What is claimed is:

1. A method comprising:

providing a halogen stream;

providing a first alkane stream;

reacting at least a portion of the halogen stream with at least a portion of the first alkane stream to form a halogenated stream, wherein the halogenated stream comprises alkyl monohalides, alkyl polyhalides, and a hydrogen halide;

providing a second alkane stream; and

reacting at least a portion of the second alkane stream with at least a portion of the alkyl polyhalides to create at least some additional alkyl monohalides.

2. The method of claim 1 further comprising:

contacting at least some of the alkyl monohalides and at least some of the additional alkyl monohalides with a catalyst to form a product stream that comprises higher hydrocarbons and hydrogen halide.

3. The method of claim 2 further comprising:

separating the hydrogen halide from the product stream; and

reacting the hydrogen halide with a source of oxygen to regenerate the halogen stream.

4. The method of claim 1 wherein the reacting at least a portion of the halogen stream with at least a portion of the first alkane stream occurs in a first zone of a reactor vessel and the reacting at least a portion of the second alkane stream with at least a portion of the alkyl polyhalides occurs in a second zone of the reactor vessel.

5. The method of claim 4 wherein the first zone of the reactor vessel is upstream of the second zone of the reactor vessel.

6. The method of claim 1 wherein the reacting at least a portion of the halogen stream with at least a portion of the first alkane stream occurs in the presence of a halogenation catalyst.

7. The method of claim 6 wherein the halogenation catalyst comprises at least one catalyst selected from the group consisting of: a zeolite, an amorphous alumino-silicate, an acidic zirconia, a tungstate, a solid phosphoric acid, a metal oxide, a mixed metal oxide, a metal halide, and a mixed metal halide.

8. The method of claim 3 wherein the reacting at least a portion of the halogen stream with at least a portion of the first alkane stream occurs in a plurality of reactors, wherein at least one of the plurality of reactors is operating at all times.

9. The method of claim 8 wherein one of the plurality of reactors undergoes decoking by introduction of an oxygen source to produce a decoking product, wherein the decoking product is combined with the hydrogen halide before reacting the hydrogen halide with a source of oxygen.

10. The method of claim 2 further comprising:

contacting the at least some of the alkyl monohalides and at least some of the additional alkyl monohalides with an isomerization catalyst to create an isomerized stream prior to contacting the isomerized stream with the catalyst to form the product stream.

11. The method of claim 2 further comprising:

contacting the product stream with a hydrodehalogenation catalyst to create a dehalogenated product stream and hydrogen halide.

12. The method of claim 11 wherein the hydrodehalogenation catalyst comprises at least one active component selected from the group consisting of: copper, copper oxide, palladium, and platinum, and supported on at least one material selected from the group consisting of: an active carbon, an alumina, a silica, and a zeolite.

13. The method of claim 2 wherein the catalyst comprises an ion exchanged zeolite, wherein the ion comprises at least one ion selected from the group consisting of: a Ag ion, a Ba ion, a Bi ion, a Ca ion, an Fe ion, a Li ion, a Mg ion, a Sr ion, a K ion, a Na ion, a

Rb ion, a Mn ion, a Co ion, a Ni ion, a Cu ion, a Ru ion, a Pb ion, a Pd ion, a Pt ion, and a Ce ion.

14. A method comprising:

providing an alkyl halide stream comprising alkyl monohalides, alkyl polyhalides, and a hydrogen halide;

providing a first alkane stream;

reacting at least a portion of the first alkane stream with at least a portion of the alkyl halide stream to create at least some additional alkyl monohalides;

contacting at least some of the alkyl monohalides and at least some of the additional alkyl monohalides with a catalyst to form a product stream that comprises higher hydrocarbons, hydrogen halide, and any unreacted portion of the first alkane stream;

separating the unreacted portion of the first alkane stream from the product stream;

providing a halogen stream; and

reacting at least some of the unreacted portion of the first alkane stream separated from the product stream with the halogen to form the alkyl halide stream.

What is claimed is:

1. A method comprising:

providing a first halogen stream;

providing a first alkane stream;

reacting at least a portion of the first halogen stream with at least a portion of the first alkane stream in a first reaction vessel to form a first halogenated stream;

providing a second alkane stream comprising C_2 and higher hydrocarbons;

providing a second halogen stream; and

reacting at least a portion of the second halogen stream with at least a portion of the second alkane stream in a second reaction vessel to form a second halogenated stream.

