

ZONE REACTOR INCORPORATING REVERSIBLE HYDROGEN HALIDE CAPTURE AND RELEASE

FIELD OF THE INVENTION

[0001] This invention relates to a process and apparatus for converting hydrocarbon feedstocks into higher hydrocarbons.

BACKGROUND OF THE INVENTION

[0002] U.S. Pat. No. 6,525,230 discloses a method of converting alkanes to alcohols and/or ethers, and a zone reactor comprised of a hollow, unsegregated interior defining first, second, and third zones. In a first embodiment, air or oxygen reacts with metal bromide in the first zone to provide bromine; bromine reacts with alkane(s) in the second zone to form alkyl bromides; and the alkyl bromides react with metal oxide in the third zone to form the corresponding product(s). Metal bromide from the third zone is transported through the vessel to the first zone, and metal oxide from the first zone is recycled to the third zone. A second embodiment differs from the first embodiment in that metal oxide is transported through the vessel from the first zone to the third zone, and metal bromide is recycled from the third zone to the first zone. In a third embodiment, the flow of gases through the vessel is reversed to convert the metal oxide back to metal bromide and to convert the metal bromide back to the metal oxide.

SUMMARY OF THE INVENTION

[0003] The present disclosure provides an improved zone reactor and a process for converting a hydrocarbon feedstock into one or more higher hydrocarbons.

[0003a] In a first aspect, there is provided a reactor for converting a hydrocarbon feedstock into one or more products, comprising: one or more hollow vessels that define multiple zones in the reactor, wherein a first zone contains a material capable of releasing hydrogen halide and a carbon-carbon coupling catalyst, a second zone is coupled to the first zone, and a third zone is coupled to the second zone and contains a carbon-carbon coupling catalyst and a material capable of capturing hydrogen halide.

[0003b] In a second aspect, there is provided a reactor for converting a hydrocarbon feedstock into higher hydrocarbons, comprising: a hollow vessel having first, second, and third zones, wherein the first zone contains partially halogenated olefins and/or partially halogenated unsaturated organic polymers, and ZSM-5 zeolites; the second zone is

coupled to the first zone and contains a metal oxide; and the third zone is coupled to the second zone and contains a microporous coupling catalyst and medium- to long-chain olefins and/or unsaturated organic polymers.

5 **[0003c]** In one embodiment, an improved zone reactor comprises a vessel having first, second, and third zones, wherein the first zone contains both a material capable of releasing hydrogen halide (HX) and a carbon-carbon coupling catalyst; the second zone is initially empty (other than an ambient atmosphere) or contains a halogenation and/or oxyhalogenation catalyst; and the third zone contains both a carbon-carbon coupling catalyst and a material capable of capturing HX. Gases can flow through each of the first, second, and third zones. Preferably a gas inlet and/or outlet is provided in each of the first, second, and third zones, including an inlet in zone 2 for introducing a gaseous hydrocarbon feedstock.

15 **[0004]** In a third aspect, there is provided a process for converting a hydrocarbon feedstock into higher hydrocarbons, comprising: forming a first stream of hydrogen halide (HX) by heating a material capable of releasing HX in the presence of air or oxygen; forming alkyl halides by reacting a hydrocarbon feedstock and the first stream of HX in the presence of air or oxygen; forming higher hydrocarbons and a second stream of HX by reacting the alkyl halides in the presence of a second carbon-carbon coupling catalyst; and capturing the second stream of HX by reacting it with a material capable of capturing HX.

20 **[0004a]** In a fourth aspect, there is provided a process for converting a hydrocarbon feedstock into higher hydrocarbons, comprising;

- (a) forming hydrogen halide (HX) and a material capable of capturing HX by heating a material capable of releasing HX in the presence of air or oxygen;
- 25 (b) forming alkyl halides by reacting a hydrocarbon feedstock with the HX formed in step (a) in the presence of air or oxygen;
- (c) forming higher hydrocarbons and additional HX by reacting the alkyl halides in the presence of a coupling catalyst; and
- (d) forming a material capable of releasing HX by reactively capturing the HX formed in step (c) with a material capable of capturing HX.

30 **[0004b]** In an embodiment of the present disclosure, an improved process for converting a hydrocarbon feedstock into higher hydrocarbons comprises forming HX by heating a material capable of releasing HX, in the presence of air or oxygen; optionally decoking a carbon-carbon coupling catalyst; forming alkyl halides by reacting a hydrocarbon feedstock with HX

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in the presence of air or oxygen; forming higher hydrocarbons and HX (and, less desirably, coke) by reacting the alkyl halides in the presence of a carbon-carbon coupling catalyst; and capturing HX by reacting it with a material capable of capturing HX. Preferably, the process is repeated multiple times, with alternating HX release and capture and alternating coking and decoking of the coupling catalyst. In one embodiment, HX is released by dehydrohalogenating a partially halogenated olefin or polyolefin, and captured by hydrohalogenating the olefin or polyolefin.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] These and other aspects and features of the invention will become more clear when considering in light of the appended drawings, wherein:

[0006] FIG. 1 is a schematic diagram of a zone reactor according to one embodiment of the invention; and

[0007] FIG. 2 is a schematic diagram of zone 2 of an improved zone reactor according to another embodiment to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The present invention provides a process and an improved zone reactor for converting a hydrocarbon feedstock into one or more useful products, i.e., "higher hydrocarbons." Generally, the process comprises forming a first stream or quantity of hydrogen halide (HX) by heating a material capable of releasing HX in air or oxygen; forming alkyl halides by reacting a hydrocarbon feedstock and the first stream of HX in air or oxygen; forming higher hydrocarbons and a second stream or quantity of HX by reacting the alkyl halides in the presence of a second carbon-carbon coupling catalyst; and capturing the second stream of HX by reacting it with a material capable of capturing HX.

