

OXYGEN CARRIER MATERIALS AND METHODS OF MAKING AND USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/489,573 filed March 10, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to oxygen carrier materials, and in particular, to oxygen carrier materials and methods of making oxygen-carrier materials.

BACKGROUND

[0003] Some chemical processes utilize oxygen carrier materials. In such processes, oxygen may be delivered or “carried” in a cycle via a reduction and subsequent oxidation of the oxygen carrier material. Oxygen carrier materials may be used in chemical processes that require oxygen. In such processes the oxygen carried by the oxygen carrier material may be utilized as the source of oxygen. In particular, oxygen carrier materials may be utilized in cyclical chemical processes where oxygen may be added to and removed from the oxygen carrier material as it is used throughout the entire process. For example, combustion reactions may utilize oxygen from an oxygen carrier material.

SUMMARY

[0004] There is a continued need for oxygen carrier materials that are suitable for use with particular chemical processes. It may be desired to have oxygen carrier materials that may be operable to selectively carry oxygen for specific chemical reactions. For example, oxygen carrier materials may be selective for the combustion of hydrogen over the combustion of hydrocarbons. It has been discovered that particular oxygen carrier compositions, according to some embodiments, may have these desirable attributes. For example, and as is described herein, oxygen carrier materials that include a redox-active metal oxide and particular alkali-including compositions may have beneficial performance over conventional oxygen carrier materials.

[0005] According to one or more embodiments of the present disclosure, an oxygen carrier material may comprise a redox-active metal oxide and an alkali-including composition. The alkali-including composition may have the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$. In the formula the sum

of u, v, and w may equal 1, the sum of x and y may equal 1, z may be greater than 1.5, and r may be from 0.02 to 20.

[0006] According to one or more additional embodiments of the present disclosure, a method of making an oxygen carrier material may comprise providing a redox-active metal oxide. The method may also comprise impregnating the redox-active metal oxide with an aqueous solution comprising one or more water-soluble alkali silicates, alkali aluminates, or alkali-alumino-silicates to produce an impregnated redox-active metal oxide. The method may also comprise drying the impregnated redox-active metal oxide and calcining the impregnated redox-active metal oxide to produce the oxygen carrier material. The oxygen carrier material may comprise a redox-active metal oxide and an alkali-including composition. The alkali-including composition may have the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$. In the formula the sum of u, v, and w may equal 1, the sum of x and y may equal 1, z may be greater than 1.5, and r may be from 0.02 to 20.

[0007] According to one or more additional embodiments of the present disclosure, a method for producing olefinic compounds may comprise contacting a feed stream comprising one or more hydrocarbons in a reactor with an oxygen carrier material. In the reactor the one or more hydrocarbons may be dehydrogenated to form hydrogen and one or more olefinic compounds and at least a portion of the hydrogen may be reacted with oxygen from the oxygen carrier material to produce water. The method may also comprise passing at least a portion of the oxygen carrier material to a regeneration unit and passing at least a portion of the oxygen carrier material from the regeneration unit to the reactor. The oxygen carrier material may comprise a redox-active metal oxide and an alkali-including composition. The alkali-including composition may have the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$. In the formula the sum of u, v, and w may equal 1, the sum of x and y may equal 1, z may be greater than 1.5, and r may be from 0.02 to 20.

[0008] Additional features and advantages of the present disclosure will be set forth in the detailed description, which follows, and in part will be apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, including the detailed description, which follows the claims, as well as the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The following detailed description of specific embodiments of the present disclosure can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

[0010] FIG. 1 is a schematic depiction of a reactor system suitable for use with oxygen carrier material, according to one or more embodiments described herein; and

[0011] FIG. 2 is a powder x-ray diffraction pattern of oxygen-carrier materials, according to one or more embodiments described herein.

[0012] Additional features and advantages of the present disclosure will be set forth in the detailed description, which follows, and in part will be apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, including the detailed description, which follows the claims, as well as the appended drawings.

[0013] It is to be understood that both the foregoing 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. The accompanying drawings are included to provide a further understanding of the various embodiments and are incorporated into and constitute a part of this specification. The drawings illustrate the various embodiments described herein, and together with the description, explain the principles and operations of the claimed subject matter.

DETAILED DESCRIPTION

[0014] Specific embodiments of the present application will now be described. The disclosure may, however, be embodied in different forms and should not be construed as limited to the embodiments set forth in this disclosure. Rather, these embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the subject matter to those skilled in the art.

[0015] Generally, described in this disclosure are various embodiments of oxygen carrier materials, embodiments of methods of making oxygen carrier materials, and embodiments of methods of using oxygen carrier materials.

[0016] According to one or more embodiments, the oxygen carrier material may comprise a redox-active metal oxide and an alkali-including composition. As used herein the term “redox-active metal oxide” refers to a metal oxide capable of undergoing reduction in the presence of a reducing agent, for example, hydrogen, and capable of undergoing oxidation in the presence of an oxidizing agent, for example, oxygen or air. The alkali-including composition may generally have the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$; where $u+v+w=1$, $x+y=1$, z is greater than 1.5, and r is from 0.02 to 20. Without being bound by theory it is believed that the combination of a redox-active metal oxide and an alkali-including composition having the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$ may form an oxygen carrier material that may be selective for the combustion of hydrogen in the presence of hydrocarbons.

[0017] As described herein, the oxygen carrier material may comprise a redox-active metal oxide and an alkali-including composition. In some embodiments, at least 90 wt.%, at least 95 wt.%, at least 99 wt.%, at least 99.5 wt.%, or even at least 99.9 wt.% of the oxygen carrier material comprises the combination of the redox-active metal oxide and the alkali-including composition. In some embodiments, the oxygen carrier material may consist of the redox-active metal oxide and an alkali-including composition.

