CATALYST AND PROCESS FOR THE DEHYDROGENATION OF ALKANES TO OLEFINS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Provisional Patent Application No. 63/236,003, filed August 23, 2021, and entitled "CATALYST AND PROCESS FOR THE DEHYDROGENATION OF ALKANES TO OLEFINS," the entirety of which is incorporated by reference herein.

BACKGROUND

Field

[0002] The present specification generally relates to catalysts and processes for the dehydrogenation of alkanes to olefins, such as catalysts and processes for converting ethane to ethylene.

Technical Background

[0003] Conventional catalysts for converting alkanes to olefins, such as converting ethane to ethylene and acetic acid, are based on molybdenum (Mo), vanadium (V), and niobium (Nb) and include promoters such as calcium (Ca), sodium (Na), antimony (Sb), or tellurium (Te). In particular, Te is a common promoter included in the conventional catalysts. Processes using such catalysts require an oxygen co-feed and utilize an oxidative dehydrogenation process at low temperature, such as below 500 °C, and low pressures, such as below 300 pounds per square inch gauge (psig) (about 20 barg).

SUMMARY

[0004] There is provided a method for converting alkanes to olefins comprises: contacting a feed stream comprising alkanes with an oxidative dehydrogenation catalyst in a reaction zone, where the oxidative dehydrogenation catalyst does not comprise tellurium; and dehydrogenating the alkanes in the reaction zone without a co-feed of oxygen to yield a product stream comprising olefins, wherein the oxidative dehydrogenation catalyst has the following formula: $Mo_vV_wNb_yA_zO_x$, where v is 1.0, w is from 0.1 to 0.5, y is from 0.001 to 0.3, A is Bi, Sb, Pr, or mixtures thereof, z is from 0.01 to 0.3, and x is an oxygen content required to charge-balance the structure, and the oxidative dehydrogenation catalyst has a crystallographic structure with

Pba2-32 space group, characterized by reflections determined with Cu-K_α X-ray diffraction (XRD) as follows:

2θ (± 0.3°)	**Rel. Intensity (%)**
5.3	0.2 – 8
6.6	1.5 – 15
7.84	2.5 – 45
8.95	4 – 21
22.17	100
27.2	20-50
28.1	10 – 30

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[0004a] According to one aspect, there is provided a method for converting alkanes to olefins comprising: contacting a feed stream comprising alkanes with an oxidative dehydrogenation catalyst in a reaction zone, where the oxidative dehydrogenation catalyst does not comprise tellurium; and dehydrogenating the alkanes in the reaction zone without a co-feed of oxygen to yield a product stream comprising olefins, wherein the dehydrogenation occurs without a presence of oxygen, and wherein the oxidative dehydrogenation catalyst has the following formula: $Mo_vV_wNb_yA_zO_x$, where v is 1.0, w is from 0.1 to 0.5, y is from 0.001 to 0.3, A is Bi, Sb, Pr, or mixtures thereof, z is from 0.01 to 0.3, and x is an oxygen content required to charge-balance the structure, and the oxidative dehydrogenation catalyst has a crystallographic structure with Pba2-32 space group, characterized by reflections determined with Cu-K_α X-ray diffraction (XRD) as follows:

2θ (± 0.3°)	**Rel. Intensity (%)**
5.3	0.2 – 8
6.6	1.5 – 15
7.84	2.5 – 45
8.95	4 – 21
22.17	100
27.2	20-50
28.1	10 – 30

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[0005] There is also provided a method for converting alkanes to olefins comprises: contacting a feed stream comprising alkanes with an oxidative dehydrogenation catalyst in a reaction zone, where the oxidative dehydrogenation catalyst has the following formula: $Mo_vV_wNb_yBi_zO_x$, where v is 1.0, w is from 0.1 to 0.5, y is from 0.001 to 0.3, z is from 0.01 to 0.3, and x is an oxygen content required to charge-balance the structure, wherein

the oxidative dehydration catalyst has a crystallographic structure with Pba2-32 space group, characterized by reflections determined with Cu-K_α X-ray diffraction (XRD) as follows:

2θ (± 0.3°)	**Rel. Intensity (%)**
5.3	0.2 – 8
6.6	1.5 – 15
7.84	2.5 – 45
8.95	4 – 21
22.17	100
27.2	20-50
28.1	10 – 30

; and

dehydrogenating the alkanes in the reaction zone to yield a product stream comprising olefins.

