METHODS FOR MAKING LIGHT OLEFINS BY DEHYDROGENATION USING CATALYSTS THAT INCLUDE IRON

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application Serial No. 63/352,015, filed June 14, 2022, which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] Embodiments described herein generally relate to chemical processing and, more specifically, to methods and systems for light olefin production.

BACKGROUND

[0003] Light olefins, such as propylene, may be used as base materials to produce many different materials, such as polypropylene, isopropanol, and acrylic acid, which may be used in, e.g., packaging, construction, and textiles. As a result of this utility, there is a worldwide demand for light olefins. Suitable processes for producing light olefins generally depend on the given chemical feed and include those that utilize fluidized catalysts. For example, light olefins may be formed by the catalytic dehydrogenation of alkanes in a fluidized bed reactor. However, there is a need for improvement in the systems and associated catalysts used to make light olefins.

SUMMARY

[0004] Some methods and associated systems used to make light olefins may utilize supplemental fuels that are combusted to heat the catalyst during the production process. For example, the catalyst may be cycled between a reactor, where light olefins are produced in an endothermic reaction, and a combustor, where the catalyst is heated by exothermic combustion of at least a supplemental fuel (sometimes along with combustion of coke). Such catalysts may have catalytic activity not only for the dehydrogenation of alkanes, but also for the combustion of supplemental fuels. Some embodiments of such suitable catalysts include, e.g., gallium and platinum on a support. In some embodiments, methane may be used in the supplemental fuel. In such embodiments, conventional catalysts used for dehydrogenation may suffer from low methane combustion activity, meaning that using methane as a supplemental fuel may not provide heat to sufficiently raise the temperature of the catalyst to the desired temperatures utilized in the

dehydrogenation reaction. Further, using conventional catalysts that may suffer from low methane combustion activity may negatively impact the safety of the dehydrogenation process, as un-combusted methane may exceed the low flammability level required in the regenerator. As is described herein, it has been discovered that catalysts that additionally include iron may enhance combustion of methane as compared with conventional catalysts that, for example, do not include iron.

[0005] According to one or more embodiments of the present disclosure, a method may comprise contacting a hydrocarbon-containing feed with a catalyst in a reactor to form an olefin-containing effluent, then at least partially separating the olefin-containing effluent from the catalyst. The catalyst may be passed to a combustor where the catalyst may be heated by combusting a supplemental fuel. The supplemental fuel may comprise methane in an amount greater than 1 mol.%. The catalyst may be passed from the combustor to the reactor, such that at least a portion of the catalyst may continuously cycle between the reactor and the combustor. The catalyst may comprise from 0.1 wt.% to 10 wt.% of one or more metals chosen from gallium, indium, thallium or combinations thereof, from 5 ppmw to 1000 ppmw of one or more metals chosen from platinum, palladium, rhodium, iridium, ruthenium, osmium, or combinations thereof, from 100 ppmw to 30000 ppmw of iron, and at least 85 wt.% support.

[0006] It is to be understood that both the preceding general description and the following detailed description describe various embodiments and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter. Additional features and advantages of the embodiments will be set forth in the detailed description and, in part, will be readily apparent to persons of ordinary skill in the art from that description, which includes the accompanying drawing and claims, or recognized by practicing the described embodiments. The drawing is included to provide a further understanding of the embodiments and, together with the detailed description, serves to explain the principles and operations of the claimed subject matter. However, the embodiment depicted in the drawing is illustrative and exemplary in nature, and not intended to limit the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The following detailed description may be better understood when read in conjunction with the following drawing, in which:

[0008] FIG. 1 schematically depicts a reactor system, according to one or more embodiments of the present disclosure.

[0009] When describing the simplified schematic illustration of FIG. 1, the numerous valves, temperature sensors, electronic controllers, and the like, which may be used and are well known to a person of ordinary skill in the art, are not included. Further, accompanying components that are often included in such reactor systems, such as air supplies, heat exchangers, surge tanks, and the like are also not included. However, it should be understood that these components are within the scope of the present disclosure.

[0010] Reference will now be made in greater detail to various embodiments, some of which are illustrated in the accompanying drawing.

DETAILED DESCRIPTION

[0011] The present disclosure is directed to methods for making light olefins by dehydrogenation where particular catalyst compositions are utilized, as are described herein. For example, catalysts useful for dehydrogenation may include a catalyst comprising: from 0.1 wt.% to 10 wt.% of one or more metals chosen from gallium, indium, thallium, or combinations thereof; from 5 ppmw to 1000 ppmw of one or more metals chosen from platinum, palladium, rhodium, iridium, ruthenium, osmium, or combinations thereof; from 100 ppmw to 30000 ppmw of iron; and at least 85 wt.% support. In one or more embodiments, such catalysts provide dual catalytic functionality for dehydrogenation of alkanes as well as combustion of supplemental fuels. Such catalysts including iron may be particularly well suited for fluidized dehydrogenation of light alkanes to light olefins, such as propane to propylene, where methane is utilized as a supplemental fuel to heat the catalyst.

[0012] Embodiments of the methods presently disclosed are described in detail herein in the context of the reactor system of FIG. 1 operating as a fluidized dehydrogenation reactor system to produce light olefins, such as propylene. However, it should be understood that the principles disclosed and taught herein may be applicable to other systems which utilize different system components oriented in different ways. For example, the concepts described herein may be equally applied to other systems with alternate reactor units and regeneration units, such as those that operate under non-fluidized conditions or include downers rather than risers. It should be further understood that not all portions of FIG. 1 should be construed as essential to the claimed subject

matter. Moreover, while the recited method steps in the appended claims are described herein in the context of FIG. 1, such recited method steps should be understood as adaptable to other systems, as would be understood by those skilled in the art.

[0013] Now referring to FIG. 1, an example reactor system 102 that may be suitable for use with the methods and/or apparatuses described herein is schematically depicted. The reactor system 102 generally comprises multiple system components, such as a reactor portion 200 and a catalyst processing portion 300. As described herein, "system components" refer to portions of the reactor system 102, such as reactors, separators, transfer lines, combinations thereof, and the like. As used herein in the context of FIG. 1, the reactor portion 200 generally refers to the portion of the reactor system 102 in which the major process reaction takes place (*e.g.*, dehydrogenation) to form the olefin-containing effluent. A hydrocarbon-containing feed enters the reactor portion 200, is contacted with a catalyst, converted to an olefin-containing effluent (containing product and unreacted feed), and exits the reactor portion 200. The reactor portion 200 comprises a reactor 202 which may include an upstream reactor section 250 and a downstream reactor section 230. According to one or more embodiments, as depicted in FIG. 1, the reactor portion 200 may additionally include a catalyst separation section 210, which serves to separate the catalyst from the olefin-containing effluent formed in the reactor 202. Also, as used herein, the catalyst processing portion 300 generally refers to the portion of the reactor system 102 where the catalyst is in some way processed, such as by combustion, to, e.g., improve catalytic activity by decoking and/or heating the catalyst. The catalyst processing portion 300 may comprise a combustor 350 and a riser 330, and may additionally comprise a catalyst separation section 310. In one or more embodiments, the catalyst separation section 210 may be in fluid communication with the combustor 350 (e.g., via standpipe 426) and the catalyst separation section 310 may be in fluid communication with the upstream reactor section 250 (e.g., via standpipe 424 and transport riser 430).

