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(54) Title: ONE POT DEHYDROCHLORINATION/CHLORINATION OF A CHLOROALKANE TO PRODUCE A MIXTURE OF CHLORINATED ALKENES AND CHLORINATED ALKANES

(57) Abstract: The present invention provides methods of preparing chlorinated alkanes and chlorinated alkanes by treating a chlorinated alkane starting material at least one Lewis acid catalyst comprising gallium metal, a gallium salt, a gallium alloy, or combinations thereof, a chlorinating agent, and an optional solvent.

ONE POT DEHYDROCHLORINATION/CHLORINATION OF A CHLOROALKANE TO PRODUCE A MIXTURE OF CHLORINATED ALKENES AND CHLORINATED ALKANES

FIELD OF THE INVENTION

[0001] The present disclosure generally relates to the one pot preparation of a mixture of chlorinated alkene products and chlorinated alkane products by dehydrochlorination/chlorination of a chloroalkane starting material.

BACKGROUND OF THE INVENTION

[0002] Halogenated alkanes are useful intermediates for many products including agricultural products, pharmaceuticals, cleaning solvents, solvents, gums, silicones, and refrigerants. The processes to prepare halogenated alkanes are varied and can be time consuming, moderately efficient, and lack reproducibility.

[0003] Typically, halogenated alkanes are formed by telomerizing a halogenated alkane starting material and an alkene or halogenated alkene to form a longer chained halogenated alkane product. This product is typically purified, and subsequently dehydrohalogenated in one reactor, using a dehydrohalogenation catalyst or caustic, and halogenated in another reactor to form higher halogenated alkanes. Generally, this method on an industrial scale has been applied to chlorinated alkanes.

[0004] Various Lewis acid catalysts have been used to accomplish the simultaneous dehydrochlorination/ chlorination of a chlorinated alkane starting material. Some of these Lewis acid catalysts include FeCl_3 , SbCl_5 , as well as others. Examples have been reported which demonstrate this simultaneous dehydrochlorination/ chlorination of a chlorinated alkane starting material. Additionally, under normal process conditions, these catalysts will also perform further dehydrochlorination/ chlorination on the desired product producing amounts of undesired by-products such as higher chlorinated alkanes and heavy by-products. US 9,139,495 claims the simultaneous dehydrochlorination/ chlorination of 1,1,1,3-tetrachloropropane to form 1,1,1,2,3-pentachloropropane.

[0005] US 8,115,038 teaches the simultaneous dehydrochlorination/ chlorination of 1,1,1,3-tetrachloropropane to produce 1,1,1,2,3-pentachloropropane using FeCl_3 . Dehydrochlorination of the 1,1,1,2,3-pentachloropropane to form 1,1,2,3-tetrachloropropene is also described. Other US patents (US 8,614,363 and US 8,912,372) use FeCl_3 in a one pot dehydrochlorination/chlorination reaction. US 2015/0045591 uses a pentavalent antimony compound, such as SbCl_5 . These processes produce significant amounts of higher chlorinated alkanes and by-products, which reduces the yields of the desired products and increases the overall manufacturing cost of the chlorinated propane.

[0006] It would be desirable to develop processes for preparing chlorinated alkenes and chlorinated alkanes that utilize a small amount of catalyst and afford high selectivity, while decreasing the production of heavy by-products. Preferably, such processes also produce the desired halogenated alkane product in high yield, and allow for the recycling of various materials.

SUMMARY OF THE INVENTION

[0007] In one aspect, disclosed herein are processes for preparing chlorinated alkenes and chlorinated alkanes. In general, the process comprises forming a reaction mixture comprising contacting at least one chloroalkane starting material, at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and optionally a solvent in a reactor under conditions detailed below. A product mixture is generated comprising anhydrous HCl , at least one chlorinated alkene product, and at least one chlorinated alkane product, wherein the concentration of the at least one chlorinated alkene within the reaction mixture is controlled between 1% and 99% by weight, by manipulating the amount of chlorinating agent supplied, process temperature, process pressure, concentration of reactants or combinations thereof.

[0008] In another aspect, disclosed herein are processes for preparing 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, from 1,1,1,3-tetrachloropropane. In general, the process comprises forming a

reaction mixture comprising 1,1,1,3-tetrachloropropane, at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and optionally a solvent in a reactor under conditions detailed below. A product mixture is generated comprising anhydrous HCl, 1,1,1,2,3-pentachloropropane, and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, wherein the concentration of the 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, within the reaction mixture is controlled between 1% and 99% by weight by manipulating the amount of chlorinating agent supplied, process temperature, process pressure, concentration of reactants or combinations thereof. In one embodiment, the reaction mixture is a liquid phase reaction mixture.

[0009] In an additional aspect, disclosed herein are processes for preparing 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, from ethylene and carbon tetrachloride. In general, the process commences by forming a reaction mixture comprising ethylene and carbon tetrachloride (CCl₄) to prepare 1,1,1,3-tetrachloropropane using a telomerization process. In the process to prepare 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, from 1,1,1,3-tetrachloropropane, a reaction mixture is formed comprising at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and optionally a solvent in a reactor under conditions detailed below. A product mixture is generated comprising anhydrous HCl, 1,1,1,2,3-pentachloropropane, and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, wherein the concentration of the 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof within the reaction mixture is controlled between 1% and 99% by weight by manipulating the amount of chlorinating agent supplied, process temperature, process pressure, concentration of reactants or combinations thereof. In one embodiment, the reaction mixture is a liquid phase reaction mixture.

[0010] In another aspect, disclosed herein are processes for preparing 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-

tetrachloropropene, or combinations thereof, from 1,1,1,3,3-pentachloropropane. In general, the process comprises forming a reaction mixture comprising 1,1,1,3,3-pentachloropropane, at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and optionally a solvent in a reactor under conditions detailed below. A product mixture is generated comprising anhydrous HCl, 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, wherein the concentration of the 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, within the reaction mixture is controlled between 1% and 99% by weight by manipulating the amount of chlorinating agent supplied, process temperature, process pressure, concentration of reactants or combinations thereof. In one embodiment, the reaction mixture is a liquid phase reaction mixture.

[0011] In yet another aspect, disclosed herein are processes for preparing 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, from vinyl chloride and carbon tetrachloride. In general, the process commences by forming a reaction mixture comprising vinyl chloride and carbon tetrachloride (CCl₄) to prepare 1,1,1,3,3-pentachloropropane using a telomerization process. The process for preparing 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof comprises forming a reaction mixture comprising 1,1,1,3,3-pentachloropropane, at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and optionally a solvent in a reactor under conditions detailed below. A product mixture is generated comprising anhydrous HCl, 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof wherein the concentration of the 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, within the reaction mixture is controlled between 1% and 99% by weight by manipulating the amount of chlorinating agent supplied, process temperature, process pressure, concentration of reactants or combinations thereof. In one embodiment, the reaction mixture is a liquid phase reaction mixture.

[0012] In still another aspect, disclosed herein are processes for preparing at least one of 1,2,2,3-tetrachloropropane, 1,1,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, or 1,1,2,2,3-pentachloropropane and at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene. In general, the process comprises forming a reaction mixture comprising at least one of 1,2,3-trichloropropane, 1,1,1,3-tetrachloropropane, 1,1,2,3-tetrachloropropane, or 1,2,2,3-tetrachloropropane, at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and optionally a solvent in a reactor under conditions detailed below. A product mixture is generated comprising anhydrous HCl, at least one of 1,2,2,3-tetrachloropropane, 1,1,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, or 1,1,2,2,3-pentachloropropane and at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene wherein the concentration of the at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene within the reaction mixture is controlled between 1% and 99% by weight by manipulating the amount of chlorinating agent supplied, process temperature, process pressure, concentration of reactants or combinations thereof. In one embodiment, the reaction mixture is a liquid phase reaction mixture.

[0013] Other features and iterations of the invention are described in more detail below.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The process commences by preparing a reaction mixture in a reactor comprising contacting a chloroalkane starting material, at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and optionally a solvent, in a reactor. After generating the liquid reaction mixture, a product mixture is formed comprising anhydrous HCl, a chlorinated alkene product, and a chlorinated alkane product wherein the concentration of the chlorinated alkene within the reaction mixture is controlled between 1% and 99% by weight by manipulating the amount of chlorinating agent supplied, process temperature,

process pressure, or combinations thereof. A surprising and unexpected results is the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof in the process, as described below, produces the chlorinated alkene product and the chlorinated alkane product in high yield with low levels of over dehydrochlorination of the chlorinated alkane product and low levels of heavy by-products. In one embodiment, the reaction mixture is a liquid phase reaction mixture.

(a). chlorinated alkane starting material

[0015] The chlorinated alkane starting material useful in this process may be a chlorinated propane, such as a dichloropropane, a trichloropropane, a tetrachloropropane, a pentachloropropane, a hexachloropropane, or combinations thereof. Non-limiting examples of dichloropropanes, trichloropropanes, tetrachloropropanes, pentachloropropanes, and hexachloropropanes include, but are not limited to 1,1-dichloropropane; 1,2-dichloropropane; 1,3-dichloropropane; 1,1,1-trichloropropane; 1,1,2-trichloropropane; 1,2,2-trichloropropane; 1,2,3-trichloropropane; 1,1,1,2-tetrachloropropane; 1,1,2,2-tetrachloropropane; 1,1,1,3-tetrachloropropane; 1,1,2,3-tetrachloropropane; 1,1,3,3-tetrachloropropane; 1,1,1,2,3-pentachloropropane; 1,1,1,2,2-pentachloropropane, 1,1,2,3,3-pentachloropropane; 1,1,2,2,3-pentachloropropane; 1,1,1,3,3-pentachloropropane; 1,1,1,3,3,3-hexachloropropane; 1,1,1,2,3,3-hexachloropropane; or combinations thereof.

