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. 63/235,996, 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 for the dehydrogenation of alkanes to olefins, such as catalysts 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) (or about 20 barg).

SUMMARY

[0004] There is provided an oxidative dehydrogenation catalyst comprises: a structure comprising oxides of molybdenum (Mo), vanadium (V), niobium (Nb), and bismuth (Bi) having a formula $Mo_vV_wNb_yBi_zO_x$, wherein v is 1, 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 the oxygen content required to charge-balance the structure, the oxidative dehydrogenation catalyst has a crystalline structure with the 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] In one aspect, there is provided an oxidative dehydrogenation catalyst comprising: a structure comprising a mixed oxide of molybdenum (Mo), vanadium (V), niobium (Nb), and bismuth (Bi) having a formula $Mo_vV_wNb_yBi_zO_x$, wherein v is 1, 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, the oxidative dehydrogenation catalyst has a crystallographic structure with the 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 forming an oxidative dehydrogenation catalyst comprises: adding a molybdenum-containing compound, a vanadium-containing compound, a bismuth-containing compound, a niobium-containing compound, and one or more organic acids to a mixture of complexing agents and water ; synthesizing $Mo_vV_wNb_yBi_zO_x$ by hydrothermal synthesis at a hydrothermal synthesis temperature for a period of time, where v is 1, 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 the oxygen content required to charge-balance the structure; and separating the $Mo_vV_wNb_yBi_zO_x$ from retained liquids.

[0005a] In another aspect, there is provided a method for forming an oxidative dehydrogenation catalyst, the method comprising: adding a molybdenum-containing compound, a vanadium-containing compound, a bismuth-containing compound, a niobium-containing compound, and one or more organic acids to a mixture of alkylene glycol or alcohol amine and water to form a starting mixture; treating the starting mixture by hydrothermal synthesis at a hydrothermal synthesis temperature that is from 180 °C to 220 °C; separating $Mo_vV_wNb_yBi_zO_x$ from retained liquids, and calcining the $Mo_vV_wNb_yBi_zO_x$ in an inert atmosphere, wherein the starting mixture comprises at least one of molybdenum trioxide (MoO_3) and vanadium pentoxide (V_2O_5).

[0006] There is also provided a method for converting paraffins to olefins comprises: contacting a feed stream comprising paraffins with the oxidative dehydrogenation catalyst; converting at least a portion of the paraffins to olefins, thereby yielding a product stream comprising paraffins and olefins; and separating the olefins from the paraffins in the product stream, wherein the oxidative dehydrogenation catalyst comprises: a structure comprising oxides of molybdenum (Mo), vanadium (V), niobium (Nb), and bismuth (Bi) having a formula $Mo_vV_wNb_yBi_zO_x$, wherein v is 1, 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 the oxygen content required to charge-balance the structure, the oxidative

dehydrogenation catalyst has a 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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As would be recognized by one of ordinary skill in the art, the relative intensity may be affected by the preferential orientation effect and the above-disclosed relative intensities take into account such effects.

[0006a] In another aspect, there is provided a method for converting paraffins to olefins, the method comprising: contacting a feed stream comprising paraffins with the oxidative dehydrogenation catalyst as defined herein; converting at least a portion of the paraffins to olefins, thereby yielding a product stream comprising paraffins and olefins; and separating the olefins from the paraffins in the product stream.

[0007] Additional features and advantages will be set forth in the detailed description that 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.

[0008] 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.

CLAIMS

1. An oxidative dehydrogenation catalyst comprising:

a structure comprising a mixed oxide of molybdenum (Mo), vanadium (V), niobium (Nb), and bismuth (Bi) having a formula $Mo_vV_wNb_yBi_zO_x$, wherein

v is 1, 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,

the oxidative dehydrogenation catalyst has a crystallographic structure with the 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. The oxidative dehydrogenation catalyst of claim 1, wherein the oxidative dehydrogenation catalyst consists of the structure comprising oxides of molybdenum (Mo), vanadium (V), niobium (Nb), and bismuth (Bi) having a formula $Mo_vV_wNb_yBi_zO_x$, wherein v is 1, 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 the oxygen content required to charge-balance the structure.

3. The oxidative dehydrogenation catalyst of claim 1, wherein the oxidative dehydrogenation catalyst is essentially free of tellurium (Te).

4. The oxidative dehydrogenation catalyst of any one of claims 1 to 3, wherein the oxidative dehydrogenation catalyst has the following formula: $MoV_{0.2-0.3}Nb_{0.1}Bi_{0.1}O_x$.

5. A method for forming an oxidative dehydrogenation catalyst, the method comprising:

adding a molybdenum-containing compound, a vanadium-containing compound, a bismuth-containing compound, a niobium-containing compound, and one or more organic acids to a mixture of alkylene glycol or alcohol amine and water to form a starting mixture;

treating the starting mixture by hydrothermal synthesis at a hydrothermal synthesis temperature that is from 180 °C to 220 °C;

separating $Mo_vV_wNb_yBi_zO_x$ from retained liquids, and

calcining the $Mo_vV_wNb_yBi_zO_x$ in an inert atmosphere,

wherein the starting mixture comprises at least one of molybdenum trioxide (MoO_3) and vanadium pentoxide (V_2O_5).

6. The method for forming an oxidative dehydrogenation catalyst of claim 5, wherein the one or more organic acids comprises at least one of citric acid ($C_6H_8O_7$), oxalic acid ($C_2H_2O_4$), and mixtures thereof.

7. The method for forming an oxidative dehydrogenation catalyst of any one of claim 5 or claim 6, wherein the niobium-containing compound is selected from the group consisting of niobium oxide, niobic acid ($Nb_2O_5 \cdot xH_2O$), ammonium niobium oxalate ($(NH_4)Nb(C_2O_4)_2xH_2O$), niobium ethoxide, and mixtures thereof.

8. The method for forming an oxidative dehydrogenation catalyst of any one of claim 5 to 7, wherein the bismuth-containing compound is selected from the group consisting of bismuth oxide (Bi_2O_3), bismuth sulfate ($Bi_2(SO_4)_3$), bismuth citrate ($BiC_6H_5O_7$), and bismuth nitrate ($Bi(NO_3)_3$).

9. The method for forming an oxidative dehydrogenation catalyst of any one of claims 5 to 8, wherein the alkylene glycol is ethylene glycol ($C_2H_6O_2$).

10. The method for forming an oxidative dehydrogenation catalyst of any one of claims 5 to 9, wherein the hydrothermal synthesis temperature is from 180 °C to 210 °C.

11. The method for forming an oxidative dehydrogenation catalyst of any one of claims 5 to 10, wherein the starting mixture comprises MoO_3 and V_2O_5.

12. A method for converting paraffins to olefins, the method comprising:

contacting a feed stream comprising paraffins with the oxidative dehydrogenation catalyst of any one of claims 1 to 4;

converting at least a portion of the paraffins to olefins, thereby yielding a product stream comprising paraffins and olefins; and

separating the olefins from the paraffins in the product stream.

13. The method of claim 12, wherein the method further comprises contacting a second stream comprising oxygen with the feed stream comprising paraffins and the oxidative dehydrogenation catalyst.

14. The method of claim 13, wherein the conversion occurs at a temperature that is from 300 °C to 700 °C, and a pressure that is from 0 barg to 20 barg.

15. The method of any of claim 13 and claim 14, wherein the conversion occurs at an alkane weight hourly space velocity (WHSV) that is from 0.1/hr to 10/hr.