[0014] Generally as is described herein, in embodiments illustrated in FIG. 1, catalyst is cycled between the reactor portion 200 and the catalyst processing portion 300. It should be understood that when "catalysts" are referred to herein, they may refer to solid materials that are catalytically active for a desired reaction. The terms "catalytic activity" and "catalyst activity" refer to the degree to which the catalyst is able to catalyze the reactions conducted in the reactor system 102. The catalyst that exits the reactor portion 200 may be deactivated catalyst. As used herein, "deactivated" may refer to a catalyst which has reduced catalytic activity or is cooler as

compared to catalyst entering the reactor portion 200. However, deactivated catalyst may maintain some catalytic activity. Reduced catalytic activity may result from contamination with a substance such as coke. Coke may form on the catalyst within the reactor portion 200. Reactivation (sometimes called "regeneration" herein) may remove the contaminant such as coke, raise the temperature of the catalyst, or both. In embodiments, deactivated catalyst may be reactivated by catalyst reactivation in the catalyst processing portion 300. The deactivated catalyst may be reactivated by, but not limited to, removing coke by combustion, oxidizing the catalyst, other reactivation process, or combinations thereof. In some embodiments, the catalyst may be heated during reactivation by combustion of a supplemental fuel, such as methane, ethane, propane, natural gas, or combinations thereof. The reactivated catalyst from the catalyst processing portion 300 is then passed back to the reactor portion 200.

[0015] As is disclosed herein, in one or more embodiments the supplemental fuel may comprise methane. For example the supplemental fuel may comprise an amount of methane greater than or equal to 1 mol.%, such as greater than or equal to 2 mol.%, greater than or equal to 3 mol.%, greater than or equal to 4 mol.%, or even greater than or equal to 5 mol.%. In some embodiments the supplemental fuel comprises methane in an amount no more than 10 mol.%. In some embodiments, the supplemental fuel may comprise methane in an amount greater than 10 mol.%, such as greater than 20 mol.%, greater than 30 mol.%, greater than 40 mol.%, greater than 50 mol.%, greater than 60 mol.%, greater than 70 mol.%, greater than 80 mol.%, greater than 90 mol.%, or even 100 mol.%. Catalysts with improved methane combustion activity, such as those described herein that include manganese, can better utilize methane as a supplemental fuel to facilitate re-heating of the catalyst. The catalyst is heated during regeneration to aid with regeneration and also because heated catalyst serves as a heat carrier to carry heat from the combustor 350 to the reactor portion 200 to facilitate the dehydrogenation reaction.

[0016] In non-limiting examples, the reactor system 102 described herein may be utilized to produce light olefins from a hydrocarbon-containing feed. According to one or more embodiments, the reaction may be a dehydrogenation reaction. According to such embodiments, the hydrocarbon-containing feed may comprise one or more of ethane, propane, n-butane, and i-butane. In one or more embodiments, the hydrocarbon-containing feed may comprise at least 50 wt.%, at least 60 wt.%, at least 70 wt.%, at least 80 wt.%, at least 90 wt.%, at least 95 wt.% or even at least 99 wt.% of ethane. In additional embodiments, the hydrocarbon-containing feed may comprise at least 50 wt.%, at least 60 wt.%, at least 70 wt.%, at least 80 wt.%, at least 90 wt.%, at

least 95 wt.% or even at least 99 wt.% of propane. In additional embodiments, the hydrocarbon-containing feed may comprise at least 50 wt.%, at least 60 wt.%, at least 70 wt.%, at least 80 wt.%, at least 90 wt.%, at least 95 wt.% or even at least 99 wt.% of n-butane. In additional embodiments, the hydrocarbon-containing feed may comprise at least 50 wt.%, at least 60 wt.%, at least 70 wt.%, at least 80 wt.%, at least 90 wt.%, at least 95 wt.% or even at least 99 wt.% of i-butane. In additional embodiments, the hydrocarbon-containing feed may comprise at least 50 wt.%, at least 60 wt.%, at least 70 wt.%, at least 80 wt.%, at least 90 wt.%, at least 95 wt.% or even at least 99 wt.% of the sum of ethane, propane, n-butane, and i-butane.

[0017] In one or more embodiments, the catalyst may comprise, consist essentially of, or consist of one or more of gallium, indium, or thallium; one or more of platinum, palladium, rhodium, iridium, ruthenium, or osmium; iron; and a support. As described herein, "consisting essentially of" refers to materials with less than 1 wt.% of the non-recited materials (i.e., consisting essentially of A and B means A and B combined are at least 99 wt.% of the composition). As is described herein, the catalyst may be solid particles suitable for fluidization.

[0018] In one or more embodiments, the catalyst may comprise one or more of gallium, indium, or thallium in an amount of from 0.1 wt.% to 10 wt.% based on the total mass of the catalyst. Such materials may catalyze the dehydrogenation of alkanes to alkenes, particularly when used in combination with one or more of platinum, palladium, rhodium, iridium, ruthenium, or osmium. Such materials may additionally catalyze the combustion of coke and supplemental fuels. For example, the catalyst may comprise one or more of gallium, indium, or thallium in an amount from 0.1 wt.% to 0.25 wt.%, from 0.25 wt.% to 0.5 wt.%, from 0.5 wt.% to 0.75 wt.%, from 0.75 wt.% to 1 wt.%, from 1 wt.% to 2 wt.%, from 2 wt.% to 3 wt.%, from 3 wt.% to 4 wt.%, from 4 wt.% to 5 wt.%, from 5 wt.% to 6 wt.%, from 6 wt.% to 7 wt.%, from 7 wt.% to 8 wt.%, from 8 wt.% to 9 wt.%, from 9 wt.% to 10 wt.%, or any combination of these ranges. In some embodiments, the catalyst may comprise one or more of gallium, indium, or thallium in an amount from 0.1 wt.% to 9 wt.%, from 0.1 wt.% to 8 wt.%, from 0.1 wt.% to 7 wt.%, from 0.1 wt.% to 6 wt.%, or from 0.1 wt.% to 5 wt.%. In some embodiments, the catalyst comprises only gallium but not indium or thallium, only indium but not gallium or thallium, or only thallium but not gallium or indium. It should be understood that the compositional ranges describing the amount of gallium, indium, and thallium represent ranges for any one of these materials, or for the combination of these materials. Without being bound by theory, it is believed that compositions having one or more of gallium, indium, or thallium in an amount less than 0.1 wt.% negatively impacts the

catalyst's ability to catalyze the alkane dehydrogenation process by lowering both the percentage of total alkane dehydrogenated and the percentage of dehydrogenated alkane that is the intended product. However, it is believed that compositions having one or more of gallium, indium, or thallium in an amount exceeding 10 wt.% may negatively impact the catalyst's ability to catalyze the alkane dehydrogenation process, negatively impact the catalyst's selectivity towards the intended product, or both.