[0018] In one or more embodiments, the ratio of the weight of redox-active metal oxide to the weight of the alkali-including composition in the oxygen carrier material may be greater than or equal to 5:1, such as greater than or equal to 10:1, greater than or equal to 15:1, greater than or equal to 20:1, greater than or equal to 25:1, greater than or equal to 30:1, greater than or equal to 35:1, greater than or equal to 40:1, greater than or equal to 45:1, or even greater than or equal to 50:1. In some embodiments, the ratio of the weight of redox-active metal oxide to the weight of alkali-including composition may be from 5:1 to 95:1. For example, the ratio of the weight of redox-active metal oxide to the weight of alkali-including composition may be from 5:1 to 90:1, such as from 5:1 to 80:1, from 5:1 to 70:1, from 5:1 to 60:1, from 5:1 to 50:1, from 5:1 to 40:1, from 5:1 to 30:1, from 5:1 to 20:1, from 5:1 to 10:1, from 10:1 to 95:1, from 10:1 to 90:1, from 10:1 to 80:1, from 10:1 to 70:1, from 10:1 to 60:1, from 10:1 to 50:1, from 10:1 to 40:1, from 10:1 to 30:1, from 10:1 to 20:1, from 20:1 to 95:1, from 20:1 to 90:1, from 20:1 to 80:1, from 20:1 to 70:1, from 20:1 to 60:1, from 20:1 to 50:1, from 20:1 to 40:1, from 20:1 to 30:1, from 30:1 to 95:1, from 30:1 to 90:1, from 30:1 to 80:1, from 30:1 to 70:1, from 30:1 to 60:1, from 30:1 to 50:1, from 30:1 to 40:1, from 40:1 to 95:1, from 40:1 to 90:1, from 40:1 to 80:1, from 40:1 to 70:1, from 40:1 to 60:1, from 40:1 to 50:1, from 50:1 to 95:1, from 50:1 to 90:1, from 50:1 to 80:1, from 50:1 to 70:1, from 50:1 to 60:1, from 50:1 to 50:1.

80:1, from 50:1 to 70:1, from 50:1 to 60:1, from 60:1 to 95:1, from 60:1 to 90:1, from 60:1 to 80:1, from 60:1 to 70:1, from 70:1 to 95:1, from 70:1 to 90:1, from 70:1 to 80:1, from 80:1 to 95:1, from 80:1 to 90:1, or from 90:1 to 95:1. Without being bound by theory it is believed that a ratio of the weight of redox-active metal oxide to the weight of the alkali-including composition in the oxygen carrier material of less than 5:1 may reduce the total oxygen capacity of the oxygen carrier material as it is believed that the alkali-including composition is not redox-active. It is also believed that the alkali-including composition may beneficially affect the selectivity of the oxygen-carrier material. It is further believed that a ratio of the weight of redox-active metal oxide to the weight of the alkali-including composition in the oxygen carrier material of greater than 5:1 may balance the non-redox-active nature of the alkali-including composition with its beneficial effect on selectivity.

[0019] As described herein, the oxygen carrier material may include a redox-active metal oxide. In one or more embodiments, the redox-active metal oxide includes binary, ternary, or other mixed metal oxides capable of undergoing reduction in the presence of a reducing agent (for example, hydrogen) and oxidation in the presence of oxidizing agent (for example, oxygen or air). In some embodiments, the redox-active metal oxide may be a metal oxide of an IUPAC group 6, 7, 8, 9, 10, 11, or 12 metal. In some embodiments, the redox-active metal oxide may be an oxide of a metal selected from Fe, Mn, Cu, Ni, Co, or Ce. In some embodiments, the redox-active metal oxide may be an oxide of a metal selected from Fe and Mn. In some embodiments, the redox-active metal oxide may be selected from Fe_2O_3 , FeO , Fe_3O_4 , Mn_2O_3 , MnO , Mn_3O_4 , MnO_2 , $(\text{Ca}_{1-x}\text{Sr}_x)\text{MnO}_3$, Mg_6MnO_8 , LaSrMnO_3 , LaSrFeO_3 , FeTiO_3 , Fe_2TiO_5 , $\text{FeTi}_3\text{O}_{10}$, BaMnO_3 , or combinations thereof. For example, other suitable redox-active metal oxides are disclosed in “Chemical Looping Combustion: Status and Development Challenges,” Energy Fuels 2020, 34, 9077–9093, “On the Attrition Evaluation of Oxygen Carriers in Chemical Looping Combustion” Fuel Processing Technology 148 (2016) 188–197, and L.S. Fan, “Chemical Looping Systems for Fossil Energy Conversions”, John Wiley & Sons (2010) which are incorporated herein by reference in their entireties.

[0020] As described herein, the oxygen carrier material may include an alkali-including composition having the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$, where $u+v+w=1$, $x+y=1$, z is greater than 1.5, and r is from 0.02 to 20. Without being bound by theory it is believed that oxygen-carrier materials comprising an alkali-including composition with the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$ and a redox-active metal oxide have improved selectivity towards hydrogen combustion over

hydrocarbons resulting in lower amount of CO_x formation when compared to oxygen-carrier materials that do not comprise the alkali-including composition, as is demonstrated in the present Examples.

[0021] In the oxygen carrier material, the alkali-including composition may act as a surface dopant, a bulk dopant or both. If the alkali-including composition acts as a surface dopant it may partially or completely coat the surface of redox-active metal oxide. If the alkali-including composition acts as a bulk dopant, the alkali-including composition may be distributed throughout the interior of the redox-active metal oxide. If the alkali-including composition acts as both a surface dopant and a bulk dopant the alkali-including composition may partially or completely coat the surface of the redox-active metal oxide and may also be distributed throughout the interior of the redox-active metal oxide.

[0022] In the formula, $u+v+w=1$ indicates that the alkali-including composition includes at least some amount of one or more of sodium, potassium, and lithium. In some embodiments, one of u , v , or w is equal to 1. In such embodiments, the alkali-including composition may include sodium, but not potassium or lithium, potassium, but not sodium or lithium, or lithium, but not sodium or potassium. In other embodiments, the alkali-including composition may include sodium and potassium but not lithium, sodium and lithium but not potassium, potassium and lithium but not sodium, or the alkali-including composition may include sodium, potassium and lithium.