[0016] One method for preparing these chloroalkane starting materials is through the telomerization process. In this process, carbon tetrachloride (Tet), an alkene or chlorinated alkene, a catalyst system comprising metallic iron, ferric chloride, and/or ferrous chloride, and a trialkylphosphate and/or a trialkylphosphite are contacted to produce the chlorinated alkanes. As an illustrative example, using ethylene as the alkene in the above described telomerization process yields tetrachloropropanes, such as 1,1,1,3-tetrachloropropane (250FB). Utilizing vinyl chloride as the chlorinated alkene, pentachloropropanes, such as 1,1,1,3,3-pentachloropropane (240FA) would result. The skilled artisan readily knows other methods for preparing the chloroalkane

starting materials. In a preferred embodiment, the chloroalkane starting materials comprises 1,1,1,3-tetrachloropropane, also known as 250FB. In another preferred embodiment, the chloroalkane starting materials comprises 1,1,1,2,3-pentachloropropane, also known as 240DB. In still another preferred embodiment, the chloroalkane starting material comprises 1,1,1,3,3-pentachloropropane, also known as 240FA. In yet another preferred embodiment, the chloroalkane starting material comprises 1,2,3-trichloropropane, 1,1,1,3-tetrachloropropane, 1,2,2,3-tetrachloropropane, 1,1,2,3-tetrachloropropane, or combinations thereof.

[0017] The chloroalkane starting material may be crude, unpurified product from the telomerization reaction or from another process, partially purified, or fully purified by means known to the skilled artisan. One common method of purifying the chlorinated alkane is distillation. Non-limiting examples of distillations may be a simple distillation, flash distillation, a fractional distillation, a steam distillation, or a vacuum distillation. Use of a stripping gas, such as carbon tetrachloride or nitrogen may also be employed to reduce the distillation temperature.

[0018] Generally, the chloroalkane starting material useful in the process may have a purity greater than 10 wt%. In various embodiments, the purity of the chloroalkane starting material may have a purity greater than 10wt%, greater than 30 wt%, greater than 50 wt%, greater than 75 wt%, greater than 90 wt%, greater than 95 wt%, or greater than 99 wt%.

(b). the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof.

[0019] A variety of Lewis acid catalysts may be used in the dehydrochlorination/chlorination process. In various embodiments, the at least one Lewis acid catalyst comprises gallium metal, a salt of gallium, a gallium alloy, or combinations thereof. As appreciated by the skilled artisan, at least part of the at least one Lewis acid catalyst may be in homogeneous or heterogeneous form.

[0020] In some embodiments, the at least one Lewis acid catalyst is gallium metal. As appreciated by the skilled artisan, gallium metal, once introduced into the

process may undergo a phase transition from a solid to a liquid since gallium's melting point is about 29.7°C. Gallium metal may also undergo chlorination to a gallium chloride salt. Gallium metal and gallium salts may be partially soluble or fully soluble in the reaction medium.

[0021] In some embodiments, the at least one Lewis acid catalyst useful in the process is a gallium alloy. Non-limiting examples of gallium containing alloys useful in the process may be Al Ga, galphenol, galinstan, or combinations thereof.

[0022] In other embodiments, the at least one Lewis acid catalyst is a gallium salt. As appreciated by the skilled artisan, gallium salts can exist in a number of oxidation states. Non-limiting oxidation states of gallium salts useful in the dehydrochlorination process may be Ga (I), Ga (II), Ga (III), or combinations thereof. As appreciated by the skilled artisan, a wide variety of anions may be part of a metal salt. Non-limiting examples of suitable anions in these transition metal salts may include acetates, acetylacetonates, alkoxides, butyrates, carbonyls, dioxides, halides, hexonates, hydrides, mesylates, octanoates, nitrates, nitrosyl halides, nitrosyl nitrates, sulfates, sulfides, sulfonates, phosphates, and combinations thereof. In a preferred embodiment, the anion in the metal salt comprises a chloride. In a preferred embodiment, the metal salt may be gallium dichloride (gallium (I,III) chloride/digallium tetrachloride), GaCl_2 (GaGaCl_4), gallium (II) chloride (Ga_2Cl_4), gallium (III) chloride, (GaCl_3), or combinations thereof.

[0023] The gallium metal, a gallium alloy, a gallium salt, or combinations thereof, once in the process, may undergo oxidation and/or reduction to produce an activated catalytic species in various oxidation states. The oxidation state of these active gallium catalytic species may vary, and may be for examples (I), (II), and (III). In an embodiment, the active gallium catalyst may be in the Ga(I) oxidation state. In another aspect, the active gallium catalyst may be Ga (II). In still another aspect, the active gallium catalyst may be in the Ga (III) oxidation state. In an additional aspect, the active gallium catalyst may comprise a mixture of Ga (I) and Ga (II). In still another aspect, the active gallium catalyst may comprise a mixture of Ga(I) and Ga (III) oxidation states. In yet another aspect, the active gallium catalyst may be in the Ga (II) and Ga (III)

oxidation states. In another aspect, the active gallium catalyst may be in the Ga (I), Ga (II) and Ga (III) oxidation states.

[0024] The at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof may further comprise an additional Lewis acid catalyst. The combination of the Lewis acid catalysts would provide a synergistic effect in the dehydrochlorination/chlorination process by increasing the kinetics of the process, improving the percent conversion, increasing the selectivity of the process, or combinations of these effects. A large variety of additional Lewis acid catalysts may be used with gallium metal, a salt of gallium, a gallium alloy, or combinations thereof in the process. In some embodiments, the additional Lewis acid catalyst may be a transition metal. As used herein, the term "transition metal" refers to a transition metal element, a transition metal containing alloy, a transition metal containing compound, or combinations thereof. Non limiting examples of transition metals in the at least one Lewis acid catalyst may be selected from the group consisting of aluminum, antimony, bismuth, chromium, cobalt, copper, gold, indium, iron, lead, magnesium, manganese, mercury, nickel, platinum, palladium, rhodium, samarium, scandium, silver, titanium, tin, zinc, zirconium, and combinations thereof. In a preferred embodiment, the additional Lewis acid catalyst comprises iron.

[0025] Non-limiting examples of transition metal containing alloys useful in the process may be an alloy of aluminum, an alloy of bismuth, an alloy of chromium, an alloy of cobalt, an alloy of copper, an alloy of gold, an alloy of indium, an alloy of iron, an alloy of lead, an alloy of magnesium, an alloy of manganese, an alloy of mercury, an alloy of nickel, an alloy of platinum, an alloy of palladium, an alloy of rhodium, an alloy of samarium, an alloy of scandium, an alloy of silver, an alloy of titanium, an alloy of tin, an alloy of zinc, an alloy of zirconium, and combinations thereof. Non-limiting common names for these alloys may be Al-Li, Alnico, Birmabright, duraluminum, hiduminum, hydroalium, magnalium, Y alloy, nichrome, stellite, ultimet, vitallium, various alloys of brass various alloys of brass, bronze, constantin, Corinthian bronze, cunife, cupronickel, cymbal metals, electrum, haptizon, manganin, nickel silver, Nordic gold, tumbaga, crown gold, colored gold, electrum, rhodite, rose gold, tumbaga, white gold, cast iron,

pig iron, Damascus steel, wrought iron, anthracite iron, wootz steel, carbon steel, crucible steel, blister steel, alnico, alumel, brightray, chromel, cupronickel, ferronickel, German silver, Inconel, monel metal, nichrome, nickel-carbon. Nicrosil, nitinol, permalloy, supermalloy, 6al-4v, beta C, gum metal, titanium gold, Babbitt, britannium, pewter, solder, terne, white metal, sterling silver, zamak, zircaloy, or combinations thereof.

[0026] In various embodiments, the additional Lewis acid catalyst may comprise a transition metal salt. Non-limiting examples of suitable transition metal salts may include a salt of aluminum, a salt of antimony a salt of bismuth, a salt of chromium, a salt of cobalt, a salt of copper, a salt of gold, a salt of indium, a salt of iron, a salt of lead, a salt of magnesium, a salt of manganese, a salt of mercury, a salt of nickel, a salt of platinum, a salt of palladium, a salt of rhodium, a salt of samarium, a salt of scandium, a salt of silver, a salt of titanium, a salt of tin, a salt of zinc, a salt of zirconium, and combinations thereof. Non-limiting examples of anion for these suitable transition metal salts may include acetates, acetylacetonates, alkoxides, butyrates, carbonyls, dioxides, halides, hexonates, hydrides, mesylates, octanates, nitrates, nitrosyl halides, nitrosyl nitrates, sulfates, sulfides, sulfonates, phosphates, and combinations thereof. Examples of suitable transition metal salts may include, iron (II) chloride, iron (III) chloride, aluminum (III) chloride, antimony (III) chloride, antimony (V) chloride, or combinations thereof.

[0027] Generally, the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof may be in various forms or configuration. Non-limiting examples of the forms or configuration of the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof may be dissolved in the liquid reaction medium or may exist as a solid. In other embodiments, the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof is heterogeneous and may be immobilized on the surface of a solid support. Non-limiting examples of suitable supports or substrate that may be alumina, silica, silica gel, diatomaceous earth, molecular sieves, carbon, clay or combinations of two or more thereof. The resulting

supported catalyst may be introduced into the reaction medium as a packing, an unstructured packing, a foil, a sheet, a screen, a wool, a wire, a ball, a plate, a pipe, a rod, a bar, a granule or a powder.