[0019] In one or more embodiments, the catalyst may comprise one or more of platinum, palladium, rhodium, iridium, ruthenium, or osmium in an amount from 5 ppmw to 1000 ppmw based on the total mass of the catalyst. Such materials may catalyze the dehydrogenation of alkanes to alkenes, particularly when used in combination with one or more of gallium, indium, or thallium. Such materials may additionally catalyze the combustion of coke and supplemental fuels. For example, the catalyst may comprise one or more of platinum, palladium, rhodium, iridium, ruthenium, or osmium in an amount from 5 ppmw to 50 ppmw, from 50 ppmw to 100 ppmw, from 100 ppmw to 200 ppmw, from 200 ppmw to 300 ppmw, from 300 ppmw to 400 ppmw, from 400 ppmw to 500 ppmw, from 500 ppmw to 600 ppmw, from 600 ppmw to 700 ppmw, from 700 ppmw to 800 ppmw, from 800 ppmw to 900 ppmw, from 900 ppmw to 1000 ppmw, or any combination of these ranges. In some embodiments, the catalyst may comprise one or more of platinum, palladium, rhodium, iridium, ruthenium, or osmium in an amount from 5 ppmw to 900 ppmw, from 5 ppmw to 800 ppmw, from 5 ppmw to 600 ppmw, from 5 ppmw to 500 ppmw, or from 10 ppmw to 400 ppmw. In some embodiments, the catalyst comprises only platinum but not palladium, rhodium, iridium, ruthenium, or osmium, only palladium but not platinum, rhodium, iridium, ruthenium, or osmium, only rhodium, but not platinum palladium, iridium, ruthenium, or osmium, only iridium, but not platinum palladium, rhodium, ruthenium, or osmium, only ruthenium but not platinum, palladium, rhodium, iridium, or osmium, or only osmium but not platinum, palladium, rhodium, iridium, or ruthenium. It should be understood that the compositional ranges describing the amount of platinum, palladium, rhodium, iridium, ruthenium, and osmium represent ranges for any one of these materials, or for the combination of these materials. Without being bound by theory, it is believed that compositions having one or more of platinum, palladium, rhodium, iridium, ruthenium, or osmium in an amount less than 5 ppmw negatively impacts the catalyst's ability to catalyze the alkane dehydrogenation process by lowering both the percentage of total alkane dehydrogenated and the percentage of dehydrogenated alkane that is the intended product. However, it is believed that compositions

having one or more of platinum, palladium, rhodium, iridium, ruthenium, or osmium in an amount exceeding 1000 ppmw may negatively impact the catalyst's ability to catalyze the alkane dehydrogenation process, negatively impact the catalyst's selectivity towards the intended product, or both.

[0020] In one or more embodiments, the catalyst may comprise iron in an amount from 100 ppmw to 30000 ppmw based on the total weight of the catalyst. The incorporation of iron may promote combustion of methane while not having significant impact on the dehydrogenation of alkanes. For example, the catalyst may comprise iron in an amount from 100 ppmw to 500 ppmw, from 500 ppmw to 1000 ppmw, from 1000 ppmw to 2500 ppmw, from 2500 ppmw to 5000 ppmw, from 5000 ppmw to 7500 ppmw, from 7500 ppmw to 10000 ppmw, from 10000 ppmw to 15000 ppmw, from 15000 ppmw to 20000 ppmw, from 20000 ppmw to 25000 ppmw, from 25000 ppmw to 30000 ppmw, or any combination of these ranges. In some embodiments, the catalyst may comprise iron in an amount from 100 ppmw to 25000 ppmw, from 150 ppmw to 20000 ppmw, from 200 ppmw to 15000 ppmw, from 300 ppmw to 12500 ppmw, from 400 ppmw to 10000 ppmw, or from 500 ppmw to 8000 ppmw. Without being bound by theory, it is believed that compositions having iron in an amount less than 100 ppmw may not sufficiently improve the methane combustion performance of the catalyst. However, it is believed that compositions having iron in an amount exceeding 30000 ppmw may negatively impact the catalyst's dehydrogenation performance by lowering both the percentage of total alkane that is dehydrogenated and the percentage of dehydrogenated alkane that is the intended product. Without being bound by theory, it is believed that iron may also help lower the rate at which the catalyst's methane combustion activity decreases over time during the operation of a dehydrogenation process.

[0021] In one or more embodiments, the catalyst may comprise iron in combination with one or more of chromium, manganese, or vanadium in a combined amount from 100 ppmw to 30000 ppmw based on the total weight of the catalyst. For example, The catalyst may comprise iron in combination of one or more of iron, chromium, manganese, or vanadium in a combined amount from 100 ppmw to 500 ppmw, from 500 ppmw to 1000 ppmw, from 1000 ppmw to 2500 ppmw, from 2500 ppmw to 5000 ppmw, from 5000 ppmw to 7500 ppmw, from 7500 ppmw to 10000 ppmw, from 10000 ppmw to 15000 ppmw, from 15000 ppmw to 20000 ppmw, from 20000 ppmw to 25000 ppmw, from 25000 ppmw to 30000 ppmw, or any combination of these ranges. In some embodiments the catalyst comprises iron and chromium but not manganese or vanadium, iron and manganese but not chromium or vanadium, iron and vanadium but not chromium or

manganese, iron, chromium, and manganese but not vanadium, iron, chromium, and vanadium but not manganese, or iron, manganese and vanadium, but not chromium.

[0022] As is described herein, in one or more embodiments, the catalyst may comprise a support. The support may comprise one or more of alumina, silica, or combinations thereof. For example, in some embodiments the support may comprise one or more of alumina, silica-containing alumina, zirconia-containing alumina, titania-containing alumina, and lanthanum-containing alumina. The support may be present in an amount of at least 85 wt.% relative to the total weight of the catalyst, such as at least 85 wt.%, at least 90 wt.%, or at least 95 wt.%. In some embodiments, the support comprises less than or equal to 99.5 wt.% of the catalyst. Generally, the wt.% of the support may fill the remainder of the total catalyst not specified by other materials.

[0023] In one or more embodiments, the catalyst may optionally comprise one or more alkali metals, one or more alkaline earth metals, or both in an amount from 0.01 wt.% to 2.5 wt.% based on the total weight of the catalyst. For example, the catalyst may comprise one or more alkali metals, one or more alkaline earth metals, or both in an amount from 0.01 wt.% to 0.05 wt.%, from 0.05 wt.% to 0.1 wt.%, from 0.1 wt.% to 0.2 wt.%, from 0.2 wt.% to 0.3 wt.%, from 0.3 wt.% to 0.4 wt.%, from 0.4 wt.% to 0.5 wt.%, from 0.5 wt.% to 0.6 wt.%, from 0.6 wt.% to 0.7 wt.%, from 0.7 wt.% to 0.8 wt.%, from 0.8 wt.% to 0.9 wt.%, from 0.9 wt.% to 1 wt.%, from 1 wt.% to 1.25 wt.%, from 1.25 wt.% to 1.5 wt.%, from 1.5 wt.% to 1.75 wt.%, from 1.75 wt.% to 2 wt.%, from 2 wt.% to 2.25 wt.%, from 2.25 wt.% to 2.5 wt.%, or any combination of these ranges. In some embodiments, the catalyst may comprise one or more alkali metals, one or more alkaline earth metals, or both from 0.01 wt.% to 1 wt.%, from 0.02 wt.% to 0.75 wt.%, from 0.03 wt.% to 0.5 wt.%, from 0.04 wt.% to 0.4 wt.%, or from 0.05 wt.% to 0.3 wt.%. In some embodiments, the one or more alkali metals or one or more alkaline earth metals may be potassium. Without being bound by theory, it is believed that compositions having alkali metals or alkaline earth metals in an amount less than 0.01 wt.% may cause the production of undesired products during the dehydrogenation reaction. However, it is believed that compositions having alkali metals or alkaline earth metals in an amount exceeding 2.5 wt.% may reduce the catalyst's dehydrogenation activity.

[0024] In one or more embodiments, the catalyst may comprise, consist essentially of, or consist of gallium, platinum, iron, and a support. For example, the catalyst may comprise, consist essentially of, or consist of from 0.1 wt.% to 10 wt.% of gallium; from 5 ppmw to 1000 ppmw of

platinum; from 100 ppmw to 30000 ppmw iron; and at least 85 wt.% of a support. In one exemplary embodiment, the catalyst may comprise, consist essentially of, or consist of from 0.1 wt.% to 5 wt.% of gallium; from 10 ppmw to 400 ppmw of platinum; from 500 ppmw to 8000 ppmw iron, and at least 85 wt.% of a support.