[0023] In the formula, $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$, $x+y$ may equal 1. Accordingly, the alkali-including composition includes at least some amount of one or both of silicon and aluminum. In some embodiments, x may be equal to 1 and the alkali-including composition may include silicon but not aluminum. In other embodiments, y may be equal to 1 and the alkali-including composition may include aluminum but not silicon. In still more embodiments, the alkali-including composition may include both silicon and aluminum. In the formula x and y may each equal any number from 0 to 1 inclusive of 0 and 1, so long as the sum of x and y is equal to 1. For example, both x and y may be equal to .5, x may be equal to .75 and y may be equal to .25, or x may be equal to .25 and y may be equal to .75.

[0024] The alkali-including composition may include oxygen. In the formula, $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$, z may be greater than or equal to 1.5 indicating that at least some amount of oxygen is present in the alkali-including composition. In one or more embodiments, z may be greater than

or equal to 1.5, such as greater than or equal to 2, greater than or equal to 2.5, greater than or equal to 3, greater than or equal to 3.5, greater than or equal to 4, greater than or equal to 4.5, or even greater than or equal to 5. In some embodiments, z may be from 1.5 to 5, such as from 1.5 to 4.5, from 1.5 to 4, from 1.5 to 3.5, from 1.5 to 3, from 1.5 to 2.5, from 1.5 to 2, from 2 to 5, from 2 to 4.5, from 2 to 4, from 2 to 3.5, from 2 to 3, from 2 to 2.5, from 2.5 to 5, from 2.5 to 4.5, from 2.5 to 4, from 2.5 to 3.5, from 2.5 to 3, from 3 to 5, from 3 to 4.5, from 3 to 4, from 3 to 3.5, from 3.5 to 5, from 3.5 to 4.5, from 3.5 to 4, from 4 to 5, from 4 to 4.5, or from 4.5 to 5.

[0025] In one or more embodiments, r in the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$ may be from 0.02 to 20. For example, r may be from 0.02 to 15, from 0.02 to 10, from 0.02 to 5, from 0.02 to 1, from 0.02 to 0.5, from 0.02 to 0.1, from 0.02 to 0.05, from 0.05 to 20, from 0.05 to 15, from 0.05 to 10, from 0.05 to 5, from 0.05 to 1, from 0.05 to 0.5, from 0.05 to 0.1, from 0.1 to 20, from 0.1 to 15, from 0.1 to 10, from 0.1 to 5, from 0.1 to 1, from 0.1 to 0.5, from 0.5 to 20, from 0.5 to 15, from 0.5 to 10, from 0.5 to 5, from 0.5 to 1, from 1 to 20, from 1 to 15, from 1 to 10, from 1 to 5, from 5 to 20, from 5 to 15, from 5 to 10, from 10 to 20, from 10 to 15, or from 15 to 20.

[0026] In one or more embodiments, the alkali-including composition may be free of boron. In further embodiments, the alkali-including composition may be selected from the group consisting of NaAlO_2 , KAlO_2 , Na_4SiO_4 , $\text{Na}_6\text{Si}_2\text{O}_7$, Na_2SiO_3 , Na_2SiO_5 , $\text{Na}_6\text{Si}_6\text{O}_{19}$, K_2SiO_3 , $\text{K}_2\text{Si}_2\text{O}_5$, or $\text{K}_2\text{Si}_4\text{O}_9$.

[0027] In one or more embodiments, the oxygen-carrier material may be capable of fluidization. In some embodiments, the oxygen carrier material may have a median particle size (D_{50}) of from 50 μm to 300 μm , such as from 50 μm to 250 μm , from 50 μm to 200 μm , from 50 μm to 150 μm , from 50 μm to 100 μm , from 100 μm to 300 μm , from 100 μm to 250 μm , from 100 μm to 200 μm , from 100 μm to 150 μm , from 150 μm to 300 μm , from 150 μm to 250 μm , from 150 μm to 200 μm , from 200 μm to 300 μm , from 200 μm to 250 μm , or from 250 μm to 300 μm .

[0028] In some embodiments, the oxygen-carrier material may exhibit properties known in the industry as “Geldart A” or “Geldart B” properties. Particles 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, which are incorporated herein by reference in their entireties.

[0029] 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 $U-U_{mf}$ (U is the velocity of the carrier gas, and U_{mf} 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 cfp; 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.

[0030] Group B is understood by those skilled in the art as representing a “sand-like” powder that starts bubbling at U_{mf} ; that exhibits moderate bed expansion; a fast deaeration; no limits on bubble size; moderate levels of solids mixing and gas backmixing, assuming equal $U-U_{mf}$; 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 (cfp) of $40\ \mu\text{m} < \text{cfp} < 500\ \mu\text{m}$ when the density (pp) is $1.4 < \text{pp} < 4\ \text{g}/\text{cm}^3$, and preferably $60\ \mu\text{m} < \text{cfp} < 500\ \mu\text{m}$ when the density (pp) is $4\ \text{g}/\text{cm}^3$ and $250\ \mu\text{m} < \text{cfp} < 100\ \mu\text{m}$ when the density (pp) is $1\ \text{g}/\text{cm}^3$.

[0031] In one or more embodiments, a method of making an oxygen-carrier material, as described herein, may comprise: providing a redox-active metal oxide, impregnating the redox-active metal oxide with an aqueous solution comprising one or more water-soluble alkali silicates, alkali aluminates, or alkali-alumino-silicates to produce an impregnated redox-active metal oxide, drying the impregnated redox-active metal oxide, and calcining the impregnated redox-active metal oxide to produce the oxygen-carrier material.

[0032] Providing the redox-active metal oxide may include any conventional technique for preparing the redox-active metal oxide, including spray drying, granulation, and solid state synthesis followed by drying and calcination. In some embodiments, the redox-active metal oxide

may be a Geldart Group A or Group B particle before impregnation. In other embodiments, the redox-active metal oxide may not be a Geldart Group A or Group B particle before impregnation.