[0028] In still another embodiment, the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof in a continuous reactor may be part of at least one fixed catalyst bed. In still another embodiment, the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof in a continuous reactor may be part of at least one cartridge. In still another embodiment, the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof may be part of a structured or un-structured packing where the at least one catalyst is a part of the packing or un-structured packing. Using a fixed catalyst bed, a cartridge, structured packing, or unstructured packing, the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof may be contained and easily replaced when consumed.

[0029] Generally, the concentration of at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof may be used in stoichiometric or catalytic amounts as compared to the chloroalkane starting material. If it is used as a catalyst, generally, less than 10% by weight is used, relative to the amount of chloroalkane in the reactor. In various embodiments, the concentration of the at least one Lewis acid in the reactor is less than about 1,000 ppm, less than about 750 ppm, less than about 500 ppm, less than about 250 ppm or less than about 100 ppm. If the gallium metal, gallium alloy, gallium salts, or combinations thereof is immobilized on the surface of a solid support, the concentration relative to the support may be from 0.1 to about 50 % by weight.

(c). chlorinating agent

[0030] A wide variety of different chlorinating agents may be used in the process. Non-limiting examples of suitable chlorinating agents may be chlorine gas, sulfuryl chloride, thionyl chloride, oxalyl chloride, PCl_3 , PCl_5 , POCl_3 , and combinations thereof.

In a preferred embodiment, the chlorinating agents may include chlorine gas, sulfuryl chloride, or combinations thereof. In a most preferred embodiment, the chlorinating agent is chlorine gas. If chlorine gas is used, it may be used at a pressure that is at least atmospheric pressure or at sub-atmospheric pressures. The chlorine gas may be diluted with a carrier gas, such as nitrogen, a noble gas, or combinations thereof. Preferably, the pressure of the chlorine gas, and the entire reaction, is at least atmospheric pressure.

[0031] Generally, the mole ratio of the chlorinating agent to the chloroalkane starting material supplied to the reaction mixture may range from about 0.01:1.0 to about 1.20:1.0. In various embodiments, the mole ratio of the chlorinating agent to the chloroalkane starting material may range from about 0.01:1.0 to about 1.20:1.0, from about 0.1:1.0 to about 1.10:1.0, from about 0.2:1.0 to about 1.1:1.0. In one embodiment, when a second chlorination reaction is to be performed, the mole ratio of the chlorinating agent to the chloroalkane starting material supplied to the reaction mixture may be substoichiometric, i.e., it may range from about 0.3:1.0 to about 0.8:1.05, from about 0.4:1.0 to about 0.7:1.0, from about 0.45:1.0 to about 0.65:1.0. As appreciated by the skilled artisan, the product distribution of the chlorinated alkene product and the chlorinated alkane product will be dependent on the number of moles of the chlorinating agent used in the process.

(d). optional solvent.

[0032] In various embodiments, the reaction mixture may further comprise a solvent. Non-limiting examples of solvents may be CCl_4 , C_2Cl_4 (tetrachloroethylene), the chloroalkane starting material, the chlorinated alkene product, the chlorinated alkane product, or combinations thereof. In one preferred embodiment, the solvent comprises carbon tetrachloride.

(e). reaction conditions

[0033] As appreciated by the skilled artisan, there are many methods to stir the contents of a reactor comprising a liquid phase, and to provide adequate mixing with the

at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof and adequate mixing of the liquid and gas phases. These methods would provide increased interaction between the liquid phase and at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof. Non-limiting methods to adequately stir the liquid phase contents of the reactor may be jet stirring, impellers, baffles in the reactor, pumps or combinations thereof.

[0034] When a solid catalyst is used, mixing maximizes solid-liquid mass-transfer by maximizing contact between the liquid phase and the solid catalyst. Therefore, the type of mixing depends on the form of the at least one Lewis acid catalyst and whether an additional Lewis acid catalyst is used with gallium metal, a salt of gallium, a gallium alloy, or combinations thereof. For example, when the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof is in powder form, an impeller with or without baffles aids in suspending, mixing, and fluidizing of the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof to maximize contact area and provide fresh liquid contact with the powder.

[0035] In another embodiment, when the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof is in the form of a fixed bed, then the liquid phase is fed directly into the fixed bed from one end of the fixed bed and exits from the other end. The fixed bed may be contained within a cylindrical or tubular container. Generally, the L/D (length/diameter) of the cylindrical or tubular container may be greater than 1. In various embodiments, the L/D (length/diameter) of the cylindrical or tubular container may be greater than 1, greater than 2, greater than 4, greater than 6, or greater than 8. The residence time and velocity of the fluid in the fixed bed may be varied by recycling a portion of the fixed bed reactor effluent back to the inlet. All components of the reaction mixture may be fed to the fixed bed, or a separate absorber may be employed in which gaseous and liquid components are mixed prior to entering the fixed bed. When a separate absorber is used, the fixed bed reactor temperature may also be independently varied from the

absorber temperature by heat exchanging the feed or the reactor recycle stream. The fixed bed temperature may also be controlled by including internal heat exchanger such as the use of multitube exchanger.

[0036] As appreciated by the skilled artisan, at least one of the methods or a combination of these may be utilized in the process.

[0037] In general, the process for the preparation of chlorinated alkene product and chlorinated alkane product will be conducted to maintain the temperature from about 20°C to about 160°C or about 30°C to about 150°C, using an internal or external heat exchanger. In various embodiments, the temperature of the reaction may be maintained from about 60°C to about 120°C.

[0038] Generally, the process may be conducted at a pressure of about atmospheric pressure (~14.7 psi) to about 200 psi so the amount of the gases absorbed into the liquid are in suitable quantities so the reaction may proceed and maintain the kinetics of the process. In various embodiments, the pressure of the process may be from about atmospheric pressure (~14.7 psi) to about 200 psi, from about 20 psi to about 150 psi, from about 25 psi to about 100 psi, from about 30 psi to about 80 psi, or from 40 psi to about 60 psi. In another embodiment, the pressure is from atmospheric pressure to 35 psi.

[0039] Generally, anhydrous HCl is produced as a by-product from the process. In various embodiments, the anhydrous HCl, under the reaction conditions described above, may be removed directly from the reactor. In another embodiment, the anhydrous HCl removed from the reactor may be chilled to condense at least a portion of the chlorine, organic constituents, or combinations thereof, and these condensed constituents may be returned to the reactor. Removing the anhydrous HCl will increase the kinetics of the process.

[0040] Generally, the concentration of the chlorinated alkene product is controlled from about 1% to about 99% by weight by manipulating the amount of chlorinating agent, process temperature, process pressure, or combinations thereof. Concentration of chlorinated alkene at the higher end of said range will improve the chlorination kinetics, thereby allowing lower chlorinating agent concentration and mitigating over-

chlorination, for instance by free radical chlorination reactions. In various embodiments, the concentration of the chlorinated alkene product may range from 1% to about 99% by weight, from about 5% to about 90% by weight, from about 10% to about 80% by weight, from about 25% to about 75% by weight, from about 30% to about 70% by weight, or from about 40% to about 60% by weight.

[0041] As appreciated by the skilled artisan, the above process may be run in a batch mode or a continuous mode where continuous mode is preferred. In another embodiment, the process in continuous modes may be stirred in various methods as appreciated by the skilled artisan.

[0042] The chlorinated alkane starting material fed to the above described process may be converted into the chlorinated alkene product and chlorinated alkane product in at least 50 wt% conversion. In various embodiments, the conversion of chlorinated alkane into the chlorinated alkene product and chlorinated alkane product may be at least 50 wt%, at least 60 wt %, at least 70 wt %, at least 80 wt %, at least 95 wt %, and at least 99 wt%

[0043] The concentration of the chlorinated alkene product may be greater than about 1 wt% as compared to concentration of all the components of the reaction mixture. In various embodiments, the concentration of the chlorinated alkene product may be greater than about 5 wt%, greater than about 10 wt%, greater than 20 wt%, greater than about 40 wt%, greater than about 75 wt%, greater than about 90 wt%, or greater than 99 wt%.

[0044] The concentration of the chlorinated alkane product as compared to the total contents of the reaction mixture may be greater than about 40 wt%. In various embodiments, the concentration of the chlorinated alkane product as compared to the total contents of the reaction mixture may be greater than about 40 wt%, greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 90 wt%, greater than about 95 wt%, or even greater than about 99 wt%.

[0045] In general, the combined percentage selectivity of the chlorinated alkane product and the chlorinated alkane product is at least 70%. In various embodiments,

the combined selectivity of the chlorinated alkane product and the chlorinated alkene product is at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, or at least 99%.

[0046] In various embodiments, the molar ratio of chlorinated propene products to chlorinated propane products in the reaction mixture is greater than 1.

(f). chloroalkene products

[0047] A wide variety of chloroalkene products can be produced using the starting materials and methods described herein. A non-exhaustive list of products that may be prepared comprises 1,1,3-trichloropropene; 3,3,3-trichloropropene; 1,3,3,3-tetrachloropropene; 1,1,3,3-tetrachloropropene; 1,1,2,3-tetrachloropropene; 1,2,3-trichloropropene; 2,3-dichloropropene; 2-chloropropene; 1-chloropropene; or combinations of two or more thereof.

(g). chloroalkane products

[0048] A wide variety of chloroalkane products can be produced using the starting materials and methods described herein. A non-exhaustive list of products that may be prepared comprises 1,1,1,2,3-pentachloropropane; 1,1,1,2,3,3-hexachloropropane; 1,2,3-trichloropropane; 1,1,2-trichloropropane; 1,2,2,3-tetrachloropropane; 1,1,2,3-tetrachloropropane; 1,1,2,2,3-pentachloropropane; or combinations of two or more thereof.