[0009] The general features and mode of operation of one embodiment of an improved zone reactor are schematically depicted in Figs. 1A and 1B. A zone reactor 10 in the form of a generally hollow vessel contains a first zone 1 which is further subdivided into two subzones, 1A and 1B; a second zone 2; and a third zone 3, which is further subdivided into zones 3A and 3B.

[0010] Initially, zone 1A contains a material capable of releasing HX, as described below. Zone 1B contains a carbon-carbon coupling catalyst, which catalyzes carbon-carbon bond formation and the generation of higher hydrocarbons. Although not bound by theory, it is believed that carbon-carbon bond formation proceeds via intermolecular -- and possibly even intramolecular -- metathesis reactions of alkyl halide molecules. In the drawing, the catalyst in zone 1B is also coated and/or impregnated with coke, as described below. When the reactor is loaded for its inaugural run, however, no coke is present. Zone 2 is either empty or

contains a halogenation and/or oxyhalogenation catalyst or cataloreactant. Zone 3B also contains a carbon-carbon coupling catalyst, and zone 3A contains a material capable of capturing HX.

[0011] A first opening or inlet 4 in the left end of the reactor allows air or oxygen to be introduced into the vessel. A second opening or inlet 5 in the middle of the reactor allows a gaseous hydrocarbon feedstock to be introduced, and a third opening or inlet 6, in the right end of the vessel allows product(s) to be withdrawn. In addition, each of the zones and subzones meet at boundaries 7 that permit the flow of gases into adjoining zones. In one embodiment, the vessel has an unsegregated interior, and adjacent zones and subzones are not physically separated from one another. In another embodiment, adjacent zones and subzones are separated by a screen, or by a wall or other divider that has at least one opening provided therein to permit gases to flow from one zone or subzone to the next. Various heaters and/or coolers (not shown) are thermally coupled to the vessel, directly or indirectly, to facilitate temperature control at each zone and subzone.

[0012] As shown in FIG. 1A, initially the reactor operates from left to right, with air or oxygen being introduced through a gas inlet 4 into zone 1A, causing the material contained therein to release gaseous HX. Heated air or oxygen and HX from zone 1A pass into zone 1B and into contact with the carbon-carbon coupling catalyst. The air or oxygen reacts with any coke that has previously been deposited in or on the catalyst and converts it to CO₂. In the presence of an excess of air or oxygen, any CO that is formed will also be converted to CO₂.

[0013] In zone 2, a gaseous, hydrocarbon feedstock is introduced into the vessel through the second gas inlet 5 and allowed to react with HX in the presence of air or oxygen and, preferably, a halogenation and/or oxyhalogenation catalyst or cataloreactant. This results in the formation of one or more alkyl halides (RX) and steam, which are carried, along with any HX that is present, into zone 3B. There, the alkyl halide(s) react in the presence of a carbon-carbon coupling catalyst and are converted to higher hydrocarbons and HX. The reaction also can, and typically will, result in the formation of coke, with coke particles being deposited on the carbon-carbon coupling catalyst as a coating and/or within the interstitial voids of the catalyst. The HX that is formed then reacts with a material capable of capturing it in zone 3A. The gaseous hydrocarbon products, CO₂, residual air (or its oxygen-depleted components), water, and possibly other species, are carried out of the reactor vessel through the third opening 6 and can be collected, separated and purified, further reacted, and/or processed in some other manner.

[0014] FIG. 1B illustrates the zone reactor ready for a run in the reverse direction, from right to left. The reactor 10 still contains zones 1-3 and subzones 1A, 1B, 3B, and 3A, but now the material in zone 3A is capable of releasing HX when heated in air or oxygen (having been hydrohalogenated when the reactor was run in the forward direction). Similarly, the

catalyst in zone 3B is now coated and/or impregnated with coke, whereas the catalyst in zone 1B has little or (ideally) no coke. The material in zone 1A is ready to react with, and thereby capture and store, HX. Air or oxygen is introduced through the third inlet 6 in zone 3A and causes the material contained therein to release HX, which flows, along with air or oxygen, into zone 3B. The air or oxygen oxidizes the coke that has been deposited on the carbon-carbon coupling catalyst. HX and air or oxygen are carried downstream into zone 2, where they react with the hydrocarbon feedstock to form alkyl halides and steam, which pass into zone 1B. The alkyl halides react in zone 1B in the presence of the carbon-carbon coupling catalyst, and form hydrocarbon products, HX, and coke (which is deposited on and/or in the catalyst). HX, CO₂, air or its components, steam, and possibly other gases then pass into zone 1A, and the HX reacts with and is captured by the material contained therein. Products and residual gases exit through the first opening 4. The reactor is again ready to be run in the forward direction. By cycling between the forward and reverse directions, the reactor can be operated continually.

