

TITLE OF THE INVENTION

COMPOSITIONS OF AND PROCESSES FOR 3,5,5-TRICHLORO-1,1,1,2,2,6,6,6-OCTAFLUOROHXANE

FIELD

[0001] The present application relates to compositions comprising fluorinated compounds, processes of preparing such compositions and their use, particularly 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd, $\text{CF}_3\text{CF}_2\text{CHClCH}_2\text{CCl}_2\text{CF}_3$).

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 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd, $\text{CF}_3\text{CF}_2\text{CHClCH}_2\text{CCl}_2\text{CF}_3$), processes of preparing such compositions and their use.

[0005] The present invention provides a process for preparing HCFC-548mafd comprising contacting 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a) with 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf) in the presence of a catalyst system comprising a metal and an organic ligand in a reactor, to obtain a process mixture comprising HCFC-548mafd.

[0006] In one embodiment, the process is performed in the presence of an excess of CFC-113a and the process mixture comprises HCFC-548mafd 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 85°C to about 165°C, preferably about 125°C to about 155°C, more preferably in the range of 135°C-150°C, and a pressure of about 50 psig to 170 psig or 100 psig to 165 psig or preferably 125 psig to 155 psig or more preferably 135 psig to 150 psig.

[0008] The present invention also provides a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, and at least one additional compound chosen from 3,3,4,4,4-pentafluoro-1-butene ($\text{CH}_2=\text{CHCF}_2\text{CF}_3$, HFO-1345zf), 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-2,2,2-trifluoroethane (CF_3CCl_3 , CFC-113a), 1-chlorobutane, 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), $\text{C}_{10}\text{H}_6\text{Cl}_3\text{F}_{13}$ isomers, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene ($\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}=\text{CFCF}_3$, HCFO-1547mafz), triphenylphosphine and tributylphosphate.

BRIEF DESCRIPTION OF THE FIGURE

[0009] Figure 1 provides a flow diagram for a process useful to prepare HCFC-548mafd according to an embodiment of this invention.

DETAILED DESCRIPTION

GENERAL TERMS

[0010] Compounds may be referred to herein by the compound name (e.g., 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane) or ASHRAE designation (e.g., HCFC-

548mafd) or chemical formula (e.g., $\text{CF}_3\text{CF}_2\text{CHClCH}_2\text{CCl}_2\text{CF}_3$) 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.

[0011] 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.

[0012] 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-1316mzz and Z-CFO-1316mxx, whereas specific isomers are identified as “E-CFO-1316mxx” and “Z-CFO-1316mxx”.

[0013] 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).

[0014] 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.

[0015] 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".

[0016] 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."

[0017] 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.

[0018] 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.

[0019] 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.

[0020] As used herein, a “catalyst system” comprises a metal and an organic ligand. The catalyst system promotes the addition of alkyl halides to olefins. By “promotes the addition of alkyl halides to olefins” is meant herein the catalyst system catalyzes or initiates the reaction an alkyl halide with an olefin.

[0021] 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.

[0022] 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.

[0023] The present invention relates broadly to compositions comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd, $\text{CF}_3\text{CF}_2\text{CHClCH}_2\text{CCl}_2\text{CF}_3$), and processes of preparing such compositions and their use.

PROCESS DESCRIPTION

[0024] The present invention describes processes for production of a mixture or composition comprising, consisting of, or consisting essentially of HCFC-548mafd ($\text{CF}_3\text{CF}_2\text{CHClCH}_2\text{CCl}_2\text{CF}_3$, 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane), and one or more additional compounds.

[0025] In one embodiment, the present invention provides a process for preparing HCFC-548mafd comprising contacting CFC-113a with HFO-1345zf in the presence of a catalyst system comprising a metal and an organic ligand in a reactor, to obtain a process mixture comprising HCFC-548mafd, wherein the process is performed at a temperature of about 85°C to about 165°C , preferably about 125°C to about 155°C , more preferably in the range of 135°C - 150°C , a pressure of about 50 psig to 170 psig or 100 psig to 165 psig or 125 psig to 155 psig or 135 psig to 150 psig.

[0026] In one embodiment for a process for preparing 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, the process is performed at a conversion of less than 80% of 1,1,1-trichloro-2,2,2-trifluoroethane. In one embodiment, the process is performed at a conversion of 30-80% of 1,1,1-trichloro-2,2,2-trifluoroethane. In one embodiment, the process is performed at a conversion of 40-70% of 1,1,1-trichloro-2,2,2-trifluoroethane. In one embodiment, the process is performed at a conversion of 50-70% of the 1,1,1-trichloro-2,2,2-trifluoroethane.