II. Separation and Recycle Streams.

[0049] The next step in the process comprises separating at least some of the components of the product mixture. In one embodiment, at least some of the anhydrous HCl is removed from the reactor as the product mixture is formed. In another embodiment, the chlorinating agent is separated from the product mixture while the HCl is being removed or after the HCl is removed. In still another embodiment, at least some of the chlorinated alkene product is separated from the product mixture together with HCl or after HCl is removed and it is recycled to the reactor, purified for use in other reactions or sent to a secondary reactor, where it undergoes one or more further reactions.

[0050] While specific purification protocols are exemplified below, it must be understood that during the processes disclosed herein, at least some of the chlorinated alkene product is at least partially purified in one or more separation devices. Similarly, at least some of the chlorinated alkane product is also at least partially purified in one or more separation devices. Similarly, the other components of the product mixture may be sent to one or more separation devices, where streams comprising the components are generated. These streams may be recycled to the reactor, used in a different reaction, purified as product or discarded – the exact fate of the stream depending on what is in it. In general, one or more separation devices are used, either in series or in parallel, with series being preferred. Examples of separation devices are known in the art and are described herein.

[0051] In one embodiment, the purified chlorinated alkene product and purified chlorinated alkane product from the liquid reaction mixture comprising the chlorinated alkene product, the chlorinated alkane product, the at least one Lewis acid comprising gallium metal, a gallium salt, or combinations thereof, the chlorinating agent, any remaining hydrogen chloride that was not removed directly from the reactor, an optional solvent, lighter by-products, heavier by-products (also referred to as heavies), and unreacted chloroalkane starting material are separated into one or more product effluent streams. Depending on the purity of the chloroalkane starting material used in the process, further components in the liquid phase reaction mixture may be a trialkylphosphate, a trialkylphosphite, and iron salts or iron hydroxide from the telomerization process. In one embodiment, the product mixture is removed from the reactor as vapor and/or a liquid and is then distilled. The chlorinated alkane product and/or the chlorinated alkene product is then isolated. The heavies are continuously or intermittently purged from the reactor or from a distillation bottom stream. In one embodiment, the product mixture further comprises at least one catalyst, which is dissolved therein, and the catalyst is removed and/or deactivated before the product mixture is purified. The catalyst may be removed by adding water, activated carbon or by using ion exchange. The catalyst may be deactivated using one or more chelating agents, such as those that contain N, S, and/or P. Examples of chelating agents

include amines, nitrites, amides, thiols, alcohols, phosphates (such as alkylphosphates) and phosphites (such as alkylphosphites). Examples of specific chelating agents that may be used include, stearyl amines, lauryl amines, cyclohexyl amines, octyl amines, 2-ethylhexylamine, 2-octylamine, tert-octylamine, diaminododecane ($\text{Cl}_2\text{H}_{28}\text{N}_2$), hexamethylenediamine, ethylenediamine, tetramethylenediamine, acetonitrile, pentanenitrile, benzonitrile, tolunitrile, N-ethylacetamide, acetanilide, aceto-p-toluidide, hexamethylenephosphoramidate dimercaprol, tributylphosphate, triethylphosphate trimethylphosphate, and triphenylphosphate.

[0052] The separation process commences by transferring at least a portion of the liquid phase reaction mixture from the reactor into a separator or multiple separators. In various embodiments, at least one of the first separator and the second separator may have a distillation column or a multistage distillation column. Additionally, at least one of the first separator and the second separator may further comprise a reboiler, a bottom stage, or a combination thereof. Various distillation columns may be used in this capacity. In one embodiment, a side draw column or a distillation column which provides an outlet stream from an intermediate stage or a dividing wall column (dividing wall column (DWC) is a single shell, fully thermally coupled distillation column capable of separating mixtures of three or more components into high purity products (product effluent streams)) may be used as a separator. A portion of various product effluent streams after separation or a portion of the anhydrous liquid reaction mixture produced by the process may be optionally recycled back into the reactor to provide increased kinetics, increased efficiencies, reduced overall cost of the process, increased selectivity of the desired halogenated alkane, increased yield of the desired halogenated alkane, and increased mixing.

[0053] In one embodiment, at least a portion of the at least one chlorinated alkene product is separated from the product mixture, either directly from the reactor or from distillation of the product mixture after leaving the reactor and the at least a portion of the at least one chlorinated alkene product that was separated from the product mixture is at least partially purified and recycled to the reactor or sent to a second reactor wherein the at least one chlorinated alkene product is contacted with a

chlorinating agent with or without the addition of a catalyst to produce the at least one chlorinated alkane product.

[0054] In another embodiment, at least a portion of the at least one chlorinated alkane product is removed from the product mixture, either directly from the reactor or from distillation of the product mixture after leaving the reactor.

[0055] In an embodiment, at least a portion of at least one of the anhydrous HCl, the at least one chlorinated alkene product or the at least one chlorinated alkane product is continuously removed from the product mixture.

[0056] Each product effluent stream, as described below, is enriched in the particular component of the liquid phase reaction mixture. Further separation may be required of each product effluent streams to produce highly pure compounds.

[0057] In another embodiment, the process may be conducted in a reactive distillation column. In this configuration, the chemical reactor and a distillation are combined in a single operating step, thus, allowing for selective removal of various components from the reaction mixture, simultaneous addition of reactants into the process, addition of various product streams, and distillation of various product effluent streams from the process.

[0058] A portion of the liquid reaction mixture is then transferred into a separator. In an embodiment, the separator may utilize at least one simple distillation, at least one vacuum distillation, at least one fractional distillation, or combinations thereof. The distillations may comprise at least one theoretical plate.

[0059] Separating the purified chlorinated alkene product and chlorinated alkane product from the liquid reaction mixture produces at least two product effluent streams. In various embodiments, separating the purified chlorinated alkene and purified chlorinated alkane product may produce three product effluent streams, four product effluent streams, or more product streams depending on the separation device utilized. As an example, the separation of the chlorinated alkene and chlorinated alkane from the contents of the reactor using three product streams is described below.

[0060] In an embodiment, the liquid reaction mixture is distilled, and the lights, comprising HCl and the chlorinating agent (typically chlorine) are removed. The HCl

and the chlorinating agent may be further separated, where the chlorinating agent can be recycled to the reactor. Alternatively, HCl can be removed before the chlorinating agent is removed. In the same distillation column or in a different distillation column, the chlorinated alkene can also be separated from the liquid reaction mixture. The chlorinated alkene can be recycled and chlorinated, to thereby generate the chlorinated alkane product. Again, in the same distillation column or in a different distillation column, the chlorinated alkane product can be isolated. Heavies can be removed from the bottom of one or more distillation columns. The heavies are optionally recycled to the reactor.

[0061] In an alternate embodiment, the lights are removed as one fraction, while the chlorinated alkene and the chlorinated alkane product are removed as a second stream. The lights containing stream can be further distilled to separate the HCl from the chlorinating agent (typically chlorine). The second stream can be further distilled and the chlorinated alkene can be recycled to the reactor, where it is chlorinated. The heavies can be recycled to the reactor or discarded.

[0062] In another embodiment, the liquid reaction mixture may be distilled to produce three product streams, product effluent streams (a), (b), and (c), after at least some of the anhydrous HCl is removed. Product effluent stream (a) typically comprises the optional solvent (but not if the solvent is chlorinated alkane product), light by-products, the chlorinating agent and any remaining anhydrous hydrogen chloride which under the process conditions described above is removed as a gas as an overhead stream during the separation. Product effluent stream (b) comprises the chlorinated alkene product and the chloroalkane starting material which may be removed as a side stream. Product (c) comprises chlorinated alkane product, heavy by-products, and the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof which comprise the bottom stream.

[0063] Generally, product effluent streams (a) comprising the optional solvent, anhydrous hydrogen chloride, the chlorinating agent, and light by-products may be further purified producing two additional product effluent streams (d) and (e) wherein product effluent stream (d) obtained as an overhead stream comprises anhydrous

hydrogen chloride, the chlorinating agent, light by-products and product effluent stream (e), obtained as the bottom stream, comprises the optional solvent. The overhead product effluent stream (d) may be further purified since anhydrous hydrogen chloride and the chlorinating agent are valuable commercial materials. Alternatively, (a) may be separated to provide anhydrous HCl overhead and all the other stuff in the bottom. The bottom stream may be separated to remove light by products overhead and a solvent/chlorine stream that can be recycled.

[0064] Product effluent stream (b) may be recycled to the reactor and at least a portion may be further purified producing two additional product effluent streams (f) and (g) where product effluent stream (f) comprises the chlorinated alkene product and product effluent stream (g) comprises the chloroalkane starting material.

[0065] Product effluent stream (c) may be further purified producing two additional product effluent streams (h) and (i) wherein product effluent stream (h) comprises the chlorinated alkane product and product effluent stream (i) comprises heavy by-products and the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof.

[0066] In order to improve the efficiency of the process, various product effluent streams may be externally recycled back into the process. In various embodiments, at least a portion of the product effluent stream (b) comprising the chlorinated alkene product and the chloroalkane starting material, product effluent stream (e) comprising the optional solvent, product effluent stream (f) comprising the chlorinated alkene product, product effluent stream (g) comprising unreacted chloroalkane starting material, and product effluent stream (i) comprising heavy by-products and the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof may be recycled back into the dehydrochlorination/chlorination process, as described above.

