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(54) Title: METHODS FOR CONVERTING ALKANES TO ALKENES AND STEAM TOLERANT DEHYDROGENATION CATALYSTS

(57) Abstract: A method for converting alkanes to alkenes includes contacting a feed stream comprising alkanes with a dehydrogenation catalyst in a reaction zone in the presence of steam, the dehydrogenation catalyst comprising zirconia and chromium. The method further includes converting at least a portion of the alkanes to alkenes, thereby yielding a product stream comprising alkanes, alkenes, and hydrogen, wherein the dehydrogenation catalyst does not require a gaseous oxidant in the feed stream or as a co-feed to catalyze conversion of alkanes to alkenes.



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METHODS FOR CONVERTING ALKANES TO ALKENES AND STEAM TOLERANT DEHYDROGENATION CATALYSTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/511,262 filed June 30, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] The present disclosure relates to methods for efficiently converting various alkanes to alkenes. In particular, the present disclosure relates to the preparation of dehydrogenation catalysts, and more particularly, dehydrogenation catalysts that tolerate steam, and methods of using the dehydrogenation catalysts to achieve a high conversion of alkanes to alkenes in the presence of steam.

BACKGROUND

[0003] Alkenes are used for a wide range of industrial applications, including producing plastics, fuels, and various downstream chemicals. Such alkenes include C₂ to C₄ materials, including ethene, propene, and butenes (also commonly referred to as ethylene, propylene, and butylenes, respectively). A variety of processes for producing these alkenes have been developed, including petroleum cracking and various synthetic processes.

[0004] One such process for producing alkenes is alkane dehydrogenation. Conventional alkane dehydrogenation is endothermic and equilibrium limited and produces multiple moles of products per mole of reactants. Therefore, to reach economically feasible levels of alkane-to-alkene conversion, conventional alkane dehydrogenation necessitates the use of low pressures and high temperatures, often in excess of 800 °C, to shift the equilibrium toward the reaction products. Additionally, radical chemistry that occurs in conventional alkane dehydrogenation processes may produce coke as a byproduct. The coke may cause blockages, which may require periodic shutdowns for decoking operations.

[0005] Maintaining the low pressures and high temperatures necessary for economically feasible alkane-to-alkene conversion can be expensive. Accordingly, a need exists for methods and catalytic systems with high alkene selectivity that operate at higher pressures and lower temperatures while reaching economically feasible levels of alkane-to-alkene conversion.

SUMMARY

[0006] Embodiments of the present disclosure address these and other needs by the methods of preparation of dehydrogenation catalysts, and more particularly, dehydrogenation catalysts that are capable of performing dehydrogenation chemistry in the presence of steam, and methods of using such dehydrogenation catalysts. A dehydrogenation catalyst, as described herein, comprises zirconia (ZrO_2) and chromium (Cr). This dehydrogenation catalyst may then be used for converting alkanes to alkenes. The dehydrogenation catalyst may be able to catalyze the conversion of alkanes to alkenes in the presence of steam.

[0007] According to one or more embodiments of the present disclosure, a method for converting alkanes to alkenes may comprise contacting a feed stream comprising alkanes with a dehydrogenation catalyst in a reaction zone under steam conditions, the dehydrogenation catalyst comprising zirconia and chromium, and converting at least a portion of the alkanes to alkenes, thereby yielding a product stream comprising alkanes, alkenes, and hydrogen.

[0008] According to one or more embodiments of the present disclosure, a method for forming a dehydrogenation catalyst may comprise obtaining a zirconia support, adding a chromium-containing precursor to the zirconia support to form a chromium-containing zirconia, and calcining and drying the chromium-containing zirconia to form a dehydrogenation catalyst.

[0009] 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 embodiments described herein, including the detailed description which follows in addition to the claims.

[0010] 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.

DETAILED DESCRIPTION

[0011] Reference will now be made in detail to embodiments of methods for preparing dehydrogenation catalysts, and more particularly, dehydrogenation catalysts that tolerate steam, and methods of using the dehydrogenation catalysts to convert alkanes to alkenes in the presence of steam. As used herein, “steam conditions” refers to reaction conditions where at least some amount of steam is present. For example, a reaction might take place under 5 volume percent (v.%) steam conditions wherein 5% of the gas volume of the reaction section would be filled with steam. The steam that leads to steam conditions may come from any source. For example, the steam that leads to steam conditions may be generated in-situ by selective hydrogen combustion materials.

[0012] As used herein, “dehydrogenation” refers to a chemical process by which hydrogen is chemically removed from a chemical compound. For example, ethane may undergo dehydrogenation to be converted to ethylene. As used herein, “dehydrogenation catalyst(s)” refers to any substance that increases the rate of a dehydrogenation reaction without itself undergoing any permanent chemical change. As used herein, “background dehydrogenation activity” refers to the dehydrogenation activity that occurs in the presence of inert material instead of a catalyst measured under the same process conditions. For example, a dehydrogenation catalyst may have an activity equal to 1.1 times background dehydrogenation activity when the dehydrogenation catalyst performs dehydrogenation at a conversion rate equal to 1.1 times the dehydrogenation activity of quartz chips under the same process conditions.

[0013] As used herein, “alkane(s)” refers to any series of hydrocarbon molecules that consist of carbon-carbon single bonds and where the carbon structure is saturated with hydrogen. Ethane, propane, and butane are examples of alkanes. As used herein, “alkene(s)” refers any series of hydrocarbon molecules, where at least two of the carbon atoms are not saturated with hydrogen and share a double bond. Ethylene, propylene, 1-butene, *trans*-2-butene, and *cis*-2-butene are examples of alkenes. Alkenes include dienes, which are hydrocarbons where at least two sets of

two of the carbon molecules, that may or may not be adjacent to each other, are not saturated with hydrogen and share a double bond.

[0014] As used herein, “chromium-containing zirconia” refers to a zirconia where chromium is present on the surface of the zirconia, and/or chromium is present in the pores of the zirconia. The chromium may be present in any form. For example, the chromium may be in the form of a metal oxide.

[0015] The use of dehydrogenation catalysts is known in the field of hydrocarbon products, such as plastics, fuels, and various downstream chemicals. For example, the Catofin propane dehydrogenation processes from Lummus Technology and the Oleflex propane dehydrogenation processes from Honeywell employ Cr/Al₂O₃ and Pt-Sn-based dehydrogenation catalysts, respectively. Additionally, chromium and zirconia catalysts are known for use in oxidative dehydrogenation of alkanes. In the oxidative dehydrogenation processes, alkanes are typically co-fed with a gaseous oxidant such as oxygen, air, carbon dioxide, or nitrogen oxides, thus shifting the equilibrium constraint of the dehydrogenation reaction.

[0016] Oxidative dehydrogenation occurs at the surface of the catalyst by a reaction of alkane and oxidant and generates water. The presence of water and alkanes at high temperatures can lead to reduced alkene selectivity through oxidation and reforming reactions that yield methane and carbon oxide products such as carbon monoxide and carbon dioxide. Furthermore, many oxidative dehydrogenation catalysts, when used in the absence of a gaseous oxidant in the feed stream or as a co-feed, exhibit significantly reduced activity in the presence of steam. Thus, not every oxidative dehydrogenation catalyst is a steam tolerant alkane dehydrogenation catalyst. In contrast, the dehydrogenation catalysts disclosed and described herein exhibit steam tolerance, even in the absence of a gaseous oxidant in the feed stream or as a co-feed. The preparation and composition of such dehydrogenation catalysts used in embodiments are discussed below.

[0017] The dehydrogenation catalyst may comprise zirconia (ZrO₂). As used herein, the zirconia used in embodiments disclosed and described herein in the dehydrogenation catalyst may be “phase pure zirconia”, which is defined herein as zirconia to which no other materials have intentionally been added during production. Thus, “phase pure zirconia” includes zirconia with small amounts of components other than zirconium (including oxides other than zirconia) that are

unintentionally present in the zirconia as a natural part of the zirconia production process, such as, for example, hafnium (Hf). Accordingly, as used herein “zirconia” and “phase pure zirconia” are used interchangeably unless specifically indicated otherwise. In other embodiments, the zirconia can be non-phase pure zirconia, such as zirconia doped with calcium (Ca), yttria (Y_2O_3), lanthanum (La), cerium (Ce), or rare earth elements.