[0027] In one embodiment, the process of this invention is performed in the presence of an excess of 1,1,1-trichloro-2,2,2-trifluoroethane.

[0028] When the process of this invention is performed at a conversion of 1,1,1-trichloro-2,2,2-trifluoroethane of less than 100% such as from 30-80% or when an excess of 1,1,1-trichloro-2,2,2-trifluoroethane is used, the process mixture produced comprises HCFC-548mafd and 1,1,1-trichloro-2,2,2-trifluoroethane. In these embodiments, the 1,1,1-trichloro-2,2,2-trifluoroethane present in the process mixture can be and is preferably separated and recycled to the process.

[0029] In certain embodiments, the metal 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.

[0030] 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.

[0031] 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 is or comprises ferric chloride. In one embodiment, the metal is or comprises ferrous chloride. In one embodiment, the metal is or comprises ferric chloride and ferrous chloride.

[0032] In one embodiment of the process of this invention, the metal is or comprises copper. When the metal is copper, the copper may be in the form of a copper salt. The copper salt may be selected from the group consisting of one or more of copper (I) chloride, copper (II), 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.

[0033] The organic ligand can be an organophosphorus compound or an organonitrogen compound.

[0034] 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.

[0035] 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. The organophosphorus compound may comprise one or more alkyl or aryl groups. An example of the organophosphorus compound includes compounds having a structural formula as follows: $PR_1R_2R_3$ where R_1 , R_2 , and R_3 independently selected to be aryl, alkyl, aryloxy or alkoxy. Another example of the organophosphorus compound includes compounds having a structural formula as follows: $OPR_1R_2R_3$ where R_1 , R_2 , and R_3 are independently selected to be aryl, aryloxy or alkyl or alkoxy.

[0036] 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.

[0037] In one embodiment, the metal comprises iron and the organic ligand comprises a trialkyl phosphate or trialkyl phosphine or triaryl phosphine.

[0038] In one embodiment of the process of this invention, the process is performed in the presence of iron as the metal and a trialkyl phosphate. In one embodiment, the metal is iron and the trialkyl phosphate is a tris(C_{1-6} alkyl)phosphate. In one embodiment, the metal is iron and the trialkyl phosphate is tributyl phosphate.

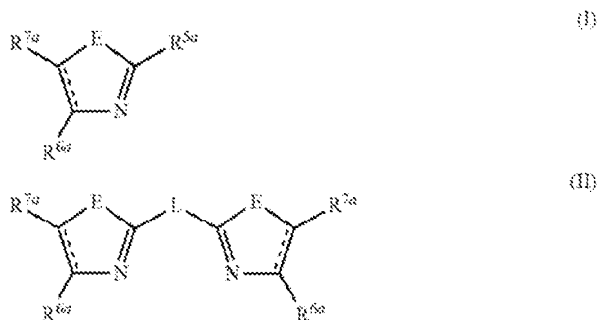
[0039] In one embodiment of the process of this invention, the metal is iron and the organic ligand comprises a phosphine. In one embodiment, the phosphine comprises an alkylphosphine or arylphosphine. In one embodiment, the phosphine is

chosen from tributyl phosphine and triphenylphosphine. In one embodiment, the organic ligand is tributyl phosphine. In one embodiment, the organic ligand is triphenylphosphine.

[0040] In one embodiment of the process of this invention, the process is performed in the presence of a catalyst system wherein the metal is copper and the organic ligand is an organonitrogen compound.

[0041] When the metal is copper, the organic ligand 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.

[0042] 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.

[0043] In one embodiment of the process of this invention, the metal is copper and the organic ligand comprises an organonitrogen compound. In one embodiment of the process of this invention, the metal is or comprises copper and the organonitrogen compound is an amine. In one embodiment of the process of this invention, the metal of the catalyst system comprises copper and the organic ligand is an amine.

[0044] In certain embodiments, the concentration of metal in the process mixture is based on ICP analysis of the process mixture. In one embodiment of this invention, the concentration of the metal ranges from 300 ppmw to 3000 ppmw of metal and the metal is iron or copper. In one embodiment, the metal is iron and the concentration of the metal ranges from 500 ppmw to 2500 ppmw. In one embodiment, the metal is copper and the concentration of the metal ranges from 500 ppmw to 2500 ppmw. In one embodiment of this invention, the concentration of the metal ranges from 750 ppmw to 2000 ppmw and the metal comprises iron or copper. In one embodiment, the metal comprises iron and the concentration of the metal ranges from 750 ppmw to 2000 ppmw. In one embodiment, the metal comprises copper and the concentration of the metal ranges from 750 ppmw to 2000 ppmw.