[0015] In an alternate embodiment, the flow of gaseous reactants always maintains the same direction, and the reaction zones are stationary. However, the solids are continuously regenerated. As the halide contained within zone 1A is depleted, solid is withdrawn at a constant rate from that zone and transported into zone 3A. Similarly, fully regenerated solid is constantly withdrawn from zone 3A and transported back to zone 1A. The solid transport between zones 1A and 3A is facilitated by gravity, pneumatic transport, other mechanical means (e.g., conveyors), or a combination of methods. In a similar manner, regenerated carbon-carbon coupling catalyst in zone 1B is continuously withdrawn and transported to zone 3B, and coked carbon-carbon coupling catalyst is transported from Zone 3B to Zone 1B for regeneration. Transport of the coupling catalyst is facilitated by gravity, pneumatic transport, other mechanical means, or a combination of methods.

[0016] As used here and in the claims, the use of the singular or the plural in reference to a compound, catalyst, or other substance is not intended to limit the substance to a particular number of molecules or quantity, nor to a particular number of different types of the substance, unless otherwise indicated. For example, "higher hydrocarbons" can include a quantity of predominately one, or exactly one, compound (e.g., a quantity of isooctane) or two or more different compounds (e.g., butane, benzene, propylene, etc.). Similarly, "olefins" refers to a quantity of a single olefin, or two or more different olefins; "zeolites" refers to a quantity of one or more different zeolites; etc.

[0017] It is contemplated that any of a number of hydrocarbon feedstocks will be used in the practice of the present invention. Nonlimiting examples include one or more light alkanes and/or olefins, e.g., methane, ethane, propane, butane, ethylene, propylene, butenes; natural gas; and other mixtures of hydrocarbons. In most embodiments, the feedstock will be primarily aliphatic in nature. Certain oil refinery processes yield light hydrocarbon streams

(so-called "light-ends," typically a mixture of C1 - C3 hydrocarbons), which can be used with or without added methane. In general, the feedstock is introduced into the reactor as a gas.

[0018] The products of the zone reactor -- one or more "higher hydrocarbons" -- will depend on the feedstock, the carbon-carbon coupling catalyst, and the reactor conditions, e.g., gas flow rates (which affects reactor residence time), temperature, and pressure. As used herein, the term "higher hydrocarbon" refers to a hydrocarbon having a higher carbon number (greater number of carbon atoms per molecule) and/or a higher bond order than one or more components of the hydrocarbon feedstock. For example, if the feedstock is pure methane (carbon number 1, bond order 1), the resulting higher hydrocarbons produced could be ethane, propane, ethylene, propylene, larger alkanes and olefins, possibly alkynes, and/or aromatic compounds. If the feedstock is pure ethane (carbon number 2; bond order 1), the resulting higher hydrocarbons could be propane (carbon number 3; bond order 1), ethylene (carbon number 2, bond order 2), etc. If the feedstock is natural gas -- typically a mixture of light hydrocarbons, predominately methane, with lesser amounts of ethane, propane, and butane, and even smaller amounts of longer hydrocarbons such as pentane, hexane, etc. -- the resulting higher hydrocarbons could include one or more C2 or higher alkanes (e.g., ethane, propane, butane, C5+ hydrocarbons and other light naphthas); olefins (e.g., ethylene, propylene, butylene, etc.); and/or aromatic hydrocarbons.

[0019] Certain classes of higher hydrocarbons are particularly desirable, including "gasoline range" hydrocarbons, e.g., C4 - C12 alkanes, more preferably C5 - C10 alkanes, with or without olefinic and/or aromatic components. C5+ alkanes with high aromatic content, but low benzene content are particularly desirable as gasolines or gasoline blending agents. Other desirable products include aromatic compounds -- benzene, toluene, xylene (especially p-xylene), mesitylene, etc.-- and especially aromatic products with low benzene content. In one embodiment, the product consists predominantly of benzene, or benzene-rich aromatics. In another embodiment, the product consists predominantly of toluene, or toluene-rich aromatics. In one embodiment, the aromatic content of the product is enriched by recycling non-aromatic components to the solid reactor. In the case of saturated aliphatic compounds, this entails re-bromination followed by carbon-carbon coupling in the presence of a coupling catalyst, whereas olefinic compounds may be coupled directly (in the presence of a coupling catalyst as described herein).