[0018] According to embodiments, the zirconia particles may include zirconia particles having a crystalline structure. The zirconia particles may include zirconia particles having monoclinic crystal form (also known as a baddeleyite structure), tetragonal crystal form, cubic crystal form, or combinations thereof.

[0019] The dehydrogenation catalyst may comprise chromium (Cr) in any suitable oxidation state. According to embodiments, the chromium may have an oxidation state of +2, +3, +4, +5, +6, or combinations thereof. In embodiments, the dehydrogenation catalyst may comprise chromium having a single oxidation state or the dehydrogenation catalyst may comprise chromium having different oxidation states.

[0020] In one or more embodiments, the dehydrogenation catalyst may comprise zirconia, where the zirconia acts as a metal oxide support. The term “metal oxide support” may refer to a support material that supports the other components of the dehydrogenation catalyst, for example, chromium.

[0021] In one or more embodiments, a method for forming a dehydrogenation catalyst may comprise obtaining a zirconia support, adding a chromium-containing precursor to the zirconia support to form a chromium-containing zirconia, and calcining and drying the chromium-containing zirconia to form a dehydrogenation catalyst. In embodiments, the chromium-containing zirconia may be calcined and dried under air at a temperature of less than or equal to 1000 °C. In one or more embodiments, a method for forming a dehydrogenation catalyst may further comprise preparing the zirconia support by precipitation reaction. In embodiments, adding a chromium-containing precursor to the zirconia support to form a chromium-containing zirconia may comprise impregnating the zirconia support with chromium-containing precursor to form a chromium-impregnated zirconia.

[0022] In one or more embodiments, the dehydrogenation catalyst may be prepared by precipitation. For example, the dehydrogenation catalyst may be prepared by co-precipitating the zirconia support and the chromium-containing precursor. In embodiments, the dehydrogenation catalyst may be prepared by a combination of impregnation and precipitation. For example, the zirconia support might first be prepared by precipitation, and then the zirconia support might be impregnated with the chromium-containing precursor by precipitation.

[0023] In one or more embodiments, adding a chromium-containing precursor to the zirconia support to form a chromium-containing zirconia may comprise any combination of adding a chromium-containing precursor to the zirconia support, wherein the zirconia support is a fluidizable zirconia support, adding a chromium-containing precursor to the zirconia support by spray drying, or adding a chromium-containing precursor to the zirconia support by granulation.

[0024] In one or more embodiments, adding a chromium-containing precursor to the zirconia support in a fluidized bed operation, wherein the zirconia support is a fluidizable zirconia support may comprise placing the zirconia support in a fluidized bed reactor and adding a chromium-containing precursor to the zirconia support. In embodiments, the chromium-containing precursor may be a dry powder or may be part of a solution or slurry. In embodiments, the chromium-containing zirconia support prepared for use in a fluidized bed operation may be spray dried. In embodiments, adding a chromium-containing precursor to the zirconia support by granulation may comprise combining powdered zirconia support with powdered chromium-containing precursor and combining the powdered zirconia support and powdered chromium-containing precursor to form chromium-containing zirconia.

[0025] In embodiments, the surface area of the zirconia particles may be greater than or equal to 5 meters squared per gram (m^2/g). For example, the surface area of the zirconia particles may be at least $5 \text{ m}^2/\text{g}$, at least $10 \text{ m}^2/\text{g}$, at least $20 \text{ m}^2/\text{g}$, at least $50 \text{ m}^2/\text{g}$, at least $75 \text{ m}^2/\text{g}$, at least $100 \text{ m}^2/\text{g}$, at least $125 \text{ m}^2/\text{g}$, or at least $150 \text{ m}^2/\text{g}$. In embodiments, the surface area of the zirconia particle may be from $5 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $10 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $20 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, such as from $30 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $40 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $50 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $60 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $70 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $80 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $90 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $100 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $110 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from $120 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, from 130

m²/g to 200 m²/g, or from 140 m²/g to 200 m²/g. In embodiments, the surface area of the zirconia particles may be from 5 m²/g to 180 m²/g, from 5 m²/g to 160 m²/g, from 5 m²/g to 140 m²/g, from 5 m²/g to 120 m²/g, from 5 m²/g to 100 m²/g, from 5 m²/g to 90 m²/g, from 5 m²/g to 80 m²/g, from 5 m²/g to 70 m²/g, from 5 m²/g to 60 m²/g, from 5 m²/g to 50 m²/g, from 5 m²/g to 40 m²/g, from 5 m²/g to 30 m²/g, from 5 m²/g to 20 m²/g, or from 5 m²/g to 10 m²/g. In embodiments, the surface area of the zirconia particles may be from 10 m²/g to 160 m²/g, from 20 m²/g to 130 m²/g, from 30 m²/g to 120 m²/g, from 40 m²/g to 110 m²/g, from 50 m²/g to 100 m²/g, from 60 m²/g to 90 m²/g, or from 70 m²/g to 80 m²/g.

[0026] It should be understood that according to embodiments, the dehydrogenation catalyst may be made by other methods that eventually lead to intimate contact between the chromium-containing precursor and zirconia. Some examples include vapor phase deposition of chromium-containing precursors (either organic or inorganic in nature), followed by their controlled decomposition.

[0027] In embodiments, the dehydrogenation catalyst is substantially free from silicon. The term “substantially free” may refer to having less than 0.5 weight percent (wt.%) of a certain component in a composition. For example, the dehydrogenation catalyst that is substantially free from silicon may have less than 0.5 wt.% silicon based on the total weight of the dehydrogenation catalyst.

[0028] In one or more embodiments, the dehydrogenation catalyst comprises from 0.5 % to 20 % chromium based on a total weight of the dehydrogenation catalyst. In embodiments, the dehydrogenation catalyst may comprise from 0.5 % to 20 % chromium, from 0.1 % to 49 %, 0.2 % to 49 %, 0.3 % to 49 %, 0.4 % to 49 %, 0.5 % to 49 %, 1 % to 49 %, 5 % to 49 %, 10 % to 49 %, 15 % to 49 %, 20 % to 49 %, 25 % to 49 %, 30 % to 49 %, 40 % to 49 %, 0.1 % to 40 %, 0.2 % to 40 %, 0.3 % to 40 %, 0.4 % to 40 %, 0.5 % to 40 %, 1 % to 40 %, 5 % to 40 %, 10 % to 40 %, 15 % to 40 %, 20 % to 40 %, 25 % to 40 %, 30 % to 40 %, 0.1 % to 30 %, 0.2 % to 30 %, 0.3 % to 30 %, 0.4 % to 30 %, 0.5 % to 30 %, 1 % to 30 %, 5 % to 30 %, 10 % to 30 %, 15 % to 30 %, 20 % to 30 %, 25 % to 30 %, 0.1 % to 20 %, 0.2 % to 20 %, 0.3 % to 20 %, 0.4 % to 20 %, 0.5 % to 20 %, 1 % to 20 %, 5 % to 20 %, 10 % to 20 %, 15 % to 20 % chromium, or any combination thereof, based on a total weight of the dehydrogenation catalyst.

[0029] In one or more embodiments, the dehydrogenation catalyst may comprise hafnium. In embodiments, the hafnium may be present in the zirconia as a natural part of the zirconia production process.

[0030] In one or more embodiments, the dehydrogenation catalyst may comprise 1 wt.% to 5 wt.% chromium metal, and 65 wt.% to 80 wt.% zirconium metal, wherein the weight percent is based on a total weight of the dehydrogenation catalyst (the total weight of the dehydrogenation catalyst including the oxygen in the oxides).

[0031] In one or more embodiments, the dehydrogenation catalyst may be a promoted dehydrogenation catalyst comprising the formula Cr-Zr-X, wherein X is selected from the group consisting of alkali metals, alkaline earth metals, tin (Sn), chloride (Cl), boron (B), phosphorous (P), sulfur (S), niobium (Nb), bismuth (Bi), antimony (Sb), and combinations thereof. In embodiments, X of the formula Cr-Zr-X may be in any thermodynamically stable oxidation state. In embodiments, X of the formula Cr-Zr-X may be an oxide. In embodiments, Zr of the formula Cr-Zr-X may comprise zirconia (ZrO₂).