[0045] In one embodiment of this invention, the concentration of the metal ranges from 800 ppmw to 1800 ppmw. In one embodiment, the metal comprises iron and the concentration of the metal ranges from 800 ppmw to 1800 ppmw. In one

embodiment, the metal comprises copper and the concentration of the metal ranges from 800 ppmw to 1800 ppmw. In one embodiment of this invention, the concentration of the metal ranges from 1000 ppmw to 1500 ppmw. In one embodiment, the metal comprises iron and the concentration of the metal ranges from 1000 ppmw to 1500 ppmw. In one embodiment, the metal comprises copper and the concentration of the metal ranges from 1000 ppmw to 1500 ppmw. In one embodiment of this invention, the concentration of the metal ranges from 1200 ppmw to 1400 ppmw. In one embodiment, the metal comprises iron and the concentration of the metal ranges from 1200 ppmw to 1400 ppmw.. In one embodiment, the metal comprises copper and the concentration of the metal ranges from 1200 ppmw to 1400 ppmw.

[0046] In one embodiment of this invention, the concentration of the metal ranges from 1000 ppmw to 1500 ppmw. In one embodiment, the metal is or comprises iron and the concentration of the metal ranges from 1000 ppmw to 1500 ppmw. In one embodiment, the metal is or comprises copper and the concentration of the catalyst ranges from 1000 ppmw to 1500 ppmw.

[0047] In one embodiment of this invention, the concentration of the metal ranges from 1200 ppmw to 1400 ppmw. In one embodiment, the metal of the catalyst system comprises iron and the concentration of the metal ranges from 1200 ppmw to 1400 ppmw.. In one embodiment, the metal of the catalyst system comprises copper and the concentration of the metal ranges from 1200 ppmw to 1400 ppmw..

[0048] In one embodiment of this invention, the concentration of the metal 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 comprises a trialkyl phosphate. In one embodiment, the organic ligand comprises a trialkyl phosphate. In one embodiment, the organic ligand comprises a trialkyl phosphate, and the trialkyl phosphate is a tri(C₁₋₆ alkyl)phosphate. In one embodiment, the tri(C₁₋₆ alkyl)phosphate is tributyl phosphate and the metal of the catalyst system comprises iron. In one embodiment of this invention, the concentration of the metal 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 comprises a phosphine. In one embodiment, the

phosphine comprises an alkylphosphine or arylphosphine. In one embodiment, the phosphine is chosen from triphenylphosphine and tributyl phosphine. In one embodiment, the phosphine is triphenylphosphine and the metal comprises iron. In one embodiment, the phosphine is tributyl phosphine and the metal comprises iron.

[0049] In one embodiment the process is performed with a molar excess of 1,1,1-trichloro-2,2,2-trifluoroethane. A molar excess of molar excess of 1,1,1-trichloro-2,2,2-trifluoroethane used is based on 1 molar equivalent of HFO-1345zf, 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 HFO-1345zf.

[0050] In one embodiment the process of this invention comprises contacting 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a) with HFO-1345zf in the presence of a catalyst system comprising a metal and an organic ligand to obtain a process mixture comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, wherein the process is performed at a temperature of about 100 to about 165°C, preferably about 125 to about 155°C, more preferably in the range of 135-150°C, and a pressure of about 50 psig to 170 psig or 100 psig to 165 psig or 125 psig to 155 psig or 135 psig to 150 psig.

[0051] In one embodiment, the catalyst is iron and the process is performed at a temperature of about 125 to about 155°C. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a temperature of about 125 to about 155°C. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a temperature of about 125 to about 155°C and at a pressure of 100 psig to 165 psig.

[0052] In one embodiment, the catalyst is iron and the process is performed at a temperature in the range of 135-150°C. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a temperature of in the range of 135-150°C. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a temperature of in the range of 135-150°C and at a pressure of 100 psig to 165 psig.

[0053] In one embodiment, the catalyst is iron and the process is performed at a pressure of about 50 psig to 170 psig. In one embodiment, the catalyst is iron, the

organic ligand is tributylphosphate, and the process is performed at a pressure of about 50 psig to 170 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 50 psig to 170 psig and at a temperature of about 125 to about 155°C.