[0025] In one or more embodiments, the catalyst may include solid particulates that are capable of fluidization. In some embodiments, the catalyst may exhibit properties known in the industry as "Geldart A" or "Geldart B" properties. Catalyst type may be classified as "Group A" or "Group B" according to D. Geldart, Gas Fluidization Technology, John Wiley & Sons (New York, 1986), 34-37; and D. Geldart, "Types of Gas Fluidization," Powder Technol. 7 (1973) 285-292, the disclosures of which are incorporated herein by reference in their entireties.

[0026] Geldart Group A is understood by those skilled in the art as representing an aeratable powder, having a bubble-free range of fluidization; a high bed expansion; a slow and linear deaeration rate; bubble properties that may include a predominance of splitting/recoalescing bubbles, with a maximum bubble size and large wake; high levels of solids mixing and gas backmixing, assuming equal U-Umf (U is the velocity of the carrier gas, and Umf is the minimum fluidization velocity, typically though not necessarily measured in meters per second, m/s, i.e., there is excess gas velocity); axisymmetric slug properties; and no spouting, except in very shallow beds. The properties listed tend to improve as the mean particle size decreases, assuming equal $d\bar{p}$; or as the < 45 micrometers (μm) proportion is increased; or as pressure, temperature, viscosity, and density of the gas increase. In general, the particles may exhibit a small mean particle size and/or low particle density (< 1.4 grams per cubic centimeter, g/cm^3), fluidize easily, with smooth fluidization at low gas velocities, and may exhibit controlled bubbling with small bubbles at higher gas velocities.

[0027] Geldart Group B is understood by those skilled in the art as representing a "sand-like" powder that starts bubbling at Umf; that exhibits moderate bed expansion; a fast deaeration; no limits on bubble size; moderate levels of solids mixing and gas backmixing, assuming equal U-Umf; both axisymmetric and asymmetric slugs; and spouting in only shallow beds. These properties tend to improve as mean particle size decreases, but particle size distribution and, with some uncertainty, pressure, temperature, viscosity, or density of gas seem to do little to improve them. In general, most of the particles having a particle size ($d\bar{p}$) of 40 μm < $d\bar{p}$ < 500 μm when the density (ρp) is 1.4 < ρp < 4 g/cm^3.

[0028] In one or more embodiments, the catalyst may be prepared via incipient wetness impregnation also known as dry impregnation or capillary impregnation. For example, such a process is described in Marceau et al., *Impregnation and Drying*, Synthesis of Solid Catalysts 59 (2008), which is incorporated herein by reference in its entirety. For example, the support may be impregnated using metal precursors, then dried at temperatures less than 200 °C, and then calcined at temperatures less than 800 °C to produce the catalyst. For example, suitable metal precursors may include nitrate or amine nitrate metal precursors. Additionally, other suitable metal precursors are contemplated herein, as would be known by those skilled in the art. In some embodiments, the method of making the catalyst may comprise impregnating the support with gallium, platinum, and iron; drying the support; and calcining the support, wherein the catalyst comprises from 0.1 wt.% to 10 wt.% of gallium, from 5 ppmw to 1000 ppmw of platinum, from 100 ppmw to 30000 ppmw of iron, and at least 85 wt.% support.

[0029] In one or more embodiments, the catalyst may be prepared by incipient wetness sequential impregnation, where materials are impregnated in a specific order, either before or after drying and calcining. In incipient wetness sequential impregnation, the catalyst is first impregnated with one or more metal precursors, dried at temperatures less than 200 °C, and then calcined at temperatures less than 800 °C. The catalyst then undergoes a least one additional cycle of impregnation, drying, and calcining with an additional metal precursor to create a finished catalyst. In incipient wetness sequential impregnation, the metals added to the catalyst can be added in sequential order in successive impregnation cycles. In one or more embodiments, the support is sequentially impregnated with gallium and platinum and then with iron. For some embodiments, the method of making a catalyst may comprise impregnating the support with gallium and platinum, drying the support, calcining the support, impregnating the support with iron following the drying and calcining, and drying and calcining the support following the impregnation with iron, wherein the catalyst comprises from 0.1 wt.% to 10 wt.% of gallium, from 5 ppmw to 1000 ppmw of platinum, from 100 ppmw to 30000 ppmw iron and at least 85 wt.% support. In additional embodiments, the method of making a catalyst may comprise impregnating the support with iron to create an iron impregnated support, drying the iron impregnated support, calcining the iron impregnated support, impregnating the iron impregnated support with gallium and platinum following the drying and calcining, and drying and calcining the iron impregnated support following the impregnation with gallium and platinum, wherein the catalyst comprises

from 0.1 wt.% to 10 wt.% of gallium, from 5 ppmw to 1000 ppmw of platinum, from 100 ppmw to 30000 ppmw of iron, and at least 85 wt.% support.

[0030] Incipient wetness sequential impregnation allows the support to be impregnated with metals in a sequential order where some metals may be impregnated onto the support before others. The order of impregnation can be therefore be altered as desired. Additionally, other suitable methods for making the catalysts described herein are contemplated, as would be known by those skilled in the art.

[0031] Now referring again to FIG. 1, the hydrocarbon-containing feed may enter feed inlet 434 into the reactor 202, and the olefin-containing effluent may exit the reactor system 102 via pipe 420. According to one or more embodiments, the reactor system 102 may be operated by feeding a hydrocarbon-containing feed (e.g., in a feed stream) and a fluidized catalyst into the upstream reactor section 250. The hydrocarbon-containing feed contacts the catalyst in the upstream reactor section 250, and each flow upwardly into and through the downstream reactor section 230 to produce an olefin-containing effluent.

[0032] Now referring to FIG. 1 in detail, the reactor portion 200 may comprise an upstream reactor section 250, a transition section 258, and a downstream reactor section 230, such as a riser. The transition section 258 may connect the upstream reactor section 250 with the downstream reactor section 230. As depicted in FIG. 1, the upstream reactor section 250 may be positioned below the downstream reactor section 230. Such a configuration may be referred to as an upflow configuration in the reactor 202. The upstream reactor section 250 may include a vessel, drum, barrel, vat, or other container suitable for a given chemical reaction. As depicted in FIG. 1, the upstream reactor section 250 may be connected to the downstream reactor section 230 via the transition section 258. The upstream reactor section 250 may generally comprise a greater cross-sectional area than the downstream reactor section 230. The transition section 258 may be tapered from the size of the cross-section of the upstream reactor section 250 to the size of the cross-section of the downstream reactor section 230 such that the transition section 258 projects inwardly from the upstream reactor section 250 to the downstream reactor section 230. For example, the transition section 258 may be a frustum.

[0033] The upstream reactor section 250 may be connected to a transport riser 430, which, in operation may provide reactivated catalyst in a feed stream to the reactor portion 200. The

reactivated catalyst and/or reactant chemicals may be mixed with a distributor 260 housed in the upstream reactor section 250. The catalyst entering the upstream reactor section 250 via transport riser 430 may be passed through standpipe 424 to a transport riser 430, thus arriving from the catalyst processing portion 300. In some embodiments, catalyst may come directly from the catalyst separation section 210 via standpipe 422 and into a transport riser 430, where it enters the upstream reactor section 250, where in such embodiments some of the catalyst is not passed through the catalyst processing portion 300. The catalyst can also be fed via standpipe 422 directly to the upstream reactor section 250 (not depicted in FIG. 1). This catalyst may be somewhat deactivated, but may still, in some embodiments, be suitable for reaction in the upstream reactor section 250, particularly when used in combination with reactivated catalyst.

