and water, e.g., converting ethane into ethylene with water being produced. In one form of oxidative dehydrogenation, an oxygen transfer agent is used to provide an oxygen source for the reaction.

SUMMARY

[0006] It has been observed that, at elevated temperatures, oxygen transfer agents may not have sufficient fluidization within the reactor used for the reaction, leading to reduced yields of the desired product. Accordingly, there is a need for improved processes for olefin production using oxidative dehydrogenation in which sufficient fluidization is maintained in the reactor at elevated temperatures. According to one or more examples described herein, it has been found that including a fluidization enhancing additive with the oxygen transfer agent allows for sufficient fluidization of the oxygen transfer agents at reaction temperatures in the reactor.

[0007] According to the present disclosure, a process for oxidative dehydrogenation of a hydrocarbon to produce an olefin and water includes contacting, in a fluidized bed, the hydrocarbon with a particulate material. The particulate material may include at least one oxygen transfer agent; and at least one fluidization enhancing additive consisting of inorganic materials. During at least a portion of the time of the contacting of the hydrocarbon with the particulate material, the fluidized bed is at a temperature at or above a melting point of one or more materials of the oxygen transfer agent. Further, during at least a portion of the time of the contacting of the hydrocarbon with the particulate material, a surface of at least a portion of the at least one oxygen transfer agent comprises a molten layer. The at least one fluidization enhancing additive does not undergo reduction in the fluidized bed during the contacting of the hydrocarbon with the particulate material at the temperature. The at least one fluidization enhancing additive is present in an amount that maintains sufficient fluidization of the particulate material.

[0007a] In one aspect, there is provided a process for oxidative dehydrogenation of a hydrocarbon to produce an olefin and water, the process comprising: contacting, in a fluidized bed, the hydrocarbon with a particulate material comprising: at least one oxygen transfer agent; and at least one fluidization enhancing additive consisting of inorganic materials; wherein: during at least a portion of the time of the contacting of the hydrocarbon with the particulate material, the fluidized bed is at a temperature at or above a melting point of one or more materials of the oxygen transfer agent; during at least a portion of the time of the contacting of the hydrocarbon with the

particulate material, a surface of at least a portion of the at least one oxygen transfer agent comprises a molten layer; the at least one fluidization enhancing additive does not undergo reduction in the fluidized bed during the contacting of the hydrocarbon with the particulate material at the temperature; the at least one fluidization enhancing additive is present in an amount that maintains sufficient fluidization of the particulate material; and the at least one oxygen transfer agent and the at least one fluidization enhancing additive are separate particles in the particulate material.

[0008] It is to be understood that both the foregoing brief summary and the following detailed description present embodiments and examples of the technology, and are intended to provide an overview or framework for understanding the nature and character of the technology as it is claimed. The accompanying drawings are included to provide a further understanding of the technology, and are incorporated into and constitute a part of this specification. The drawings illustrate various embodiments and examples and, together with the description, serve to explain the principles

and operations of the technology. Additionally, the drawings and descriptions are meant to be merely illustrative, and are not intended to limit the scope of the claims in any manner.

[0009] Additional features and advantages of the described embodiments and examples will be set forth in the detailed description that follows. The additional features and advantages of the described embodiments and examples will be, in part, readily apparent to those skilled in the art from that description or recognized by practicing the described embodiments and examples, including the detailed description that follows as well as the drawings and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] 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:

[0011] FIGURE (FIG.) 1 shows the reduction/oxidation of an oxygen transfer agent with concurrent formation of useful products, in accordance with embodiments described herein;

[0012] FIG. 2 is a schematic diagram of an apparatus for lab-scale fluidization experiments;

[0013] FIG. 3 is a chart of differential pressure versus superficial gas velocity from Example 1;

[0014] FIG. 4 is a chart of differential pressure versus bed temperature from Example 2; and

[0015] FIG. 5 is a chart of ethane conversion vs. olefin selectivity from Example 4.

DETAILED DESCRIPTION

[0016] According to one or more embodiments described herein, a process for oxidative dehydrogenation of a hydrocarbon to produce an olefin and water may include contacting, in a fluidized bed, the hydrocarbon with a particulate material comprising at least one oxygen transfer

CLAIMS

1. A process for oxidative dehydrogenation of a hydrocarbon to produce an olefin and water, the process comprising:

contacting, in a fluidized bed, the hydrocarbon with a particulate material comprising:

at least one oxygen transfer agent; and

at least one fluidization enhancing additive consisting of inorganic materials;

wherein:

during at least a portion of the time of the contacting of the hydrocarbon with the particulate material, the fluidized bed is at a temperature at or above a melting point of one or more materials of the oxygen transfer agent;

during at least a portion of the time of the contacting of the hydrocarbon with the particulate material, a surface of at least a portion of the at least one oxygen transfer agent comprises a molten layer;

the at least one fluidization enhancing additive does not undergo reduction in the fluidized bed during the contacting of the hydrocarbon with the particulate material at the temperature;

the at least one fluidization enhancing additive is present in an amount that maintains sufficient fluidization of the particulate material; and

the at least one oxygen transfer agent and the at least one fluidization enhancing additive are separate particles in the particulate material.