[0033] As described hereinabove, the method of making an oxygen-carrier material may comprise impregnating the redox-active metal oxide with an aqueous solution. The aqueous solution may comprise one or more water-soluble alkali silicates, alkali aluminates, or alkali-alumino-silicates. In some embodiments, the aqueous solution may comprise one or more of sodium silicate, potassium silicate, lithium silicate, sodium aluminate, potassium aluminate, lithium aluminate, or combinations thereof. In one or more embodiments, the aqueous solution may have a pH of greater than 7. For example, the aqueous solution may have a pH of greater than 7.5, greater than 8, greater than 8.5, greater than 9, greater than 9.5, greater than 10, greater than 10.5, greater than 11, or even greater than 11.5.

[0034] In one or more embodiments, the redox-active metal oxide may be impregnated via dry impregnation, also referred to as incipient wetness impregnation. In one or more embodiments, the redox-active metal oxide may be impregnated via wet impregnation. In some embodiments, the redox-active metal oxide may be impregnated more than once with the aqueous solution.

[0035] The impregnated redox-active metal oxide may then be dried after impregnation. In some embodiments, the impregnated redox-active metal oxide may be dried under air. In one or more embodiments, the impregnated redox-active metal oxide may be dried at a temperature of less than 200 °C, such as less than 175 °C, less than 150 °C, less than 125 °C, less than 100 °C, less than 75 °C, or even less than 50 °C. In embodiments where the redox-active metal oxide is impregnated more than once with the aqueous solution, the impregnated redox-active metal oxide may be dried between each impregnation.

[0036] The dried impregnated redox-active metal oxide may then be calcined to produce the oxygen-carrier material. In one or more embodiments, the dried impregnated redox-active metal oxide may be calcined at a temperature of less than 1200 °C, such as less than 1100 °C, less than 1000 °C, less than 900 °C, less than 800 °C, less than 700 °C, less than 600 °C, or even less than 500 °C. In one or more embodiments, the dried impregnated redox-active metal oxide may be calcined under air.

[0037] According to one or more embodiments of the present disclosure, a method for producing olefinic compounds is provided using the oxygen carrier materials described herein. As

used herein, the term “olefinic compounds” refers to hydrocarbons having one or more carbon-carbon double bonds apart from the formal double bonds in aromatic compounds. For example, ethylene and styrene are olefinic compounds, but ethylbenzene would not be an olefinic compound as the only double bonds present in ethylbenzene are formal double bonds present as part of the aromatic structure. Now referring to FIG. 1, a reactor system 100 that may be used with the methods of the present disclosure is shown, but other reactor systems as would be known by one of skill in the art are contemplated herein. For example, the oxygen carrier materials of the present disclosure may be utilized in the systems and methods that are disclosed in WO 2020/046978, the teachings of which are incorporated by reference in their entirety herein.

[0038] Referring back to FIG. 1, the reactor system 100 may include a reactor 110 and a regeneration unit 120. In one or more embodiments, the reactor 110 may be a fluidized bed reactor. A feed stream 101 may be passed into the reactor 110. In one or more embodiments, the feed stream 101 may comprise one or more hydrocarbons. In one or more embodiments, the one or more hydrocarbons may comprise one or more of ethane, propane, butane, or ethylbenzene. According to one or more embodiments, the one or more hydrocarbons 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 one or more hydrocarbons 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 one or more hydrocarbons 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 butane. In additional embodiments, the one or more hydrocarbons 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 ethylbenzene. In additional embodiments, the one or more hydrocarbons 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, butane and ethylbenzene.

[0039] In the reactor 110, feed stream 101 may be contacted with an oxygen carrier material and the one or more hydrocarbons may be dehydrogenated to form hydrogen and one or more olefinic compounds. At least a portion of the hydrogen is reacted with oxygen from the oxygen carrier material to form water. Reacting the hydrogen with oxygen from the oxygen carrier material may reduce the oxygen carrier material. The dehydrogenation reaction in the fluidized bed reactor 110 may be thermally driven or may be catalytically driven.

[0040] In one or more embodiments, the dehydrogenation reaction may utilize a dehydrogenation catalyst. The dehydrogenation catalyst may be any suitable catalyst as would be known by one skilled in the art. For example, suitable catalysts are described in *Chem. Rev.* 2014, 114, 20, 10613–10653, which is incorporated herein by reference in its entirety and U.S. Pat. No. 8,669,406, which is incorporated herein by reference in its entirety. Alternatively, no catalyst may be utilized to perform the dehydrogenation reaction.

[0041] The reduced oxygen carrier material may need to be re-oxidized before being used again in the reactor 110. Reduced oxygen carrier material may be passed from the reactor 110 to the regeneration unit 120 via stream 103. In the regeneration unit 120 the reduced oxygen carrier material may be re-oxidized. In some embodiments, the oxygen carrier material is re-oxidized by exposing it to an oxygen-containing gas, for example, air or oxygen. The re-oxidized oxygen carrier material may then be passed back to the reactor 110 from the regeneration unit 120 via stream 104. As such, the oxygen carrier material may be looped or cycled through the reactor system 100. In some embodiments the re-oxidized oxygen carrier material may be partially reduced before being passed to the reactor 110.

