 further comprising, regenerating the fluorination catalyst after the catalyst has decreased in activity, wherein a regenerating step comprises treating the catalyst with oxygen or air at elevated temperature in the condition majority organic materials are purged away,
32. The process of any of claims 1-31, wherein the process is performed at a molar ratio of HF to HCFC-353maf from about 3:1 to about 50:1.
33. The process of claim 20 wherein the molar ratio of HF to HCFC-353maf is from about 10:1 to about 45:1 or 15:1 to 40:1.
34. The process of any of claims 1-33, further comprising adding an oxygen-containing gas to the process.
35. The process of claim 34 wherein the amount of oxygen added to the process from the oxygen-containing gas is greater than greater than 0 mole % and less than 10 mole %.

36. The process of claim 34 wherein the amount of oxygen added to the process from the oxygen-containing gas is from about 0.2 mole % to about 5 mole %, or from about 1 mole %.
37. The process of any of claims 1-36, wherein the process mixture comprising 3,3,4,4,4-pentafluoro-1-butene further comprises unreacted HF and the unreacted HF is recovered and recycled to the process.
38. The process of any of claims 1-37, wherein the process mixture comprises intermediates and unreacted 353maf, and the unreacted 353maf and intermediates are recovered and recycled to the process.
39. The process of claim 38, wherein the intermediates comprise HCFO-1343 isomers, HCFO-1344 isomers, or mixtures thereof.
40. A composition comprising 3,3,4,4,4-pentafluoro-1-butene, and at least one additional compound chosen from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd), dichlorotrifluorobutene isomers (HCFO-1343 isomers), chlorotetrafluorobutene isomers (HCFO-1344 isomers), chloropentafluorobutene isomers (HCFO-1335 isomers), chlorotrifluorobutene isomers (HCFO-1353 isomers), hexafluorobutene isomers (HFO-1336 isomers), pentafluorobutene isomers (HFO-1345 isomers), chloropentafluorobutane isomers (HCFC-355 isomers), 1,1,1,4,4,4-hexafluorobutane (HFC-356mff), 1,1,1-trifluoroethane (HFC-143a), trifluoromethane (HFC-23), chlorotrifluoromethane (CFC-13), heptafluorobutane isomers (HFC-347 isomers), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,3,3,3-tetrafluoropropene (HFO-1234ze), 2-chloro-1,1,1,3,3,3-hexafluoro-2-butene (HCFO-1326mxz), heptafluorobutene isomers (HFO-1327 isomers), 2,2,3,3,3-pentafluoropropanal and 2,2,4-trichloro-1,1,1-trifluorobutane (353maf).
41. The composition of claim 40, wherein the composition comprises one or more of chlorotetrafluorobutene isomers, dichlorotrifluorobutene isomers and chloropentafluorobutene isomers.
42. The composition of claim 41, wherein the composition comprises chlorotetrafluorobutene isomers.

43. The composition of claim 42 wherein the chlorotetrafluorobutene isomers is one or more of *Z*-4-chloro-1,1,1,2-tetrafluoro-2-butene (*Z*-HCFO-1344myz), *E*-4-chloro-1,1,1,2-tetrafluoro-2-butene (*E*-HCFO-1344myz), *Z*-2-chloro-1,1,1,4-tetrafluoro-2-butene (*Z*-HCFO-1344mxz), *E*-2-chloro-1,1,1,4-tetrafluoro-2-butene (*E*-HCFO-1344mxz), 3-chloro-3,4,4,4-tetrafluoro-1-butene (HCFO-1344fzb), *E*-2-chloro-1,1,1,3-tetrafluoro-2-butene (*E*-HCFO-1344mxy), or *Z*-2-chloro-1,1,1,3-tetrafluoro-2-butene (*Z*-HCFO-1344mxy).
44. The composition of claim 41, wherein the composition comprises dichlorotrifluorobutene isomers.
45. The composition of claim 44, wherein the dichlorotrifluorobutene isomers is one or more of *E*-2,4-dichloro-1,1,1-trifluoro-2-butene (*E*-HCFO-1343mxz), 3,3-dichloro-4,4,4-trifluoro-1-butene (HCFO-1343maz), and *Z*-2,4-dichloro-1,1,1-trifluoro-2-butene (*Z*-HCFO-1343mxz).
46. The composition of claim 41, wherein the composition comprises chloropentafluorobutene isomers.
47. The composition of claim 46, wherein the chloropentafluorobutene isomers is one or more of *E*-1-chloro-3,3,4,4,4-pentafluoro-1-butene (*E*-HCFO-1335dz), *E*-1-chloro-1,1,4,4,4-pentafluoro-2-butene (*E*-HCFO-1335lzz), *Z*-1-chloro-1,1,4,4,4-pentafluoro-2-butene, (*Z*-HCFO-1335lzz), and *E*-2-chloro-1,1,1,4,4-pentafluoro-2-butene (*E*-HCFO-1335mxz).
48. The composition of claim 41, wherein the composition comprises two or more of dichlorotrifluorobutene isomers, chlorotetrafluorobutene isomers and chloropentafluorobutene isomers.
49. The composition of claim 41, wherein the composition comprises at least one dichlorotrifluorobutene isomer and chlorotetrafluorobutene isomers.
50. The composition of claim 41, wherein the composition comprises dichlorotrifluorobutene isomers and chloropentafluorobutene isomers.
51. The composition of claim 41, wherein the composition comprises chlorotetrafluorobutene isomers and chloropentafluorobutene isomers.