[0034] In one or more embodiments, the catalyst may have a residence time within the reactor portion 200 of less than or equal to 3 minutes. As the term is used herein, "residence time" refers to the average amount of time the catalyst or other specified material spends within the reactor portion 200. As it is an average, the amount of time the catalyst may spend within the reactor portion 200 during any given cycle may not be equal to the average, but over time will average out to be equal to about the residence time. In some embodiments, the catalyst may have a residence time within the reactor portion 200 of less than or equal to 2.5 min., less than or equal to 2 min., less than or equal to 1.5 min., less than or equal to 1 min., less than or equal to 0.5, or less than or equal to 0.1 min. Without being bound by theory, it is believed that catalyst residence time greater than 3 minutes may increase equipment costs without a matching increase in catalyst dehydrogenation performance. However, it is believed that catalyst residence time less than 0.1 minutes may not allow the catalyst to sufficiently catalyze the dehydrogenation reaction.

[0035] Still referring to FIG. 1, in one or more embodiments, based on the shape, size, and other processing conditions (such as temperature and pressure) in the upstream reactor section 250 and the downstream reactor section 230, the upstream reactor section 250 may operate as a fluidized bed, such as in a fast fluidized, turbulent, or bubbling bed upflow reactor, while the downstream reactor section 230 may operate in more of a plug flow manner, such as in a riser reactor. For example, the reactor 202 of FIG. 1 may comprise an upstream reactor section 250 operating as a fast fluidized, turbulent, or bubbling bed reactor and a downstream reactor section 230 operating as a dilute phase riser reactor, with the result that the average catalyst and gas flow moves concurrently upward. As the term is used herein, "average flow" refers to the net flow, i.e., the total upward flow minus the retrograde or reverse flow, as is typical of the

behavior of fluidized particles in general. As described herein, a "fast fluidized" reactor may refer to a reactor utilizing a fluidization regime wherein the superficial velocity of the gas phase is greater than the choking velocity and may be semi-dense in operation. As described herein, a "turbulent" reactor may refer to a fluidization regime where the superficial velocity of less than the choking velocity and is more dense than the fast fluidized regime. As described herein, a "bubbling bed" reactor may refer to a fluidization regime wherein well defined bubbles in a highly dense bed are present in two distinct phases. The "choking velocity" refers to the minimum velocity required to maintain solids in the dilute-phase mode in a vertical conveying line. As described herein, a "dilute phase riser" may refer to a riser reactor operating at above choking velocity.

[0036] According to embodiments, the olefin-containing effluent and the catalyst may be passed out of the downstream reactor section 230 to a separation device 220 in the catalyst separation section 210, where the catalyst is at least partially separated from the olefin-containing effluent, which is transported out of the catalyst separation section 210. According to one or more embodiments, following separation from vapors in the separation device 220, the catalyst may generally move through the stripper 224 to the catalyst outlet port 222 where the catalyst is transferred out of the reactor portion 200 via standpipe 426 and into the catalyst processing portion 300.

[0037] According to one or more embodiments, the separation device 220 may be a cyclonic separation system, which may include two or more stages of cyclonic separation. In embodiments where the separation device 220 comprises more than one cyclonic separation stages, the first separation device into which the fluidized stream enters is referred to a primary cyclonic separation device. The fluidized effluent from the primary cyclonic separation device may enter into a secondary cyclonic separation device for further separation. Primary cyclonic separation devices may include, for example, primary cyclones, and systems commercially available under the names VSS (commercially available from UOP), LD2 (commercially available from Stone and Webster), and RS2 (commercially available from Stone and Webster). Primary cyclones are described, for example, in U.S. Patent Nos. 4,579,716; 5,190,650; and 5,275,641, which are each incorporated by reference in their entirety herein. In some separation systems utilizing primary cyclones as the primary cyclonic separation device, one or more set of additional cyclones, e.g. secondary cyclones and tertiary cyclones, are employed for further separation of the

catalyst from the product gas. It should be understood that any primary cyclonic separation device may be used in embodiments of the present disclosure.

[0038] Still referring to FIG. 1, the separated catalyst is passed from the catalyst separation section 210 to the combustor 350. In the combustor 350, the catalyst may be processed by, for example, combustion of coke with oxygen. For example, and without limitation, the catalyst may be de-coked and/or supplemental fuel may be combusted to heat the catalyst. The catalyst is then passed out of the combustor 350 and through the riser 330 to a riser termination separator 378, where the gas and solid components from the riser 330 are at least partially separated. The vapor and remaining solids are transported to a secondary separation device 320 in the catalyst separation section 310 where the remaining catalyst is separated from the gases from the catalyst processing (e.g., gases emitted by combustion of spent catalyst or supplemental fuel, referred to herein as flue gas). The flue gas may pass out of the catalyst processing portion 300 via outlet pipe 432. The separated catalyst is then passed through the oxygen treatment zone 370 within the catalyst separation section 310 to the upstream reactor section 250 via standpipe 424 and transport riser 430, where it is further utilized in a catalytic reaction. Thus, the catalyst, in operation, may cycle between the reactor portion 200 and the catalyst processing portion 300. In general, the processed chemical streams, including the hydrocarbon-containing feed and olefin-containing effluent may be gaseous, and the catalyst may be fluidized particulate solid.

[0039] Referring now to the catalyst processing portion 300, as depicted in FIG. 1, the combustor 350 of the catalyst processing portion 300 may include one or more lower reactor portion inlet ports 352 and may be in fluid communication with the riser 330. Oxygen-containing gas, such as air, may be passed through pipe 428 into the combustor 350. The combustor 350 may be in fluid communication with the catalyst separation section 210 via standpipe 426, which may supply spent catalyst from the reactor portion 200 to the catalyst processing portion 300 for regeneration. The combustor 350 and riser 330, collectively referred to as the catalyst combustion reactor 302, may operate with similar or identical fluidization regimes as to what was disclosed with respect to the upstream reactor section 250 and downstream reactor section 230 of the reactor portion 200. That is, the combustor 350 may operate as a fluidized bed, such as in a fast fluidized, turbulent, or bubbling bed upflow reactor, while the riser 330 may operate in more of a plug flow manner, such as in a riser reactor. Geometries as described with respect to the upstream reactor section 250 and downstream reactor section 230 may equally apply to the combustor 350 and riser

330. Additionally, the combustor 350 may also include a fuel inlet 354, which may supply a fuel, such as a hydrocarbon stream, to the combustor 350.

[0040] As described herein, the catalyst may be heated in the catalyst processing portion 300 by combustion of supplemental fuels. Supplemental fuels may combust with oxygen to heat the catalyst, and supplemental fuels such as a supplemental fuel, such as hydrogen, methane, ethane, propane, natural gas, or combinations thereof. Without being bound by any theory, when methane is utilized in the supplemental fuel, catalysts as described herein that include iron may better catalyze the combustion of methane to heat the catalyst. Catalysts which do not contain iron, when methane is utilized in the supplemental fuel, may be deficient by not promoting heating of the catalyst to a temperature needed for dehydrogenation.