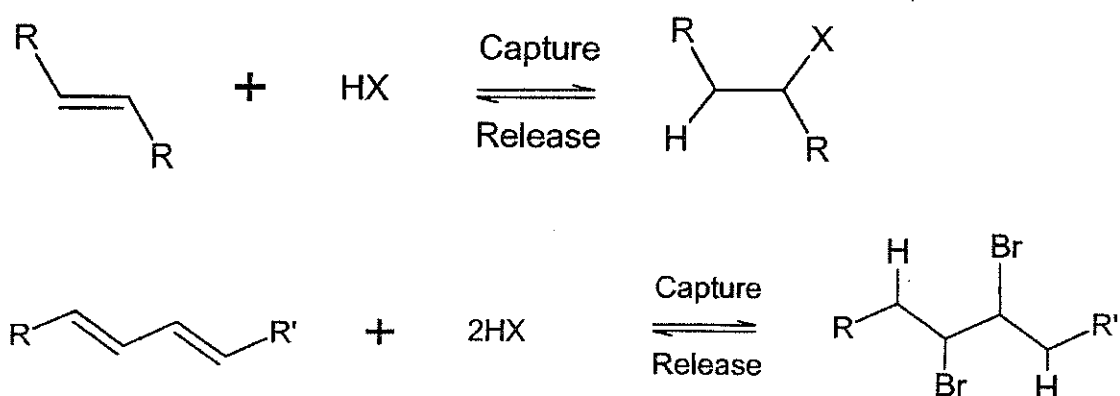
[0020] Representative hydrogen halides (HX) include hydrogen bromide (HBr) and hydrogen chloride (HCl). It is also contemplated that hydrogen fluoride (HF) and hydrogen iodide (HI) can be used, though not necessarily with equivalent results. Some of the problems associated with fluorine can likely be addressed by using dilute streams of HF (e.g., HF gas carried by helium, nitrogen, or other diluent). It is expected, however, that more vigorous reaction conditions will be required for alkyl fluorides to couple and form higher hydrocarbons, due to the strength of the fluorine-carbon bond. Similarly, problems

associated with HI (such as the endothermic nature of certain iodine reactions) can likely be addressed by carrying out the halogenation and/or coupling reactions at higher temperatures and/or pressures. The use of HBr or HCl is preferred, with HBr being most preferred.

[0021] A number of materials are capable of reversibly capturing and releasing HX and, in particular, HCl and HBr. As a first example, such materials comprise medium- to long-chain olefins, i.e., olefins having 10-100, preferably 15-80, more preferably 20-50 carbon atoms per molecule. In general, such olefins will have more than one carbon-carbon double bond per molecule. Nonlimiting specific examples include 1-dodecene, 1,12-dodecadiene, and i-eicosane. Unsaturated olefins undergo addition reactions with HX to form partially halogenated olefins or alkanes, and thereby "reactively capture" HX. When the materials are heated, they release HX and revert to olefins.

[0022] As a second example, unsaturated organic polymers can capture HX to form partially halogenated organic polymers, which, in turn, can release HX. Nonlimiting examples include polyacetylene, polyethylene that has been partially dehydrogenated, polypropylene that has been partially dehydrogenated, and mixtures thereof. Polyethylene and polypropylene can be dehydrogenated according to methods well known to those skilled in the art, e.g., via halogenation followed by dehydrohalogenation. Polybutadiene is another example of an unsaturated organic polymer that may be used to capture, and then release, HX.

[0023] Olefins and unsaturated organic polymers capture HX by reacting with it to form partially halogenated compounds. The reaction can be reversed by heating the materials in the presence of air or oxygen. The following equations are nonlimiting examples of the basic scheme:



[0024] In one embodiment, the unsaturated material is carried on a support, such as silica, titania, or a similar heat-resistant, inorganic, generally inert material. As one example, silica pellets are coated with polyethylene by combining the pellets and polyethylene, heating the mixture to a temperature above the glass transition temperature of the polyethylene, and then

adding halogen to the pellets and exposing the combination to ultraviolet light, thereby halogenating the polymer.

[0025] In zone 2, alkyl halides are formed by reacting a hydrocarbon feedstock with HX and O₂ (oxyhalogenation) and/or by reacting alkyl halides with X₂ (halogenation). UV light and/or heat can drive the reaction. In a preferred embodiment, the reaction takes place in the presence of a halogenation and/or oxyhalogenation catalyst or cataloreactant. Nonlimiting examples include metal oxides, such as copper oxide (CuO), and metal halides, such as CuCl₂, CuBr₂, etc. Mixtures of catalysts can be used. The catalytic materials can be supported or unsupported.

[0026] In FIG. 1, the catalyst is located throughout zone 2. In an alternate embodiment shown in FIG. 2, the halogenation and/or oxyhalogenation catalyst is confined to downstream and upstream regions 8 of zone 2, leaving an empty central area 9.

[0027] In Zones 1B and 3B, a carbon-carbon coupling catalyst is utilized to facilitate the conversion of alkyl halides to higher hydrocarbons. As used herein, the term "carbon-carbon coupling catalyst" refers to a material capable of catalyzing carbon-carbon bond formation, and includes both "true" catalysts, which presumably participate in the reaction on a mechanistic level, but are not consumed in the process, as well as "cataloreactants," which are chemically transformed in the course of the reaction, but can be returned to their original form via a regeneration reaction. For example, oxygen atoms in the cataloreactant could be replaced by halogen atoms during the carbon-carbon coupling reaction, and then regenerated (with halogen being replaced by oxygen) in a subsequent regeneration step, such as by the passage of air or oxygen over the initially transformed cataloreactant material. Carbon-carbon coupling catalysts are also referred to as "oligomerization catalysts," or simply, "coupling catalysts."