[0054] In one embodiment, the catalyst is iron and the process is performed at a pressure of about 100 psig to 165 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 100 psig to 165 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 100 psig to 165 psig and at a temperature of about 125 to about 155°C.

[0055] In one embodiment, the catalyst is iron and the process is performed at a pressure of about 125 psig to 155 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 125 psig to 155 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 125 psig to 155 psig and at a temperature of about 125 to about 155°C.

[0056] In one embodiment, the catalyst is iron and the process is performed at a pressure of about 135 psig to 150 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 135 psig to 150 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 135 psig to 150 psig and at a temperature of about 125 to about 155°C.

[0057] In one embodiment, the catalyst is iron and the process is performed at a pressure of about 135 psig to 150 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 135 psig to 150 psig. In one embodiment, the catalyst is iron, the organic ligand is tributylphosphate, and the process is performed at a pressure of about 135 psig to 150 psig and at a temperature in the range of 135-150°C.

[0058] 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 HFO-1345zf 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.

[0059] 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 /condenser to facilitate separating reactants, components of the catalyst system, and by-products from the reactor process mixture.

[0060] 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.

[0061] 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 HFO-1345zf.

[0062] 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-548mafd) from the remaining process mixture.

[0063] For example, in one embodiment, the distillation system comprises a distillation column to remove compounds having boiling points below CFC-113a 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-548mafd.

[0064] 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-548mafd.

[0065] A final product of the distillation system is a purified HCFC-548mafd product.

[0066] The purified HCFC-548mafd product may be used, for example, in manufacture of other fluorochemicals, including, for example, *E*-1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene (*E*-HFO-153-10mczz).

COMPOSITION

[0067] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd), and at least one additional compound chosen from 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf), 1,1-dichloro-1,2,2,2-tetrafluoroethane (CFC-114a), 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a), 1-chlorobutane, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane (CFC-316maa), 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (CFO-1316mxx), C₁₀H₆Cl₃F₁₃ isomers, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz), triphenylphosphine and tributylphosphate.

[0068] In one embodiment of this disclosure is provided a composition comprising HCFC-548mafd, HFO-1345zf and CFC-113a. In one embodiment, this composition further comprises CFC-114a. In one embodiment, this composition further comprises HCFO-1547mafz.

[0069] In one embodiment of this disclosure is provided a composition comprising HCFC-548mafd, HFO-1345zf and CFC-113a and further comprising CFC-114a.

[0070] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, HFO-1345zf and CFC-113a and further comprising CFC-114a or 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz).

[0071] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, 2,2,3,3-tetrachloro-1,1,1,4,4,4-

hexafluorobutane (CFC-316maa), 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (CFO-1316mxx).

[0072] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, at least one additional compound chosen from 3,3,4,4,4-pentafluoro-1-butene, 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, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane, 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, trichlorotriskafluorodecane, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene, 1-chlorobutane.

[0073] In one embodiment, a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, 3,3,4,4,4-pentafluoro-1-butene, 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, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane, 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, trichlorotriskafluorodecane, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene, 1-chlorobutane.

[0074] The composition of claim 53 wherein the composition comprises 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene.

[0075] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, HFO-1345zf and CFC-113a and further comprising CFC-114a and/or 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz) and/or 1-chlorobutane.

[0076] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, HFO-1345zf and CFC-113a and further comprising CFC-114a, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz), and 1-chlorobutane.

[0077] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, HFO-1345zf and CFC-113a and further comprising 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz) and/or 1-chlorobutane and tributylphosphate.

[0078] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene and further comprising HFO-1345zf and 113a.

[0079] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene, HFO-1345zf and CFC-113a and further comprising CFC-114a.

[0080] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene, HFO-1345zf and CFC-113a and further comprising CFC-114a and/or 1-chlorobutane.

[0081] In one embodiment of this disclosure is provided a composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene, HFO-1345zf, CFC-113a and further comprising tributylphosphate.

[0082] Compounds disclosed herein are provided in Table 1.