[0032] In one or more embodiments, the dehydrogenation catalyst may be a promoted dehydrogenation catalyst comprising the formula Cr-Zr-Q, wherein Q is selected from the group consisting of lanthanum (La), cerium (Ce), neodymium (Nd), samarium (Sm), gadolinium (Gd), dysprosium (Dy), praseodymium (Pr), europium (Eu) and combinations thereof. In embodiments, Q of the formula Cr-Zr-Q may be in any thermodynamically stable oxidation state. In embodiments, Q of the formula Cr-Zr-Q may be an oxide. In embodiments, Zr of the formula Cr-Zr-Q may comprise zirconia (ZrO₂).

[0033] In one or more embodiments, the dehydrogenation catalyst may be a promoted dehydrogenation catalyst comprising the formula of a least one of Cr-Zr-X and Cr-Zr-Q. In embodiments, the dehydrogenation catalyst may be a promoted dehydrogenation catalyst comprising the formula Cr-Zr-Z, wherein Z selected from the group consisting of tungsten (W), vanadium (V), niobium (Nb), and combinations thereof. In embodiments, Z of the formula Cr-Zr-Z may be in any thermodynamically stable oxidation state. In embodiments, Z of the formula Cr-Zr-Z may be an oxide. In embodiments, Zr of the formula Cr-Zr-Z may comprise zirconia (ZrO₂). In embodiments, the dehydrogenation catalyst may be a promoted dehydrogenation catalyst,

wherein the promoter is selected from the group comprising transition metals, lanthanides, and combinations thereof.

[0034] In one or more embodiments, a method for converting alkanes to alkenes may comprise contacting a feed stream comprising alkanes with a dehydrogenation catalyst in a reaction zone. In embodiments, the feed stream may comprise C₂-C₄ alkanes. In embodiments, the feed stream may comprise ethane, propane, butanes, or combinations thereof. In embodiments, the feed stream may be contacted with the dehydrogenation catalyst for a controlled time of exposure. In embodiments, the controlled time of exposure may be selected based on the desired catalyst to feed stream mass to mass ratio. In embodiments, the controlled time of exposure may be from 5 seconds (sec) to 1 hour (h). In embodiments, the controlled time of exposure may be from 5 seconds (sec) to 1 h, from 10 sec to 30 minutes (min), from 15 sec to 15 min, from 20 sec to 10 min, from 25 sec to 5 min, from 25 sec to 30 sec, from 30 sec to 1 min, or any combination thereof.

[0035] In one or more embodiments, the reaction zone may be a zone inside a reactor adapted to allow the feed stream to be contacted with the dehydrogenation catalyst. In one or more embodiments, the reactor may be a fixed-bed reactor, including but not limited to a dual tube fixed-bed reactor. In embodiments, the reactor may be a circulating fluidized bed reactor. In embodiments, the reactor may be two or more reactors in series or parallel, and each reactor in series or parallel may be the same type of reactor as other reactors in the series, or may be a different type of reactor from other reactors in the series. In embodiments, the reaction zone may house a material that converts gaseous hydrogen to water.

[0036] In one or more embodiments, a method for converting alkanes to alkenes may comprise converting at least a portion of the alkanes to alkenes, thereby yielding a product stream comprising alkanes, alkenes, and hydrogen. In embodiments, the product stream may comprise ethylene, propylene, butylene, hydrogen, or combinations thereof. In embodiments, the product stream may comprise ethane, propane, butane, ethylene, propylene, butylene, hydrogen, or combinations thereof.

[0037] In one or more embodiments, at least a portion of the hydrogen in the product stream is combusted and yields water. In embodiments, the water may be in the form of steam. In embodiments, the steam may comprise gaseous water, liquid water, aerosolized water, or

combinations thereof. Because of this hydrogen combustion, water—such as steam—will be present in the reaction zone during dehydrogenation of the alkanes in the feed stream. As mentioned above, many oxidative dehydrogenation catalysts lose conversion and selectivity when they are exposed to water and require a significant amount of oxidative gas to offset the loss of conversion and selectivity. However, the dehydrogenation catalysts disclosed and described herein retain catalytic activity in the presence of water and retain all or some of their conversion or selectivity when the hydrogen is combusted and forms water. Therefore, the catalysts disclosed and described herein can operate in the presence of water without the addition of oxidative gas.

[0038] In one or more embodiments, the dehydrogenation catalyst may have an alkene selectivity of greater than or equal to 40 carbon mole percent (Cmol%), greater than or equal to 45 Cmol%, greater than or equal to 50 Cmol%, greater than or equal to 55 Cmol %, greater than or equal to 65 Cmol%, greater than or equal to 75 Cmol%, greater than or equal to 85 Cmol%, greater than or equal to 95 Cmol %, greater than or equal to 97 Cmol%, greater than or equal to 98 Cmol%, or greater than or equal to 99 Cmol%.

[0039] In one or more embodiments, the dehydrogenation catalyst comprises a dehydrogenation activity of greater than or equal to 1.1 times background dehydrogenation activity. In embodiments, the dehydrogenation catalyst comprises a dehydrogenation activity of greater than or equal to 1.1 times, 1.5 times, 2 times, 3 times, 4 times, 5 times, or 10 times background dehydrogenation activity.

[0040] In one or more embodiments, the dehydrogenation catalyst retains at least some dehydrogenation activity above background dehydrogenation activity under greater than or equal to 5 v.% steam conditions based on a total volume of gaseous components in the reaction zone. In embodiments, the dehydrogenation catalyst retains at least some dehydrogenation activity above background dehydrogenation activity under greater than or equal to 5 v.%, 10 v.%, 15 v.%, 20 v.%, 25 v.%, 30 v.%, 35 v.%, 40 v.%, 45 v.%, or 50 v.% steam conditions based on a total volume of gaseous components in the reaction zone.

[0041] In embodiments, the dehydrogenation catalyst comprises a dehydrogenation activity of greater than or equal to 1.1 times, 1.5 times, 2 times, 3 times, 4 times, 5 times, or 10 times background dehydrogenation activity under greater than or equal to 5 v.%, 10 v.%, 15 v.%, 20

v.%, 25 v.%, 30 v.%, 35 v.%, 40 v.%, 45 v.%, or 50 v.% steam conditions based on a total volume of gaseous components in the reaction zone.

[0042] In one or more embodiments, the method for converting alkanes to alkenes may further comprise contacting the feed stream comprising alkanes with at least one other catalyst. In embodiments, the at least one other catalyst may comprise a selective hydrogen combustion material (interchangeably called an oxygen carrier material). For example, oxygen-carrier materials such as those disclosed in U.S. App. No. 62/725,504, entitled “METHODS OF PRODUCING HYDROGEN-SELECTIVE OXYGEN-CARRIER MATERIALS,” filed on, August 31, 2018, and U.S. App. No. 62/725,508, entitled “HYDROGEN-SELECTIVE OXYGEN-CARRIER MATERIALS AND METHODS OF USE,” filed on, August 31, 2018, are contemplated as suitable for the presently disclosed processes, and the teachings of these references are incorporated by reference herein. In one or more additional embodiments, the oxygen-carrier material may include those of U.S. Pat. No. 5,430,209, U.S. Pat. No. 7,122,495, and/or WO 2018/232133, each of which are incorporated by reference in their entireties.