[0067] In another embodiment, at least a portion of product effluent stream (b), product effluent stream (e), product effluent stream (f), product effluent stream (g), product effluent stream (i), or combinations thereof may be mixed with fresh liquid feed (comprising non-recycled chloroalkane starting material, and optional solvent) before

being recycled back into the reactor in batch mode or continuous mode. In various embodiments, the product effluent streams and fresh liquid feeds may be introduced into the reactor separately or mixed together before entering the process. To be clear, fresh feed streams may contain all or less than all of the following: the chloroalkane starting material, the chlorinated alkene product, the chlorinating agent, the catalyst or catalysts, and the optional solvent. The introduction of these fresh liquid feeds into the reactor or mixing the recycle streams with fresh liquid feeds increases the efficiency of the process, reduces the overall cost, maintains the kinetics, maintains the reaction conversion, increase the through-put, and reduces the by-products produced by the process. The amounts of the product effluent streams recycled to the reactor or fresh liquid feeds added to the reactor may be the same or different. One way to measure the amount of product effluent streams and/or fresh liquid feeds being added to the reactor is to identify the mass flow of the materials. The product effluent stream being recycled to the reactor has a product effluent stream mass flow, while the fresh liquid feeds being added to the reactor has a fresh liquid feed mass flow. Mass flows may be measured using methods known in the art.

[0068] Generally, the ratio of the product effluent stream mass flow being recycled to the fresh liquid feed mass flow is adjusted to not only maintain the conversion of the process but also maintain the kinetics of the process.

(III). Preferred Embodiments: Preparation of 1,1,1,2,3-Pentachloropropane and 1,1,3-Trichloropropene, 3,3,3-Trichloropropene, or Combinations thereof, from 1,1,1,3-Tetrachloropropane.

(a) process for preparing 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, from 1,1,1,3-tetrachloropropane

[0069] Another aspect of the present disclosure encompasses process for preparing 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, from 1,1,1,3-tetrachloropropane. The

process commences by preparing a liquid phase reaction mixture comprising 1,1,1,3-tetrachloropropane; at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and an optional solvent. The at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof is described above in Section (I)(b), the chlorinating agent is described above in Section (I)(c), and the optional solvent is described above in Section (I)(d). The process is controlled by manipulating the amount of chlorinating agent supplied, the concentration of the 1,1,1,3-tetrachloropropane, process temperature, process pressure, or combinations thereof wherein the concentration of the 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof within the reaction mixture is controlled between 1% and 99% by weight.

(b) reaction conditions

[0070] The reaction conditions are described above in Section (I)(e).

(c) output from the process to prepare 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, from 1,1,1,3-tetrachloropropane.

[0071] The 1,1,1,3-tetrachloropropane fed to the above described process may be converted to 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof in at least 30 wt% conversion. In various embodiments, the conversion of 1,1,1,3-tetrachloropropane to 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof may be at least 50 wt%, at least 60 wt%, at least 75 wt%, at least 85 wt%, at least 95 wt%, and at least 99 wt%.

[0072] The concentration of 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof may be greater than about 1 wt% as compared to concentration of all the components of the reaction mixture. In various embodiments, the concentration of 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof may be greater than about 5 wt%, greater than about 10 wt%, greater than 20 wt%,

greater than about 40 wt%, greater than about 75 wt%, greater than about 90 wt%, or greater than 99 wt%.

[0073] The concentration of 1,1,1,2,3-pentachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%. In various embodiments, the concentration of 1,1,1,2,3-pentachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%, greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 90 wt%, greater than about 95 wt%, or even greater than about 99 wt%.

(d) separation of 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof and recycling product effluent streams.

[0074] The process for separating the 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof from the reactor contents is described above in Section (II). Specific recycle streams useful in improving the efficiency of the process are described above in Section (II).

[0075] The product effluent stream (f) from the separator comprising the 1,1,3-trichloropropene; 3,3,3-trichloropropene, or combinations thereof produced in the process may have a yield of at least about 10%. In various embodiments, product effluent stream (f) comprising 1,1,3-trichloropropene; 3,3,3-trichloropropene, or combinations thereof produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

[0076] The product effluent stream (h) from the separator comprising 1,1,1,2,3-pentachloropropane produced in the process may have a yield of at least about 10%. In various embodiments, product effluent stream (h) comprising 1,1,1,2,3-pentachloropropane produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

(IV). Preferred Embodiments: Preparation of 1,1,1,2,3-Pentachloropropane and 1,1,3-Trichloropropene, 3,3,3-Trichloropropene, or Combinations Thereof, from Ethylene and Carbon Tetrachloride.

(a) process for preparing 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, from ethylene and carbon tetrachloride.

[0077] Another aspect of the present disclosure encompasses process for preparing 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof from ethylene and carbon tetrachloride. The process commences by preparing a liquid phase reaction mixture comprising ethylene, carbon tetrachloride, at least one Lewis acid catalyst comprising ferric chloride, metallic iron or iron alloy, and a ligand forming 1,1,1,3-tetrachloropropane (250FB) using a telomerization process.

[0078] The process for preparing 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof from 1,1,1,3-tetrachloropropane commences by forming a liquid phase reaction mixture comprising 1,1,1,3-tetrachloropropane, gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and an optional solvent. The at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof is described above in Section (I)(b), the chlorinating agent is described above in Section (I)(c), and the optional solvent is described above in Section (I)(d). The process is controlled by manipulating the amount of chlorinating agent supplied, the concentration of carbon tetrachloride, process temperature, process pressure, or combinations thereof wherein the concentration of the 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof within the reaction mixture is controlled between 1% and 99% by weight.

(b) reaction conditions

[0079] The reaction conditions are described above in Section (I)(e).

(c) output from the process to prepare 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, from ethylene and carbon tetrachloride.

[0080] The 1,1,1,3-tetrachloropropane fed to the above described process from the telomerization process may be converted to 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof in at least 50 wt% conversion. In various embodiments, the conversion of 1,1,1,3-tetrachloropropane to 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof may be at least 50 wt%, at least 60 wt%, at least 75 wt%, at least 85 wt%, at least 95 wt%, and at least 99 wt%.

[0081] The concentration of 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof may be greater than about 5 wt% as compared to concentration of all the components of the reaction mixture. In various embodiments, the concentration of 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof may be greater than about 5 wt%, greater than about 10 wt%, greater than 20 wt%, greater than about 40 wt%, greater than about 75 wt%, greater than about 90 wt%, or greater than 99 wt%.

[0082] The concentration of 1,1,1,2,3-pentachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%. In various embodiments, the concentration of 1,1,1,2,3-pentachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%, greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 90 wt%, greater than about 95 wt%, or even greater than about 99 wt%.

(d) separation of 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof and recycling product effluent streams.

[0083] The process for separating the 1,1,1,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof from the reactor contents is described above in Section (II). Specific recycle streams useful in improving the efficiency of the process are described above in Section (II).

[0084] The product effluent stream (f) from the separator comprising the 1,1,3-trichloropropene; 3,3,3-trichloropropene, or combinations thereof produced in the process may have a yield of at least about 10%. In various embodiments, product effluent stream (f) comprising 1,1,3-trichloropropene; 3,3,3-trichloropropene, or combinations thereof produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

[0085] The product effluent stream (h) from the separator comprising 1,1,1,2,3-pentachloropropane produced in the process may have a yield of at least about 10%. In various embodiments, product effluent stream (h) comprising 1,1,1,2,3-pentachloropropane produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

(V). Preferred Embodiments: Preparation of 1,1,1,2,3,3-Hexachloropropane and 1,1,3,3-Tetrachloropropene, 1,3,3,3-Tetrachloropropene, or Combinations Thereof, from 1,1,1,3,3-Pentachloropropane.

(a) process for preparing 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, from 1,1,1,3,3-pentachloropropane.

[0086] Another aspect of the present disclosure encompasses process for preparing 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, from 1,1,1,3,3-pentachloropropane.. The

process commences by preparing a liquid phase reaction mixture comprising 1,1,1,3,3-pentachloropropane; at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof, a chlorinating agent, and an optional solvent. The at least one Lewis acid catalyst comprising gallium metal, a gallium alloy, a gallium salt, or combinations thereof is described above in Section (I)(b), the chlorinating agent is described above in Section (I)(c), and the optional solvent is described above in Section (I)(d). The process is controlled by manipulating the amount of chlorinating agent supplied, the concentration of the 1,1,1,3,3-pentachloropropane, process temperature, process pressure, or combinations thereof wherein the concentration of the 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof within the reaction mixture is controlled between 1% and 99% by weight.

(b) reaction conditions

[0087] The reaction conditions are described above in Section (I)(e).

(c) output from the process to prepare 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, from 1,1,1,3,3-pentachloropropane.

[0088] The 1,1,1,3,3-pentachloropropane fed to the above described process may be converted to 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof in at least 50 wt% conversion. In various embodiments, the conversion of 1,1,1,3,3-pentachloropropane to 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof may be at least 50 wt%, at least 60 wt%, at least 75 wt%, at least 85 wt%, at least 95 wt%, and at least 99 wt%.

[0089] The concentration of 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof may be greater than about 5 wt% as compared to concentration of all the components of the reaction mixture. In various embodiments, the concentration of 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof may be greater than about 5 wt%, greater

than about 10 wt%, greater than 20 wt%, greater than about 40 wt%, greater than about 75 wt%, greater than about 90 wt%, or greater than 99 wt%.

[0090] The concentration of 1,1,1,2,3,3-hexachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%. In various embodiments, the concentration of 1,1,1,2,3,3-hexachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%, greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 90 wt%, greater than about 95 wt%, or even greater than about 99 wt%.

(d) separation of 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof

[0091] The process for separating the 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof from the reactor contents is described above in Section (II). Specific recycle streams useful in improving the efficiency of the process are described above in Section (II).