52. The composition of claim 41, wherein the composition comprises dichlorotrifluorobutene isomers, chlorotetrafluorobutene isomers and chloropentafluorobutene isomers.
53. The composition of claim 40, wherein the composition comprises hexafluorobutene isomers.
54. The composition of claim 53, wherein the hexafluorobutene isomers is one or more of *E*-1,1,1,4,4,4-hexafluoro-2-butene (*E*-HFO-1336mzz), *Z*-1,1,1,4,4,4-hexafluoro-2-butene (*Z*-HFO-1336mzz), 2,3,3,4,4,4-hexafluoro-1-butene (HFO-1336yf), and 1,3,3,4,4,4-hexafluoro-1-butene (HFO-1336ze).
55. The composition of claim 40, wherein the composition comprises HCFO-1353 isomers.
56. The composition of claim 55, wherein the HCFO-1353 isomers comprises HCFO-1353mxz.
57. The composition of claim 40, wherein the composition comprises 1,3,3,4,4,4-hexafluoro-1-butene (HFO-1336ze) and at least one additional compound chosen from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 1-chloro-3,3,3-trifluoropropene (1233zd), *Z*-4-chloro-1,1,1,2-tetrafluoro-2-butene (*Z*-HCFO-1344myz), *E*-4-chloro-1,1,1,2-tetrafluoro-2-butene (*E*-HCFO-1344myz), *Z*-2-chloro-1,1,1,4-tetrafluoro-2-butene (*Z*-HCFO-1344mxz), *E*-2-chloro-1,1,1,4-tetrafluoro-2-butene (*E*-HCFO-1344mxz), 3-chloro-3,4,4,4-tetrafluoro-1-butene (HCFO-1344fzb), *E*-2-chloro-1,1,1,3-tetrafluoro-2-butene (*E*-HCFO-1344mxy), *Z*-2-chloro-1,1,1,3-tetrafluoro-2-butene (*Z*-HCFO-1344mxy), *E*-1-chloro-3,3,4,4,4-pentafluoro-1-butene (*E*-HCFO-1335dz), *E*-1-chloro-1,1,4,4,4-pentafluoro-2-butene (*E*-HCFO-1335lzz), *Z*-1-chloro-1,1,4,4,4-pentafluoro-2-butene, (*Z*-HCFO-1335lzz), *E*-2-chloro-1,1,1,4,4-pentafluoro-2-butene (*E*-HCFO-1335mxz), *E*-2,4-dichloro-1,1,1-trifluoro-2-butene (*E*-HCFO-1343mxz), 3,3-dichloro-4,4,4-trifluoro-1-butene (HCFO-1343maz), *Z*-2,4-dichloro-1,1,1-trifluoro-2-butene (*Z*-HCFO-1343mxz), 4-chloro-1,1,1,2,2-pentafluorobutane (HCFC-355of), 1,1,1,4,4,4-hexafluorobutane (HFC-356mff), 3-chloro-4,4,4-trifluoro-2-butene (HCFO-1353mxz), 1,1,4,4,4-pentafluoro-2-butene (HFO-1345mzz), 1,1,1-trifluoroethane (HFC-143a), trifluoromethane (HFC-23), chlorotrifluoromethane (CFC-13), 2,3,3,3-tetrafluoropropene (HFO-1234yf),

- 1,3,3,3-tetrafluoropropene (HFO-1234ze), 2-chloro-1,1,1,3,3,3-hexafluoro-2-butene (HCFO-1326mxz), heptafluorobutene isomers (HFO-1327 isomers), *E*-1,1,1,4,4,4-hexafluoro-2-butene (*E*-HFO-1336mzz), *Z*-1,1,1,4,4,4-hexafluoro-2-butene (*Z*-HFO-1336mzz), 2,3,3,4,4,4-hexafluoro-1-butene (HFO-1336yf), 1,3,3,4,4,4-hexafluoro-1-butene (HFO-1336ze), 2,2,3,3,3-pentafluoropropanal and 2,2,4-trichloro-1,1,1-trifluorobutane (HCFC-353maf).
58. The composition of claim 40, wherein the composition comprises 2,3,3,4,4,4-hexafluoro-1-butene (HFO-1336yf), and at least one additional compound chosen from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 1-chloro-3,3,3-trifluoropropene (1233zd), dichlorotrifluorobutene isomers (HCFO-1343 isomers), chlorotetrafluorobutene isomers (HCFO-1344 isomers), chloropentafluorobutene isomers (HCFO-1335 isomers), chloropentafluorobutane isomers (HCFC-355 isomers), 1,1,1,4,4,4-hexafluorobutane (HFC-356mff), 3-chloro-4,4,4-trifluoro-2-butene (HCFO-1353mxz), 1,1,4,4,4-pentafluoro-2-butene (HFO-1345mzz), 1,1,1-trifluoroethane (HFC-143a), trifluoromethane (HFC-23), chlorotrifluoromethane (CFC-13), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,3,3,3-tetrafluoropropene (HFO-1234ze), 2-chloro-1,1,1,3,3,3-hexafluoro-2-butene (HCFO-1326mxz), heptafluorobutene isomers (HFO-1327 isomers), 2,2,3,3,3-pentafluoropropanal and 2,2,4-trichloro-1,1,1-trifluorobutane (353maf).
59. The composition of claim 40 wherein the composition comprises 1,1,4,4,4-pentafluoro-2-butene (HFO-1345mzz).
60. The composition of claim 40 prepared according to the process of any of claims 1-39.
61. Use of the composition of any of claims 40-59 in a heat transfer application.
62. Use of the composition of any of claims 40-59 as a dielectric liquid.
63. Use of the composition of any of claims 40-59 as a cleaning solvent.