[0043] In embodiments, the dehydrogenation catalyst and the selective hydrogen combustion materials are both present in the reaction zone. In embodiments, the dehydrogenation catalyst and the selective hydrogen combustion material may be present in a mass to mass ratio of from 10:1 to 1:10. In embodiments, the dehydrogenation catalyst and the selective hydrogen combustion material may be present in a mass to mass ratio of from 10:1 to 1:10, from 10:1 to 1:10, from 2:1 to 1:10, from 1:1 to 1:10, from 10:1 to 1:5, from 10:1 to 1:5, from 2:1 to 1:5, from 1:1 to 1:5, from 10:1 to 1:2, from 10:1 to 1:2, from 2:1 to 1:2, from 1:1 to 1:2, from 10:1 to 1:1, from 10:1 to 1:1, or from 2:1 to 1:1. In embodiments, the dehydrogenation catalyst and the selective hydrogen combustion material may be in contact with each other. In embodiments, the dehydrogenation catalyst and the selective hydrogen combustion material may have been mixed or otherwise combined prior to being placed in the reaction zone. In embodiments, the dehydrogenation catalyst and the selective hydrogen combustion material may be mixed in the reaction zone. In embodiments, the dehydrogenation catalyst and the selective hydrogen combustion material may be separate.

[0044] As mentioned above, many conventional alkane dehydrogenation processes, such as oxidative dehydrogenation processes, require the use of gaseous oxidants, such as oxygen, air, carbon dioxide, or nitrogen oxides, in the feed stream or as a co-feed. The term “gaseous oxidant(s)” may refer to a substance or substances other than water that may oxidize hydrogen. However, in one or more embodiments of the present disclosure, the dehydrogenation catalyst maintains the conversion of alkanes to alkenes without the presence of a gaseous oxidant in the feed stream or as a co-feed. In some embodiments, the dehydrogenation catalyst maintains the conversion of alkanes to alkenes with the presence of only a small amount of a gaseous oxidant in the feed stream or as a co-feed. In some embodiments, the dehydrogenation catalyst maintains the conversion of alkanes to alkenes with the presence of less than 5 v.%, less than 4 v.%, less than 3 v.%, less than 2 v.%, less than 1 v.%, less than 0.5 v.%, less than 0.25 v.%, or less than 0.1 v.% gaseous oxidant in the feed stream or as a co-feed.

[0045] In one or more embodiments, the dehydrogenation catalyst and the feed stream have a mass to mass ratio that is from 5:1 to 200:1. This mass ratio is defined as the ratio between the mass feed rate of catalyst to the reaction zone and the mass feed rate of alkane to the reaction zone. In embodiments, the dehydrogenation catalyst and the feed stream have a mass to mass ratio that is from 5:1 to 200:1, from 10:1 to 200:1, from 25:1 to 200:1, from 50:1 to 200:1, from 75:1 to 200:1, from 100:1 to 200:1, from 150:1 to 200:1, from 5:1 to 150:1, from 10:1 to 150:1, from 25:1 to 150:1, from 50:1 to 150:1, from 75:1 to 150:1, from 100:1 to 150:1, from 5:1 to 100:1, from 10:1 to 100:1, from 25:1 to 100:1, from 50:1 to 100:1, from 75:1 to 100:1, from 5:1 to 75:1, from 10:1 to 75:1, from 25:1 to 75:1, from 50:1 to 75:1, from 5:1 to 50:1, from 10:1 to 50:1, from 25:1 to 50:1, from 5:1 to 25:1, from 10:1 to 25:1, or from 5:1 to 10:1.

[0046] In one or more embodiments, the dehydrogenation catalyst and the feed stream may have a weight hourly space velocity (WHSV) of from 1 to 12 per hour (h^{-1}), where WHSV is defined as the weight of the feed stream flow per weight of the dehydrogenation catalyst present in the reaction zone per hour. In embodiments, the dehydrogenation catalyst and the feed stream may have a WHSV of from 1 to 12 h^{-1} , from 1 to 10 h^{-1} , from 1 to 8 h^{-1} , from 1 to 5 h^{-1} , from 1 to 3 h^{-1} , or from 1 to 2 h^{-1} .

[0047] In one or more embodiments, the converting at least a portion of the alkanes to alkenes occurs at a temperature that is less than or equal to 750 °C. In embodiments, the converting at least a portion of the alkanes to alkenes occurs at a temperature that is less than or equal to 780 °C, less than or equal to 750 °C, less than or equal to 725 °C, less than or equal to 700 °C, less than or equal to 675 °C, or less than or equal to 650 °C.

[0048] In one or more embodiments, the converting at least a portion of the alkanes to alkenes occurs at a pressure that is equal to atmospheric pressure. In embodiments, the converting at least a portion of the alkanes to alkenes occurs at a pressure from 1-20 bar, when measured as an absolute pressure (bara). In embodiments, the converting at least a portion of the alkanes to alkenes occurs at a pressure from 1-20 bara, from 1-15 bara, from 1-10 bara, or from 1-5 bara.

[0049] In one or more embodiments, the method of converting alkanes to alkenes may further comprise removing spent dehydrogenation catalyst from the reaction zone and introducing the spent dehydrogenation catalyst into a regeneration zone. In embodiments, the regeneration zone may be part of the reactor. In embodiments, the regeneration zone may be separate from the reactor.

[0050] In embodiments, the method of converting alkanes to alkenes may further comprise regenerating the spent dehydrogenation catalyst, thereby forming regenerated dehydrogenation catalyst. In embodiments, regenerating the dehydrogenation catalyst may comprise contacting the dehydrogenation catalyst with a regeneration stream comprising gaseous oxygen, air, or combinations thereof. In embodiments, the regeneration zone is purged with gaseous nitrogen prior to contacting the dehydrogenation catalyst with the regeneration stream. In embodiments, the dehydrogenation catalyst may be regenerated at a temperature of greater than or equal to 650 °C. In one or more embodiments, the dehydrogenation catalyst may be regenerated for a time of greater than or equal to 1 minute (min), greater than 5 min, greater than 10 min, or greater than 30 min. In embodiments, the dehydrogenation catalyst may be heated prior to sending the dehydrogenation catalyst back to the reaction zone.

[0051] In embodiments, the method of converting alkanes to alkenes may further comprise regenerating the spent selective hydrogen combustion material, thereby forming regenerated selective hydrogen combustion material. Regenerating the selective hydrogen combustion

material may comprise contacting the selective hydrogen combustion material with a regeneration stream comprising gaseous oxygen, air, or combinations thereof. In embodiments, the regeneration zone is purged with gaseous nitrogen prior to contacting the selective hydrogen combustion material with the regeneration stream. In embodiments, the selective hydrogen combustion material may be regenerated at a temperature of greater than or equal to 650 °C. In one or more embodiments, the selective hydrogen combustion material may be regenerated for a time of greater than or equal to 1 minute (min), greater than 5 min, greater than 10 min, or greater than 30 min. In embodiments, the selective hydrogen combustion material may be heated prior to sending the selective hydrogen combustion material back to the reaction zone to close heat balance. In embodiments, the selective hydrogen combustion material and the dehydrogenation catalyst may be regenerated together.

[0052] In one or more embodiments, the method of converting alkanes to alkenes may further comprise returning regenerated dehydrogenation catalyst to the reaction zone where it is contacted with the feed stream.

EXAMPLES

[0053] EXAMPLE 1

[0054] A Cr/ZrO₂ catalyst was prepared by incipient wetness impregnation method. Monoclinic ZrO₂ support (NORPRO SZ31164 3 mm extrudates, BET = 100 m²/g, pore volume determined by deionized (DI) water 0.4 mL/g) was crushed and sieved to 40-80 mesh size. Then, 5 g of the ZrO₂ support was impregnated with 2 mL of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt) until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogeneously distributed over the support. The impregnated catalyst was dried and calcined under air in the box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750°C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0055] EXAMPLE 2

[0056] A Cr/ZrO₂ catalyst was prepared by incipient wetness impregnation method. First, 10 g of zirconium hydroxide Zr(OH)₄ (DKKK L30036, pore volume determined by DI water 0.67 g/mL) was impregnated with 6.7 mL of DI water until the water was no longer drawn into the pores of the support and the water was homogenously distributed over the support. The material was dried and calcined under air in the box oven using the following temperature program: room temperature to 120°C at 3 deg/min, dwell 2 h, 120 to 500°C at 3 deg/min, dwell 4 h, cool down to room temperature. The calcined support was compacted and sieved to 40-80 mesh size.