[0028] Nonlimiting examples of coupling catalysts include non-crystalline alumino silicates (amorphous solid acids), tungsten/zirconia super acids, sulfated zirconia, alumino phosphates such as SAPO-34 and its framework-substituted analogues (substituted with, e.g., Ni or Mn), Zeolites, such as ZSM-5 and its ion-exchanged analogs, and framework substituted ZSM-5 (substituted with Ti, Fe, Ti + Fe, B, or Ga). and other microporous minerals. The catalysts can be natural or synthetic, doped or undoped, supported or unsupported.

[0029] Preferred catalysts for producing liquid-at-room-temperature hydrocarbons include ion-exchanged ZSM-5 having a SiO₂/Al₂O₃ ratio of less than 300:1, preferably less than 100:1, and most preferably 30:1 or less. Nonlimiting examples of preferred exchanged ions include ions of Ag, Ba, Bi, Ca, Fe, Li, Mg, Sr, K, Na, Rb, Mn, Co, Ni, Cu, Ru, Pb, Pd, Pt, and Ce. These ions can be exchanged as pure salts or as mixtures of salts. The preparation of doped zeolites and their use as carbon-carbon coupling catalysts is described in

Patent Publication No. US 2005/0171393 A1, at pages 4-5, which is incorporated by reference herein in its entirety.

[0030] Zeolites are available from a variety of sources, including Zeolyst International (Valley Forge, PA). Specific examples include doped-ZSM-5 and doped mordenite (where, e.g., calcium and/or magnesium are the dopants). In one embodiment of the invention a Mn-exchanged ZSM-5 zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30 is used as the coupling catalyst. Under certain process conditions, it can produce a tailored selectivity of liquid hydrocarbon products.

[0031] Product distribution can be shifted in favor of more aromatic content, less aromatic content, gasoline grade materials by altering the properties of the zeolite or other catalyst. Pore size and acidity are expected to be important. Acidity may be used to control product chain length and functionality, and pore size may control chain length and functionality. Zeolites having a particular pore size may selectively produce benzene, toluene, para-xylene, ortho-xylene, meta-xylene, mixed xylenes, ethylbenzene, styrene, linear alkylbenzene, and/or other aromatic products. Pore size can also be expected to affect formation of non-aromatic products.

[0032] In various aspects of the invention, air or oxygen is used to accomplish a desired result, for example, decoking, oxyhalogenation, HX release, cataloreactant regeneration, etc. It is to be understood that the term "air or oxygen" in this context includes any of a number of oxygen-based or oxygen-containing gas streams. Nonlimiting examples include ordinary air, pure oxygen gas (O_2), oxygen gas containing minor amounts of other gaseous components, dilute streams of oxygen gas in a carrier gas (e.g., helium), oxygen-enriched air, etc.

[0033] To facilitate the various steps of HX capture and release, catalyst decoking, halogenation and/or oxyhalogenation, and product formation, different zones of the reactor are operated at appropriate pressures and temperatures, taking into account the feedstock, catalysts, gas flow rates, and desired product(s). In one embodiment, the reactor is operated at, or slightly above, atmospheric pressure. Zone 1A or 3A is heated to a temperature of from 0 to 500 °C, preferably 100 to 400 °C, more preferably 200 to 300 °C, to facilitate HX release. Zone 3A or 1A is heated to a slightly lower temperature, e.g., 0 to 400 °C, preferably 100 to 300 °C, more preferably 150 to 250 °C, to facilitate HX capture. Decoking of the coupling catalyst is facilitated by heating zone 1B or 3B to a higher temperature, e.g., about 500 °C. Halogenation and/or oxyhalogenation of the hydrocarbon feedstock occurs in zone 2, which is heated to a temperature of 150 to 600 °C, preferably 400 to 600 °C, more preferably 450 to 515 °C. Product formation (carbon-carbon coupling) is facilitated by heating zone 3B or 1B to a temperature of 150 to 600 °C, preferably 275 to 425 °C.

[0034] There are a number of alternate embodiments for practicing the invention. For example, instead of a single vessel defining three zones, the zone reactor can comprise three separate vessels, each defining a separate zone, 1, 2, or 3. As another example, certain

reactor designs offer the possibility of improved heat transfer. Thus, the reactor can be configured as a series of small tubes (inner diameter less than 6 inches, more preferably from 2 to 4 inches). As a third example, instead of an in-line configuration, the tubes can be arranged in parallel and enclosed in a larger vessel, in which a suitable heat transfer fluid is circulated. Alternatively, the bundle of tubes can have air or another inert gas directed across their surface to facilitate cooling and/or heating.