[0041] As described in one or more embodiments, following separation of flue gas from catalyst in the riser termination separator 378 and secondary separation device 320, treatment of the processed catalyst with an oxygen-containing gas is conducted in the oxygen treatment zone 370. In some embodiments, the oxygen treatment zone 370 includes a fluid solids contacting device. The fluid solids contacting device may include baffles or grid structures to facilitate contact of the processed catalyst with the oxygen-containing gas. Examples of fluid solid contacting devices are described in further detail in U.S. Patent Nos. 9,827,543 and 9,815,040. The fluidization regime within the oxygen treatment zone may be bubbling bed type fluidization. The oxygen treatment zone 370 may include an oxygen-containing gas inlet 372, which may supply an oxygen-containing gas to the oxygen treatment zone 370 for oxygen treatment of the catalyst.

[0042] As is disclosed herein, in one or more embodiments the catalyst may be exposed to an oxygen-containing gas in oxygen treatment zone 370. For example, the catalyst may be exposed to an oxygen-containing gas for from 2 min. to 20 min., such as from 2 min. to 4 min., from 4 min. to 6 min., from 6 min. to 8 min., from 8 min. to 10 min., from 10 min. to 12 min., from 12 min. to 14 min., from 14 min. to 16 min., from 16 min. to 18 min., from 18 min. to 20 min., or any combination of these ranges. In some embodiments the catalyst may be exposed to an oxygen containing gas from 4 min. to 18 min., from 6 min. to 17 min., from 8 min. to 16 min., or from 10 min. to 15 min. Without being bound by theory, it is believed that exposure of the catalyst to an oxygen-containing gas for more than 20 minutes may increase equipment costs without a matching increase in catalyst regeneration efficiency. However, it is believed that

oxygen-containing gas exposure for less than 2 minutes may lead to less efficient regeneration of the catalyst which may reduce the catalyst's dehydrogenation activity.

[0043] In one or more embodiments, the light olefins may be present in a "product stream" sometimes called an "olefin-containing effluent" and include light olefins. Such a stream exits the reactor system of FIG. 1 and may be subsequently processed. As used in the present disclosure, the term "light olefins" refers to one or more of ethylene, propylene, and butene. The term butene includes any isomers of butene, such as α-butylene, cis-β-butylene, trans-β-butylene, and isobutylene. In some embodiments, the olefin-containing effluent includes at least 25 wt.% light olefins based on the total weight of the olefin-containing effluent. For example, the olefin-containing effluent may include at least 35 wt.% light olefins, at least 45 wt.% light olefins, at least 55 wt.% light olefins, at least 65 wt.% light olefins, or at least 75 wt.% light olefins based on the total weight of the olefin-containing effluent. The olefin-containing effluent may further comprise unreacted components of the hydrocarbon-containing effluent, as well as other reaction products that are not considered light olefins. The light olefins may be separated from unreacted components in subsequent separation steps.

Examples

[0044] The various embodiments of the present disclosure will be further clarified by the following examples. The examples are illustrative in nature and should not be understood to limit the subject matter of the present disclosure.

Example 1 – Effect of Iron loading

[0045] In Example 1, 12 different samples of catalytically active particles (i.e., catalysts) were prepared and the effect of iron loading on catalytically active particles was observed. For the purposes of Example 1, the samples were prepared by first preparing microspheroidal alumina support by spray drying a mixture of hydrated alumina and Ludox® Silica and then heating the resulting spray dried particles at a temperature of at least 1000 °C sufficient to achieve particles with particle size ranging from 5 μm to 300 μm, pore volume of 0.20 ± 0.10 ml/g, surface area of 70 ± 20 m^2/g, and silica content 2.5 ± 2.5 wt.%. The catalyst materials were prepared using an incipient wetness impregnation method to load the designated metal or metals to the support using nitrate or amine nitrate metal precursors followed by drying at a temperature less than 200 °C, and

then calcination at a temperature less than 800 °C. The exact compositions of the samples are provided in Table 1.

[0046] The samples were tested at ambient pressure under conditions of 0.5 grams (g) of the sample was mixed with 1.0 g inert silicon carbide and loaded into a quartz reactor. The reaction combustion reactivation cycle was carried out for 10 break in cycles followed by dehydrogenation and regeneration testing cycles. The break in cycles were run by performing two steps: a dehydrogenation step where a dehydrogenation process was performed at 625 °C with weight hourly space velocity "WHSV" propane of 10 hr^{-1} and feed composition of 90% propane/10% nitrogen for 60 seconds; and a reactivation step where the catalyst was heated to 730 °C under 100% air with a flow rate of 50 standard cubic centimeters per minute (sccm) for 5 minutes. After the catalyst had been run through 10 break in cycles it was tested in the dehydrogenation and regeneration testing cycles. The dehydrogenation and regeneration testing cycles were run be performing three steps: a dehydrogenation step using the same conditions as the dehydrogenation step of the break in cycles where dehydrogenation performance data were collected at 30 seconds time on stream; a combustion step where combustion was performed at 730 °C under 2.5 mol% Methane/balance air with a total flow of 50 sccm and a WHSV of Methane of 0.1hr^{-1} for 3 minutes where combustion performance data were collected at 60 seconds time on stream; and a reactivation step where the samples were heated to 730 °C under 100% air with a flow rate of 50 sccm for 2 minutes. The dehydrogenation and combustion performances of the samples were reported in Table 1 after 25 cycles.

Table 1

Sample	Pt [ppm]	Ga [wt.%]	K [wt.%]	Fe [ppm]	Propane Conversion [%]	Propylene Selectivity [%]	Methane Conversion [%]
A	300	1.6	0.25	0	39.4	98.7	85.2
1	300	1.6	0.25	1000	48.2	99.1	94.8
2	300	1.6	0.25	1500	48.7	99.2	94.2
3	300	1.6	0.25	3000	46.1	99.0	98.2
4	300	1.6	0.25	5000	44.7	99.1	99.5
5	300	1.6	0.25	8000	33.6	98.2	100
6	300	1.6	0.25	10000	27.8	97.0	100
B	0	0	0.25	3000	1.7	62.6	89.0
C	0	0	0.25	30000	4.3	72.1	100

D	0	1.6	0.25	3000	6.2	92.3	91.7
E	300	0	0.25	3000	3.1	83.7	99.7
F	0	0	0	3000	2.4	80.0	91.8

[0047] As indicated by Table 1, all samples with iron (i.e., Samples 1-6) saw an improvement in methane conversion. Some samples with iron saw improvement in methane conversion, propane conversion, and propylene selectivity. For example, Comparative Example A (void of iron) has worse propane conversion, propylene selectivity and methane conversion than samples 1-4 which are identical to Comparative Example A except for the presence of iron. Table 1 also indicated that while increasing iron composition in the samples continued to improve methane conversion up to 100%, samples with high iron loading (i.e., Sample 6) saw a decrease in propane conversion and propylene selectivity when compared to samples with lower iron loading (i.e., samples 1-4). Samples with higher iron loading still provided acceptable propane conversion and propylene selectivity. Further, Table 1 indicates that samples without both platinum and gallium (i.e., Comparative Examples B-F) had lower propane conversion and propylene selectivity than samples with both platinum and gallium (i.e., Samples 1-6). That is, Table 1 indicates that the overall catalyst composition of platinum, gallium, and iron, is important for improving methane conversion while maintaining acceptable propane conversion and propylene selectivity.

Example 2 – Effect of Multiple Metal Promoters

[0048] In Example 2, 2 samples of catalytically active particles (i.e., catalysts) were prepared and the effect of multiple metal promoters on catalyst performance was observed. The samples were prepared and tested using the catalyst preparation procedure of Example 1. The composition of the samples and their dehydrogenation and combustion performances were reported in Table 2.