[0057] Then, 1.5 g of the calcined and sieved ZrO₂ support (monoclinic and tetragonal phases) was impregnated with 0.6 mL of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt) until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogenously distributed over the support. The impregnated catalyst was dried and calcined under air in the box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0058] When analyzed using x-ray powder diffraction (XRD), the catalyst showed the presence of monoclinic and tetragonal zirconia.

[0059] EXAMPLE 3

[0060] A Cr/ZrO₂ catalyst was prepared by incipient wetness impregnation method. Monoclinic ZrO₂ support (NORPRO SZ31164 3 mm extrudates, BET = 100 m²/g, pore volume determined by DI water 0.4 mL/g) was crushed and sieved to 40-80 mesh size. Then, 5 g of ZrO₂ support was impregnated with 2 mL of DI water until the water was no longer drawn into the pores of the support and the water was homogenously distributed over the support. The material was dried and calcined under air in a box oven using the following temperature program: room temperature to 120 °C at 3 deg/min, dwell 2 h, 120 to 500 °C at 3 deg/min, dwell 4 h, cool down to room temperature.

[0061] Then, the ZrO₂ support (1.5 g) was impregnated with 0.6 mL of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt) until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogeneously distributed over the support. The impregnated catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0062] **EXAMPLE 4**

[0063] A Cr/ZrO₂ catalyst was prepared by incipient wetness method, as described in Example 3, but used 0.6 mL of 1 M ammonium chromate solution in DI water instead of 1 M Cr (III) nitrate nonahydrate solution to impregnate 1.5 g of pre-calcined ZrO₂ support.

[0064] **EXAMPLE 5**

[0065] A Cr/ZrO₂ catalyst was prepared by co-precipitation and incipient wetness impregnation method. A three neck round bottom flask equipped with a magnetic stir bar, a pH probe, a thermometer, and a dropping funnel was placed in a water bath. The water bath was placed on heating plate. Then, 400 mL of DI water was added to the three neck round bottom flask. The heating plate was set and controlled at a temperature of 60±2 °C. Then, 275 mL of zirconyl nitrate 35 percent weight (%wt) in nitric acid was added dropwise along with 14.6 M ammonium hydroxide solution in DI water (base) under continuous stirring at a speed of 500 rpm. The rate of chemical addition was controlled to keep pH constant at 7.0 ±0.3. A precipitate formed and was recovered and centrifuged to separate solid from liquid. The precipitate was dried and calcined under air in a box oven using the following temperature program: room temperature to 120 °C at 5 deg/min, dwell 2 h, 120 to 750 °C at 5 deg/min, dwell 4 h, cool down to room temperature. The as prepared ZrO₂ support was compacted (static press 7 tonnes / 10 min) and then crushed and sieved to 40-80 mesh size.

[0066] Then, 5 g of the as prepared ZrO₂ support (monoclinic and tetragonal phases) was impregnated with 0.99 mL of 1.92 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt) until the impregnation solution was no longer drawn into the pores of the support

and the impregnation solution was homogeneously distributed over the support. The impregnated catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0067] When analyzed using x-ray powder diffraction (XRD), the catalyst of Example 5 showed the presence of monoclinic and tetragonal zirconia.

[0068] EXAMPLE 6

[0069] A Cr/ZrO₂ catalyst was prepared by co-precipitation and incipient wetness impregnation method. First, a ZrO₂ support was prepared using the same ZrO₂ support preparation method described in Example 5.

[0070] Then, 5 g of the ZrO₂ support was impregnated with 0.99 mL of 1.92 M ammonium dichromate solution in DI water until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogeneously distributed over the support. The impregnated catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0071] When analyzed using x-ray powder diffraction (XRD), the catalyst showed the presence of monoclinic and tetragonal zirconia.

[0072] COMPARATIVE EXAMPLE 1

[0073] Commercially available quartz chips (Pyromatics part # 7359-05010) were used to determine background dehydrogenation activity.

[0074] COMPARATIVE EXAMPLE 2

[0075] A dehydrogenation catalyst that is known to effectively perform the dehydrogenation of propylene to propane under the conditions described in US patent number 9834496, the entirety of which is hereby incorporated by reference, was used in the form of 70 micron particles.

[0076] COMPARATIVE EXAMPLE 3

[0077] A Cr/SiO₂-Al₂O₃ catalyst was prepared by incipient wetness method. Siralox 1 from SASOL in the form of extrudates (1.7/250 M10596 spec Z600200, pore volume determined by DI water 0.5 ml/g) was used as a SiO₂-Al₂O₃ support. The support was crushed and sieved to 40-80 mesh size prior to use. Then, 1.5 g of SiO₂-Al₂O₃ support was impregnated with 0.6 mL of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt) until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogenously distributed over the support. The impregnated catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0078] COMPARATIVE EXAMPLE 4

[0079] A Cr/SiO₂ catalyst was prepared by incipient wetness method. The SiO₂ support was SS61138 from NORPRO in the form of 3 mm extrudates (250 m²/g, pore volume determined by DI water 1.0 m²/g). The support was crushed and sieved to 40-80 mesh size prior to use. Then, 2 mL of impregnation solution was prepared by mixing 1.2 mL of DI water with 0.8 mL of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt). Then, 2 g of SiO₂ support was impregnated with the impregnation solution until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogenously distributed over the support. The impregnated catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0080] COMPARATIVE EXAMPLE 5

[0081] A Cr/Nb₂O₅ catalyst was prepared by incipient wetness method. The Nb₂O₅ support was prepared by thermal decomposition of ammonium niobate (V) oxalate hydrate at 500 °C for 4 h under air (BET surface area 50 m²/g, pore volume determined by DI water 0.4 mL/g). The support was sized to 40-80 mesh size prior to use. Then, 0.85 g of Nb₂O₅ support was impregnated with 0.34 ml of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt) until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogenously distributed over the support. The impregnated catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0082] COMPARATIVE EXAMPLE 6

[0083] A Cr/HfO₂ catalyst was prepared by incipient wetness method. The HfO₂ support was prepared by thermal decomposition of hafnium (IV) nitrate at 500 °C for 4 h under air (32 m²/g, pore volume determined by DI water 0.13 mL/g) was compacted and sized to 40-80 mesh size prior to use. Then, 0.83 g of HfO₂ support was impregnated with 0.11 mL of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt) until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogenously distributed over the support. The impregnated catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0084] COMPARATIVE EXAMPLE 7

[0085] A Cr/SnO₂ catalyst was prepared by incipient wetness method. The SnO₂ support, commercially available from Sigma Aldrich (pore volume determined by DI water 0.31 m²/g), was compacted and sieved to 40-80 mesh size prior to use. Then, 1.5 g of SnO₂ support was impregnated with 0.47 mL of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt) until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogenously distributed over the support. The impregnated

catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0086] COMPARATIVE EXAMPLE 8

[0087] A Cr/MgO catalyst was prepared by incipient wetness method. The MgO support (13 m²/g, pore volume determined by DI water 0.31 mL/g) was compacted and sieved to 40-80 mesh size prior to use. Then, 0.67 mL of impregnation solution was prepared by mixing 0.19 mL DI water with 0.48 mL of 1 M Cr (III) nitrate solution in DI water (prepared from the nonahydrate salt). Then, 1 g of MgO support was impregnated with the impregnation solution until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogenously distributed over the support. The impregnated catalyst was dried and calcined under air in a box oven using the following temperature program: room temperature to 177 °C at 5 deg/min, dwell 2 h, 177 °C to 750 °C at 5 deg/min, dwell 1 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh.

[0088] COMPARATIVE EXAMPLE 9

[0089] Monoclinic ZrO₂ support (NORPRO SZ31164 3 mm extrudates, BET = 100 m²/g, pore volume determined by DI water 0.4 mL/g) was crushed and sieved to 40-80 mesh size. Then, 22 mL of impregnation solution was prepared by mixing 12.375 mL DI water with 9.625 ml of 2 M Zn (II) nitrate hexahydrate solution in DI water. Then, 10 g of ZrO₂ support was impregnated with 4 mL of the impregnation solution until the impregnation solution was no longer drawn into the pores of the support and the impregnation solution was homogenously distributed over the support. The material was dried and calcined under air in a box oven using the following temperature program: room temperature to 120 °C at 3 deg/min, dwell 2 h, 120 to 550 °C at 3 deg/min, dwell 4 h, cool down to room temperature. The catalyst was sieved after calcination to remove fine particles smaller than 80 mesh and recalcined under air in the box oven for 1 h at 750 °C (ramp rate 5 deg/min).