[0042] The one or more olefinic compounds produced in the reactor 110 may exit the reactor 110 via product stream 102. In one or more embodiments, the olefinic compounds may comprise one or more of ethylene, propylene, butylene, or styrene. The term butylene includes any isomers of butylene, such as α -butylene, cis- β -butylene, trans- β -butylene, and isobutylene. In some embodiments, the olefin-containing effluent may comprise at least 20 wt. %, at least 30 wt. %, at least 40 wt. %, at least 50 wt. %, or even at least 60 wt. % of ethylene. In additional embodiments, the olefin-containing effluent may comprise at least 20 wt. %, at least 30 wt. %, at least 40 wt. %, at least 50 wt. %, or even at least 60 wt. % of propylene. In additional embodiments, the olefin-containing effluent may comprise at least 20 wt. %, at least 30 wt. %, at least 40 wt. %, at least 50 wt. %, or even at least 60 wt. % of butylene. In additional embodiments, the olefin-containing effluent may comprise at least 20 wt. %, at least 30 wt. %, at least 40 wt. %, at least 50 wt. %, or even at least 60 wt. % of styrene. In additional embodiments, the olefin-containing effluent may comprise at least 20 wt. %, at least 30 wt. %, at least 40 wt. %, at least 50 wt. %, or even at least 60 wt. % of the sum of one or more of ethylene, propylene, butylene, and styrene. The product stream 102 may further comprise unreacted components of the feed stream, as well as other

reaction products that are not considered olefinic compounds. The olefinic compounds may be separated from unreacted components in subsequent separation steps.

EXAMPLES

[0043] 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 – Sample Preparation

[0044] Comparative Example A was non-redox-active inert quartz chips that were used as received. Comparative Example B was calcium manganese oxide (CaMnO_3), Comparative Example C was manganese oxide (MnO_2), Comparative Example D was copper oxide (CuO), Comparative Example E was Cerium Oxide (CeO_2), and Comparative Example F was iron oxide (Fe_2O_3). Comparative Examples A-F were all procured commercially and used as received.

[0045] Comparative Examples C1-C4 were prepared by impregnating Comparative Example D with an aqueous solution of sodium nitrate. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting comparative examples were listed in Table 2.

[0046] Comparative Examples C5-C6 were prepared by impregnating Comparative Example E with SiO_2 and calcining the mixture in air at a temperature less than 1000 °C. The composition of the resulting comparative examples were listed in Table 3.

[0047] Samples 1-3 were prepared by impregnating Comparative Example B. First, sodium aluminate, obtained commercially from Sigma Aldrich (#13404), was dissolved in water to form an impregnation solution. The impregnation solution was then added to a given amount of Comparative Example B to form an impregnated material. The impregnated material was then dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 1. Further, FIG. 1 shows a powder x-ray diffraction pattern of Sample 1 and Sample 3, where Sample 3 has a higher amount of sodium aluminate loading.

[0048] Samples 4-7 were prepared by impregnating Comparative Example B. First, potassium silicate solutions were obtained commercially from Zaclon (Zacsil 30 or Zacsil 865) and were

used as the impregnation solution. Given amount of impregnation solution was added to given amount of Comparative Example B to form an impregnated material. The impregnated material was then dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 1.

[0049] Samples 8-10 were prepared by impregnating Comparative Example B. First, sodium silicate solution was obtained commercially from Sigma Aldrich (#338443) and was used as the impregnation solution. Impregnation solution was added to given amount of Comparative example B to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 1.

[0050] Samples 11-13 were prepared by impregnating Comparative Example B. First, sodium silicate and sodium aluminate were obtained commercially and combined to form an aqueous impregnation solution. Impregnation solution was then added to given amount of Comparative Example B to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 1.

[0051] Samples 14-17 were prepared by impregnating Comparative Example C. First, sodium silicate solution was obtained commercially and used as the impregnation solution. Impregnation solution was then added to given amount of Comparative Example C to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 2.

[0052] Samples 18-19 were prepared by impregnating Comparative Example C. First, sodium silicate solution and sodium hydroxide were obtained commercially and combined to form an aqueous impregnation solution. Impregnation solution was then added to given amount of Comparative Example C to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 2.

[0053] Samples 20-22 were prepared by impregnating Comparative Example D. First, potassium silicate solutions were obtained commercially from Zaclon (Zacsil 30) and were

combined with potassium hydroxide to form the impregnation solution. Impregnation solution was then added to given amount of Comparative Example D to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples was listed in Table 2.

[0054] Samples 23-25 were prepared by impregnating Comparative Example C. First, sodium aluminate, obtained commercially, was dissolved in water to form an impregnation solution. Impregnation solution was then added to given amount of Comparative Example C to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 2.

[0055] Samples 26 was prepared by impregnating Comparative Example D. First, sodium silicate solution was obtained commercially and used as the impregnation solution. Impregnation solution was then added to given amount of Comparative Example E to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 3.

[0056] Samples 27 was prepared by impregnating Comparative Example E. First, sodium silicate solution was obtained commercially and used as the impregnation solution. Impregnation solution was then added to given amount of Comparative Example E to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 4.

[0057] Samples 28-30 were prepared by impregnating Comparative Example F. First, sodium silicate solution was obtained commercially and used as the impregnation solution. The impregnation solution was then added to a given amount of Comparative Example E to form an impregnated material. The impregnated material was dried at a temperature of less than 200 °C followed by calcination in air at less than 1000 °C for 6 hours. The compositions of the resulting Samples were listed in Table 5.

Example 2 – Ethane Dehydrogenation Performance

[0058] Testing of oxygen carrying materials were performed in a fixed bed laboratory reactor. A 0.5 g portion of the sample was loaded into a 0.5 in. OD quartz bulb connected to 6.5 mm OD quartz tubing. The sample bed was supported on a pill of quartz wool and a layer of 0.5-1.0 mm quartz chips. The empty space in the quartz bulb above the sample bed was filled with 0.5-1.0 mm quartz chips. The reactor was installed into a clamshell furnace and a flow of helium at 50 sccm was started through the reactor tube. The reactor was then heated, under 40 standard cubic centimeters (sccm) of air flow, from room temperature to 780 °C. The oxygen carrying materials were subjected to several cyclic sequences—each cycle comprising ethane dehydrogenation (reduction) and air regeneration (oxidation) with inert nitrogen purging if the reactor tube in-between reduction and oxidation pulses. The ethane dehydrogenation steps were done at a weight hourly space velocity (WHSV) of 7 hr⁻¹. Specifically, 52.72 sccm of a gas mixture containing 90 mol% ethane and 10 mol% helium were fed through the reactor for 60 seconds while the reactor was held at 780 °C. Analysis of the product gas composition was taken at 30 seconds into the dehydrogenation reaction pulse (halfway through). During the air regeneration steps, 40 sccm of air was fed through the reactor for 10 minutes. Between each of ethane dehydrogenation and air regeneration steps, the reactor tube was purged with 40 sccm of nitrogen for 2 minutes. The product gas compositions were analyzed by a Siemens Maxim Process Gas Chromatograph. For each oxygen carrying material, multiple replicate reduction-oxidation cycles were performed and the average ethane conversion, ethylene selectivity, CO_x selectivity, and hydrogen:ethylene ratio are reported.

