

TITLE OF THE INVENTION

COMPOSITIONS OF AND PROCESSES FOR 2,2,4-TRICHLORO-1,1,1-TRIFLUOROBUTANE

FIELD

[0001] The present application relates to compositions comprising fluorinated compounds, processes of preparing such compositions and their use, particularly 2,2,4-trichloro-1,1,1-trifluorobutane, (HCFC-353maf, $\text{CH}_2\text{ClCH}_2\text{CCl}_2\text{CF}_3$).

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 *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), are believed to meet both goals. In particular, 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). Accordingly, there is a need to develop new processes and intermediate compositions for preparing *E*-1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene.

SUMMARY

[0004] The present invention relates to compositions comprising 2,2,4-trichloro-1,1,1-trifluorobutane (HCFC-353maf, $\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$), processes of preparing such compositions and their use.

[0005] The present invention provides a process for preparing HCFC-353maf comprising contacting 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a) with ethylene

in the presence of a catalyst system comprising a metal and an organic ligand in a reactor to obtain a process mixture comprising HCFC-353maf.

[0006] In one embodiment, the process is performed in the presence of an excess of CFC-113a and the process mixture comprises HCFC-353maf and CFC-113a. In certain embodiments, the CFC-113a may be recovered from the process mixture and recycled to the process.

[0007] The process may be performed at a temperature of about 80°C to about 150°C, a pressure of about 50 to 150 psig. Preferably, the temperature is in the range of about 85°C to about 125°C, or in the range of about 95°C to about 115°C.

[0008] The present invention also provides a composition comprising HCFC-353maf, and at least one additional compound chosen from ethylene, CF₃CCl₃ (CFC-113a), CF₃CFCl₂ (CFC-114a), CF₃CHCl₂ (HCFC-123), CHCl₂CHClF (HCFC-131), C₄H₃F₃Cl₄ isomers (HCFC-343 isomers), CF₃CCl₂CH₂CH₃ (HCFC-363maf), 1-chlorobutane, 1-chlorobutene, 1,3-dichlorobutane, CF₃CCl₂CCl₂CF₃ (CFC-316maa), CF₃CCl=CClCF₃ (CFO-1316mxx), C₆H₈Cl₃F₃ (trichlorotrifluorohexane isomers, HCFC-593 isomers), dichlorotrifluorooctene isomers (C₈H₁₁Cl₂F₃ isomers), dichlorotrifluorobutene isomers (HCFO-1343 isomers), C₆H₂Cl₃F₇ isomers, 1-butanol, 2-butoxyethanol and organic ligand. The composition may be prepared by the process disclosed herein.

[0009] In one embodiment, the present invention provides a composition comprising HCFC-353maf and ethylene, or, HCFC-353maf and CF₃CFCl₂ (CFC-114a), or HCFC-353maf and CF₃CHCl₂ (HCFC-123), or HCFC-353maf and CF₃CCl₂CH₂CH₃ (HCFC-363maf), or HCFC-353maf and 1-chlorobutane, or HCFC-353maf and CF₃CCl₂CCl₂CF₃ (CFC-316maa), or HCFC-353maf and CF₃CCl=CClCF₃ (CFO-1316mxx), or HCFC-353maf and C₆H₈Cl₃F₃ (trichlorotrifluorohexane isomers, HCFC-593 isomers), or HCFC-353maf and dichlorotrifluorooctene isomers (C₈H₁₁Cl₂F₃ isomers), or HCFC-353maf and CHCl₂CHClF (1,1,2-trichloro-2-fluoroethane, HCFC-131), or HCFC-353maf and dichlorotrifluorobutene.

[0010] In one embodiment, the present invention provides a composition comprising HCFC-353maf and ethylene and CF₃CFCl₂ (CFC-114a), or HCFC-353maf and CF₃CFCl₂ (CFC-114a) and CF₃CHCl₂ (HCFC-123), or HCFC-353maf

and CF_3CHCl_2 (HCFC-123) and $\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_3$ (HCFC-363maf), or HCFC-353maf and 1-chlorobutene and dichlorotrifluorobutene, or HCFC-353maf and $\text{C}_6\text{H}_8\text{Cl}_3\text{F}_3$ (trichlorotrifluorohexane isomers, HCFC-593 isomers) and CFO-1316mxx, or HCFC-353maf and dichlorotrifluorooctene ($\text{C}_8\text{H}_{11}\text{Cl}_2\text{F}_3$) and $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_3$.

[0011] The present invention also provides a composition comprising HCFC-353maf, and at least one isomer of trichlorotrifluorohexane isomers, (HCFC-593 isomers).

BRIEF DESCRIPTION OF THE FIGURE

[0012] Figure 1 illustrates a flow diagram for a process useful to prepare HCFC-353maf according to an embodiment of this invention.

DETAILED DESCRIPTION

[0013] The present invention relates broadly to compositions comprising 2,2,4-trichloro-1,1,1-trifluorobutane (HCFC-353maf, $\text{CH}_2\text{ClCH}_2\text{CCl}_2\text{CF}_3$), processes of preparing such compositions and their use.

GENERAL TERMS

[0014] Compounds may be referred to herein by the compound name (e.g., 2,2,4-trichloro-1,1,1-trifluorobutane) or ASHRAE designation (e.g., HCFC-353maf) or chemical formula (e.g., $\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$) 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.

[0015] 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.

[0016] 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, CFO-1316mxx may include one or both of E-CFO-1316mxx and Z-CFO-1316mxx, whereas specific isomers are identified as “E-CFO-1316mxx” and “Z-CFO-1316mxx”.

[0017] 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).

[0018] 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.

[0019] 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”.

[0020] 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.”

[0021] 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.

[0022] 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.

[0023] 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.

[0024] As used herein, a “catalyst system” comprises a metal and an organic ligand. The catalyst system effects the addition of alkyl halides to olefins. By “effects the addition of alkyl halides to olefins” is meant herein the catalyst system catalyzes or initiates the reaction of an alkyl halide with an olefin.

[0025] 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.

[0026] 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

[0027] The present invention describes processes for preparing a mixture or a composition comprising, consisting of, or consisting essentially of HCFC-353maf ($\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$, 2,2,4-trichloro-1,1,1-trifluorobutane), and one or more additional compounds.