[0092] The product effluent stream (f) from the separator comprising the 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof produced in the process may have a yield of at least about 10%. In various embodiments, product effluent stream (f) comprising 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

[0093] The product effluent stream (h) from the separator comprising 1,1,1,2,3,3-hexachloropropane produced in the process may have a yield of at least about 10%. In various embodiments, product effluent stream (h) comprising 1,1,1,2,3,3-hexachloropropane produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

(VI). Preferred Embodiments: Preparation of 1,1,1,2,3,3-Hexachloropropane and 1,1,3,3-Tetrachloropropene, 1,3,3,3-Tetrachloropropene, or Combinations Thereof, from Vinyl Chloride and Carbon Tetrachloride.

(a) process for preparing 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, from vinyl chloride and carbon tetrachloride.

[0094] Another aspect of the present disclosure encompasses process for preparing 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, from vinyl chloride and carbon tetrachloride. The process commences by preparing a liquid phase reaction mixture comprising vinyl chloride, carbon tetrachloride, at least one Lewis acid catalyst comprising ferric chloride, metallic iron or iron alloy, and a ligand forming 1,1,1,3,3,3-tetrachloropropane (240FA) using a telomerization process.

[0095] The process for preparing 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof from 1,1,1,3,3,3-pentachloropropane commences by preparing a liquid phase reaction mixture comprising 1,1,1,3,3,3-pentachloropropane, at least one Lewis acid catalyst comprising gallium metal, a gallium alloy, a gallium salt, or combinations thereof, a chlorinating agent, and an optional solvent. The at least one Lewis acid catalyst comprising gallium metal, a gallium alloy, a gallium salt, or combinations thereof is described above in Section (I)(b), the chlorinating agent is described above in Section (I)(c), and the optional solvent is described above in Section (I)(d). The process is controlled by manipulating the amount of chlorinating agent supplied, the concentration of carbon tetrachloride, process temperature, process pressure, or combinations thereof wherein the concentration of the 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof within the reaction mixture is controlled between 1% and 99% by weight.

(b) reaction conditions

[0096] The reaction conditions are described above in Section (I)(e).

(c) output from the process to prepare 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, from vinyl chloride and carbon tetrachloride

[0097] The 1,1,1,3,3-tetrachloropropane fed to the above described process from the telomerization process may be converted to 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof in at least 50 wt% conversion. In various embodiments, the conversion of vinyl chloride and carbon tetrachloride to 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof may be at least 50 wt%, at least 60 wt%, at least 75 wt%, at least 85 wt%, at least 95 wt%, and at least 99 wt%.

[0098] The concentration of 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof may be greater than about 5 wt% as compared to concentration of all the components of the reaction mixture. In various embodiments, the concentration of 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof may be greater than about 5 wt%, greater than about 10 wt%, greater than 20 wt%, greater than about 40 wt%, greater than about 75 wt%, greater than about 90 wt%, or greater than 99 wt%.

[0099] The concentration of 1,1,1,2,3,3-hexachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%. In various embodiments, the concentration of 1,1,1,2,3,3-hexachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%, greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 90 wt%, greater than about 95 wt%, or even greater than about 99 wt%.

(d) separation of 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof

[0100] The process for separating the 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof from the reactor contents is described above in Section (II). Specific recycle streams useful in improving the efficiency of the process are described above in Section (II).

[0101] The product effluent stream (f) from the separator comprising the 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof produced in the process may have a yield of at least about 10%. In various embodiments, product effluent stream (f) comprising 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

[0102] The product effluent stream (h) from the separator comprising 1,1,1,2,3,3-hexachloropropane produced in the process may have a yield of at least about 10%. In various embodiments, product effluent stream (h) comprising 1,1,1,2,3-pentachloropropane produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

(VII). Preferred Embodiments: Preparation of At Least One of 1,2,2,3-Tetrachloropropane, 1,1,1,2,3-Pentachloropropane, or 1,1,2,2,3-Pentachloropropane and At Least One of 1,1,3-Trichloropropene, 3,3,3-Trichloropropene, 1,2,3-Trichloropropene, or 2,3-Dichloropropene from at least one of 1,2,3-Trichloropropane, 1,1,1,3-Tetrachloropropane, 1,1,2,3-tetrachloropropane, or 1,2,2,3-Tetrachloropropane

(a) process for preparing at least one of 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, or 1,1,2,2,3-pentachloropropane and at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene, from at least one of 1,2,3-

trichloropropane, 1,1,1,3-tetrachloropropane, 1,1,2,3-tetrachloropropane, or 1,2,2,3-tetrachloropropane.

[0103] Another aspect of the present disclosure encompasses process for preparing at least one of 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, or 1,1,2,2,3-pentachloropropane and at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene from at least one of 1,2,3-trichloropropane, 1,1,1,3-tetrachloropropane, 1,1,2,3-tetrachloropropane, or 1,2,2,3-tetrachloropropane. The process commences by preparing a liquid phase reaction mixture comprising the at least one of 1,2,3-trichloropropane, 1,1,1,3-tetrachloropropane, or 1,2,2,3-tetrachloropropane; at least one Lewis acid catalyst comprising gallium metal, a gallium alloy, a gallium salt, or combinations thereof, a chlorinating agent, and an optional solvent. The at least one Lewis acid catalyst comprising gallium metal, a gallium alloy, a gallium salt, or combinations thereof is described above in Section (I)(b), the chlorinating agent is described above in Section (I)(c), and the optional solvent is described above in Section (I)(d). The process is controlled by manipulating the amount of chlorinating agent supplied, concentration of 1,2,3-trichloropropane, 1,1,1,3-tetrachloropropane, or 1,2,2,3-tetrachloropropane, process temperature, process pressure, or combinations thereof wherein the concentration of the at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene within the reaction mixture is controlled between 1% and 99% by weight

(b) reaction conditions

[0104] The reaction conditions are described above in Section (I)(e).

(c) output from the process to prepare 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, and 1,1,2,2,3-pentachloropropane and 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof from 1,2,3-trichloropropane, 1,1,1,3-tetrachloropropane, or 1,2,2,3-tetrachloropropane.

[0105] The at least one 1,2,3-trichloropropane, 1,1,1,3-tetrachloropropane, or 1,2,2,3-tetrachloropropane fed to the above described process may be converted to at least one of 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, or 1,1,2,2,3-pentachloropropane and at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene, or combinations thereof in at least 50 wt% conversion. In various embodiments, the conversion of 1,1,1,3,3-pentachloropropane to at least one of 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, or 1,1,2,2,3-pentachloropropane and at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene, or combinations thereof may be at least 50 wt%, at least 60 wt%, at least 75 wt%, at least 85 wt%, at least 95 wt%, and at least 99 wt%.

[0106] The concentration of at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene may be greater than about 5 wt% as compared to concentration of all the components of the reaction mixture. In various embodiments, the concentration of at least one of 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, or 2,3-dichloropropene may be greater than about 5 wt%, greater than about 10 wt%, greater than 20 wt%, greater than about 40 wt%, greater than about 75 wt%, greater than about 90 wt%, or greater than 99 wt%.

[0107] The concentration of at least one of 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, or 1,1,2,2,3-pentachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%. In various embodiments, the concentration of at least one of 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, or 1,1,2,2,3-pentachloropropane as compared to the total contents of the reaction mixture may be greater than about 40 wt%, greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 90 wt%, greater than about 95 wt%, or even greater than about 99 wt%.

(d) separation of 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropane, 1,3,3,3-tetrachloropropane, or combinations thereof

[0108] The process for separating the 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropane, 1,3,3,3-tetrachloropropane, or combinations thereof from the reactor contents will utilize several different separation devices (such as those described above), which will allow for the purification of various product mixture components, such as 1,1,1,2,3,3-hexachloropropane and 1,1,3,3-tetrachloropropane, 1,3,3,3-tetrachloropropane, or combinations thereof. During the purification, various effluent streams may be purified, recycled to one or more reactors or used in a different process, without further purification. The exact purification protocol is apparent to the skilled person.

[0109] The yield of the 1,1,3,3-tetrachloropropane, 1,3,3,3-tetrachloropropane, or combinations thereof produced in the process may be at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

[0110] The yield of the 1,1,1,2,3,3-hexachloropropane produced in the process may be at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

DEFINITIONS

[0111] When introducing elements of the embodiments described herein, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0112] Having described the invention in detail, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

EXAMPLES

[0113] The following examples illustrate various embodiments of the invention.

Example 1: Preparation of 1,1,1,2,3 pentachloropropane from 1,1,1,3-tetrachloropropane using homogeneous catalyst with low formation of tri or tetrachloropropene

[0114] A 250 mL three necked flask equipped with a dry ice condenser, magnetic stir bar and a sparge tube was charged with 50 g (274.72 mmol) of 1,1,1,3-tetrachloropropane (Synquest Laboratories, cat. no. 1100-5-33, lot# 00009664) and 50 g of CCl₄ (Acros Organics, 99+%, cat. no. 16772, lot# B0754464). The vent line from the condenser was connected to a scrubber containing 20% sodium hydroxide solution. Nitrogen was sparged through this solution for 3 minutes before adding 400 ppm of gallium trichloride (Alfa Aesar, ultra dry, 99.999% metals basis, cat. no. 43879, lot# T31D002). The reaction mixture was stirred and heated to 50-55 °C for 2 minutes. Chlorine gas (Praxair, lot# U700017107C2) was then introduced slowly through the sparge tube maintaining the reaction temperature at about 50-55 °C throughout the reaction time. Chlorine was passed through the reaction mixture for about 35 to 45 minutes until chlorine consumption appeared to have stopped (appearance of yellow gas in the scrubber). The reaction mixture was analyzed by GC using ethylene dichloride as external standard. The GC yield of 1,1,1,2,3 pentachloropropane obtained was 93% with 98% conversion of 1,1,1,3-tetrachloropropane. The byproducts were found to be higher chlorinated and heavier compounds than 1,1,1,2,3-pentachloropropane. The formation of tri or tetrachloropropene byproducts was below detection limit (about 50ppm or less).