2. The method of claim 1 wherein the first halogenated stream, the second halogenated stream, or both comprise alkyl monohalides and alkyl polyhalides and further comprising reacting at least a portion of the alkyl polyhalides with an additional alkane stream to create at least some additional alkyl monohalides.

3. The method of claim 1 further comprising:

contacting at least a portion of the first halogenated stream, the second halogenated stream, or both with a catalyst to form a product stream that comprises higher hydrocarbons and hydrogen halide.

4. The method of claim 3 further comprising:

separating the hydrogen halide from the product stream; and

reacting the hydrogen halide with a source of oxygen to regenerate a halogen stream.

5. The method of claim 1 where the first reaction vessel, the second reaction vessel, or both comprise a halogenation catalyst.

6. The method of claim 5 wherein the halogenation catalyst comprises at least one catalyst selected from the group consisting of: a zeolite, an amorphous alumino-silicate, an acidic

zirconia, a tungstate, a solid phosphoric acid, a metal oxide, a mixed metal oxide, a metal halide, and a mixed metal halide.

7. A method comprising:

providing a halogen stream;

providing a first alkane stream;

reacting at least a portion of the halogen stream with at least a portion of the first alkane stream to form a halogenated stream, wherein the halogenated stream comprises alkyl monohalides, alkyl polyhalides, and hydrogen halide; and

contacting at least some of the alkyl monohalides with a coupling catalyst to form a product stream that comprises higher hydrocarbons and hydrogen halide.

8. The method of claim 7 further comprising:

providing a second alkane stream;

reacting at least a portion of the second alkane stream with at least a portion of the higher alkyl halides to create at least some additional alkyl monohalides; and

contacting at least some of the additional alkyl monohalides with the catalyst to form at least some higher hydrocarbons and hydrogen halide.

9. The method of claim 7 further comprising:

separating the hydrogen halide from the product stream; and

reacting the hydrogen halide with a source of oxygen to regenerate the halogen stream.

10. The method of claim 7 wherein the coupling catalyst comprises a reduced aluminum content ZSM-5 zeolite.

11. The method of claim 10 further comprising forming the reduced aluminum content ZSM-5 zeolite by contacting a zeolite with a dealumination agent, wherein the dealumination agent comprises at least one material selected from the group consisting of: a mineral acid, hydrochloric acid, hydrofluoric acid, a chelating agent, ethylenediaminetetraacetic

acid, oxalic acid, malonic acid; steam, an exchange reagent, $SiCl_4$, $NH_4[SiF_6]$, NH_4HF_2, AlF_3, a trialkyl phosphates, an organic phosphites, and a combination thereof.

12. The method of claim 7 wherein the the catalyst comprises a plurality of catalytic materials wherein each catalytic material is disposed in a different reaction vessel.

13. The method of claim 8 wherein the higher hydrocarbons comprise light olefins.

14. The method of claim 13 wherein the catalyst comprises at least one material selected from the group consisting of: a crystalline silico-alumino-phosphate; an alumino silicate; SAPO-34; a silico-alumino-phosphate substituted with Co, Ni, Mn, Ga, or Fe; a ZSM-5, a ZSM doped with Mg, Ca, Sr, Ba, K, Ag, P, La, or Zn; erionite; ferrierite; ALPO-5; MAPO-36; ZSM-12; ZSM-57; ZSM-23; ZSM-22; MCM-22; and a combination thereof.

15. The method of claim 7 wherein the catalyst comprises a ZSM-5 catalyst modified with mixture comprising copper oxide and zinc oxide, wherein the higher hydrocarbons comprise mesitylene.

16. The method of claim 7 further comprising:

providing a Lewis base molecule; and

contacting the Lewis base molecule with the catalyst contemporaneously with the contacting of at least some of the alkyl monohalides with the coupling catalyst to form the product stream.

17. The method of claim 16 wherein the Lewis base molecule is present in an amount less than about 15% by weight of the total feed to the coupling catalyst.

18. A method comprising:

providing an alkyl halide stream;

contacting at least some of the alkyl halides with a coupling catalyst to form a product stream comprising higher hydrocarbons and hydrogen halide;

contacting the product stream with an aqueous solution comprising a metal halide to remove at least a portion of the hydrogen halide from the product stream;

separating at least some of the metal halide from the aqueous solution; and

heating the separated metal halide to generate a corresponding halogen.