[0028] In one embodiment, the present invention provides a process for preparing HCFC-353maf comprising contacting CFC-113a with ethylene in the presence of a catalyst system comprising a metal and an organic ligand in a reactor to obtain a process mixture comprising HCFC-353maf, wherein the process is performed at a temperature of about 80°C to about 150°C , and a pressure of about 50 to 150 psig. Preferably, the temperature is in the range of about 85°C to about 125°C , or in the range of about 95°C to about 115°C .

[0029] In one embodiment, the process of this invention is performed at a conversion of CFC-113a of less than 100%, such as from 30-80% conversion of CFC-113a.

[0030] In one embodiment for a process for preparing HCFC-353maf, the process is performed at a conversion of less than 80% of the CFC-113a. In one embodiment, the process is performed at a conversion of 30-80% of the CFC-113a. In one embodiment, the process is performed at a conversion of 40-70% of the CFC-113a. In one embodiment, the process is performed at a conversion of 50-70% of the CFC-113a.

[0031] In one embodiment, the process of this invention is performed in the presence of an excess of CFC-113a.

[0032] When conversion of 1,1,1-trichloro-2,2,2-trifluoroethane is less than 100% or when an excess of CFC-113a is used, the process mixture comprises HCFC-353maf and CFC-113a. In these embodiments, the CFC-113a present in the

process mixture may be and is preferably separated from the process mixture and recycled to the process.

[0033] The process of this invention involves reaction of CFC-113a with ethylene to produce HCFC-353maf in the presence of a catalyst system comprising a metal and an organic ligand. Many metals have been found to promote the addition of haloalkanes to olefins with good selectivity. Of particular interest in this invention are systems based on iron, copper, ruthenium and nickel and more particularly here, are systems based on iron or copper.

[0034] In certain embodiments, the metal of the catalyst system is or comprises iron or copper. In one embodiment of the process of this invention, the metal is or comprises iron. In one embodiment, the metal is or comprises copper.

[0035] In one embodiment of the process of this invention, the metal is or comprises iron powder, iron wire, iron screen or iron turnings or combinations of two or more thereof. In one embodiment, the metal comprises iron powder. In one embodiment, the metal comprises iron wire. In one embodiment, the metal comprises iron screen. In one embodiment, the metal comprises iron turnings.

[0036] In one embodiment of the process of this invention, the metal is or comprises an iron salt such as ferric chloride or ferrous chloride. In one embodiment, the metal comprises ferric chloride. In one embodiment, the metal comprises ferrous chloride. In one embodiment, the metal comprises ferric chloride and ferrous chloride.

[0037] In one embodiment of the process of this invention, the metal is or comprises copper. The copper may be in the form of a copper salt such as copper(I) chloride or copper (II) chloride. Other copper salts may also be used including copper(I) bromide, copper (II) bromide, copper (I) iodide, copper (II) acetate and copper (II) sulfate. In one embodiment, the metal comprises copper (I) chloride. In one embodiment, the metal comprises copper (II) chloride. In one embodiment, the metal comprises copper(I) chloride and copper (II) chloride.

[0038] The organic ligand can be an organophosphorus compound or an organonitrogen compound.

[0039] In one embodiment, when the organic ligand is an organophosphorus compound, the metal is iron. In one embodiment, when the organic ligand is an organonitrogen compound, the metal is copper.

[0040] When the organic ligand is an organophosphorus compound, the organic ligand may be selected from the group consisting of a phosphine, phosphinite, phosphonate, phosphite, a phosphine oxide or a phosphate, and mixtures of two or more thereof. When the organic ligand is an organonitrogen compound, the organic ligand may be selected from the group consisting of an amine, a nitrile, an amide, a thiamide, and mixtures of two or more thereof.

[0041] In one embodiment of the process of this invention, the metal is iron and the organic component comprises an organophosphorus compound. The organophosphorus compound may be phosphine, phosphinite, phosphonate, phosphite, phosphine oxide or phosphate, each comprising one or more alkyl or aryl groups. In one embodiment, the organophosphorus compound includes compounds having a structural formula as follows: $PR_1R_2R_3$ where each R_1 , R_2 , and R_3 is independently aryl, alkyl, aryloxy or alkoxy. In another embodiment, the organophosphorus compound includes compounds having a structural formula as follows: $O=PR_1R_2R_3$ where each R_1 , R_2 , and R_3 is independently aryloxy or alkoxy.

[0042] In one embodiment, the metal of the catalyst system comprises iron and the organic ligand of the catalyst system comprises a trialkyl phosphate or trialkyl phosphine or triaryl phosphine.

[0043] In one embodiment of the process of this invention, the process is performed in the presence a catalyst system comprising iron and an alkyl phosphate, wherein the alkyl phosphate is a monoalkyl phosphate, a dialkyl phosphate or a trialkyl phosphate or a combination of two or more thereof. In one embodiment of the process of this invention, the alkyl phosphate is a monoalkyl phosphate. In one embodiment of the process of this invention, the alkyl phosphate is a dialkyl phosphate. In one embodiment of the process of this invention, the alkyl phosphate is a trialkyl phosphate. In one embodiment of the process of this invention, the alkyl phosphate is a combination of two or more of monoalkyl phosphate, dialkyl phosphate and trialkyl phosphate.

[0044] In one embodiment, the metal of the catalyst system comprises iron and the organic ligand is trialkyl phosphate, wherein the trialkyl phosphate is a tris(C₁₋₆ alkyl)phosphate. In one embodiment, the metal of the catalyst system is iron and the organic ligand is tributyl phosphate.

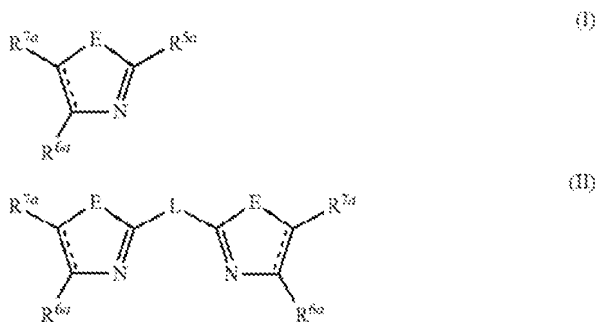
[0045] In one embodiment of the process of this invention, the metal of the catalyst system is iron and the organic ligand of the catalyst system comprises a phosphine. In one embodiment, the phosphine comprises an alkylphosphine or arylphosphine. In one embodiment, the phosphine is chosen from tributyl phosphine and triphenyl phosphine. In one embodiment, the organic ligand is tributyl phosphine. In one embodiment, the organic ligand is triphenyl phosphine.