[0090] CATALYST CHARACTERIZATION**[0091] X-RAY FLUORESCENCE (XRF) MEASUREMENTS**

[0092] Catalyst composition was determined by X-ray Fluorescence (XRF). XRF data were collected at room temperature (RT) with a PANalytical PW4400 spectrometer using an X-ray tube with a rhodium anode. The catalyst compositions are shown in Table 1. Elements that were below the detection limit or not present are represented as blank in the table. Oxygen represented the balance of the elemental composition.

Table 1: Composition of Catalysts in Examples 1-6 and Comparative Examples 1-9

	Cr (wt. %)	Zr (wt. %)	Hf (wt. %)	Si (wt. %)	Mg (wt.%)	Ca (wt. %)	Sn (wt. %)	Zn (wt. %)	Al (wt. %)	Nb (wt.%)
Example 1	1.8	69.8	2.6							
Example 2	2.16	69	2.6							
Example 3	1.9	69.2	2.6							
Example 4	1.9	69.2	2.6							
Example 5	0.93	70.7	2.6							
Example 6	3	68	2.6							
Comparative Example 1										
Comparative Example 2	Dehydrogenation catalyst known to effectively perform the dehydrogenation of propylene to propane.									

Comparative Example 3	2.7			0.8					49.7	
Comparative Example 4	2.5			44.9						
Comparative Example 5	2.5									66.1
Comparative Example 6	0.84	0.47	82.9							
Comparative Example 7	1.25						77			
Comparative Example 8	5.6			0.13	41.9	0.7			10.9	
Comparative Example 9		69.3	2.5					2.6		

[0093] CATALYST PERFORMANCE TESTING

[0094] The performance of the catalysts of both in the examples and the comparative examples was assessed under both wet and dry conditions. The reaction conditions of both the wet and dry conditions are shown in Table 2.

Table 2: Reaction Conditions Used to Assess Catalyst Performance

Condition	Type	Temperature Range (°C)	Ethane [v.%]	H ₂ O [v.%]	N ₂ [v.%]	Catalyst Load [g]	WHSV [h ⁻¹]	Pressure [bara] (psia)	Catalyst/Ethane (mass/mass)
Condition 1	Dry test	650-750°C	60	0	40	0.3	11.8	1.08 (16)	10-12
Condition 2	Wet test	650-750°C	60	20	20	0.3	11.8	1.08 (16)	10-12

[0095] The catalysts of the examples and the comparative examples were tested for selectivity and activity in a dual tube fixed-bed reactor. The catalysts were sized to a 40-80 mesh size. The reactor bed comprised 300 milligrams (mg) of catalyst mixed with 1.5 grams (g) of 40-80 mesh size quartz chips. In Comparative Example 1, the catalyst was replaced with quartz chips. The

reactor pressure was set at 1.08 bara (16 psia) and the catalysts were evaluated under the two sets of conditions summarized in Table 2.

[0096] First, the reactor was purged with nitrogen gas (N₂) where the pressure was 16 psia. The temperature was ramped to 400 °C under N₂ flow and then the N₂ flow was switched to 60% ethane – 20% H₂O – 20% N₂ flow. Water inlet flow was controlled by a high pressure liquid chromatography (HPLC) pump. An evaporator was used to evaporate water to the gas phase. Feed analysis was performed by analyzing the feed gas composition using online gas chromatography (GC).

[0097] Then, the reactor was purged with N₂ and the temperature was ramped to 650 °C followed by switching from the N₂ to air. The catalyst was regenerated at 650 °C for 6 minutes (min) followed by a N₂ purge step. Then, the feed composition was directed to the reactor at a controlled time of exposure (25-30 seconds (s) on stream corresponding to catalyst to ethane mass to mass ratio of 12-10). This completes a single cycle at a given temperature set point.

[0098] Regeneration of the catalyst after exposure to ethane-containing feed was performed at the same temperature as the corresponding reaction step. Every catalyst was evaluated under two sets of condition specified in Table 2. The wet test was done first, followed by a dry test. For each condition and each temperature set point, 3 cycles (reaction-purge-regeneration) were completed. The average values were then calculated and reported in Table 3 and Table 4.

[0099] Alkane conversion and carbon based selectivities are calculated using the following equations:

$$S_j \text{ (Cmol\%)} = [\alpha_j \cdot \eta_{j, \text{out}} / \sum \alpha_j \cdot \eta_{j, \text{out}}] \cdot 100$$

(Equation 1)

$$\text{Carbon Balance (\%)} = \sum \alpha_j \cdot \eta_{j, \text{out}} / \eta_{\text{C}_2\text{H}_6, \text{in}} \cdot 100$$

(Equation 2)

$$\text{Ethane Conversion (\%)} = [(\eta_{\text{C}_2\text{H}_6, \text{in}} - \eta_{\text{C}_2\text{H}_6, \text{out}}) / \eta_{\text{C}_2\text{H}_6, \text{in}}] \cdot 100$$

(Equation 3)

$$\text{Reforming Product sel. (Cmol\%)} = S_{\text{CH}_4} + S_{\text{CO}} + S_{\text{CO}_2}$$

(Equation 4)

where “ η_{in} ” is defined as the molar inlet flow of the component (mol/min), “ η_{out} ” is the molar outlet flow of the component (mol/min), “ S_j ” is defined as the carbon based selectivity to product j (%), “ α_j ” the number of carbon atoms for product j .

Table 3: Performance Data for the Examples

Example	Condition	T [°C]	Carbon Balance (%)	Ethane Conversion (%)	Ethylene Selectivity (Cmol%)	Reforming Product Selectivity (Cmol%)
Example 1	1	650	97.2	25.9	93.0	3.3
Example 1	1	700	96.4	27.1	94.4	3.8
Example 1	1	750	96.5	23.3	94.9	4.1
Example 1	1	780	96.7	24.5	94.5	3.7
Example 1	2	650	100.5	12.1	88.4	6.8
Example 1	2	700	100.7	31.0	77.9	12.6
Example 1	2	750	100.6	55.5	59.5	19.2
Example 1	2	780	99.7	60.3	61.5	17.2
Example 2	1	650	97.8	24.3	92.1	3.9
Example 2	1	700	96.8	27.8	94.3	4.0
Example 2	1	725	96.5	26.0	94.6	4.2
Example 2	1	750	96.0	23.6	94.8	4.5
Example 2	2	650	100.6	8.4	90.1	9.9
Example 2	2	700	101.3	28.4	78.5	21.4
Example 2	2	725	101.4	40.5	68.7	30.9
Example 2	2	750	101.4	53.1	54.4	45.0
Example 3	1	650	94.5	31.6	89.9	6.8
Example 3	1	700	91.0	38.7	90.6	7.6
Example 3	1	725	90.7	37.9	90.5	7.8
Example 3	1	750	91.0	36.3	90.6	7.5
Example 3	2	650	100.4	22.6	82.0	17.9
Example 3	2	700	101.1	45.2	61.2	38.4
Example 3	2	725	102.1	59.6	45.4	54.1
Example 3	2	750	100.3	67.9	42.2	57.2
Example 4	1	650	90.6	36.1	79.9	16.2
Example 4	1	700	77.1	54.0	76.9	20.7