[0035] In some applications, where the outlet from zone 2 must be cooled before entering the product formation (metathesis) zone (zone 1B or 3B), a precooler can be used. In one embodiment, the precooler comprises an air-cooled bundle of tubes, or tubes enclosed in a shell in which a suitable heat transfer fluid is circulated around the tubes. The use of a precooler can decrease the required reactor volume in the metathesis zone. The requirement of heat removal during metathesis can strongly influence reactor design.

[0036] Another alternative is to use an inert heat carrier within the interior of the reactor itself. For example, an excess of alkane feedstock can be introduced to dissipate the heat, thereby allowing the reactor to be in a packed bed configuration instead of a tube-shell arrangement. The use of an internal heat carrier should allow the reactor to be operated adiabatically. An inert stream that can be separated easily from the reaction product stream can also be used as a heat carrier in this configuration. It is expected that an adiabatic packed bed scheme can significantly reduce reactor cost.

[0037] In still another embodiment of the invention, a zone reactor is used in combination with a post-reactor bed packed with ZSM-5 zeolites or other materials that facilitate production of gasoline-range hydrocarbons. For example, a zone reactor can be used to form light olefins, which are then fed into a zeolite bed to facilitate coupling of the light olefins into gasoline-range hydrocarbons.

[0038] A number of materials of construction may be employed to enhance the lifetime of the zone reactor. Nonlimiting examples include Hastelloy alloys, aluminum- and chromium-enriched metal alloys, titanium, zirconium, tantalum and nickel metal and their alloys, silica-, alumina-, and zirconia-coated metals, and heat conducting ceramic materials such as silicon carbide. Reactor vessels also can be constructed of insulating, corrosion-resistant materials, for example, alumina, silica, and zirconia, each lined with a corrosion-resistant, but not necessarily temperature-resistant, material, such as polytetrafluoroethylene. Under some conditions, the vessel can be operated isothermally, with heating and/or cooling provided by a heat transfer fluid passed through pipes constructed of the types of heat-conducting materials listed above. Alternatively, the reactor can be operated adiabatically.

Examples

[0039] The following are nonlimiting examples of the invention.

[0040] Preparation of Materials Capable of Releasing and Capturing HBr

Reagents A and B

[0041] High surface area ($>300 \text{ m}^2/\text{g}$) silica pellets are coated with polyethylene by combining the pellets and polyethylene and heating to a temperature above the glass transition temperature of the polyethylene. Bromine is added to the pellets and the combination is exposed to UV light, resulting in bromination of the polymer. Half of the material is separated and heated to 225°C , resulting in the release of HBr and formation of a material, Reagent A, capable of capturing HBr. The other half of the material, Reagent B, is kept for use as a material capable of releasing HBr.

Reagents C and D

[0042] Formation of an adsorbent. High surface area ($>300 \text{ m}^2/\text{g}$) silica pellets are coated with polyethylene by combining the pellets and polyethylene and heating to a temperature above the glass transition temperature of the polyethylene. Chlorine is added to the pellets and the combination is exposed to UV light, resulting in chlorination of the polymer. Half of the material is separated and heated to 225°C , resulting in the release of HCl. The other half of the material is kept for use as an HCl-containing adsorbent.

Example 1

[0043] A zone reactor as shown in Fig. 1 is loaded with the following materials:

Zone 1A: Reagent B.

Zone 1B: ZSM-5 coupling catalyst.

Zone 2 : copper oxide catalyst.

Zone 3B: ZSM-5 coupling catalyst.

Zone 3A: Reagent A.

In step 1, air is passed through zone 1A at a temperature of 225°C , converting Reagent B to Reagent A and releasing HBr. The air and HBr from zone 1A pass first into zone 1B at a temperature of 500°C (in subsequent runs this will regenerate (decoke) the coupling catalyst), and then into zone 2, where natural gas is oxybrominated at 400°C . The products of zone 2 pass over the coupling catalyst in zone 3B at 400°C , producing higher hydrocarbon and HBr. In zone 3A, HBr is captured by Reagent A (which is converted to Reagent B) at a temperature of 150°C .

In step 2, air is passed through zone 3A at a temperature of 225°C , converting Reagent B to Reagent A and releasing HBr. The air and HBr from zone 3A pass into zone 3B at a temperature of 500°C , regenerating (decoking) the coupling catalyst. In zone 2, natural gas is oxybrominated at 400°C . The products of zone 2 pass over the coupling catalyst in zone 1B at 400°C producing higher hydrocarbons and HBr. In zone 1A, HBr is captured by Reagent A (which is converted to Reagent B) at a temperature of 150°C .

Example 2.

[0044] The hydrocarbon products of Example 1 are passed over a ZSM-5 catalyst at a temperature of 350 to 450 °C, so as to change the average molecular weight of the products.

Example 3

[0045] The procedure of example 1 is followed, but instead of ZSM-5, a mixture of tungsten oxide and zirconia (WZA) is used as the carbon-carbon coupling catalyst.

Example 4

[0046] The hydrocarbon products of Example 3 are passed over a ZSM-5 catalyst at a temperature of 350 to 450 °C, so as to change the average molecular weight of the products.

Example 5.