Example 2: Preparation of 1,1,1,2,3 pentachloropropane from 1,1,1,3-tetrachloropropane using homogeneous catalyst with low formation of trichloropropene

[0115] The experiment in example 1 was repeated, but with using 1000ppm of Ga metal in place of GaCl₃ as catalyst. A yield of 92.65% of 1,1,1,2,3-

pentachloropropane product was observed, with 99.6% conversion of 1,1,1,3-tetrachloropropane. Again trichloropropene byproducts were below detection limit.

Example 3: Preparation of 1,1,1,2,3 pentachloropropane from 1,1,1,3-tetrachloropropane using homogeneous catalyst with higher formation of trichloropropene

[0116] The experiment in example 1 was repeated, but with using 416ppm of GaCl₃ as catalyst without using CCl₄ as diluent. After 116 minutes of run time at 25oC temperature, 250FB conversion was found to be about 41.7% with selectivity to 1,1,3-trichloropropene of 4.6%, 1230XA of 0.1%, 240FA of 2.5%, and 240DB of 91.7% and heavies and other byproducts of 1.4%.

Example 4: Preparation of 1,1,1,2,3 pentachloropropane from 1,1,1,3-tetrachloropropane using homogeneous catalyst with low formation of trichloropropene

[0117] The experiment in example 3 was repeated using 199ppm GaCl₃ and at temperature of 20-36oC. After 30 min of chlorination, the conversion of 250FB was found to be 95.5% with 1,1,3-trichloropropene below detection limit. The selectivity to 1230XA was found to be 0.02%, 240FA of 0.9%, and 240DB of 94% while heavies and other byproducts of 5.3%.

Example 5: Preparation of 1,1,1,2,3 pentachloropropane from 1,1,1,3-tetrachloropropane using heterogeneous catalyst with low formation of trichloropropene

[0118] A 23.8 ml Monel reactor tube (0.43 inch ID and 10 inches long) was charged with 12.9 g catalyst. The catalyst was 20% GaCl₃ (Aldrich) on activated carbon (Norit). The catalyst was prepared by insipient wetness technique using a GaCl solution in water and was dried in an oven at a maximum temperature of 150°C under nitrogen purge. The reactor tube was mounted in an oven at a 45° angle, and the oven temperature was controlled at 85°C. Feed of 1,1,1,3-tetrachloropropane (Synquest

Laboratories) was introduced to the bottom end of the reactor at 0.15 ml/min using a piston pump. Chlorine gas (Aldrich, 99.5% pure) was fed to the bottom end of the reactor at 29.6 sccm through a mass flow controller. The reactor was maintained essentially at atmospheric pressure, with effluent flowing through an open tube into a bottle. The reaction mixture exiting the reactor was sampled and was analyzed by GC. The GC conversion of 1,1,1,3-tetrachloropropane was 65%. The selectivity of 1,1,1,2,3-pentachloropropane was 73%, of 1,1,3-trichloropropane was 11%, and of 1230xa was 9%. Other byproducts were predominantly higher chlorinated and heavier compounds than 1,1,1,2,3-pentachloropropane, and their total selectivity was about 7%. Catalyst activity, as observed by conversion of 1,1,1,3-tetrachloropropane was stable for 73 hours.

CLAIMS

What is claimed is:

1. Methods of preparing chlorinated alkanes and chlorinated alkenes, the methods comprising:
 - (a) forming a reaction mixture comprising at least one chloroalkane starting material, chlorinating agent, and at least one Lewis acid catalyst in a reactor; and
 - (b) generating a product mixture comprising at least one chlorinated alkane product, at least one chlorinated alkene product, and anhydrous HCl; wherein the concentration of the at least one chlorinated alkene within the reaction mixture is controlled between 1% and 99% by weight by manipulating the amount of chlorinating agent supplied, reaction temperature, reaction pressure, reaction concentration or combinations thereof.
2. The methods according to claim 1, wherein the at least one Lewis acid catalyst comprises gallium metal, a salt of gallium, a gallium alloy, or combinations thereof.
3. The methods according to claim 2, wherein the at least one Lewis acid catalyst comprises GaCl₃.
4. The methods according to any one of claims 1-3, wherein the chlorinating agent comprises chlorine gas, sulfuryl chloride, or combinations thereof.
5. The methods according to any one of claims 1-4, wherein the reaction mixture further comprises a solvent.
6. The methods according to claim 5, wherein the solvent comprises at least one of CCl₄, the chloroalkane starting material, the chlorinated alkane product, or the chlorinated alkene product.
7. The methods according to any one of claims 1-6, wherein the chloroalkane starting material is a chlorinated propane starting material and the chlorinated alkane product is a chlorinated propane product.
8. The methods according to claim 7, wherein the chlorinated propane starting material comprises at least two chlorine atoms.

9. The methods according to the claim 7 or 8, wherein the chlorinated propane product comprises at least one more chlorine atom than the chlorinated propane starting material.
10. The methods according to any one of claims 7-9, wherein the chlorinated propane starting material comprises 1,1,1,3-tetrachloropropane; 1,1,1,3,3-pentachloropropane; 1,2-dichloropropane; 1,2,3-trichloropropane; 1,1,2-trichloropropane; 1,2,2,3-tetrachloropropane, 1,1,2,3- tetrachloropropane or combinations thereof.
11. The methods according to any one of claims 1-10, wherein the reaction is conducted in the liquid phase.
12. The methods according to any one of claims 1-11, wherein at least part of the Lewis acid catalyst is in homogeneous or heterogeneous form.
13. The methods according to any one of claims 1-12, wherein at least part of the at least one Lewis acid catalyst is a heterogeneous catalyst and is deposited on a substrate comprising alumina, silica, silica gel, diatomaceous earth, molecular sieves, carbon, clay or combinations of two or more thereof.
14. The methods according to claim 13, wherein the Lewis acid catalyst deposited on a substrate is contained in a catalyst bed.
15. The methods according to claim 14, wherein the reaction mixture contacts the catalyst bed by, for example, flowing through it.
16. The methods according to any one of claims 1-15, wherein the at least one Lewis acid catalyst further comprises Fe metal, FeCl_2 , FeCl_3 , AlCl_3 , SbCl_3 , SbCl_5 , bismuth or combinations of two or more thereof.
17. The methods according to any one of claims 12-16, wherein the total amount of homogeneous Lewis acid catalyst in the reaction mixture is less than about 1000 ppm.
18. The methods according to any one of claims 1-17, wherein the reaction mixture has a process temperature that is from about 20°C to about 160°C and preferably from about 60°C to about 120°C.

19. The methods according to any one of claims 1-18, wherein the reaction mixture has a process pressure that is from about 0 psig to about 1000 psig or preferably from about 0 psig to about 200 psig.
20. The methods according to any one of claims 1-19, wherein the at least one chlorinated alkane product comprises at least one of 1,1,1,2,3-pentachloropropane; 1,1,1,2,3,3-hexachloropropane; 1,2,3-trichloropropane; 1,1,2-trichloropropane; 1,2,2,3-tetrachloropropane; 1,1,2,3-tetrachloropropane; or 1,1,2,2,3-pentachloropropane.
21. The methods of any one of the claims 1-20, wherein the at least one chlorinated alkene product comprises at least one of 1,1,3-trichloropropene; 3,3,3-trichloropropene; 1,3,3,3-tetrachloropropene; 1,1,3,3-tetrachloropropene; 1,1,2,3-tetrachloropropene, 1,2,3-trichloropropene; 2,3-dichloropropene; 2-chloropropene; or 1-chloropropene.
22. The methods of any one of the claims 1-21, wherein the concentration of the at least one chlorinated alkene product is greater than 5 wt%, when compared to the concentration of all of the components of the reaction mixture.
23. The methods of any one of the claims 1-22, wherein at least a portion of the anhydrous HCl is removed from the product mixture, either directly from the reactor or from distillation of the product mixture after leaving the reactor.
24. The methods of any one of claims 1-23, wherein at least a portion of the at least one chlorinated alkene product is separated from the product mixture, either directly from the reactor or from distillation of the product mixture after leaving the reactor and the at least a portion of the at least one chlorinated alkene product that was separated from the product mixture is at least partially purified and recycled to the reactor or sent to a second reactor wherein the at least one chlorinated alkene product is contacted with a chlorinating agent with or without the addition of a catalyst to produce the at least one chlorinated alkane product.
25. The methods of any one of claims 1-24, wherein at least a portion of the at least one chlorinated alkane product is removed from the product mixture, either directly from the reactor or from distillation of the product mixture after leaving the reactor.

26. The methods according to any one of claims 23-25, wherein at least a portion of at least one of the anhydrous HCl, the at least one chlorinated alkene product or the at least one chlorinated alkane product is continuously removed from the product mixture.

27. The methods of any one of the claims 1-26, wherein the chlorinating agent is chlorine.

28. The methods of any one of the claims 1-27, wherein the concentration of the at least one chlorinated alkane product is greater than 40 wt% as compared to the total contents of the reaction mixture.

29. The methods of any one of the claims 1-28, wherein greater than 50 wt % of the at least one chloroalkane starting material is converted into a mixture of the at least one chlorinated alkane product and the at least one chlorinated alkene product.

30. The methods of any one of the claims 1-29, wherein at least a portion of the at least one chloroalkane starting material in the product mixture leaves the reactor, is separated from the product mixture and is returned to the reactor.

31. The methods of any one of claims 1-30, wherein the chlorinated alkane product is 1,1,1,2,3-pentachloropropane, the chlorinated alkene product comprises at least one of 1,1,3-trichloropropene or 3,3,3-trichloropropene, and the chloroalkane starting material comprises 1,1,1,3-tetrachloropropane.