TABLE 1

Name	Formula	Compound
3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane	$\text{CF}_3\text{CF}_2\text{CHClCH}_2\text{CCl}_2\text{CF}_3$	HCFC-548mafd
3,3,4,4,4-pentafluoro-1-butene	$\text{CH}_2=\text{CHCF}_2\text{CF}_3$	HFO-1345zf
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-2,2,2-trifluoroethane	CF_3CCl_3	CFC-113a
1-chlorobutane	$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{CH}_3$	
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

Name	Formula	Compound
	$C_{10}H_6Cl_3F_{13}$	$C_{10}H_6Cl_3F_{13}$ isomers
5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene	$CF_3CCl_2CH_2CH=CFCF_3$	HCFO-1547mafz
1-chlorobutane	$CH_2ClCH_2CH_2CH_3$	
tributylphosphate	$(CH_3CH_2CH_2CH_2O)_3PO$	
triphenylphosphine	$P(C_6H_5)_3$	

DESCRIPTION OF THE FIGURE

[0083] Figure 1 provides a flow diagram for a process useful to prepare HCFC-548mafd according to an embodiment of this invention. In Figure 1, there is provided a reaction system **100** which includes reactor **101** and a distillation system downstream of reactor **101**. In this system, reactant HFO-1345zf feed **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**. Recycled process stream **113** is also introduced to reactor **101**. Reactor **101** contains catalyst system (iron- or copper-based), which is not illustrated in Figure 1. Metal is fed from bed **105** to reactor **101** along with cooled recycled process stream **110**. While certain reactants (HFO-1345zf, 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**.

[0084] The metal component of the catalyst system described herein may be fed from metal solids 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 solids bed **105** 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+} .

[0085] A vent condenser may be attached to reactor **101** to remove inert materials, such as nitrogen.

[0086] 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 cooled recycled process stream 110, which includes unreacted reactant (CFC-113a and HFO-1345zf), as well as a portion of the catalyst system.

[0087] A second portion 108 of process stream 106 comprising reactants (CFC-113a and HFO-1345zf), product (HCFC-548mafd) and byproducts proceeds to first distillation column 112a. An overhead stream 111 is removed. The overhead stream 111 may comprise, for example, noncondensable gases, such as nitrogen or anhydrous HCl. A liquid distillate stream is removed from column 112a and recycled to reactor 101 as cooled recycled process stream 113. Cooled recycled process stream 113 comprises reactants (CFC-113a and HFO-1345zf). A separated stream 114 is taken from the bottom of column 112a. Separated stream 114 proceeds through heat exchanger 115 to evaporator 116 then condenser 117. A purge 118 may be removed from evaporator 116.

[0088] From condenser 117, an overhead stream 119 is removed. Overhead stream 119 comprises inert gases such as N₂, residual reactants such as HFO-1345zf, or other impurities. A condensed stream 120 proceeds from condenser 117 through pump 131 to second distillation column 112b.

[0089] In distillation column 112b, condensed stream 120 is separated into stream 121 comprising CFC-113a and components having a boiling point below HCFC-548mafd and stream 122 comprising HCFC-548mafd and components having a boiling point above HCFC-548mafd.

[0090] Stream 121 proceeds to third distillation column 112c, in which CFC-113a is separated from components having a boiling point below HCFC-548mafd to provide recycle CFC-113a stream 123. A purge may be removed from both the top and the bottom of third distillation column 112c. As illustrated, purge stream 124, may comprise, among others, HFC-123. As illustrated, purge stream 125 may comprise CFC-113.

[0091] In distillation column **112d**, stream **122** comprising HCFC-548mafd and components having a boiling point above HCFC-548mafd is separated into stream **126** comprising purified HCFC-548mafd from column **112d**.

[0092] As illustrated in Figure 1, a purge stream **128** may be removed from distillation column **112d** and purified stream comprising HCFC-548mafd is removed as product stream **126** as final product. The final product comprising HCFC-548mafd may be stored in tank **127** for future or immediate use in manufacture of 1,1,1,2,2,5,5,6,6-decafluoro-3-hexene (HFO-153-10mczz).

[0093] Additional components not shown in Figure 1 may include purge lines, heat exchangers, pumps, and vacuum equipment for distillation columns.

[0094] 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.

EXAMPLES

Example 1. Synthesis of 3,5,5-Trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)

[0095] To a dry 400 ml shaker tube was added 9.56 g of iron powder, 4.25 g of iron trichloride, 18.23 g of triphenylphosphine, and 343 g of R113a. The solution was degassed with N₂ pressure/vacuum sweep. While under vacuum, the tube was placed in dry ice and 100 g of HFO-1345zf was added. The tube was heated to 110°C until pressure stabilized. The reactor was cooled, unloaded, and the reaction mixture was analyzed by GC/MS (FID). Results are provided in Table 2.