19. The method of claim 18 wherein the metal halide comprises a metal with multiple stable oxidation states.

20. The method of claim 18 wherein the metal halide comprses CuBr or $CuBr_2$.

21. The method of claim 18 wherein the separating the metal halide from the aqueous solution comprises at least one process selected from the group consisting of: crystallization, evaporation, evaporative crystallization, filtration, and centrifugation.

22. The method of claim 18 wherein the the metal halide is separated from the aqueous solution at a temperature below about 200 °C.

23. The method of claim 18 wherein the separated metal halide is heated to a temperature above about 275 °C.

24. The method of claim 181 further comprising:

combining the heated metal halide with an aqueous solution to form the aqueous solution comprising a metal halide.

25. The method of claim 18 further comprising:

providing an alkane stream; and

contacting the alkane stream and the corresponding halogen to generate the alkyl halide stream.

26. A method comprising:

providing an alkyl halide stream;

contacting at least some of the alkyl halides with a coupling catalyst to form a product stream comprising higher hydrocarbons and hydrogen halide;

contacting the product stream with a solid reactant to remove at least a portion of the hydrogen halide from the product stream; and

reacting the solid reactant with a source of oxygen to generate a corresponding halogen.

27. The method of claim 26 wherein contacting the product stream with a solid reactant and reacting the solid reactant with a source of oxygen occur at different temperatures.

28. The method of claim 26 wherein the solid reactant comprises a calcium silicate.

29. The method of claim 28 wherein the calcium silicate is doped with an alkali metal.

30. The method of claim 26 wherein the solid reactant comprises at least one material selected from the group consisting of: a nickel oxide, a cobalt oxide, a copper oxide, a calcium oxide, an iron oxide, and a combination thereof.

31 The method of claim 30 wherein the solid reactant is synthesized using a sol-gel method, a sol-gel method coupled with oil-drop method, a co-precipitation based method, or a combination thereof.

32. The method of claim 26 wherein the solid reactant comprises a fluorinated alumina.

33. The method of claim 32 wherein the solid reactant comprises an impregnated metal oxide.

34. The method of claim 32 wherein the solid reactant is doped with an alkali or alkali earth metal.

35. The method of claim 32 wherein the solid reactant is formed by contacting an alumina with a fluorinated agent.

36. The method of 26 further comprising:

combining an aqueous fluid with the product stream in a quench column to lower the temperature of the product stream prior to contacting the product stream with the solid reactant.

37. The method of 36 wherein the aqueous fluid is water.

38. The method of 36 wherein the quench column comprises at least one column type selected from the group consisting of: a packed bed column, and a spray tower.

39. The method of claim 26 further comprising:

contacting the products stream with at least a portion of the hydrogen halide removed with an organic solvent to absorb at least some of the higher hydrocarbons; and

separating the organic solvent comprising at least some of the higher hydrocarbons from the higher hydrocarbons.

40. The method of claim 39 wherein the organic solvent is contacted with the products stream in an absorber.

41. The method of claim 39 wherein the organic solvent comprises a non-volatile hydrocarbon.

42. The method of claim 41 wherein the non-volatile hydrocarbon comprises at least one hydrocarbon selected from the group consisting of: mesitylene, diesel, a mixture of C_8 and higher hydrocarbons, and a combination thereof.

43. The method of claim 39 wherein the higher hydrocarbons are separated from the organic solvent in a series of separators to produce a plurality of streams with different hydrocarbon fractions.

44. The method of claim 26 wherein the alkyl halide stream further comprises light hydrocarbons.

45. The method of claim 44 further comprising:

passing the products stream through an expansion valve, wherein the products stream comprises at least some of the light hydrocarbons, wherein the temperature of the products stream drops during expansion.

separating any heavier hydrocarbons that condense from the light hydrocarbons.

46. The method of claim 45 further comprising:

thermally contacting the separated light hydrocarbons with the products stream in a heat exchanger prior to the products stream passing through the expansion valve.

47. A method comprising:

providing an alkyl halide stream;

contacting at least some of the alkyl halides with a coupling catalyst to form a product stream comprising higher hydrocarbons and hydrogen halide;

separating at least some of the product stream from the hydrogen halide; and

contacting the hydrogen halide with oxygen and an aqueous solution comprising a metal capable of forming multiple stable oxidation states to generate a corresponding halogen and water.