[0005a] In another aspect, there is provided a method for converting alkanes to olefins comprising: contacting a feed stream comprising alkanes with an oxidative dehydrogenation catalyst in a reaction zone, where the oxidative dehydrogenation catalyst has the following formula: $Mo_vV_wNb_yBi_zO_x$, where v is 1.0, w is from 0.1 to 0.5, y is from 0.001 to 0.3, z is from 0.01 to 0.3, and x is an oxygen content required to charge-balance the structure,wherein the oxidative dehydrogenation catalyst has a crystallographic structure with Pba2-32 space group, characterized by reflections determined with Cu-K_α X-ray diffraction (XRD) as follows:

2θ (± 0.3°)	**Rel. Intensity (%)**
5.3	0.2 – 8
6.6	1.5 – 15
7.84	2.5 – 45
8.95	4 – 21
22.17	100
27.2	20-50
28.1	10 – 30

; and dehydrogenating the alkanes in the reaction zone to yield a product stream comprising olefins, wherein the dehydrogenation occurs without a presence of oxygen.

[0006] Additional features and advantages will be set forth in the detailed description, which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the examples described herein, including the detailed description which follows and the claims.

[0007] It is to be understood that both the foregoing general description and the following detailed description describe various examples and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWING

[0008] The FIG. is a schematic drawing of a system for processing alkanes to olefins according to embodiments disclosed and described herein.

DETAILED DESCRIPTION

[0009] Reference will now be made in detail to embodiments of processes for dehydrogenation of alkanes to olefins and of catalysts for the dehydrogenation of alkanes to olefins, such as processes and catalysts for converting ethane to ethylene.

[0010] One issue with conventional oxidative dehydrogenation processes is that they require a feed stream of oxygen gas (O_2). This adds costs to the process by requiring equipment that can produce pure, or nearly pure, oxygen to use in the process. In addition, the presence of oxygen in the process increases the chances for undesired, dangerous combustion as the oxygen and hydrocarbons mix. Finally, because of the nature of the catalyst, and the oxygen requirement for dehydrogenation of alkanes, conventional oxidative dehydrogenation processes for converting alkanes to olefins are conducted in fixed bed reactors, which require down time to remove, replace, and/or regenerate the catalyst. Accordingly, there is a need for improved catalyst that can convert alkanes to olefins.

[0011] It has unexpectedly been found that compositional modifications of the conventional oxidative dehydrogenation catalysts, as disclosed and described herein, allow for stable reduction and oxidation (redox) cycling of the materials. Catalysts disclosed and described herein have oxygen carrying capacity that is high enough so that selective conversion of ethane to ethylene is obtained in a circulating reactor fed with oxygenated solids. By using catalysts disclosed and described herein, circulation rates that are industrially viable in circulating reactors may be used and adequate conversion and selectivity of ethane to ethylene is achieved. This eliminates the need for feeding gas phase oxygen to the reactor. Moreover, air can be used to regenerate the spent catalyst. In addition, the reactor/regenerator system used for the ethane conversion is exothermic and, thus, can be operated without additional heat input.