[0046] In one embodiment of the process of this invention, the process is performed in the presence of a catalyst system wherein the metal of the catalyst system comprises copper and the organic ligand of the catalyst system is a nitrogen-containing organic ligand.

[0047] When the metal of the catalyst system is copper, the organic ligand of the catalyst system may comprise an organonitrogen compound. For example, the organonitrogen compound may be selected from the group consisting of an amine, a nitrile, or an amide, or combinations of two or more thereof. The amine may be selected from the group consisting of monoalkyl amine, dialkylamine, trialkyl amine and cyclic amine. The amine may be selected from the group consisting of tert-butylamine, *n*-butylamine, sec-butylamine, 2-propylamine, benzylamine, tri-*n*-butylamine, ethanolamine, piperidine and pyridine. In one embodiment the amine is tert-butylamine. The nitrile may be selected from the group consisting of acetonitrile, propionitrile, *n*-butyronitrile, benzonitrile, and phenylacetonitrile. In one embodiment, the nitrile is acetonitrile. The amide may be selected from the group consisting of hexamethylphosphoramide and dimethylformamide. In one embodiment, the amide is hexamethylphosphoramide.

[0048] When the metal is copper, the organic ligand may comprise a nitrogen-containing heterocyclic compound. Suitable heterocyclic compounds include those selected from the group consisting of imidazoles, imidazolines, oxadiazoles, oxazoles, oxazolines, isoxazoles, thiazoles, thiazolines, pyrrolines, pyridines, trihydropyrimidines, pyrazoles, triazoles, triazolium salts, isothiazoles, tetrazoles,

tetrazolium salts, thiadiazoles, pyridazines, pyrazines, oxazines and dihydrooxazine. In certain embodiments, the heterocyclic compound is selected from the group having Formula (I) or Formula (II) as follows: where E is selected from O, S, Se, CH₂ and N(R^{8a}); R^{5a} is selected from the group consisting of CH₃ and C₂H₅ (and is preferably CH₃); R^{6a} and R^{7a} are selected from the group consisting of H, CH₃, C₆H₅ (i.e., phenyl), CH₂C₆H₅, CH(CH₃)₂, and fused phenyl; L is selected from the group consisting of O, S, Se, N(R^{8a}), C₆H₄-, 2,6-pyridyl-, -OC₆H₄-C₆H₄O-, -CH₂CH₂OCH₂CH₂- and -(CH₂)_p-, where p is an integer from 0 to 6; and each R^{8a} is selected from the group consisting of H and C_mH_{2m+1} where m is an integer from 1 to 6. The bond between each pair of carbon atoms respectively attached to R^{6a} and R^{7a}



(as represented by the dashed bond lines in Formula (I) and Formula (II)) can be either a single or a double bond.

[0049] In one embodiment of the process of this invention, the metal of the catalyst system is copper and the organic ligand of the catalyst system comprises an organonitrogen compound. In one embodiment of the process of this invention, when the metal is or comprises copper and the organic ligand is an organonitrogen compound and the organonitrogen compound is an amine.

[0050] In the present invention, the concentration of the metal of the catalyst system as discussed herein refers to the concentration of the metal, based on ICP analysis of the process mixture.

[0051] In one embodiment of this invention, the concentration of the metal from the catalyst system in the process mixture, ranges from 300 ppmw to 3000 ppmw of metal and the metal is iron or copper. In one embodiment, the metal of the catalyst

is iron and the concentration of the metal in the process mixture ranges from 300 ppmw to 3000 ppmw. In one embodiment, the metal of the catalyst system is copper and the concentration of the metal in the process mixture ranges from 300 ppmw to 3000 ppmw.

[0052] In one embodiment of this invention, the concentration of the metal from the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw of metal and the metal is iron or copper. In one embodiment, the metal of the catalyst system is iron and the concentration of the metal in the process mixture ranges from 500 ppmw to 2500 ppmw. In one embodiment, the metal of the catalyst system is copper and the concentration of the metal in the process mixture ranges from 500 ppmw to 2500 ppmw.

[0053] In one embodiment of this invention, the concentration of the metal from the catalyst system in the process mixture ranges from 750 ppmw to 2000 ppmw of metal and the metal is iron or copper. In one embodiment, the metal of the catalyst system is iron and the concentration of the metal in the process mixture ranges from 750 ppmw to 2000 ppmw. In one embodiment, the metal of the catalyst system is copper and the concentration of the metal in the process mixture ranges from 750 ppmw to 2000 ppmw.

[0054] In one embodiment of this invention, the concentration of the metal from the catalyst system in the process mixture ranges from 800 ppmw to 1800 ppmw of metal and the metal is iron or copper. In one embodiment, the metal of the catalyst system is iron and the concentration of the metal in the process mixture ranges from 800 ppmw to 1800 ppmw. In one embodiment, the metal of the catalyst system is copper and the concentration of the metal in the process mixture ranges from 800 ppmw to 1800 ppmw.

[0055] In one embodiment of this invention, the concentration of the metal from the catalyst system in the process mixture ranges from 1000 ppmw to 1500 ppmw of metal and the metal is iron or copper. In one embodiment, the metal of the catalyst system is iron and the concentration of the metal in the process mixture ranges from 1000 ppmw to 1500 ppmw. In one embodiment, the metal of the catalyst system is copper and the concentration of the metal in the process mixture ranges from 1000 ppmw to 1500 ppmw.

[0056] In one embodiment of this invention, the concentration of the metal from the catalyst system in the process mixture ranges from 1200 ppmw to 1400 ppmw of metal and the metal is iron or copper. In one embodiment, the metal of the catalyst system is iron and the concentration of the metal in the process mixture ranges from 1200 ppmw to 1400 ppmw. In one embodiment, the metal of the catalyst system is copper and the concentration of the metal in the process mixture ranges from 1200 ppmw to 1400 ppmw.

[0057] In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises a trialkyl phosphate. In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises a trialkyl phosphate. In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises a tri(C₁₋₆ alkyl)phosphate. In one embodiment of this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises tributyl phosphate.

[0058] In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises a phosphine. In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises an alkylphosphine or arylphosphine. In one embodiment

of the process this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises triphenyl phosphine or tributyl phosphine. In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises triphenyl phosphine. In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises iron and the organic ligand of the catalyst system comprises tributyl phosphine.