2. The process of claim 1, wherein the at least one oxygen transfer agent comprises a compound that undergoes reduction during the oxidative dehydrogenation thereby providing oxygen for formation of the water.

3. The process of claim 1 or claim 2, wherein the at least one oxygen transfer agent comprises:

a mixed oxide comprising Mg_6MnO_8.

4. The process of claim 3, wherein the at least one oxygen transfer agent further comprises at least two promoters comprising tungsten and an alkali metal, an alkaline earth metal, or a combination of the alkali metal and the alkaline earth metal.

5. The process of claim 1 or claim 2, wherein the at least one oxygen transfer agent comprises:

at least one reducible metal-containing oxide selected from the group consisting of manganese oxide, tin oxide, indium oxide, germanium oxide, lead oxide, antimony oxide, bismuth oxide, praseodymium oxide, terbium oxide, cerium oxide, iron oxide, ruthenium oxide, and a combination of two or more thereof;

at least one alkali metal species, said alkali metal species comprising elemental alkali metal or a compound comprising the alkali metal;

at least one boron-containing species, said boron-containing species comprising elemental boron or a compound comprising boron; and

at least one alkaline earth metal-containing species, said alkaline earth metal-containing species comprising elemental alkaline earth metal or a compound comprising alkaline earth metal.

6. The process of claim 5, wherein the at least one oxygen transfer agent comprises a mixed oxide of formula (1):

$$ML_aB_bC_cO_x \qquad (1)$$

where

M is selected from the group consisting of manganese, tin, indium, germanium, lead, antimony, bismuth, praseodymium, terbium, cerium, iron, ruthenium, and a combination of two or more thereof;

L is at least one alkali metal;

B is boron;

C is at least one alkaline earth metal;

O is oxygen;

a is from 0.01 to 10;

b is from 0.1 to 20;

c is from 0.1 to 100; and

x is a number of oxygen atoms required due to valence states of M, L, B, and C.

7. The process of claim 5, wherein the at least one oxygen transfer agent comprises a mixed oxide of formula (2):

$$MB_bC_cO_x \qquad (2)$$

where

M is selected from the group consisting of manganese, tin, indium, germanium, lead, antimony, bismuth, praseodymium, terbium, cerium, iron, ruthenium, and a combination of two or more thereof;

B is boron;

C is at least one alkaline earth metal;

O is oxygen;

a is from 0.01 to 10;

b is from 0.1 to 20;

c is from 0.1 to 100; and

x is a number of oxygen atoms required due to valence states of M, L, B, and C.

8. The process of claim 1 or claim 2, wherein the oxygen transfer agent is perovskite.

9. The process of any preceding claim, wherein during at least a portion of the time of the contacting of the hydrocarbon with the particulate material, the fluidized bed is at a temperature from 650 °C to 1500 °C.

10. The process of any preceding claim, wherein the fluidization enhancing additive is selected from the group consisting of non-reducible oxides, zeolites, clays, fluid catalytic cracking catalysts, and combinations of two or more thereof.

11. The process of any preceding claim, wherein the fluidization enhancing additive comprises a non-reducible oxide comprising an inorganic material comprising a chemical species selected from the group consisting of alumina, silica, silicon carbide, metal carbide, metal nitride, titanium dioxide, alkaline earth metal oxide, alkali sulfate, alkaline earth sulfate, calcium sulfate, hydrates of calcium sulfate, alkali carbonate, alkaline earth carbonate, lanthanum oxide, rare earth metal oxide, boric acid, salts of boric acid, boric oxide, zinc oxide, cerium oxide, gallium oxide, and a combination of two or more thereof.

12. The process of any preceding claim, wherein the fluidization enhancing additive comprises at least one zeolite of formula (3):

$$M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O \qquad (3)$$

where

y is an integer from 2 to 1,000,000,000;

n is a valence of a cationic portion of the at least one zeolite of formula (3);

M is a metal selected from the group consisting of Zr, Mg, Ti, and a combination of two or more thereof; and

w is a number of water molecules per zeolite unit structure, such that at least 5% of n is due to proton charge.

13. The process of any preceding claim, wherein the fluidization enhancing additive comprises at least one fluid catalytic cracking catalyst.

14. The process of claim 13, wherein the at least one fluid catalytic cracking catalyst is stabilized by addition of one or more additives.

15. The process of any preceding claim, wherein a weight ratio of the at least one oxygen transfer agent to the at least one fluidization enhancing additive is from 50:50 to 99:1.