[0096]

TABLE 2

Chemical Name	Formula	GC Area %
3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf)	$\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$	19.2648%
1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a)	CF_3CCl_3	28.0933%
2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (CFO-1316mxx)	$\text{CF}_3\text{CCl}=\text{CClCF}_3$	0.1670%
2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane (CFC-316maa)	$\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_3$	0.0613%
1-chlorobutane	$\text{C}_4\text{H}_9\text{Cl}$	1.3676%
5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz)	$\text{CF}_3\text{CCl}_2\text{CH}_2\text{CH}=\text{CFCF}_3$	2.6030%
3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)	$\text{CF}_3\text{CF}_2\text{CHClCH}_2\text{CCl}_2\text{CF}_3$	42.3580%
triphenylphosphine	$\text{P}(\text{C}_6\text{H}_5)_3$	1.5645%
Other compounds		4.4818%

Example 2. Purification of 3,5,5-Trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)

The product from Example 1 is purified according to methods disclosed herein to provide a product comprising the composition disclosed in Table 3.

TABLE 3

Chemical Name	GC Area %
5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz)	0.2500%
3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)	99.5000%
Other compounds	0.2500%

Example 3. Synthesis of 3,5,5-Trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)

[0097] Iron wire was added to a 1-gallon C-276 autoclave and secured to an internal cooling coil. The autoclave was pre-charged with the liquid from a previous run, which produced 548mafd. The autoclave was agitated at 1500 rpm and heated to a 150°C internal temperature using an electric heater on the body and an internal cooling coil. CFC-113a (329.8 g/hr) and tributylphosphate (9.7 g/hr) were continuously fed into the autoclave headspace. HFO-1345zf (203.7 g/hr average) was fed to the autoclave through a dip tube as required to maintain the pressure at 165 psig. Liquid was taken off the bottom of the autoclave as required to maintain the autoclave liquid level at about 75% full. The liquid residence time was 5.6 hours. The liquid from the autoclave was collected for over 24 hours then analyzed by GC. The CFC-113a conversion was 61.7% and the HFO-1345zf conversion was 77.1%. The CFC-113a selectivity to 548mafd was 90.9% and the selectivity of HFO-1345zf to 548mafd was 89.9%. The autoclave productivity to 548mafd was 135.5 g/liter-hr. In addition to CFC-113a, HFO-1345zf and HCFC-548mafd, the composition further comprised C₁₀H₆Cl₃F₁₃ isomers, CF₃CCl₂CH₂CH=CFCF₃ (HCFO-1547mafz), and 1-chlorobutane.

Example 4. Synthesis of 3,5,5-Trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)

[0098] A 1-gallon C-276 autoclave containing immobilized iron wire was pre-charged with the liquid from a previous run. The autoclave was agitated at 1500 rpm and heated to 150°C internal temperature using an electric heater on the body. CFC-113a (284.4 g/hr) and TBP (8.4 g/hr) were continuously fed into the autoclave headspace. HFO-1345zf (154.0 g/hr average) was fed into the autoclave through a dip tube as required to maintain the pressure at 145 psig. Liquid was taken off the bottom of the autoclave as required to maintain the autoclave liquid level at about 80% full. The liquid residence time was 7.2 hours. The liquid from the autoclave was collected for over 24 hours then analyzed by GC. The 113a conversion was 56.3% and the HFO-1345zf conversion was 78.6%. The 113a selectivity to 548mafd was 92.0% and the HFO-1345zf selectivity to 548mafd was 92.8%. The autoclave productivity to HCFC-548mafd was 103.5 g/liter-hr.

Comparison Example - Synthesis of 3,5,5-Trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)

[0099] Example 4 was repeated except HFO-1345zf was continuously added via a submerged dip tube as required to maintain the autoclave internal pressure at 175 psig. In comparison to Example 4, conversion of CFC-113a decreased by about 10% and the 548mafd selectivity decreased by about 20%. Thus, lower pressure showed improved results.

Example 5. Synthesis of 3,5,5-Trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)

[0100] Iron wire was added to a 1-gallon C-276 autoclave and secured to the internal cooling coil. The autoclave was pre-charged with the liquid from a previous run. The autoclave was agitated at 1500 rpm and heated to a 140°C internal temperature using an electric heater on the body and an internal cooling coil. CFC-113a (258.4 g/hr) and TBP (6.3 g/hr) were continuously fed into the autoclave headspace. HFO-1345zf (122.4 g/hr average) was fed to the autoclave through a dip tube as required to maintain the pressure at 135 psig. Liquid was taken off the bottom of the autoclave as required to maintain the autoclave liquid level at about 75% full. The liquid residence time was 8.1 hours. The autoclave was operated for over 4 days then a liquid sample was collected and analyzed by GC. The CFC-113a conversion was 51.1% and the HFO-1345zf conversion was 78.4%. The CFC-113a selectivity to HCFC-548mafd was 90.2%, and the selectivity of HFO-1345zf to HCFC-548mafd was 95.3%. The autoclave productivity to 548mafd was 87.8 g/liter-hr.