[0059] In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture, ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises copper and the organic ligand of the catalyst system is an alkyl amine. In one embodiment of the process of this invention, the concentration of the metal of the catalyst system in the process mixture, ranges from 500 ppmw to 2500 ppmw or 750-2000 ppmw or 800 ppmw to 1800 ppmw or 1000 ppmw to 1500 ppmw and the metal comprises copper and the organic ligand of the catalyst system is tributyl amine.

[0060] In one embodiment the process is performed with a molar excess of 1,1,1-trichloro-2,2,2-trifluoroethane. A molar excess of 1,1,1-trichloro-2,2,2-trifluoroethane used is based on 1 molar equivalent of ethylene, for example, greater than 1 molar equivalent, greater than 2 molar equivalents, greater than 5 molar equivalents, or greater than 10 molar equivalents of 1,1,1-trichloro-2,2,2-trifluoroethane is used based on 1 molar equivalent of ethylene.

[0061] In one embodiment of this invention, there is provided a reaction system comprising a reactor and a distillation system downstream of the reactor. The reaction system includes feed lines to introduce reactants to the reactor. The feed lines include a feed line for a reactant ethylene feed, and a fresh reactant CFC-113a

feed, an organic ligand feed and a recycled CFC-113a feed. There is also a feed of metal to introduce metal to the reactor, such as from a bed. Any of the feeds may be combined and introduced to the reactor as a single feed. In certain embodiments, fresh reactant CFC-113a feed and recycled CFC-113a feed are combined in a single feed for CFC-113a to be introduced to the reactor. In certain embodiments, the organic ligand is combined with the fresh reactant CFC-113a feed or the recycled CFC-113a feed prior to introducing the reactor.

[0062] The reaction system further comprises an exit stream from the reactor, which provides the process mixture. In certain embodiments, the reaction system comprises a distillation system to separate the desired product from the reactor process mixture. The distillation system may comprise multiple distillation columns, evaporator (reboiler)/condenser to facilitate separating reactants, components of the catalyst system, and by-products from the reactor process mixture.

[0063] The reactor process mixture may proceed through a mechanism to separate a portion of the reaction process mixture, which is preferably cooled and then recycled to the reactor.

[0064] In one embodiment, the distillation system comprises a distillation column to separate a stream comprising reactants from the process mixture. The separated reactants comprise CFC-113a and optionally, ethylene.

[0065] In one embodiment, after separating CFC-113a from the process mixture, the distillation system comprises one or more additional distillation columns to separate the desired product (HCFC-353maf) from the remaining process mixture.

[0066] For example, in one embodiment, the distillation system comprises a distillation column to remove compounds having boiling points below ethylene from the process mixture. In another embodiment, the distillation system comprises a distillation column to remove compounds having boiling points above the boiling point of HCFC-353maf.

[0067] The distillation system may further comprise one or more purge lines to remove material from the process mixtures. For example, a purge line may be used to remove high boiling components from the process mixture. For purposes herein,

“high boiling components” comprises compounds having boiling points above the boiling point of HCFC-353maf.

[0068] Following the distillation system, the reaction system provides a purified product comprising HCFC-353maf. The reaction system may comprise a storage tank to store the purified HCFC-353maf. The purified HCFC-353maf product may be used as a starting material to produce 3,3,4,4,4-pentafluorobut-1-ene (HFO-1345zf), and optionally subsequently, 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 (*E*-HFO-153-10mczz).

COMPOSITION

[0069] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least one additional compound chosen from ethylene, CF₃CCl₃ (CFC-113a), CF₃CFCl₂ (CFC-114a), CF₃CHCl₂ (HCFC-123), CHCl₂CHClF (HCFC-131), C₄H₃F₃Cl₄ (HCFC-343 isomers), CF₃CCl₂CH₂CH₃ (HCFC-363maf), 1-chlorobutane, 1-chlorobutene, 1,3-dichlorobutane, CF₃CCl₂CCl₂CF₃ (CFC-316maa), CF₃CCl=CClCF₃ (CFO-1316mxx), C₆H₈Cl₃F₃ (trichlorotrifluorohexane, HCFC-593 isomers), dichlorotrifluorooctene (C₈H₁₁Cl₂F₃ isomers), dichlorotrifluorobutene (HCFO-1343 isomers), C₆H₂Cl₃F₇ isomers, 1-butanol, 2-butoxyethanol and organic ligand.

[0070] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, ethylene and CFC-113a.

[0071] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, ethylene and CFC-113a and further comprising CFC-114a.

[0072] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, ethylene and CFC-113a and further comprising CFC-114a and/or HCFC-363maf.

[0073] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, ethylene and CFC-113a and further comprising CFC-114a and/or HCFC-363maf and/or 1-chlorobutane, and/or CFC-316maa, and/or CFO-1316mxx.

[0074] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, ethylene and CFC-113a and further comprising CFC-114a and/or HCFC-363maf and/or 1-chlorobutane and/or dichlorotrifluoroctene.

[0075] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, ethylene and CFC-113a and further comprising CFC-114a and/or HCFC-363maf and/or 1-chlorobutane and/or dichlorotrifluoroctane and/or organic ligand. In one embodiment, the organic ligand is tributylphosphate. In one embodiment, the organic ligand is triphenylphosphine.

[0076] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and HCFC-593 isomers.

[0077] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf and 1,1,1-trifluoro-2,2,6-trichlorohexane (HCFC-593mafff).

[0078] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf and 1,3,6-trichloro-3-trifluoromethylpentane.

[0079] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and HCFC-593 isomers and further comprising ethylene and CFC-113a.

[0080] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, HCFC-593 isomers, ethylene and CFC-113a and further comprising CFC-114a.

[0081] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, HCFC-593 isomers, ethylene and CFC-113a and further comprising CFC-114a and/or HCFC-363maf.

[0082] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, HCFC-593 isomers, ethylene and CFC-113a and further comprising CFC-114a and/or 363maf and/or 1-chlorobutane and/or CFC-316maa, and/or CFO-1316mxx.

[0083] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, CFC-316maa and CFO-1316mxx.

[0084] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, HCFC-593 isomers, ethylene and CFC-113a and further comprising CFC-114a and/or HCFC-363maf and/or 1-chlorobutane and/or dichlorotrifluoroethane.