[0047] A zone reactor as shown in Fig. 1 is loaded with the following materials:

Zone 1A: Reagent D.

Zone 1B: ZSM-5 coupling catalyst.

Zone 2 : copper oxide catalyst.

Zone 3B: ZSM-5 coupling catalyst.

Zone 3A: Reagent C.

In step 1, air is passed through zone 1A at a temperature of 225 °C , converting Reagent D to Reagent C and releasing HCl. The air and HCl from zone 1A pass into zone 1B at a temperature of 500 °C (in subsequent runs, this will regenerate (decoke) the coupling catalyst), and then into zone 2, where natural gas is oxychlorinated at 400 °C. The products of zone 2 pass over the coupling catalyst in zone 3B at 400 °C, producing higher hydrocarbon and HCl. In zone 3A, HCl is captured by Reagent C (which is converted to Reagent D) at a temperature of 150 °C.

In step 2, air is passed through zone 3A at a temperature of 225 °C , converting Reagent D to Reagent C and releasing HCl. The air and HCl from zone 3A pass into zone 3B at a temperature of 500 °C, regenerating (decoking) the coupling catalyst. In zone 2, natural gas is oxychlorinated at 400 °C. The products of zone 2 pass over the coupling catalyst in zone 1B at 400 °C, producing higher hydrocarbons and HCl. In zone 1A, HCl is captured by Reagent C (which is converted to Reagent D) at a temperature of 150 °C.

Example 6

[0048] The hydrocarbon products of Example 5 are passed over a ZSM-5 catalyst at a temperature of 350 to 450 °C, so as to change the average molecular weight of the product.

Example 7.

[0049] The procedure of example 5 is followed, but instead of ZSM-5, a mixture of tungsten oxide and zirconia (WZA) is used as the carbon-carbon coupling catalyst.

Example 8.

[0050] The hydrocarbon products of Example 7 are passed over a ZSM-5 catalyst at a temperature of 350 and 450 °C, so as to change the average molecular weight of the products.

[0051] The invention has been described with reference to various embodiments, figures, and examples, but is not limited thereto. Persons having ordinary skill in the art will appreciate that the invention can be modified in a number of ways without departing from the invention, which is limited only by the appended claims and equivalents thereof.

WHAT IS CLAIMED IS:

1. A reactor for converting a hydrocarbon feedstock into one or more products, comprising:
one or more hollow vessels that define multiple zones in the reactor, wherein a first zone contains a material capable of releasing hydrogen halide and a carbon-carbon coupling catalyst, a second zone is coupled to the first zone, and a third zone is coupled to the second zone and contains a carbon-carbon coupling catalyst and a material capable of capturing hydrogen halide.
2. A reactor as recited in claim 1, wherein the reactor comprises a single vessel and the first zone is located at a first end of the vessel, the second zone is located in the middle of the vessel, and the third zone is located at a second end of the vessel, and wherein gas can flow from the first zone to the second zone and from the second zone to the third zone.
3. A reactor as recited in claim 1, wherein: the first zone is located in a first vessel, the second zone is located in a second vessel, and the third zone is located in a third vessel, and wherein gas can flow from the first zone to the second zone and from the second zone to the third zone.
4. A reactor as recited in claim 1, wherein the material capable of releasing hydrogen halide is located in a first subzone in the first zone, the carbon-carbon coupling catalyst in the first zone is located in a second subzone in the first zone, the carbon-carbon coupling catalyst in the third zone is located in a first subzone in the third zone, and the material capable of capturing hydrogen halide is located in a second subzone in the third zone.
5. A reactor as recited in claim 1, wherein the material capable of releasing hydrogen halide comprises partially halogenated olefins.
6. A reactor as recited in claim 5, wherein the partially halogenated olefins comprise 10-100 carbon atoms per molecule.
7. A reactor as recited in claim 5, wherein the partially halogenated olefins comprise 15-80 carbon atoms per molecule.
8. A reactor as recited in claim 5, wherein the partially halogenated olefins comprise 20-50 carbon atoms per molecule.

9. A reactor as recited in claim 5, wherein the partially halogenated olefins comprise partially halogenated 1-dodecene, 1,12-dodecadiene, and/or 1-eicosane.
10. A reactor as recited in claim 5, wherein the material capable of releasing hydrogen halide comprises partially halogenated organic polymers.
11. A reactor as recited in claim 10, wherein the partially halogenated organic polymers are selected from the group consisting of partially halogenated polyacetylene, polyethylene that has been partially dehydrogenated and partially halogenated, polypropylene that has been partially dehydrogenated and partially halogenated, and mixtures thereof.
12. A reactor as recited in claim 10, wherein the partially halogenated organic polymers comprise partially halogenated polybutadiene.
13. A reactor as recited in claim 1, wherein the material capable of capturing hydrogen halide comprises olefins that comprise 10-100 carbon atoms per molecule.
14. A reactor as recited in claim 13, wherein the olefins comprise 15-80 carbon atoms per molecule.
15. A reactor as recited in claim 13, wherein the olefins comprise 20-50 carbon atoms per molecule.
16. A reactor as recited in claim 1, wherein the material capable of capturing hydrogen halide comprises unsaturated organic polymers.
17. A reactor as recited in claim 16, wherein the unsaturated organic polymers are selected from the group consisting of polyacetylene, polyethylene that has been partially dehydrogenated, polypropylene that has been partially dehydrogenated, and mixtures thereof.
18. A reactor as recited in claim 16, wherein the unsaturated organic polymers comprise polybutadiene.
19. A reactor as recited in claim 1, wherein the second zone contains a halogenation and/or oxyhalogenation catalyst.
20. A reactor as recited in claim 19, wherein the halogenation and/or oxyhalogenation catalyst comprises copper oxide.