Example 6. Synthesis of 3,5,5-Trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd)

[0101] Iron wire (258 grams) was installed into a 1-gallon C-276 autoclave which was then filled with liquid from the previous run. The autoclave was agitated at 1500 rpm and maintained at 140°C internal temperature using an electric heater on the body and an internal cooling coil. During one period of operation, CFC-113a (179.4 g/hr) and TBP (5.6 g/hr) were fed continuously into the autoclave headspace. HFO-1345zf (88.6 g/hr) was continuously added via a submerged dip tube as required to

maintain the autoclave internal pressure at 135 psig. Liquid was continuously removed from the bottom of the autoclave as required to maintain a liquid volume of 2.4 liters. The reactor was allowed to reach steady state conditions. The liquid composition in the autoclave was 8.6 mol% HFO-1345zf, 39.6 mol% CFC-113a, 43.4 mol% HCFC-548mafd and 8.4 mol% other compounds. The CFC-113a conversion was 54.2% and the HFO-1345zf conversion was 84.6%. Selectivity from CFC-113a to HCFC-548mafd was 92.7% and selectivity from HFO-1345zf to HCFC-548mafd was 92.1%. Reactor productivity was 66.3 g 548mafd / liter-hr.

CLAIMS

What is claimed is:

1. A process for preparing 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane comprising contacting 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a) with 3,3,4,4,4-pentafluoro-1-butene in the presence a catalyst system comprising a metal and an organic ligand in a reactor, to obtain a process mixture comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane, wherein the process is performed at a temperature of about the process is performed at a temperature of about 100 to about 165°C.
2. The process of claim 1 wherein the temperature is about 125 to about 155°C.
3. 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 (CFC-113a).
4. 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.
5. 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.
6. 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.
7. The process of claim 1 wherein the metal comprises iron or copper.
8. The process of claim 6 wherein the metal comprises iron.
9. The process of claim 6 wherein the metal comprises copper.
10. The process of claim 7 wherein the catalyst is or comprises iron powder, iron wire, iron screen or iron turnings.
11. The process of claim 7 wherein the catalyst comprises an iron salt.
12. The process of claim 11, wherein the iron salt is ferric chloride or ferrous chloride or a combination thereof.

13. The process of any of claims 9-12, 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 a trialkyl phosphate or phosphine ligand.
15. The process of claim 13 wherein the process is performed in the presence of the catalyst system wherein the organic ligand is a trialkyl phosphate.
16. The process of claim 13 wherein the trialkyl phosphate is a tri(C1-6 alkyl)phosphate.
17. The process of claim 13 wherein the trialkyl phosphate is tributyl phosphate.
18. The process of claim 8 wherein the organic ligand comprises a phosphine.
19. The process of claim 18 wherein the phosphine comprises an alkylphosphine or arylphosphine.
20. The process of claim 19 wherein the phosphine ligand is chosen from triphenylphosphine and tributyl phosphine.
21. The process of claim 9, 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.
22. The process of claim 21, wherein the organic ligand is an amine, a nitrile, or an amide.
23. The process of claim 22, 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.
24. The process of claim 23, wherein the organic ligand is tert-butylamine.
25. The process of claim 24, wherein the organic ligand is a nitrile, selected from the group consisting of acetonitrile, propionitrile, n-butyronitrile, benzonitrile, and phenylacetonitrile.
26. The process of claim 25, wherein the organic ligand is acetonitrile.