48. The method of claim 47 wherein the metal capable of forming multiple oxidation states comprises at least one metal selected from the group consisting of: Cu, Fe, Sb, Mn, V, As, Ru, and a combination thereof.

49. The method of claim 47 wherein the aqueous solution has a pH less than about 7.0.

50. The method of claim 47 wherein the contacting of the hydrogen halide, oxygen, and the aqueous solution takes place at a temperature from about 65 °C to about 300 °C.

51. The method of claim 47 wherein the contacting of the hydrogen halide, oxygen, and the aqueous solution takes place at a pressure from about 0.1 atm to about 40 atm.

52. The method of claim 47 further comprising separating the corresponding halogen and the water.

53. The method of claim 52 wherein the steps of contacting the hydrogen halide with oxygen and an aqueous solution and separating the corresponding halogen and the water both take place in a reactive distillation unit.

54. The method of claim 52 further comprising:

providing an alkane stream;

contacting the alkane stream with the separated corresponding halogen to form the alkyl halide stream.

55. A system comprising:

a coupling reactor comprising a coupling catalyst for receiving an alkyl halide stream and contacting at least a portion of the alkyl halide stream with the coupling catalyst to form a product stream comprising higher hydrocarbons and hydrogen halide;

a separator unit for separating at least some of the product stream from the hydrogen halide; and

an oxidation reactor comprising an aqueous solution comprising a metal capable of forming multiple stable oxidation states for receiving a source of oxygen and at least a portion of the hydrogen halide from the separator unit and generating a corresponding halogen and water.

56. The system of claim 55 wherein the metal capable of forming multiple oxidation states in the oxidation reactor comprises at least one metal selected from the group consisting of: Cu, Fe, Sb, Mn, V, As, Ru, and a combination thereof.

57. The system of claim 55 wherein the aqueous solution in the oxidation reactor has a pH less than about 7.0.

58. The system of claim 55 wherein the oxidation reactor is at a temperature from about 65 °C to about 300 °C.

59. The system of claim 55 wherein the oxidation reactor is at a pressure from about 0.1 atm to about 40 atm.

60. The system of claim 55 wherein the oxidation reactor comprises at least one reactor type selected from the group consisting of: a continuous stirred tank reactor, a plu flow reactor, a packed column reactor, a fixed bed reactor, and a fluidized bed reactor.

61. The system of claim 55 further comprising a product separator for receiving the products of the oxidation reactor and separating the corresponding halogen and the water.

62. The system of claim 55 further comprising a halogenation reactor for receiving a halogen stream and an alkane stream and generating the alkyl halide stream.

63. A method comprising:

providing a halogen stream;

providing an alkane stream;

providing a decoking agent; and

reacting at least a portion of the halogen stream with at least a portion of the alkane stream in the presence of a halogenation catalyst and the decoking agent to form a halogenated stream.

64. The method of claim 63 further comprising a metal bromide catalyst downstream of the halogenation catalyst.

65. The method of claim 64 further comprising a metal bromide catalyst disposed between two sections of the halogenation catalyst.

66. The method of claim 63 wherein the decoking agent comprises at least one agent selected from the group consisting of water, oxygen, and a combination thereof.

67. The method of claim 63 further comprising:

contacting at least a portion of the halogenated stream with a catalyst to form a product stream that comprises higher hydrocarbons and hydrogen halide.

68. The method of claim 63 wherein the flow direction of the halogen stream, the alkane stream, and the decoking agent cycles relative to the halogenation catalyst.

69. The method of claim 63 wherein the reacting at least a portion of the halogen stream with at least a portion of the alkane stream in the presence of a halogenation catalyst and the decoking agent to form a halogenated stream occurs in a reactor comprising at least one reactor type selected from the group consisting of: a fixed bed reactor, a vertical fixed bed reactor, and a radial bed reactor.

70. The method of claim 64 wherein the metal halide catalyst comprises at least one material selected from the group consisting of: copper oxide, mangesium oxide, yttrium oxide, nickel oxide, cobalt oxide, iron oxide, calcium oxide, vanadium oxide, molybdenum oxide, chromium oxide, manganese oxide, zinc oxide, lanthanum oxide, tungsten oxide, tin oxide, indium oxide, bismuth oxide, a copper halide, a mangesium halide, a yttrium halide, a nickel halide, a cobalt halide, an iron halide, a calcium halide, a vanadium halide, a molybdenum halide, a chromium halide, a manganese halide, a zinc halide, a lanthanum halide, a tungsten halide, a tin halide, a indium halide, a bismuth halide, and a combination thereof.