21. A reactor as recited in claim 19, wherein the halogenation and/or oxyhalogenation catalyst comprises a copper halide.
22. A reactor as recited in claim 21, wherein the copper halide comprises copper bromide or copper chloride.
23. A reactor as recited in claim 1, wherein the carbon-carbon coupling catalyst in the first zone and/or the carbon-carbon coupling catalyst in the third zone comprises a microporous material.
24. A reactor as recited in claim 23, wherein the microporous material comprises supported or unsupported zeolites.
25. A reactor as recited in claim 24, wherein the zeolites comprise doped zeolites.
26. A reactor as recited in claim 24, wherein the zeolites comprise ZSM-5-type zeolites.
27. A reactor as recited in claim 1, wherein the first, second, and thirds zones are located inside a single hollow vessel; the first and second zones are separated by a first divider having at least one opening therein; and the second and third zones are separated by a second divider having at least one opening therein.
28. A reactor as recited in claim 27, wherein the first and second dividers comprises a screen.
29. A reactor for converting a hydrocarbon feedstock into higher hydrocarbons, comprising:
a hollow vessel having first, second, and third zones, wherein the first zone contains partially halogenated olefins and/or partially halogenated unsaturated organic polymers, and ZSM-5 zeolites; the second zone is coupled to the first zone and contains a metal oxide; and the third zone is coupled to the second zone and contains a microporous coupling catalyst and medium- to long-chain olefins and/or unsaturated organic polymers.
30. A reactor as recited in claim 29, wherein the metal oxide comprises copper oxide.
31. A reactor as recited in claim 29, wherein the microporous coupling catalyst comprises ZSM-5 zeolites.

32. A reactor as recited in claim 29, wherein the partially halogenated olefins and/or the partially halogenated unsaturated organic polymers are located in a first subzone in the first zone; the ZSM-5 zeolites are located in a second subzone in the first zone; the microporous coupling catalyst is located in a first subzone in the third zone; and the medium-to long-chain olefins and/or the unsaturated organic polymers are located in a second subzone in the third zone.

33. A process for converting a hydrocarbon feedstock into higher hydrocarbons, comprising:

forming a first stream of hydrogen halide (HX) by heating a material capable of releasing HX in the presence of air or oxygen;

forming alkyl halides by reacting a hydrocarbon feedstock and the first stream of HX in the presence of air or oxygen;

forming higher hydrocarbons and a second stream of HX by reacting the alkyl halides in the presence of a second carbon-carbon coupling catalyst; and

capturing the second stream of HX by reacting it with a material capable of capturing HX.

34. A process as recited in claim 33, further comprising decoking the first and second coupling catalysts.

35. A process as recited in claim 33, wherein the material capable of releasing HX comprises partially halogenated olefins.

36. A process as recited in claim 35, wherein the partially halogenated olefins comprise 10-100 carbon atoms per molecule.

37. A process as recited in claim 36, wherein the material capable of releasing HX comprises partially halogenated organic polymers.

38. A process as recited in claim 37, wherein the partially halogenated organic polymers are selected from the group consisting of partially halogenated polyacetylene, polybutadiene, polyethylene that has been partially dehydrogenated and partially halogenated, polypropylene that has been partially dehydrogenated and partially halogenated, and mixtures thereof.

39. A process as recited in claim 33, wherein the material capable of capturing HX comprises olefins that comprise 10-100 carbon atoms per molecule.

40. A process as recited in claim 33, wherein the material capable of capturing HX comprises unsaturated organic polymers.

41. A process as recited in claim 40, wherein the unsaturated organic polymers are selected from the group consisting of polyacetylene, polybutadiene, polyethylene that has been partially dehydrogenated, polypropylene that has been partially dehydrogenated, and mixtures thereof.

42. A process for converting a hydrocarbon feedstock into higher hydrocarbons, comprising;

(a) forming hydrogen halide (HX) and a material capable of capturing HX by heating a material capable of releasing HX in the presence of air or oxygen;

(b) forming alkyl halides by reacting a hydrocarbon feedstock with the HX formed in step (a) in the presence of air or oxygen;

(c) forming higher hydrocarbons and additional HX by reacting the alkyl halides in the presence of a coupling catalyst; and

(d) forming a material capable of releasing HX by reactively capturing the HX formed in step (c) with a material capable of capturing HX.

43. A process as recited in claim 42, further comprising coking and decoking the coupling catalyst.