[0085] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least one of ethylene, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane, 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, trichlorotrifluoroethane, 1,5,5-trichloro-6,6,6-trifluoroethane, and 2,2,4-trichloro-1,1,1-trifluorobutane.

[0086] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least two of ethylene, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane, 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, trichlorotrifluoroethane, 1,5,5-trichloro-6,6,6-trifluoroethane, and 2,2,4-trichloro-1,1,1-trifluorobutane.

[0087] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least three of ethylene, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane, 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, trichlorotrifluoroethane, 1,5,5-trichloro-6,6,6-trifluoroethane, and 2,2,4-trichloro-1,1,1-trifluorobutane.

[0088] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least four of ethylene, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane, 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, trichlorotrifluoroethane, 1,5,5-trichloro-6,6,6-trifluoroethane, and 2,2,4-trichloro-1,1,1-trifluorobutane.

[0089] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and ethylene, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane, 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, trichlorotrifluoroethane, 1,5,5-trichloro-6,6,6-trifluoroethane, and 2,2,4-trichloro-1,1,1-trifluorobutane.

[0090] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least one of 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-

dichloro-1,1,1-trifluoroethane, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluorobutane, 1,5,5-trichloro-6,6,6-trifluorohexane, 1,3,6-trichloro-3-trifluoromethylpentane, dichlorotrifluoroctene, and tributylphosphate.

[0091] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least two of 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluoroethane, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluorobutane, 1,5,5-trichloro-6,6,6-trifluorohexane, 1,3,6-trichloro-3-trifluoromethylpentane, dichlorotrifluoroctene, and tributylphosphate.

[0092] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least three of 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluoroethane, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluorobutane, 1,5,5-trichloro-6,6,6-trifluorohexane, 1,3,6-trichloro-3-trifluoromethylpentane, dichlorotrifluoroctene, and tributylphosphate.

[0093] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least four of 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluoroethane, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluorobutane, 1,5,5-trichloro-6,6,6-trifluorohexane, 1,3,6-trichloro-3-trifluoromethylpentane, dichlorotrifluoroctene, and tributylphosphate.

[0094] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluoroethane, 1,1,1-trichloro-2,2,2-trifluoroethane, 1-chlorobutane, 1,1-dichloro-1,2,2,2-tetrafluoroethane, 2,2-dichloro-1,1,1-trifluorobutane, 1,5,5-trichloro-6,6,6-trifluorohexane, 1,3,6-trichloro-3-trifluoromethylpentane, dichlorotrifluoroctene, and tributylphosphate.

[0095] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least one isomer of trichlorotrifluorohexane, HCFC-593 isomers, ethylene and CFC-113a and further comprising 114a and/or 363maf and/or 1-chlorobutane and/or tributylphosphate.

[0096] In one embodiment of this disclosure is provided a composition comprising HCFC-353maf, and at least one isomer of trichlorotrifluorohexane, HCFC-593 isomers, ethylene, CFC-113a and further comprising tributylphosphate.

[0097] In one embodiment, this disclosure provides a composition comprising HCFC-353maf and at least one of $\text{CHCl}_2\text{CHClF}$ (HCFC-131), $\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$ (HCFC-343 isomers), dichlorotrifluorobutene (HCFO-1343 isomers), 1-chlorobutene, $\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers, and 1,3-dichlorobutane.

[0098] In one embodiment, this disclosure provides a composition comprising HCFC-353maf and at least two of $\text{CHCl}_2\text{CHClF}$ (HCFC-131), $\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$ (HCFC-343 isomers), dichlorotrifluorobutene (HCFO-1343 isomers), 1-chlorobutene, $\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers, and 1,3-dichlorobutane.

[0099] In one embodiment, this disclosure provides a composition comprising HCFC-353maf and at least three of $\text{CHCl}_2\text{CHClF}$ (HCFC-131), $\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$ (HCFC-343 isomers), dichlorotrifluorobutene (HCFO-1343 isomers), 1-chlorobutene, $\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers, and 1,3-dichlorobutane.

[0100] In one embodiment, this disclosure provides a composition comprising HCFC-353maf and at least four of $\text{CHCl}_2\text{CHClF}$ (HCFC-131), $\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$ (HCFC-343 isomers), dichlorotrifluorobutene (HCFO-1343 isomers), 1-chlorobutene, $\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers, and 1,3-dichlorobutane.

[0101] In one embodiment, this disclosure provides a composition comprising HCFC-353maf, $\text{CHCl}_2\text{CHClF}$ (HCFC-131), $\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$ (HCFC-343 isomers), and dichlorotrifluorobutene (HCFO-1343 isomers).

[0102] In one embodiment, this disclosure provides a composition comprising HCFC-353maf, $\text{CHCl}_2\text{CHClF}$ (HCFC-131), $\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$ (HCFC-343 isomers), and dichlorotrifluorobutene (HCFO-1343 isomers) and further comprises 1-chlorobutene, $\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers, or 1,3-dichlorobutane.

[0103] In one embodiment, this disclosure provides a composition comprising HCFC-353maf, $\text{CHCl}_2\text{CHClF}$ (HCFC-131), $\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$ (HCFC-343 isomers), and dichlorotrifluorobutene (HCFO-1343 isomers) and further comprises 1-chlorobutene, $\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers, and 1,3-dichlorobutane.

[0104] Compounds disclosed herein are provided in Table 1.