Table 2

Sample	Pt [ppm]	Ga [wt.%]	K [wt.%]	Fe [ppm]	Cr [ppm]	Mn [ppm]	Propane Conversion [%]	Propylene Selectivity [%]	Methane Conversion [%]
7	300	1.6	0.25	750	750	0	46.1	98.9	97.0
8	300	1.6	0.25	750	0	750	44.0	98.7	94.6

[0049] As indicated by Tables 1 and 2, Sample 7 with both iron and chromium as promoters saw improved methane conversion, propane conversion, and propylene conversion when compared to the base catalyst of Comparative Example A. Tables 1 and 2 further indicate that Sample 8 with both iron and manganese as promoters saw improved methane conversion and propane conversion with identical propylene selectivity when compared to Comparative Example A.

Example 3 – Effect of Sequential Impregnation

[0050] In Example 3, a sample of catalytically active particles (i.e., catalysts) was prepared and the effect of sequential impregnation on catalytically active particle's dehydrogenation and combustion performance were examined. The sample in Example 3 was prepared by using a base catalyst (i.e., Comparative Example A) prepared using the catalyst preparation procedure of Example 1. This pre-made catalyst was then promoted by impregnating with iron (III) nitrate solution in DI water followed by drying at a temperature less than 200 °C, and then calcination at a temperature less than 800 °C. The composition of the sample and its dehydrogenation and combustion performances is reported in Table 3.

Table 3

Sample	Fe [ppm]	Propane Conversion [%]	Propylene Selectivity [%]	Methane Conversion [%]
9	Catalyst A + 3000ppm Fe	43.1	99.0	94.6

[0051] As indicated by Tables 1 and 3, the sample prepared by sequential impregnation (i.e., Sample 9) did not losing significant dehydrogenation or combustion activity when compared to samples prepared by co-impregnation (i.e., Sample 3). That is, the catalyst can be prepared using either sequential impregnation or co-impregnation.

Example 4 – Effect of Order of Sequential Impregnation

[0052] In Example 4, 2 different samples of catalytically active particles (i.e., catalysts) were prepared and the effect of sequential impregnation on catalytically active particle's dehydrogenation and combustion performance was observed. The samples in Example 4 were prepared by using sequential impregnation to load the metals followed by drying at a temperature

less than 200 °C, and then calcination at a temperature less than 800 °C after each impregnation step. The composition of the samples, the order of their impregnation, and their dehydrogenation and combustion performances were reported in Table 4.

Table 4

Sample	Prep method	Pt [ppm]	Ga [wt.%]	K [wt.%]	Fe [ppm]	Propane Conversion [%]	Propylene Selectivity [%]	Methane Conversion [%]
6	Co-impregnation	300	1.6	0.25	10000	27.8	97.0	100
10	Sequential 1st impregnation: Pt/Ga/K 2nd impregnation: Fe	300	1.6	0.25	10000	27.3	97.6	100
11	Sequential 1st impregnation: Fe 2nd impregnation: Pt/Ga/K	300	1.6	0.25	10000	25.1	97.7	100

[0053] As Table 4 indicates, samples prepared by sequential impregnation (i.e., Samples 10 and 11) did not losing significant dehydrogenation or combustion activity when compared to a sample prepared by co-impregnation (i.e., Sample 6). That is, the catalyst can be prepared using either sequential impregnation or co-impregnation.

Example 5 – Effect of Gallium and Platinum Composition on Catalyst Performance

[0054] In Example 5, 3 different samples of catalytically active particles (i.e., catalysts) were prepared and the effect of varying compositions on dehydrogenation and combustion activity was observed. The samples in Example 6 were prepared using the catalyst preparation procedure of Example 1. The composition of the samples and their dehydrogenation and combustion performances were reported in Table 5.

Table 5

Sample	Pt [ppm]	Ga [wt.%]	K [wt.%]	Fe [ppm]	Propane Conversion [%]	Propylene Selectivity [%]	Methane Conversion [%]
12	10	0.4	0.25	3000	35.4	98.9	92.7
13	80	3	0.25	4500	49.2	98.7	96.0
14	300	0.4	0.1	3000	43.5	99.2	98.2

[0055] As indicated by Table 5 samples with iron showed improvement in methane conversion with acceptable propane conversion and propylene selectivity across a range of platinum and gallium compositions. For example, Sample 13 had improved methane conversion, propane conversion, and propylene selectivity when compared to Comparative Example A even though Sample 13 had less platinum and more gallium than Comparative Example A. All samples in Table 5 (i.e., Samples 12-14) had improved methane conversion compared to Comparative Example A.

Example 6 – Effect of Fuel Used During Combustion

[0056] In Example 6, 3 different samples of catalytically active particles (i.e., catalysts) were prepared and the effect of fuel composition on dehydrogenation and combustion activity was observed. In Example 6, the catalytically active particles were prepared using the catalyst preparation procedure from Example 1. They were then run through dehydrogenation and regeneration testing cycles as described in Example 1, but the combustion step was changed to be combustion at 730 °C under 2.5 mol% H_2/balance air (100% H_2 fuel) with a flow rate of 50 sccm for 3 minutes. Combustion data was still collected at 60 seconds time on stream as in the previous examples. The composition of the samples and their dehydrogenation and combustion performances were reported in Table 6.

Table 6

Sample	Pt [ppm]	Ga [wt.%]	K [wt.%]	Fe [ppm]	Fuel Used	Propane Conversion [%]	Propylene Selectivity [%]	Fuel Conversion [%]
A	300	1.6	0.25	0	H_2	41.3	98.7	100
3	300	1.6	0.25	3000		49.2	99.1	100
4	300	1.6	0.25	5000		44.3	98.9	100

A	300	1.6	0.25	0	CH_4	38.9	98.4	80.9
3	300	1.6	0.25	3000		50.2	98.9	95.4
4	300	1.6	0.25	5000		45.0	98.8	99.2

[0057] As indicated by Table 6 samples with iron (i.e., Samples 3 and 4) showed improved propane conversion and propylene selectivity when compared to samples without iron (i.e., Comparative Example A) even when the process is run without the use of methane as a supplemental fuel. Samples with iron (i.e., Samples 3 and 4) saw the most significant improvement in fuel conversion and in propane conversion when compared to Comparative Example A, which is void of iron, in the presence of methane fuel, but still saw some improvement in propane conversion when compared to Comparative Example A when methane is not used as a fuel.

[0058] In a first aspect of the present disclosure, light olefins may be made by dehydrogenation by a method comprising contacting a hydrocarbon-containing feed with a catalyst in a reactor to form an olefin-containing effluent, then at least partially separating the olefin-containing effluent from the catalyst. Passing the catalyst to a combustor and heating the catalyst by combusting a supplemental fuel. The supplemental fuel comprises methane in an amount greater than or equal to 1 mol.%. Passing the catalyst from the combustor to the reactor, such that at least a portion of the catalyst continuously cycles between the reactor and the combustor. The catalyst comprises from 0.1 wt.% to 10 wt.% of one or more metals chosen from gallium, indium, thallium or combinations thereof, from 5 ppmw to 1000 ppmw of one or more metals chosen from platinum, palladium, rhodium, iridium, ruthenium, osmium, or combinations thereof, from 100 ppmw to 30000 ppmw of iron, and at least 85 wt.% support.

[0059] A second aspect of the present disclosure may include the first aspect where the method further comprises passing the catalyst from the combustor to an oxygen treatment zone and exposing the catalyst to an oxygen-containing gas for from 2 minutes to 20 minutes and passing the catalyst from the oxygen treatment zone to the reactor.