Table 1

Sample	Oxygen carrier	Promoter(s)	Promoter loading [wt. %]	C ₂ H ₆ conv. [%]	C ₂ H ₄ sel. [%]	CO _x sel. [%]	H ₂ /C ₂ H ₄ ratio
A	none	none	0	22.9	96.7	0.1	1.02
B	CaMnO ₃	none	0	31.7	89.4	7.3	0.33
1	CaMnO ₃	NaAlO ₂	1.0	30.1	94.1	2.2	0.54
2	CaMnO ₃	NaAlO ₂	2.9	29.4	94.1	2.4	0.39
3	CaMnO ₃	NaAlO ₂	8.3	24.6	94.4	2.5	0.35
4	CaMnO ₃	K ₂ O(SiO ₂) _{3.9}	0.9	26.9	93.9	2.9	0.54
5	CaMnO ₃	K ₂ O(SiO ₂) _{3.9}	1.7	32.9	93.0	3.0	0.48
6	CaMnO ₃	K ₂ O(SiO ₂) _{3.3}	1.2	26.4	93.2	3.6	0.59
7	CaMnO ₃	K ₂ O(SiO ₂) _{3.3}	2.3	34.1	91.7	4.3	0.39
8	CaMnO ₃	Na ₂ O(SiO ₂) _{3.5}	1.0	30.6	93.4	2.9	0.45
9	CaMnO ₃	Na ₂ O(SiO ₂) _{3.5}	3.1	31.1	92.8	3.4	0.32
10	CaMnO ₃	Na ₂ O(SiO ₂) _{3.5}	5.0	29.7	92.7	3.8	0.27
11	CaMnO ₃	NaAlO ₂ + Na ₂ O(SiO ₂) _{3.5}	1.0 + 1.0	27.4	94.1	2.6	0.49

12	CaMnO ₃	NaAlO ₂ + Na ₂ O(SiO ₂) _{3.5}	2.9 + 1.0	30.6	93.8	2.4	0.53
13	CaMnO ₃	NaAlO ₂ + Na ₂ O(SiO ₂) _{3.5}	8.2+ 1.0	23.1	94.6	2.4	0.51

[0059] As shown in Table 1, the presence of an oxygen-carrier (Comparative Example B) improves the ethane conversion percentage and the ratio of hydrogen to ethylene when compared to a reaction with no oxygen-carrier (Comparative Example A). However, the oxygen-carrier without the presence of a promoter (Comparative Example B) was not as selective for the combustion of hydrogen over the combustion of the hydrocarbons in the reactor resulting in a significantly higher CO_x selectivity percentage than any sample with a promoter present (Samples 1-13) indicating the combustion of hydrocarbons with the oxygen from the oxygen-carrier occurred at a higher rate for the un-promoted oxygen carrier.

Table 2

Sample	Oxygen carrier	Promoter	Promoter loading [wt.%]	C ₂ H ₆ conversion [%]	C ₂ H ₄ selectivity [%]	CO _x selectivity [%]	H ₂ /C ₂ H ₄ ratio
C	MnO ₂	none	0	47.2	51.7	46.0	0.09
C1	MnO ₂	Na ₂ O	1.4	32.1	77.1	19.9	0.17
C2	MnO ₂	Na ₂ O	4.0	37.0	76.5	20.3	0.11
C3	MnO ₂	Na ₂ O	6.7	33.5	76.8	20.3	0.13
C4	MnO ₂	Na ₂ O	9.9	33.8	78.6	18.3	0.14
C5	MnO ₂	SiO ₂	2.0	45.6	52.6	45.1	0.11
C6	MnO ₂	SiO ₂	5.0	47.3	55.3	41.7	0.14
14	MnO ₂	Na ₂ O(SiO ₂) _{3.5}	1.1	29.9	86.7	8.9	0.16
15	MnO ₂	Na ₂ O(SiO ₂) _{3.5}	3.1	24.5	93.6	2.7	0.21
16	MnO ₂	Na ₂ O(SiO ₂) _{3.5}	5.0	26.5	94.4	1.8	0.27
17	MnO ₂	Na ₂ O(SiO ₂) _{3.5}	6.5	31.6	93.1	2.6	0.42
18	MnO ₂	Na ₂ O(SiO ₂) _{1.0}	5.0	24.8	94.2	2.2	0.45
19	MnO ₂	Na ₂ O(SiO ₂) _{0.3}	5.0	34.0	91.5	4.2	0.19
20	MnO ₂	K ₂ O(SiO ₂) _{3.9}	3.0	26.0	88.4	8.3	0.19
21	MnO ₂	K ₂ O(SiO ₂) _{1.0}	3.0	33.0	77.8	16.1	0.11
22	MnO ₂	K ₂ O(SiO ₂) _{0.3}	3.0	30.4	69.6	24.8	0.13
23	MnO ₂	NaAlO ₂	1.0	34.0	72.7	24.8	0.15
24	MnO ₂	NaAlO ₂	2.9	38.3	74.2	22.5	0.11
25	MnO ₂	NaAlO ₂	8.3	31.3	81.8	14.9	0.14

[0060] As shown in Table 2, Samples with a promoter, Comparative Examples C1-C6 and Samples 14-25, all had significantly lower CO_x selectivity than the Sample without a promoter, Comparative Example C. Table 2 also shows that samples with a promoter of the formula Na_uK_vLi_w(Si_xAl_yO_z)_t, as described hereinabove, (e.g. Samples 14-25) had one or more of improved ethane conversion, improved ethylene selectivity, improved CO_x selectivity, or an improved

hydrogen to ethylene ratio when compared to Comparative Examples C1-C7 which had promoters that do not have the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_t$, as described hereinabove.