TABLE 1

Name	Formula	Compound
2,2,4-trichloro-1,1,1-trifluorobutane	$\text{CH}_2\text{ClCH}_2\text{CCl}_2\text{CF}_3$	HCFC-353maf
ethylene	$\text{CH}_2=\text{CH}_2$	
1,1-dichloro-1,2,2,2-tetrafluoroethane	CF_3CFCl_2	CFC-114a
2,2-dichloro-1,1,1-trifluoroethane	CF_3CHCl_2	HCFC-123
1,1,1-trichloro-2,2,2trifluoroethane	CF_3CCl_3	CFC-113a
1,1,2-trichloro-2-fluoroethane	$\text{CHCl}_2\text{CHClF}$	HCFC-131
tetrachlorotrifluorobutane isomers	$\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$	HCFC-343 isomers
dichlorotrifluorobutene isomers	$\text{C}_4\text{H}_3\text{Cl}_2\text{F}_3$	HCFO-1343 isomers
1-chlorobutane	$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{CH}_3$	
1-chlorobutene	$\text{CHCl}=\text{CHCH}_2\text{CH}_3$	
1,3-dichlorobutane	$\text{CH}_2\text{ClCH}_2\text{CHClCH}_3$	
2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane	$\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_3$	CFC-316maa
2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene	$\text{CF}_3\text{CCl}=\text{CClCF}_3$	CFO-1316mxx
2,2-dichloro-1,1,1-trifluorobutane	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_3$	HCFC-363maf
trichlorotrifluorohexane	$\text{C}_6\text{H}_8\text{Cl}_3\text{F}_3$	HCFC-593 isomers
	$\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$	$\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers
1,5,5-trichloro-6,6,6-trifluorohexane	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	HCFC-593mafff
1,3,6-trichloro-3-trifluoromethylpentane	$\text{CH}_2\text{ClCH}_2\text{CCl}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{Cl}$	HCFC-593syme
	$\text{C}_8\text{H}_{11}\text{Cl}_2\text{F}_3$	$\text{C}_8\text{H}_{11}\text{Cl}_2\text{F}_3$ isomers
1-butanol	$\text{CH}_2\text{OHCH}_2\text{CH}_2\text{CH}_3$	
2-butoxyethanol	$\text{CH}_2\text{OHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	
tributylphosphate	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{P}=\text{O}$	

DESCRIPTION OF THE FIGURE

[0105] Figure 1 provides a flow diagram for a process useful to prepare 2,2,4-trichloro-1,1,1-trifluorobutane according to an embodiment of this invention. In Figure 1, there is provided a reaction system **100** which includes reactor **101** and distillation system downstream of reactor **101**. In the reaction system **100**, reactant ethylene **102** and fresh reactant CFC-113a feed **103** are introduced to reactor **101**. In addition, organic ligand **104** component of the catalyst system described herein is also introduced to reactor **101**. A cooled recycled process stream **110** is also introduced to reactor **101**. Reactor **101** may be pre-loaded with metal component of the catalyst system (iron or copper based), which is not illustrated in Figure 1. While certain reactants (ethylene, fresh and recycled CFC-113a and organic ligand) are illustrated as being separately introduced to reactor **101**, it should be understood that two or more of the reactants can be combined, including combining into a single feed stream along with cooled recycled process stream **110** from metal solids bed **105**.

[0106] The metal component of the catalyst system described herein may be fed from metal bed **105** to reactor **101**. Metal solids bed **105** contains additional metal (iron or copper). The additional metal may be any form of solid, metal (0) or metal salt. In one particular embodiment, the metal bed contains iron (0) which not only serves as a source of metal, but also is able to reduce Fe^{3+} that may be produced in reactor **101** to Fe^{2+} .

[0107] A vent condenser (not shown) may be attached to reactor **101** to remove inert materials. The vent condenser may be operated periodically.

[0108] Process stream **106** exits reactor **101** proceeds through pump **130**. Process stream **106** is split following pump **130** into a first portion **107** and a second portion **108**. First portion **107** of process stream **106** proceeds through heat exchanger **109** to cool first portion **107** of process stream **106**. After cooling first portion **107** of process stream **106** proceeds through metal solids bed **105**, allowing introducing additional metal to the stream, which exits metal solids bed **105** as recycled process stream **110**.

[0109] A second portion **108** of process stream **106** comprising unreacted starting materials, product and byproducts proceeds to first distillation column **112a**. Low boilers are removed overhead from column **112a**, providing separated stream **111**.

“Low boilers” may comprise ethylene and components having a boiling point below the boiling point of ethylene. Separated stream **111** proceeds through heat exchanger **113** to evaporator **114** then condenser **115**. A purge **116** may be removed from evaporator **114**. Purge **116** may comprise undissolved metal, metal chlorides.

[0110] From condenser **115**, a stream of noncondensables is removed at **117** and the condensed stream **118** proceeds to second distillation column **112b** after pump **131**. Noncondensables may comprise nitrogen, ethylene, anhydrous HCl, hydrogen, and low boiling fluorinated compounds.

[0111] In distillation column **112b**, condensed stream **118** is separated into stream **119** comprising CFC-113a and components having a boiling point below HCFC-353maf and a stream **120** comprising HCFC-353maf and components having a boiling point above HCFC-353maf.

[0112] Stream **119** proceeds to third distillation column **112c**, from which CFC-113a is separated from components having a boiling point below HCFC-353maf to provide recycle CFC-113a stream **121**. A purge may be removed from the bottom of third distillation column **112c**.

[0113] In distillation column **112d**, stream **120** comprising HCFC-353maf and components having a boiling point above HCFC-353maf is separated into stream **122** comprising purified HCFC-353maf from the column.

[0114] As illustrated in Figure 1, a purge stream **124** of high boilers is removed from distillation column **112d** and purified stream comprising HCFC-353maf is removed as product stream **122** as final product. The final product comprising HCFC-353maf may be stored in tank **123** for future use, such as, for example, in the manufacture of 3,3,4,4,4-pentafluorobut-1-ene (HFO-1345zf).

[0115] Additional components not shown in Figure 1 may include heat exchangers, pumps, vacuum equipment for distillation columns and evaporator.

[0116] 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.

[0117] The following Examples are provided to illustrate certain aspects of the invention and shall not limit the scope of the appended claims.

EXAMPLES

[0118] 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

[0119] To a 600 ml pressure reactor, equipped with a gas entrainment stirrer, cooling loop, thermocouple well and diptube, was added 8.73 grams of iron wire. The wire was secured to the cooling loop. The reactor was closed and flushed with nitrogen. Then a solution of CFC-113a (504 grams, 2.69 moles) and tributyl phosphate (17.97 grams, 0.0672 moles) was added through diptube of the reactor. The solution was deoxygenated and heated to 95°C. Ethylene gas (28 grams, 1 mole) was then slowly fed by mass flow controller through diptube at a rate such that the pressure did not to exceed 305 psig. After about 4 hours, the ethylene flow was stopped and the pressure was allowed to stabilize below 55 psig. The reactor was then cooled, sampled and analyzed by GC/MS. Results are provided below in Table 2.