CLAIMS

1. A method for converting alkanes to olefins comprising:

contacting a feed stream comprising alkanes with an oxidative dehydrogenation catalyst in a reaction zone, where the oxidative dehydrogenation catalyst does not comprise tellurium; and

dehydrogenating the alkanes in the reaction zone without a co-feed of oxygen to yield a product stream comprising olefins, wherein the dehydrogenation occurs without a presence of oxygen, and wherein

the oxidative dehydrogenation catalyst has the following formula:

$Mo_vV_wNb_yA_zO_x$, where

v is 1.0,

w is from 0.1 to 0.5,

y is from 0.001 to 0.3,

A is Bi, Sb, Pr, or mixtures thereof,

z is from 0.01 to 0.3, and

x is an oxygen content required to charge-balance the structure, and

the oxidative dehydrogenation catalyst has a crystallographic structure with Pba2-32 space group, characterized by reflections determined with Cu-K_α X-ray diffraction (XRD) as follows:

2θ (± 0.3°)	**Rel. Intensity (%)**
5.3	0.2 – 8
6.6	1.5 – 15
7.84	2.5 – 45
8.95	4 – 21
22.17	100
27.2	20-50
28.1	10 – 30

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2. A method for converting alkanes to olefins comprising:

contacting a feed stream comprising alkanes with an oxidative dehydrogenation catalyst in a reaction zone, where the oxidative dehydrogenation catalyst has the following formula:

$Mo_vV_wNb_yBi_zO_x$, where

v is 1.0,

w is from 0.1 to 0.5,

y is from 0.001 to 0.3,

z is from 0.01 to 0.3, and

x is an oxygen content required to charge-balance the structure,

wherein the oxidative dehydration catalyst has a crystallographic structure with Pba2-32 space group, characterized by reflections determined with Cu-K_α X-ray diffraction (XRD) as follows:

2θ (± 0.3°)	**Rel. Intensity (%)**
5.3	0.2 – 8
6.6	1.5 – 15
7.84	2.5 – 45
8.95	4 – 21
22.17	100
27.2	20-50
28.1	10 – 30

; and

dehydrogenating the alkanes in the reaction zone to yield a product stream comprising olefins, wherein the dehydrogenation occurs without a presence of oxygen.

3. The method of claim 1 or 2, wherein the dehydrogenating comprises contacting the feed stream with the oxidative dehydration catalyst in the reaction zone at a temperature from 300 °C to 700 °C.

4. The method of claim 1 or 2, wherein the dehydrogenating comprises contacting the feed stream with the oxidative dehydration catalyst in the reaction zone at a temperature from 400 °C to 500 °C.

5. The method of any one of claims 1 to 4, wherein the dehydrogenating comprises contacting the feed stream with the oxidative dehydration catalyst in the reaction zone at a pressure from 0 bar(g) (0 KPa) to 20 bar(g) (2000 KPa).

6. The method of any one of claims 1 to 5, wherein the dehydrogenating comprises contacting the feed stream with the oxidative dehydration catalyst in the reaction zone at a pressure from 0 bar(g) (0 KPa) to 10 bar(g) (1000 KPa).

7. The method of any one of claims 1 to 6, wherein the dehydrogenating comprises contacting the feed stream with the oxidative dehydration catalyst in the reaction zone where the feed stream has a weight hour space velocity (WHSV) from 1/hr to 10/hr.

8. The method of any one of claims 1 to 7, wherein

the reaction zone is selected from the group consisting of a fluidized bed reactor, a moving bed reactor, a fixed bed reactor, a reverse flow reactor, or an ebullated bed reactor.

9. The method of claim 8, wherein the reaction zone is a fluidized bed reactor.

10. The method of claim 8 or 9, wherein the oxidative dehydration catalyst is regenerated in a regeneration zone using an oxygen-containing gas stream having from 2 vol% to 22 vol% oxygen.

11. The method of claim 10, wherein the oxygen-containing gas stream is diluted or undiluted air.

12. The method of any one of claims 9 to 11, wherein a pressure in the regeneration zone is from 0 bar(g) (100 KPa) to 21 bar(g) (1000 KPa).

13. The method of any one of claims 1 to 12, wherein the product stream is further processed to remove at least one of oxygenates, carbon monoxide, carbon dioxide, and alkanes from the product stream.