Table 3

Sample	Oxygen carrier	Promoter	Promoter loading [wt.%]	C ₂ H ₆ conversion [%]	C ₂ H ₄ selectivity [%]	CO _x selectivity [%]	H ₂ /C ₂ H ₄ ratio
D	CuO	none	0	28.7	49.9	47.8	0.25
26	CuO	Na ₂ O(SiO ₂) _{3.5}	5	38.8	56.3	40.3	0.13

[0061] As shown in Table 3, Samples with a promoter (e.g. Sample 26) had significantly higher C₂H₄ selectivity and significantly lower CO_x selectivity than Comparative Example D which did not have a promoter.

Table 4

Sample	Oxygen carrier	Promoter	Promoter loading [wt.%]	C ₂ H ₆ conversion [%]	C ₂ H ₄ selectivity [%]	CO _x selectivity [%]	H ₂ /C ₂ H ₄ ratio
E	CeO ₂	none	0	29.1	72.6	21.2	1.72
27	CeO ₂	Na ₂ O(SiO ₂) _{3.5}	5	21.5	95.1	1.6	0.88

[0062] As shown in Table 4, Samples with a promoter (e.g. Sample 27) had significantly higher C₂H₄ selectivity and significantly lower CO_x selectivity than Comparative Example E which did not have a promoter.

Table 5

Sample	Oxygen carrier	Promoter	Promoter loading [wt.%]	C ₂ H ₆ conv. [%]	C ₂ H ₄ sel. [%]	CO _x sel. [%]	H ₂ /C ₂ H ₄ ratio
E	Fe ₂ O ₃	None	0	28.4	72.4	23.7	0.86
29	Fe ₂ O ₃	Na ₂ O(SiO ₂) _{3.5}	1.1	26.2	80.5	15.2	0.11
30	Fe ₂ O ₃	Na ₂ O(SiO ₂) _{3.5}	2.1	36.3	79.7	14.8	0.09
31	Fe ₂ O ₃	Na ₂ O(SiO ₂) _{3.5}	3.4	25.4	83.9	12.1	0.16

[0063] As shown in Table 5, Samples with a promoter (e.g. Samples 29-30) have significantly improved hydrogen to ethylene ratio and CO_x selectivity when compared to Comparative Example D with the same oxygen carrier but no promoter.

Example 3 - Powder X-ray diffraction pattern of sample oxygen carrier materials

[0064] FIG. 2 is a powder x-ray diffraction pattern of Samples 1 and 3. As shown in FIG. 2, the peaks associated with sodium aluminate are only detectable at the higher loadings of Sample 3. The presence of the sodium aluminate peaks in the pattern of Sample 3 indicates that the impregnation successfully introduced sodium aluminate as a promoter to the oxygen carrier. The low levels of promoter in Sample 1, mean that even though the sodium aluminate peaks are not visible it can be inferred from the peaks of Sample 3 that the impregnation of Sample 1 also successfully introduced sodium aluminate to the oxygen carrier.

[0065] According to a first aspect of the present disclosure an oxygen carrier material may comprise a redox-active metal oxide and an alkali-including composition. The alkali-including composition may have the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$. In the formula the sum of u, v, and w may equal 1, the sum of x and y may equal 1, z may be greater than 1.5, and r may be from 0.02 to 20.

[0066] A second aspect of the present disclosure may include the first aspect where a weight ratio of the redox-active metal oxide to the alkali-including composition is greater than or equal to 5:1.

[0067] A third aspect of the present disclosure may include any previous aspect or combination of aspects, where the redox-active metal oxide is an oxide of a metal selected from Fe, Mn, Cu, Ni, Co, or Ce.

[0068] A fourth aspect of the present disclosure may include any previous aspect or combination of aspects, where the redox-active metal oxide is an oxide of a metal selected from Fe and Mn.

[0069] A fifth aspect of the present disclosure, may include any previous aspect or combination of aspects, where the redox-active metal oxide is selected from Fe₂O₃, FeO, Mn₂O₃, MnO, CaMnO₃, Mg₆MnO₈, LaSrMnO₃, LaSrFeO₃, FeTiO₃, Fe₂TiO₅, Fe₃Ti₃O₁₀, or BaMnO₃.

[0070] A sixth aspect of the present disclosure may include any previous aspect or combination of aspects, where r is from 0.1 to 10.

[0071] A seventh aspect of the present disclosure may include any previous aspect or combination of aspects, where x or y is equal to 1.

[0072] An eight aspect of the present disclosure may include any previous aspect or combination of aspects, where one of u, v, or w is equal to 1.

[0073] A ninth aspect of the present disclosure may include any previous aspect or combination of aspects, where the alkali-including composition is free of boron.

[0074] A tenth aspect of the present disclosure may include any previous aspect or combination of aspects, where the alkali-including composition is selected from the group consisting of NaAlO_2 , KAlO_2 , Na_4SiO_4 , $\text{Na}_6\text{Si}_2\text{O}_7$, Na_2SiO_3 , Na_2SiO_5 , $\text{Na}_6\text{Si}_6\text{O}_{19}$, K_2SiO_3 , $\text{K}_2\text{Si}_2\text{O}_5$, or $\text{K}_2\text{Si}_4\text{O}_9$.

[0075] An eleventh aspect of the present disclosure may include any previous aspect or combination of aspects, where at least 95 wt.% of the oxygen carrier material comprises the combination of the redox-active metal oxide and the alkali-including composition.