Example 4	1	725	69.3	62.7	72.5	25.6
Example 4	1	750	59.3	72.3	65.7	32.7
Example 4	2	650	101.4	27.0	73.0	26.8
Example 4	2	700	102.9	55.8	41.1	58.5
Example 4	2	725	100.2	69.4	32.1	67.2
Example 4	2	750	91.2	78.9	28.5	70.9
Example 5	1	650	100.0	12.4	98.0	1.9
Example 5	1	700	100.3	19.9	97.6	1.5
Example 5	1	725	100.7	25.3	96.7	1.7
Example 5	1	750	99.8	31.2	94.8	2.7
Example 5	2	650	100.1	6.7	97.9	2.1
Example 5	2	700	101.7	10.8	96.3	3.5
Example 5	2	725	102.3	15.3	95.3	4.0
Example 5	2	750	102.7	23.0	94.0	4.8
Example 6	1	650	100.0	21.8	95.1	3.0
Example 6	1	700	99.0	20.8	96.0	3.0
Example 6	1	725	98.9	19.0	95.9	3.2
Example 6	1	750	98.9	18.5	95.7	3.3
Example 6	2	650	100.5	11.4	91.4	8.6
Example 6	2	700	100.7	24.6	86.0	13.8
Example 6	2	725	100.2	31.6	83.4	16.4
Example 6	2	750	100.6	43.1	77.3	22.2

Table 4: Performance Data for the Comparative Examples

Example	Condition	T [°C]	Carbon Balance (%)	Ethane Conversion (%)	Ethylene Selectivity (Cmol%)	Reforming Product Selectivity (Cmol%)
C. Ex. 1	1	650	99.9	0.3	99.3	0.7
C. Ex. 1	1	700	100.5	1.5	99.0	0.9
C. Ex. 1	1	725	100.6	4.6	98.7	1.0
C. Ex. 1	1	750	101.0	11.0	98.3	1.3
C. Ex. 1	2	650	100.1	0.1	99.4	0.6
C. Ex. 1	2	700	101.3	1.1	99.1	0.8
C. Ex. 1	2	725	102.1	4.0	98.8	0.9
C. Ex. 1	2	750	102.4	10.5	98.3	1.2
C. Ex. 2	1	650	100.6	26.4	99.6	0.1
C. Ex. 2	1	700	100.6	33.3	98.8	0.6
C. Ex. 2	1	725	100.2	37.0	98.3	0.9
C. Ex. 2	1	750	99.0	41.1	97.6	1.5
C. Ex. 2	2	650	98.1	3.9	90.0	9.9
C. Ex. 2	2	700	101.1	2.9	91.9	7.5
C. Ex. 2	2	725	99.8	7.1	93.1	6.0
C. Ex. 2	2	750	101.3	12.4	94.4	4.2
C. Ex. 3	1	650	100.9	11.2	98.3	1.2

C. Ex. 3	1	700	99.6	30.4	95.1	2.4
C. Ex. 3	1	725	96.4	42.2	92.4	4.2
C. Ex. 3	1	750	92.0	51.0	89.1	7.3
C. Ex. 3	2	650	99.3	2.7	87.0	13.0
C. Ex. 3	2	700	99.7	5.6	88.1	11.4
C. Ex. 3	2	725	99.9	8.6	88.7	10.7
C. Ex. 3	2	750	100.2	15.1	86.8	12.0
C. Ex. 4	1	650	99.9	4.8	99.3	0.4
C. Ex. 4	1	700	98.8	11.1	98.0	1.4
C. Ex. 4	1	725	98.7	15.2	97.7	1.6
C. Ex. 4	1	750	99.4	20.4	97.2	1.8
C. Ex. 4	2	650	96.8	4.0	98.8	1.2
C. Ex. 4	2	700	98.8	3.3	98.4	1.5
C. Ex. 4	2	725	98.9	4.6	97.4	2.0
C. Ex. 4	2	750	100.3	7.9	96.9	2.3
C. Ex. 5	1	650	99.8	0.3	98.8	1.2
C. Ex. 5	1	700	99.9	1.2	98.0	1.8
C. Ex. 5	1	725	100.0	3.3	97.3	1.9
C. Ex. 5	1	750	100.4	8.5	94.4	4.5
C. Ex. 5	2	700	101.4	0.4	97.9	1.3
C. Ex. 5	2	725	102.4	2.0	97.6	1.4
C. Ex. 5	2	750	102.9	7.9	97.1	1.7
C. Ex. 6	1	650	100.6	4.3	95.6	4.3
C. Ex. 6	1	700	100.9	8.7	96.2	3.3
C. Ex. 6	1	725	100.8	11.7	96.6	2.3
C. Ex. 6	1	750	101.1	15.9	96.1	2.2
C. Ex. 6	2	700	103.1	1.0	95.9	3.6
C. Ex. 6	2	725	103.5	4.8	95.4	3.9
C. Ex. 6	2	750	104.2	11.7	94.8	3.9
C. Ex. 7	1	650	99.9	0.5	98.7	1.3
C. Ex. 7	1	700	99.8	1.0	97.3	2.7
C. Ex. 7	1	725	99.7	1.8	95.8	4.2
C. Ex. 7	1	750	99.5	3.7	94.4	5.2
C. Ex. 7	2	650	99.3	1.3	97.3	2.7
C. Ex. 7	2	700	100.3	1.8	97.7	1.6
C. Ex. 7	2	725	100.3	3.8	97.6	1.7
C. Ex. 7	2	750	100.3	7.3	96.9	2.2
C. Ex. 8	1	650	100.0	2.7	99.6	0.4
C. Ex. 8	1	700	100.8	7.5	97.5	2.3
C. Ex. 8	1	725	100.5	17.9	96.0	2.7
C. Ex. 8	1	750	99.2	23.1	94.9	3.3
C. Ex. 8	2	650	100.1	0.2	97.5	2.5
C. Ex. 8	2	700	101.1	1.0	98.0	1.3
C. Ex. 8	2	725	100.9	4.1	97.7	1.5
C. Ex. 8	2	750	101.5	9.5	96.9	1.9
C. Ex. 9	1	650	100.5	6.9	99.3	1.0

C. Ex. 9	1	700	100.7	17.5	98.1	1.3
C. Ex. 9	1	725	99.5	21.5	97.3	1.8
C. Ex. 9	1	750	98.9	27.3	95.6	2.8
C. Ex. 9	2	650	100.7	<0.5	98.5	3.5
C. Ex. 9	2	700	100.3	1.2	97.6	4.5
C. Ex. 9	2	725	101.3	8.5	95.3	5.7
C. Ex. 9	2	750	101.9	21.1	92.8	6.3
C. Ex. 10	1	650	100.7	25.9	97.5	0.9
C. Ex. 10	1	700	99.1	36.1	96.7	1.4
C. Ex. 10	1	725	95.4	41.6	95.9	2.3
C. Ex. 10	1	750	92.6	46.7	94.4	3.6
C. Ex. 10	2	700	103.6	0.5	95.5	3.8
C. Ex. 10	2	725	104.2	5.5	78.2	21.1
C. Ex. 10	2	750	104.3	18.6	86.8	12.1

[00100] As shown in Table 3, Examples 1-6 demonstrate that catalysts containing Cr and ZrO₂ demonstrate high activity under “dry” or “wet” ethane dehydrogenation conditions and retain some or all of their activity in the presence of 20% steam by volume. The catalysts of the examples also demonstrate substantial activity above the background dehydrogenation activity (as measured in Comparative Example 1 by using quartz chips in lieu of a catalyst).

[00101] While Comparative Example 2 shows high activity and ethylene selectivity in the absence of steam, its activity is notably suppressed and essentially no different than the background dehydrogenation activity in the presence of 20% steam by volume across all temperatures studied.

[00102] Comparative Examples 3-8 demonstrate that Cr and ZrO₂ are important elements of a steam tolerant catalyst. Cr supported on alternative supports shows either overall low activity or significant rate suppression in the presence of steam.

[00103] Comparative Example 9 further demonstrates that Cr and ZrO₂ are important elements of a steam tolerant catalyst by showing that Zn supported by ZrO₂ has significant rate suppression under wet conditions despite having high activity in the absence of steam.

[00104] The present disclosure includes one or more non-limiting aspects. A first aspect includes a method for converting alkanes to alkenes, the method including contacting a feed stream comprising alkanes with a dehydrogenation catalyst in a reaction zone in the presence of

steam, the dehydrogenation catalyst comprising zirconia and chromium, and converting at least a portion of the alkanes to alkenes, thereby yielding a product stream comprising alkanes, alkenes, and hydrogen, wherein the dehydrogenation catalyst does not require a gaseous oxidant in the feed stream or as a co-feed to catalyze conversion of alkanes to alkenes.