TABLE 2

Compound	Chemical Formula	GC Area%
ethylene	$\text{CH}_2=\text{CH}_2$	1.95
CFC-113a	CF_3CCl_3	45.3
HCFC-353maf	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$	43.6
HCFC-593 isomers	$\text{C}_6\text{H}_8\text{Cl}_3\text{F}_3$	0.59
HCFC-593mafff	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0.16
CFO-1316mxx	$\text{CF}_3\text{CCl}=\text{CClCF}_3$	0.30
CFC-316maa	$\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_3$	0.10
Other Compounds		8.00

EXAMPLE 2

[0120] Iron wire (250 grams) was installed inside a 1-gallon C-276 autoclave which was then filled half full of liquid from a previous run. The autoclave was agitated at 1500 rpm and maintained at 105°C internal temperature using an electric heater on the body and an internal cooling coil. During one period of operation, CFC-113a (431 grams/hr) and tributylphosphate (0.159 ml/min) were fed continuously into the autoclave headspace. Ethylene (45 to 48 grams/hr) was continuously added via a submerged dip tube as required to maintain the autoclave internal pressure at 100 psig. Liquid was continuously removed from the bottom of the autoclave as required to maintain the liquid level at 50%. The liquid residence time was about 5 hours. The liquid from the autoclave was collected over 24 hours then analyzed by GC (FID) and is reported as mole %. The run was repeated, and the results of the runs are provided in Table 3.

TABLE 3

Compound	Chemical Formula	Run 1	Run 2
		mole %	
ethylene	$\text{CH}_2=\text{CH}_2$	0.08	0.085
CFC-114a	CF_3CFCl_2	1.955	2.04
HCFC-123	CF_3CHCl_2	0.24	0.23
CFC-113a	CF_3CCl_3	33.415	36.375
HCFC-363maf	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_3$	0.21	0.19
1-chlorobutane	$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{CH}_3$	0.075	0.00
HCFC-353maf	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Cl}$	58.53	56.25
HCFC-593 isomers	$\text{C}_6\text{H}_8\text{Cl}_3\text{F}_3$	0.18	0.14
HCFC-593mafff	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	1.235	1.095
HCFC-593syne	$\text{CH}_2\text{ClCH}_2\text{CCl}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{Cl}$	2.025	1.685
	$\text{C}_8\text{H}_{11}\text{Cl}_2\text{F}_3$	0.04	0.04
tributylphosphate	$\text{C}_{12}\text{H}_{27}\text{O}_4\text{P}$	0.845	0.79
Other compounds		1.16	1.01

EXAMPLE 3

[0121] Example 2 was repeated except ethylene was continuously added via a submerged dip tube as required to maintain the autoclave internal pressure at 125 psig. In comparison to Example 2, conversion of CFC-113a and HCFC-353maf

selectivity were similar (less than 5% difference). Thus, operating at a pressure of 125 psig showed consistently good results.

EXAMPLE 4 – COMPARISON

[0122] Example 2 was repeated except ethylene was continuously added via a submerged dip tube as required to maintain the autoclave internal pressure at 175 psig. In comparison to Example 2, conversion of CFC-113a decreased by about 10% and the HCFC-353maf selectivity decreased by about 20%.

EXAMPLE 5

[0123] A product produced in accordance with Example 2, Run 2, was purified using methods disclosed herein of including distillation. The composition after purification is provided in Table 4.

TABLE 4

Compound	Chemical Formula	GC Area%
HCFC-353maf	$\text{CH}_2\text{ClCH}_2\text{CCl}_2\text{CF}_3$	99.72
HCFO-1343 isomers	$\text{C}_6\text{H}_8\text{Cl}_3\text{F}_3$	0.04
HCFC-131	CH_2FCCl_3	0.03
HCFC-343 isomers	$\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$	0.03
1-chlorobutene	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0.02
1-butanol	$\text{CF}_3\text{CCl}=\text{CClCF}_3$	0.02
$\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers	$\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$	0.01
1,3-dichlorobutane	$\text{CH}_2\text{ClCH}_2\text{CHClCH}_3$	0.01
2-butoxyethanol	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OH}$	< 0.01
Other Compounds		0.11

CLAIMS

What is claimed is:

1. A process for preparing 2,2,4-trichloro-1,1,1-trifluorobutane comprising contacting ethylene with 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a) in the presence a catalyst system comprising a metal and an organic ligand in a reactor to obtain a process mixture comprising 2,2,4-trichloro-1,1,1-trifluorobutane (HCFC-353maf), wherein the process is performed at a temperature of about 80 to about 150°C, and a pressure of about 50 to 150 psig.
2. The process of claim 1, wherein the process is performed at a conversion of 80% or less of the 1,1,1-trichloro-2,2,2-trifluoroethane.
3. The process of claim 2 wherein the process is performed at a conversion of 30-80% of the 1,1,1-trichloro-2,2,2-trifluoroethane.
4. The process of claim 2 wherein the process is performed at a conversion of 40-70% of the 1,1,1-trichloro-2,2,2-trifluoroethane.
5. The process of claim 2 wherein the process is performed at a conversion of 50-70% of the 1,1,1-trichloro-2,2,2-trifluoroethane.
6. The process of claim 1 wherein the metal of the catalyst system comprises iron or copper.
7. The process of claim 6 wherein the metal comprises iron.
8. The process of claim 6 wherein the metal comprises copper.
9. The process of claim 7 wherein the metal is or comprises iron powder, iron wire, iron screen or iron turnings.
10. The process of claim 7 wherein the metal comprises an iron salt.
11. The process of claim 10, wherein the iron salt is ferric chloride or ferrous chloride or a combination thereof.
12. The process of any of claims 9-11, wherein the organic ligand is an organophosphorus compound.