71. The method of claim 63 wherein the decoking agent comprises less than about 5% by volume of the feed to the reaction.

72. The method of claim 65 further comprising:

separating the hydrogen halide from the product stream; and

reacting the hydrogen halide with a source of oxygen to regenerate a halogen stream.

73. The method of claim 67 wherein the halogenation catalyst comprises at least one catalyst selected from the group consisting of: a zeolite, an amorphous alumino-silicate, an acidic zirconia, a tungstate, a solid phosphoric acid, a metal oxide, a mixed metal oxide, a metal halide, and a mixed metal halide.

74. A method comprising:

providing a gas phase stream comprising an elemental halide;

contacting the gas phase stream with a chilled brine in the liquid phase, wherein the chilled brine comprises an aqueous solution and a salt;

separating the elemental halogen along with the chilled brine from the remainder of the gas phase stream that remains in the gas phase; and

separating the elemental halide from the chilled brine.

75. The method of claim 74 wherein the elemental halide comprises at least one halide selected from the group consisting of: bromine, chlorine, fluorine, and iodine.

76. The method of claim 74 wherein the chilled brine lowers the temperature of the gas phase stream from about 10 °C to about -30 °C.

77. The method of claim 74 wherein the salt is a halide salt and wherein the halide of the halide salt is the same halide as the elemental halogen.

78. The method of claim 74 wherein the chilled brine comprises from about 0.1% to about 60% by weight of the salt.

79. The method of claim 74 wherein the elemental halide is separated from the chilled brine by liquid-liquid phase separation.

80. The method of claim 74 wherein the elemental halide is separated from the chilled brine by heating the chilled brine to vaporize the elemental halide.

81. The method of claim 74 further comprising:

providing a product stream comprising a hydrogen halide; and

contacting the product stream with an oxidation catalyst in the presence of oxygen to generate the gas phase stream comprising an elemental halide and water.

82. The method of claim 74 further comprising:

providing a first alkane stream;

reacting at least a portion of the halogen stream with at least a portion of the first alkane stream to form a halogenated stream, wherein the halogenated stream comprises alkyl monohalides, higher alkyl halides, and a hydrogen halide;

providing a second alkane stream; and

reacting at least a portion of the second alkane stream with at least a portion of the higher alkyl halides to create at least some additional alkyl monohalides.

83. The method of claim 82 further comprising:

contacting at least some of the alkyl monohalides and at least some of the additional alkyl monohalides with a catalyst to form a product stream that comprises higher hydrocarbons and hydrogen halide.

84. A method comprising:

providing an alkyl halide stream;

contacting at least some of the alkyl halides with a coupling catalyst to form a product stream comprising higher hydrocarbons and hydrogen halide;

separating the hydrogen halide from the product stream; and

reacting the hydrogen halide with a source of oxygen in the presence of an oxidation catalyst to generate a corresponding halogen.

85. The method of claim 84 wherein the hydrogen halide is separated from the product stream using temperature swing absorption.

86. The method of claim 85 further comprising:

providing an aqueous hydrogen halide stream;

providing an absorption vessel;

providing a separation vessel;

contacting the product stream with the aqueous hydrogen halide stream in the absorption vessel to absorb at least some of the hydrogen halide in the product stream in the aqueous hydrogen halide stream;

transferring the aqueous hydrogen halide stream containing at least some of the hydrogen halide to the separation vessel, wherein at least a portion of the hydrogen halide in the aqueous hydrogen halide stream is removed through heating; and

recycling the aqueous hydrogen halide stream to the absorption vessel.

87. The method of claim 86 wherein the aqueous hydrogen halide stream entering the absorption vessel has a hydrogen halide concentration of at least about 48 % by weight.

88. The method of claim 86 wherein the aqueous hydrogen halide stream exiting the absorption vessel has a hydrogn halide concentration from about 50% to about 80% by weight of the aqueous hydrogen halide stream.

89. The method of claim 86 wherein the aqueous hydrogen halide stream is heated in the separation vessel to greater than about 125 °C.