[0076] In a twelfth aspect of the present disclosure a method of making an oxygen carrier material may comprise providing a redox-active metal oxide, impregnating the redox-active metal oxide with an aqueous solution comprising one or more water-soluble alkali silicates, alkali aluminates, or alkali-alumino-silicates to produce an impregnated redox-active metal oxide, drying the impregnated redox-active metal oxide, and calcining the impregnated redox-active metal oxide to produce the oxygen carrier material. The oxygen carrier material may comprise a redox-active metal oxide and an alkali-including composition. The alkali-including composition may have the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$. In the formula the sum of u, v, and w may equal 1, the sum of x and y may equal 1, z may be greater than 1.5, and r may be from 0.02 to 20.

[0077] A thirteenth aspect of the present disclosure may include the twelfth aspect, where the aqueous solution has a pH of greater than 7.

[0078] In a fourteenth aspect of the present disclosure a method for producing olefinic compounds may comprise contacting a feed stream comprising one or more hydrocarbons in a reactor with an oxygen carrier material. In the reactor the one or more hydrocarbons may be dehydrogenated to form hydrogen and one or more olefinic compounds and at least a portion of the hydrogen may be reacted with oxygen from the oxygen carrier material to produce water. The method may also comprise passing at least a portion of the oxygen carrier material to a

regeneration unit and passing at least a portion of the oxygen carrier material from the regeneration unit to the reactor. The oxygen carrier material may comprise a redox-active metal oxide and an alkali-including composition. The alkali-including composition may have the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$. In the formula the sum of u , v , and w may equal 1, the sum of x and y may equal 1, z may be greater than 1.5, and r may be from 0.02 to 20.

[0079] A fifteenth aspect of the present disclosure may include the fourteenth aspect, where the one or more hydrocarbons comprise ethane and the one or more olefinic compounds comprise ethylene.

[0080] 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.

[0081] 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.

[0082] 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.

[0083] 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.

[0084] 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.

[0085] 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.”

[0086] 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.

[0087] As would be understood in the context of the term as used herein, the term “passing” may include directly passing a substance between two portions of the disclosed system and, in some other instances, to mean indirectly passing a substance between two portions of the disclosed system. For example, indirect passing may include steps where the named substance passes through an intermediate operations unit, valve, sensor, etc.

CLAIMS

1. An oxygen carrier material comprising:
a redox-active metal oxide; and
an alkali-including composition having the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$, wherein:
 $u + v + w = 1$;
 $x + y = 1$;
 z is greater than 1.5; and
 r is from 0.02 to 20.
2. The oxygen carrier material of claim 1, wherein the weight ratio of the redox-active metal oxide to the alkali-including composition is greater than or equal to 5:1.
3. The oxygen carrier material of any preceding claim, wherein the redox-active metal oxide is an oxide of a metal selected from Fe, Mn, Cu, Ni, Co, or Ce.
4. The oxygen carrier material of any preceding claim, wherein the redox-active metal oxide is an oxide of a metal selected from Fe and Mn.
5. The oxygen carrier material of claim 1, wherein the redox-active metal oxide is selected from Fe_2O_3 , FeO , Mn_2O_3 , MnO , CaMnO_3 , Mg_6MnO_8 , LaSrMnO_3 , LaSrFeO_3 , FeTiO_3 , Fe_2TiO_5 , $\text{Fe}_3\text{Ti}_3\text{O}_{10}$, or BaMnO_3 .
6. The oxygen carrier material of any preceding claim, wherein r is from 0.1 to 10.
7. The oxygen carrier material of any preceding claim, wherein one of x or y is equal to 1.
8. The oxygen carrier material of any preceding claim, wherein one of u , v , or w is equal to 1.
9. The oxygen carrier material of any preceding claim, wherein the alkali-including composition is free of boron.

10. The oxygen carrier material of claim 1, wherein the alkali-including composition is selected from the group consisting of NaAlO_2 , KAlO_2 , Na_4SiO_4 , $\text{Na}_6\text{Si}_2\text{O}_7$, Na_2SiO_3 , Na_2SiO_5 , $\text{Na}_6\text{Si}_6\text{O}_{19}$, K_2SiO_3 , $\text{K}_2\text{Si}_2\text{O}_5$, or $\text{K}_2\text{Si}_4\text{O}_9$.
11. The oxygen carrier material of any preceding claim, wherein at least 95 wt.% of the oxygen carrier material comprises the combination of the redox-active metal oxide and the alkali-including composition.
12. A method of making an oxygen carrier material comprising:
providing a redox-active metal oxide;
impregnating the redox-active metal oxide with an aqueous solution comprising one or more water-soluble alkali silicates, alkali aluminates, or alkali-alumino-silicates to produce an impregnated redox-active metal oxide;
drying the impregnated redox-active metal oxide; and
calcining the impregnated redox-active metal oxide to produce the oxygen carrier material;
wherein the oxygen carrier material comprises:
a redox-active metal oxide; and
an alkali-including composition having the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$,
wherein:
 $u + v + w = 1$;
 $x + y = 1$;
 z is greater than 1.5; and
 r is from 0.02 to 20.
13. The method of claim 11, wherein the aqueous solution has a pH greater than 7.
14. A method for producing olefinic compounds, the method comprising:
contacting a feed stream comprising one or more hydrocarbons in a reactor with an oxygen carrier material, wherein in the reactor:
the one or more hydrocarbons are dehydrogenated to form hydrogen and one or more olefinic compounds; and

at least a portion of the hydrogen is reacted with oxygen from the oxygen carrier material to produce water;
passing at least a portion of the oxygen carrier material to a regeneration unit; and
passing at least a portion of the oxygen carrier material from the regeneration unit to the reactor;
wherein the oxygen carrier material comprises:
a redox-active metal oxide; and
an alkali-including composition having the formula $\text{Na}_u\text{K}_v\text{Li}_w(\text{Si}_x\text{Al}_y\text{O}_z)_r$,
wherein:
 $u + v + w = 1$;
 $x + y = 1$;
 z is greater than 1.5; and
 r is from 0.02 to 20..

15. The method of claim 14, wherein the one or more hydrocarbons comprise ethane and the one or more olefinic compounds comprise ethylene.