32. The methods of claim 31, wherein the method further comprises preparing 1,1,1,3-tetrachloropropane by reacting ethylene and CCl₄ in the presence of a catalyst that comprises a metal chloride, such as FeCl₃, metallic iron or iron alloy, and tributyl phosphate.

33. The methods of any one of claims 1-32, wherein the chlorinated alkane product comprises 1,1,1,2,3,3-hexachloropropane, the chlorinated alkene product comprises at least one of 1,1,3,3-tetrachloropropene or 1,3,3,3-tetrachloropropene, and the chlorinated alkane starting material comprises 1,1,1,3,3-pentachloropropane.

34. The methods of claim 33, wherein the method further comprises preparing 1,1,1,3,3-pentachloropropane by reacting vinyl chloride and CCl₄ in the presence of a Lewis acid catalyst that comprises a metal chloride, such as FeCl₃, metallic iron or iron alloy, and tributyl phosphate.

35. The methods of any one of claims 1-34, wherein the at least one chlorinated alkane product comprises at least one of 1,2,2,3-tetrachloropropane; 1,1,1,2,3-pentachloropropane; 1,1,2,2,3-pentachloropropane; the chlorinated alkene product comprises at least one of 1,1,3-trichloropropene; 3,3,3-trichloropropene; 1,2,3-trichloropropene; or 2,3-dichloropropene; and the chlorinated alkane starting materials comprise at least one of 1,2,3-trichloropropane; 1,1,1,3-tetrachloropropane; or 1,2,2,3-tetrachloropropane.
36. The methods of any one of the claims 1-35, wherein at least a portion of the chloroalkane starting material is directly chlorinated to the chlorinated alkane product without the formation of the chlorinated alkene product.
37. The methods of any one of claims 1-36, wherein the product mixture contains unreacted chlorinating agent, wherein the unreacted chlorinating agent is removed from the product mixture and recycled to the reactor.
38. The methods of claim 37, wherein fresh chlorinating agent is added to the unreacted chlorinating agent, before it is recycled to the reactor.
39. The methods of any of claims 1-38 wherein the molar ratio of chlorinated propene products to chlorinated propane products in the reaction mixture is greater than 1.
40. The method of any one of the claims 1-39, wherein the heavies contain active or deactivated catalyst and the heavies are continuously or intermittently purged from the reactor.
41. The method of any of claims 1-40, wherein the product mixture further comprises at least one catalyst, which is dissolved therein, and the catalyst is removed and/or deactivated before the product mixture is purified.
42. The method of claim 41, wherein the catalyst is removed by adding water, activated carbon, or via ion exchange.
43. The method of claims 41 or 42, wherein the catalyst is deactivated by adding a chelating agent to the product mixture.
44. The method of claim 43 wherein the chelating agent contains N, S, and/or P.

45. The method of claim 44, wherein the chelating agent comprises at least one of stearyl amines, lauryl amines, cyclohexyl amines, octyl amines, 2-ethylhexylamine, 2-octylamine, tert-octylamine, diaminododecane ($\text{Cl}_2\text{H}_{28}\text{N}_2$), hexamethylenediamine, ethylenediamine, tetramethylenediamine, acetonitrile, pentanenitrile, benzonitrile, tolunitriles, N-ethylacetamide, acetanilide, aceto-p-toluidide, hexamethylenephosphoramidate dimercaprol, tributylphosphate, triethylphosphate trimethylphosphate, or triphenylphosphate.

AMENDED CLAIMS

received by the International Bureau on 24 January 2020 (24.01.2020)

1. Methods of preparing chlorinated alkanes and chlorinated alkenes, the methods comprising:
 - (a) forming a reaction mixture comprising at least one chloroalkane starting material, chlorinating agent, and at least one Lewis acid catalyst in a reactor; and
 - (b) generating a product mixture comprising at least one chlorinated alkane product, at least one chlorinated alkene product, and anhydrous HCl; wherein the at least one Lewis acid catalyst comprises gallium metal, a salt of gallium, a gallium alloy, or combinations thereof; and wherein dehydrochlorination and chlorination reactions occur in the reactor.
2. The methods according claim 1, wherein the at least one Lewis acid catalyst comprises GaCl_3 and wherein the chlorinating agent comprises chlorine gas, sulfuryl chloride, or combinations thereof.
3. The methods according to any one of claims 1-2, wherein the reaction mixture further comprises a solvent, wherein the solvent comprises at least one of CCl_4 , the chloroalkane starting material, the chlorinated alkane product, or the chlorinated alkene product.
4. The methods according to any one of claims 1-3, wherein the chloroalkane starting material comprises 1,1,1,3-tetrachloropropane; 1,1,1,3,3-pentachloropropane; 1,2-dichloropropane; 1,2,3-trichloropropane; 1,1,2-trichloropropane; 1,2,2,3-tetrachloropropane, 1,1,2,3- tetrachloropropane or combinations thereof;
wherein the at least one chlorinated alkane product comprises at least one of 1,1,1,2,3-pentachloropropane; 1,1,1,2,3,3-hexachloropropane; 1,2,3-trichloropropane; 1,1,2-trichloropropane; 1,2,2,3-tetrachloropropane; 1,1,2,3-tetrachloropropane; or 1,1,2,2,3-pentachloropropane; and
wherein the at least one chlorinated alkene product comprises at least one of 1,1,3-trichloropropene; 3,3,3-trichloropropene; 1,3,3,3-tetrachloropropene; 1,1,3,3-

tetrachloropropene; 1,1,2,3-tetrachloropropene, 1,2,3-trichloropropene; 2,3-dichloropropene; 2-chloropropene; or 1-chloropropene.

5. The methods according to any one of claims 1-4, wherein at least part of the at least one Lewis acid catalyst is a heterogeneous catalyst and is deposited on a substrate comprising alumina, silica, silica gel, diatomaceous earth, molecular sieves, carbon, clay or combinations of two or more thereof.

6. The methods according to any one of claims 1-5, wherein the at least one Lewis acid catalyst further comprises Fe metal, FeCl_2 , FeCl_3 , AlCl_3 , SbCl_3 , SbCl_5 , bismuth or combinations of two or more thereof.

7. The methods according to any one of claims 1-6, wherein the total amount of homogeneous Lewis acid catalyst in the reaction mixture is less than about 1000 ppm.

8. The methods according to any one of claims 1-7, wherein the reaction mixture has a process temperature that is from about 20°C to about 160°C and preferably from about 60°C to about 120°C.

9. The methods of any one of claims 1-8, wherein at least a portion of the anhydrous HCl is removed from the product mixture, either directly from the reactor or from distillation of the product mixture after leaving the reactor.

10. The methods of any one of claims 1-9, wherein at least a portion of the at least one chlorinated alkene product is separated from the product mixture, either directly from the reactor or from distillation of the product mixture after leaving the reactor and the at least a portion of the at least one chlorinated alkene product that was separated from the product mixture is at least partially purified and recycled to the reactor or sent to a second reactor wherein the at least one chlorinated alkene product is contacted with a chlorinating agent with or without the addition of a catalyst to produce the at least one chlorinated alkane product.

11. The methods of any one of claims 1-10, wherein at least a portion of the at least one chlorinated alkane product is removed from the product mixture, either directly from the reactor or from distillation of the product mixture after leaving the reactor.

12. The methods according to any one of claims 10-11, wherein at least a portion of at least one of the anhydrous HCl, the at least one chlorinated alkene product or the at least one chlorinated alkane product is continuously removed from the product mixture.

13. The methods of any one of claims 1-12, wherein at least a portion of the at least one chloroalkane starting material in the product mixture leaves the reactor, is separated from the product mixture and is returned to the reactor.
14. The methods of any one of claims 1-13, wherein the chlorinated alkane product is 1,1,1,2,3-pentachloropropane, the chlorinated alkene product comprises at least one of 1,1,3-trichloropropene or 3,3,3-trichloropropene, and the chloroalkane starting material comprises 1,1,1,3-tetrachloropropane.
15. The methods of any one of claims 1-14, wherein the chlorinated alkane product comprises 1,1,1,2,3,3-hexachloropropane, the chlorinated alkene product comprises at least one of 1,1,3,3-tetrachloropropene or 1,3,3,3-tetrachloropropene, and the chlorinated alkane starting material comprises 1,1,1,3,3-pentachloropropane.
16. The methods of any one of claims 1-15, wherein the at least one chlorinated alkane product comprises at least one of 1,2,2,3-tetrachloropropane; 1,1,1,2,3-pentachloropropane; or 1,1,2,2,3-pentachloropropane; the chlorinated alkene product comprises at least one of 1,1,3-trichloropropene; 3,3,3-trichloropropene; 1,2,3-trichloropropene; or 2,3-dichloropropene; and the chlorinated alkane starting materials comprise at least one of 1,2,3-trichloropropane; 1,1,1,3-tetrachloropropane; or 1,2,2,3-tetrachloropropane.
17. The methods of any one of claims 1-16, wherein the product mixture contains unreacted chlorinating agent, wherein the unreacted chlorinating agent is removed from the product mixture and recycled to the reactor; and the heavies contain active or deactivated catalyst and the heavies are continuously or intermittently purged from the reactor.
18. The method of any of claims 1-17, wherein the product mixture further comprises at least one catalyst, which is dissolved therein, and the catalyst is removed and/or deactivated before the product mixture is purified.
19. The method of any of claims 1-18, wherein the at least one Lewis acid catalyst comprising gallium metal, a salt of gallium, a gallium alloy, or combinations thereof may be dissolved in the liquid reaction medium.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/047845

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/10 C07C17/25 C07C19/01 C07C21/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

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Further documents are listed in the continuation of Box C.



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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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