27. The process of claim 21, wherein the organic ligand is an amide, selected from the group consisting of hexamethylphosphoramide and dimethylformamide.
28. The process of claim 27, wherein the amide is hexamethylphosphoramide.
29. The process of claim 1 wherein the catalyst is iron and the process is performed at a temperature of about 125 to about 155°C.
30. The process of claim 29 wherein the organic ligand is tributylphosphate.
31. The process of claim 30, wherein the process is performed at a pressure of 100 psig to 165 psig.
32. The process of claim 1 wherein the catalyst is iron and the process is performed at a temperature in the range of 135-150°C.
33. The process of claim 32, wherein the organic ligand is tributylphosphate, and the process is performed at a temperature of in the range of 135-150°C.
34. The process of claim 33, wherein the process is performed at a pressure of 100 psig to 165 psig.
35. The process of claim 1 wherein the catalyst is iron and the process is performed at a pressure of about 50 psig to 170 psig.
36. The process of claim 35 wherein the organic ligand is tributylphosphate.
37. The process of claim 27 wherein the process is performed at a temperature of about 125 to about 155°C.
38. The process of claim 1 wherein the catalyst is iron and the process is performed at a pressure of about 100 psig to 165 psig.
39. The process of claim 38, wherein the organic ligand is tributylphosphate.
40. The process of any of claims 1-39, wherein the concentration of the metal ranges from 500 ppmw to 2500 ppmw.
41. The process of claim 40 wherein the concentration of the metal ranges from 750 ppmw to 2000 ppmw.
42. The process of claim 41 wherein the concentration of the metal ranges from 800 ppmw to 1800 ppmw.

43. The process of claim 41 wherein the concentration of the metal ranges from 1000 ppmw to 1500 ppmw.
44. The process of claim 41 wherein the concentration of the metal ranges from 1200 ppmw to 1400 ppmw.
45. The process of any of claims 41-44 wherein the metal is iron and the organic ligand comprises a trialkyl phosphate or phosphine ligand.
46. The process of claim 45 wherein the organic ligand comprises a trialkyl phosphate.
47. The process of claim 46 wherein the trialkyl phosphate is a tri(C1-6 alkyl)phosphate.
48. The process of claim 45 wherein the trialkyl phosphate is tributyl phosphate.
49. The process of claim 45 wherein the organic ligand comprises a phosphine.
50. The process of claim 49 wherein the phosphine comprises an alkylphosphine or arylphosphine.
51. The process of claim 50 wherein the phosphine ligand is chosen from triphenylphosphine and tributyl phosphine.
52. The composition prepared by the process of claim 1.
53. A composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane (HCFC-548mafd), and at least one additional compound chosen from 3,3,4,4,4-pentafluoro-1-butene (HFO-1345zf), 1,1-dichloro-1,2,2,2-tetrafluoroethane (CFC-114a), 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a), 1-chlorobutane, 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane (CFC-316maa), 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (CFO-1316mxx), C₁₀H₆Cl₃F₁₃ isomers, 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz), triphenylphosphine and tributylphosphate.
54. A composition comprising 3,5,5-trichloro-1,1,1,2,2,6,6,6-octafluorohexane(HCFC-548mafd), and at least one additional compound

chosen from 1-chlorobutane, $C_{10}H_6Cl_3F_{13}$ isomers, and 5,5-dichloro-1,1,1,2,6,6,6-heptafluoro-2-hexene (HCFO-1547mafz).

55. The composition of claim 53 wherein the composition comprises at least one additional compound chosen from HFO-1345zf, CFC-113a, CFC-114a, HCFC-123, CFC-113a, 1-chlorobutane, $C_{10}H_6Cl_3F_{13}$ isomers, HCFO-1547mafz, triphenylphosphine and tributylphosphate.
56. The composition of claim 55 comprising 3,3,4,4,4-pentafluoro-1-butene and CFC-113a.
57. The composition of claim 56 further comprising CFO-1316mxx, CFC-316maa, 1-chlorobutane, or HCFO-1547mafz.
58. The composition of claim 56 further comprising CFO-1316mxx and CFC-316maa and HCFO-1547mafz.
59. The composition of claim 56 further comprising CFC-114a.
60. The composition of claim 53 comprising at least one of HCFO-1547mafz, $C_{10}H_6Cl_3F_{13}$ isomers, and 1-chlorobutane.
61. The composition of claim 53 comprising HCFO-1547mafz $C_{10}H_6Cl_3F_{13}$ isomers, and 1-chlorobutane.
62. The composition of claim 60 further comprising CFC-114a.
63. The composition of claim 53 comprising tributylphosphate.
64. The composition of claim 53 comprising triphenylphosphine.
65. The composition of claim 53 comprising HCFO-1547mafz.
66. The composition of claim 65 further comprising HFO-1345zf and CFC-113a.
67. The composition of claim 55 comprising HFO-1345zf, CFC-113a and CFC-114a.
68. The composition of claim 55 comprising HFO-1345zf, CFC-113a and CFC-114a.
69. The composition of claim 55 comprising HFO-1345zf and CFC-113a and 1-chlorobutane.

70. The composition of claim 53 comprising HFO-1345zf, CFC-113a and tributylphosphate.
71. The composition of claim 53 comprising HFO-1345zf, CFC-113a and triphenylphosphine.