13. The process of claim 12, wherein the organic ligand is selected from the group consisting of phosphine, phosphinite, phosphonate, phosphite, a phosphine oxide or a phosphate, and mixtures of two or more thereof.
14. The process of claim 13 wherein the organic ligand comprises one or more alkyl or aryl groups.
15. The process of claim 14, wherein the organic ligand is a compound having a structural formula of $PR_1R_2R_3$, where each R_1 , R_2 , and R_3 is independently aryl, alkyl, aryloxy or alkoxy.
16. The process of claim 14, wherein the organic ligand is a compound having a structural formula of $O=PR_1R_2R_3$ where each R_1 , R_2 , and R_3 is independently aryloxy or alkoxy.
17. The process of claim 13 wherein the process is performed in the presence a catalyst system comprising iron and an alkyl phosphate, wherein the alkyl phosphate is a monoalkyl phosphate, a dialkyl phosphate or a trialkyl phosphate or a combination of two or more thereof.
18. The process of claim 17 wherein the alkyl phosphate is a trialkyl phosphate.
19. The process of claim 18 wherein the trialkyl phosphate is a tris(C1-6 alkyl)phosphate.
20. The process of claim 19 wherein the trialkyl phosphate is tributyl phosphate.
21. The process of claim 13 wherein the organic ligand comprises a phosphine.
22. The process of claim 21 wherein the phosphine comprises an alkylphosphine or arylphosphine.
23. The process of claim 22 wherein the phosphine ligand is chosen from triphenyl phosphine and tributyl phosphine.
24. The process of claim 8, wherein the organic ligand of the catalyst system is a nitrogen-containing organic ligand.
25. The process of claim 24, wherein the organic ligand is selected from the group consisting of an amine, a nitrile, an amide, a thiamide, and mixtures of two or more thereof.

26. The process of claim 25, wherein the organic ligand is an amine, a nitrile, or an amide.
27. The process of claim 26, wherein the organic ligand is an amine, selected from the group consisting of tert-butylamine, *n*-butylamine, sec-butylamine, 2-propylamine, benzylamine, tri-*n*-butylamine, ethanolamine, piperidine and pyridine.
28. The process of claim 27, wherein the organic ligand is tert-butylamine.
29. The process of claim 26, wherein the organic ligand is a nitrile, selected from the group consisting of acetonitrile, propionitrile, *n*-butyronitrile, benzonitrile, and phenylacetonitrile.
30. The process of claim 29, wherein the organic ligand is acetonitrile.
31. The process of claim 26, wherein the organic ligand is an amide, selected from the group consisting of hexamethylphosphoramide and dimethylformamide.
32. The process of claim 31, wherein the amide is hexamethylphosphoramide.
33. The process of any of claims 1-32, wherein the temperature is in the range of about 85 to about 125°C.
34. The process of any of claims 1-32, wherein the temperature is in the range of about 95 to about 115°C.
35. The process of any of claims 1-34, wherein the concentration of the metal of the catalyst system ranges from 500 ppmw to 2500 ppmw based on ICP analysis of the process mixture.
36. The process of claim 35 wherein the concentration of the metal of the catalyst system ranges from 750 ppmw to 2000 ppmw based on ICP analysis of the process mixture.
37. The process of claim 35 wherein the concentration of the metal of the catalyst system ranges from 800 ppmw to 1800 ppmw based on ICP analysis of the process mixture.

38. The process of claim 35 wherein the concentration of the metal of the catalyst system ranges from 1000 ppmw to 1500 ppmw based on ICP analysis of the process mixture.
39. The process of claim 35 wherein the concentration of the metal of the catalyst system ranges from 1200 ppmw to 1400 ppmw based on ICP analysis of the process mixture.
40. The process of any of claims 30-34 wherein the organic ligand comprises a trialkyl phosphate or phosphine ligand.
41. The process of claim 35 wherein the organic ligand comprises a trialkyl phosphate.
42. The process of claim 41 wherein the trialkyl phosphate is a tris(C1-6 alkyl)phosphate.
43. The process of claim 42 wherein the trialkyl phosphate is tributyl phosphate.
44. The process of claim 35 wherein the organic ligand comprises a phosphine.
45. The process of claim 44 wherein the phosphine comprises an alkylphosphine or arylphosphine.
46. The process of claim 45 wherein the phosphine ligand is chosen from triphenyl phosphine and tributyl phosphine.
47. A composition comprising 2,2,4-trichloro-1,1,1-trifluorobutane, and at least one additional compound chosen from ethylene, CF₃CCl₃ (CFC-113a), CF₃CFCl₂ (CFC-114a), CF₃CHCl₂ (HCFC-123), CHCl₂CHClF (HCFC-131), C₄H₃F₃Cl₄ isomers (HCFC-343 isomers), CF₃CCl₂CH₂CH₃ (HCFC-363maf), 1-chlorobutane, 1-chlorobutene, 1,3-dichlorobutane, CF₃CCl₂CCl₂CF₃ (CFC-316maa), CF₃CCl=CClCF₃ (CFO-1316mxx), C₆H₈Cl₃F₃ (trichlorotrifluorohexane isomers, HCFC-593 isomers), dichlorotrifluorooctene isomers (C₈H₁₁Cl₂F₃ isomers), dichlorotrifluorobutene isomers (HCFO-1343 isomers), C₆H₂Cl₃F₇ isomers, 1-butanol, 2-butoxyethanol and organic ligand.
48. The composition of claim 47 comprising ethylene and CFC-113a.
49. The composition of claim 48 further comprising CFC-114a.

50. The composition of any of claims 47-49 further comprising HCFC-363maf.
51. The composition of any of claims 47-49, wherein the composition comprises 1-chlorobutane.
52. The composition of any of claims 47-49, wherein the composition comprises dichlorotrifluorooctene isomers.
53. The composition of any of claims 47-49, wherein the composition comprises organic ligand.
54. The composition of claim 53 wherein the organic ligand is tributylphosphate.
55. A composition comprising 2,2,4-trichloro-1,1,1-trifluorobutane, and at least one isomer of trichlorotrifluorohexane isomers.
56. The composition of claim 55, wherein the composition comprises 1,1,1-trifluoro-2,2,6-trichlorohexane.
57. The composition of claim 56, wherein the composition comprises 1,3,6-trichloro-3-trifluoromethylpentane.
58. The composition of any of claims 55-57 further comprising ethylene and CFC-113a.
59. The composition of any of claims 55-58 further comprising CFC-114a.
60. The composition of any of claims 55-59 further comprising HCFC-363maf.
61. The composition of any of claims 55-60 further comprising 1-chlorobutane.
62. The composition of any of claims 55-61 further comprising dichlorotrifluorooctene isomers.
63. The composition of any of claims 55-62 further comprising tributylphosphate.
64. A composition comprising HCFC-353maf and at least one of $\text{CHCl}_2\text{CHClF}$ (HCFC-131), $\text{C}_4\text{H}_3\text{F}_3\text{Cl}_4$ isomers (HCFC-343 isomers), dichlorotrifluorobutene isomers (HCFO-1343 isomers), 1-chlorobutene, $\text{C}_6\text{H}_2\text{Cl}_3\text{F}_7$ isomers, and 1,3-dichlorobutane.