[0060] A third aspect of the present disclosure may include the second aspect where the catalyst is exposed to the oxygen-containing gas in the oxygen treatment zone for from 8 minutes to 20 minutes.

[0061] A fourth aspect of the present disclosure may include any of the previous aspects where the supplemental fuel comprises at least 3 mol.% methane.

[0062] A fifth aspect of the present disclosure may include any of the previous aspects where the catalyst has a residence time within the reactor of less than or equal to 3 minutes.

[0063] A sixth aspect of the present disclosure may include any of the previous aspects where the catalyst has a residence time within the reactor of less than or equal to 1 minute.

[0064] A seventh aspect of the present disclosure may include any of the previous aspects where the catalyst comprises from 0.1 wt.% to 10 wt.% of gallium and from 5 ppmw to 1000 ppmw of platinum.

[0065] An eighth aspect of the present disclosure may include any of the previous aspects where the catalyst comprises from 0.1 wt.% to 5 wt.% of gallium and from 10 ppmw to 400 ppmw of platinum.

[0066] A ninth aspect of the present disclosure may include any of the previous aspects where the catalyst comprises from 500 ppmw to 10000 ppmw of iron.

[0067] A tenth aspect of the present disclosure may include any of the previous aspects where the catalyst further comprises from 0.01 wt.% to 2.5 wt.% of one or more alkali or alkaline earth metals.

[0068] An eleventh aspect of the present disclosure may include the first aspect where the catalyst further comprises from 0.01 wt.% to 2.5 wt.% of potassium.

[0069] A twelfth aspect of the present disclosure may include any of the previous aspects where the catalyst comprises from 0.1 wt.% to 5 wt.% of gallium, from 10 ppmw to 400 ppmw of platinum, and from 500 ppmw to 8000 ppmw of iron.

[0070] A thirteenth aspect of the present disclosure may include any of the previous aspects where the support comprises one or more of alumina, silica, or combinations thereof.

[0071] A fourteenth aspect of the present disclosure may include any of the previous aspects where the catalyst has Geldart group A or Geldart group B properties.

[0072] A fifteenth aspect of the present disclosure may include any of the previous aspects where the hydrocarbon-containing feed comprises propane and the olefin-containing effluent comprises propylene.

[0073] It will be apparent to those skilled in the art that various modifications and variations can be made to the presently disclosed technology without departing from the spirit and scope of the technology. Since modifications combinations, sub-combinations and variations of the disclosed embodiments incorporating the spirit and substance of the presently disclosed technology may occur to persons skilled in the art, the technology should be construed to include everything within the scope of the appended claims and their equivalents. Additionally, although some aspects of the present disclosure may be identified herein as preferred or particularly advantageous, it is contemplated that the present disclosure is not limited to these aspects.

[0074] It is noted that the various details described in this disclosure should not be taken to imply that these details relate to elements that are essential components of the various embodiments described in this disclosure, even in cases where a particular element is illustrated in each of the drawings that accompany the present description. Unless specifically identified as such, no feature disclosed and described herein should be construed as "essential". Contemplated embodiments of the present technology include those that include some or all of the features of the appended claims.

[0075] For the purposes of describing and defining the present disclosure it is noted that the term "about" are utilized in this disclosure to represent the inherent degree of uncertainty that may be attributed to any quantitative comparison, value, measurement, or other representation. The term "about" are also utilized in this disclosure to represent the degree by which a quantitative representation may vary from a stated reference without resulting in a change in the basic function of the subject matter at issue.

[0076] In relevant cases, where a composition is described as "comprising" one or more elements, embodiments of that composition "consisting of" or "consisting essentially of" those one or more elements is contemplated herein.

[0077] It should be appreciated that compositional ranges of a chemical constituent in a stream or in a reactor should be appreciated as containing, in some embodiments, a mixture of isomers of that constituent. For example, a compositional range specifying butene may include a mixture of various isomers of butene. It should be appreciated that the examples supply compositional ranges for various streams, and that the total amount of isomers of a particular chemical composition can constitute a range.

[0078] It is noted that one or more of the following claims and the detailed description utilize the terms "where" or "wherein" as a transitional phrase. For the purposes of defining the present technology, it is noted that this term is introduced in the claims as an open-ended transitional phrase that is used to introduce a recitation of a series of characteristics of the structure and should be interpreted in like manner as the more commonly used open-ended preamble term "comprising."

[0079] It should be understood that any two quantitative values assigned to a property may constitute a range of that property, and all combinations of ranges formed from all stated quantitative values of a given property are contemplated in this disclosure. Where multiple ranges for a quantitative value are provided, these ranges may be combined to form a broader range, which is contemplated in the embodiments described herein.

CLAIMS

1. A method for making light olefins by dehydrogenation, the method comprising:

contacting a hydrocarbon-containing feed with a catalyst in a reactor to form an olefin-containing effluent;

at least partially separating the olefin-containing effluent from the catalyst;

passing the catalyst to a combustor and heating the catalyst by combusting a supplemental fuel, wherein the supplemental fuel comprises methane in an amount of greater than or equal to 1 mol.%;

passing the catalyst from the combustor to the reactor, such that at least a portion of the catalyst continuously cycles between the reactor and the combustor;

wherein the catalyst comprises:

from 0.1 wt.% to 10 wt.% of one or more metals chosen from gallium, indium, thallium, or combinations thereof;

from 5 ppmw to 1000 ppmw of one or more metals chosen from platinum, palladium, rhodium, iridium, ruthenium, osmium, or combinations thereof;

from 100 ppmw to 30000 ppmw of iron;

and at least 85 wt.% support.

2. The method of claim 1 further comprising:

passing the catalyst from the combustor to an oxygen treatment zone and exposing the catalyst to an oxygen-containing gas for from 2 minutes to 20 minutes; and

passing the catalyst from the oxygen treatment zone to the reactor.

3. The method of claim 2, wherein the catalyst is exposed to the oxygen-containing gas in the oxygen treatment zone for from 8 minutes to 20 minutes.

4. The method of any of the previous claims, wherein the supplemental fuel comprises methane in an amount of at least 3 mol.%.

5. The method of any of the previous claims, wherein the catalyst has a residence time within the reactor of less than or equal to 3 minutes.

6. The method of any of the previous claims, wherein the catalyst has a residence time within the reactor of less than or equal to 1 minute.

7. The method of any of the previous claims, wherein the catalyst comprises:
from 0.1 wt.% to 10 wt.% of gallium; and
from 5 ppmw to 1000 ppmw of platinum.

8. The method of any of the previous claims, wherein the catalyst comprises:
from 0.1 wt.% to 5 wt.% of gallium; and
from 10 ppmw to 400 ppmw of platinum.

9. The method of any of the previous claims, wherein the catalyst comprises from 500 ppmw to 10000 ppmw of iron.

10. The method of any of the previous claims, wherein the catalyst further comprises from 0.01 wt.% to 2.5 wt.% of one or more alkali or alkaline earth metals.

11. The method of claim 1, wherein the catalyst further comprises from 0.01 wt.% to 2.5 wt.% of potassium.

12. The method of any of the previous claims, wherein the catalyst comprises:
from 0.1 wt.% to 5 wt.% of gallium;
from 10 ppmw to 400 ppmw of platinum; and
from 500 ppmw to 8000 ppmw of iron.

13. The method of any of the previous claims, wherein the support comprises one or more of alumina, silica, or combinations thereof.

14. The method of any of the previous claims, wherein the catalyst has Geldart group A or Geldart group B properties.

15. The method of any of the previous claims, wherein the hydrocarbon-containing feed comprises propane and the olefin-containing effluent comprises propylene.