[00105] A second aspect of the present disclosure includes the first aspect, further including combusting at least a portion of the hydrogen to yield steam.

[00106] A third aspect of the present disclosure includes the first or second aspect, wherein the dehydrogenation catalyst comprises an alkene selectivity greater than or equal to 40 Cmol%.

[00107] A fourth aspect of the present disclosure includes any of the first through third aspects, wherein the dehydrogenation catalyst retains at least some dehydrogenation activity above background dehydrogenation activity under greater than or equal to 5 v.% steam conditions based on a total volume of gaseous components in the reaction zone.

[00108] A fifth aspect of the present disclosure includes any of the first through fourth aspects, further including contacting the feed stream comprising alkanes with a selective hydrogen combustion material, wherein the dehydrogenation catalyst and the selective hydrogen combustion material are both present in the reaction zone.

[00109] A sixth aspect of the present disclosure includes any of the first through fifth aspects, wherein the dehydrogenation catalyst comprising zirconia and chromium comprises chromium impregnated zirconia.

[00110] A seventh aspect of the present disclosure includes any of the first through sixth aspects, wherein the dehydrogenation catalyst comprises from 0.5 % to 20 % chromium metal based on a total weight of the dehydrogenation catalyst.

[00111] An eighth aspect of the present disclosure includes any of the first through seventh aspects, wherein the dehydrogenation catalyst comprises 1 wt.% to 5 wt.% chromium, and 65 wt.% to 80 wt.% zirconium, wherein the weight percent is based on a total weight of the dehydrogenation catalyst.

[00112] A ninth aspect of the present disclosure includes any of the first through eighth aspects, wherein the dehydrogenation catalyst is substantially free from silicon.

[00113] A tenth aspect of the present disclosure includes any of the first through ninth aspects, wherein the dehydrogenation catalyst is a promoted dehydrogenation catalyst comprising the formula of a least one of Cr-Zr-X and Cr-Zr-Q, wherein X is selected from the group consisting of alkali metals, alkaline earth metals, tin, chloride, boron, phosphorous, sulfur, niobium, bismuth, antimony, and combinations thereof, and Q is selected from the group consisting of lanthanum, cerium, neodymium, samarium, gadolinium, dysprosium, praseodymium, europium, and combinations thereof.

[00114] An eleventh aspect of the present disclosure includes any of the first through tenth aspects, wherein the dehydrogenation catalyst and the feed stream have a mass to mass ratio that is from 5:1 to 200:1.

[00115] A twelfth aspect of the present disclosure includes any of the first through eleventh aspects, wherein the converting at least a portion of the alkanes to alkenes occurs at a temperature that is less than or equal to 750 °C, a pressure from 1 bara to 20 bara, and a WHSV of from 1 h⁻¹ to 12 h⁻¹.

[00116] A thirteenth aspect of the present disclosure includes any of the first through twelfth aspects, wherein the method further includes removing spent dehydrogenation catalyst from the reaction zone, introducing the spent dehydrogenation catalyst into a regeneration zone, regenerating the spent dehydrogenation catalyst, thereby forming regenerated dehydrogenation catalyst, and returning regenerated dehydrogenation catalyst to the reaction zone where it is contacted with the feed stream.

[00117] A fourteenth aspect of the present disclosure includes any of the first through thirteenth aspects, wherein the dehydrogenation catalyst comprises a conversion rate of greater than or equal to 1.1 times background dehydrogenation activity.

[00118] A fifteenth aspect of the present disclosure includes a method for forming a dehydrogenation catalyst, the method including obtaining a zirconia support, adding a chromium-

containing precursor to the zirconia support to form a chromium-containing zirconia, and calcining and drying the chromium-containing zirconia to form a dehydrogenation catalyst.

[00119] A sixteenth aspect of the present disclosure includes the fifteenth aspect, wherein adding the chromium-containing precursor to the zirconia support to form a chromium-containing zirconia is a process selected from the group consisting of: adding the chromium-containing precursor to the zirconia support, wherein the zirconia support is a fluidizable zirconia support, adding the chromium-containing precursor to the zirconia support by spray drying, adding the chromium-containing precursor to the zirconia support by granulation, and combinations thereof.

[00120] The subject matter of the present disclosure has been described in detail and by reference to specific embodiments. It should be understood that any detailed description of a component or feature of an embodiment does not necessarily imply that the component or feature is essential to the particular embodiment or to any other embodiment. Further, it should be apparent to those skilled in the art that various modifications and variations can be made to the described embodiments without departing from the spirit and scope of the claimed subject matter.

[00121] It is noted that one or more of the following claims utilize the term “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.”

[00122] It should be understood that where a first component is described as “comprising” a second component, it is contemplated that, in embodiments, the first component “consists” or “consists essentially of” that second component. It should further be understood that where a first component is described as “comprising” a second component, it is contemplated that, in embodiments, the first component comprises at least 10%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, at least 95%, or even at least 99% that second component (where % can be weight % or molar %).

[00123] It is also noted that recitations herein of “at least one” component, element, etc., should not be used to create an inference that the alternative use of the articles “a” or “an” should be limited to a single component, element, etc.

CLAIMS

1. A method for converting alkanes to alkenes, the method comprising:
contacting a feed stream comprising alkanes with a dehydrogenation catalyst in a reaction zone in the presence of steam, the dehydrogenation catalyst comprising zirconia and chromium;
and
converting at least a portion of the alkanes to alkenes, thereby yielding a product stream comprising alkanes, alkenes, and hydrogen;
wherein the dehydrogenation catalyst does not require a gaseous oxidant in the feed stream or as a co-feed to catalyze conversion of alkanes to alkenes.
2. The method of claim 1, further comprising combusting at least a portion of the hydrogen to yield steam.
3. The method of any of the preceding claims, wherein the dehydrogenation catalyst comprises an alkene selectivity greater than or equal to 40 Cmol%.
4. The method of any of the preceding claims, wherein the dehydrogenation catalyst retains at least some dehydrogenation activity above background dehydrogenation activity under greater than or equal to 5 v.% steam conditions based on a total volume of gaseous components in the reaction zone.
5. The method of any of the preceding claims, further comprising contacting the feed stream comprising alkanes with a selective hydrogen combustion material, wherein the dehydrogenation catalyst and the selective hydrogen combustion material are both present in the reaction zone.
6. The method of any of the preceding claims, wherein the dehydrogenation catalyst comprising zirconia and chromium comprises chromium impregnated zirconia.
7. The method of any of the preceding claims, wherein the dehydrogenation catalyst comprises from 0.5 % to 20 % chromium metal based on a total weight of the dehydrogenation catalyst.
8. The method of any of the preceding claims, wherein the dehydrogenation catalyst comprises:

1 wt.% to 5 wt.% chromium; and

65 wt.% to 80 wt.% zirconium;

wherein the weight percent is based on a total weight of the dehydrogenation catalyst.

9. The method of any of the preceding claims, wherein the dehydrogenation catalyst is substantially free from silicon.

10. The method of any of the preceding claims, wherein the dehydrogenation catalyst is a promoted dehydrogenation catalyst comprising the formula of a least one of Cr-Zr-X and Cr-Zr-Q, wherein:

X is selected from the group consisting of alkali metals, alkaline earth metals, tin, chloride, boron, phosphorous, sulfur, niobium, bismuth, antimony, and combinations thereof; and

Q is selected from the group consisting of lanthanum, cerium, neodymium, samarium, gadolinium, dysprosium, praseodymium, europium, and combinations thereof.

11. The method of any of the preceding claims, wherein the dehydrogenation catalyst and the feed stream have a mass to mass ratio that is from 5:1 to 200:1.

12. The method of any of the preceding claims, wherein the converting at least a portion of the alkanes to alkenes occurs at a temperature that is less than or equal to 750 °C, a pressure from 1 bara to 20 bara, and a WHSV of from 1 h⁻¹ to 12 h⁻¹.

13. The method of any of the preceding claims, wherein the method further comprises:
removing spent dehydrogenation catalyst from the reaction zone;
introducing the spent dehydrogenation catalyst into a regeneration zone;
regenerating the spent dehydrogenation catalyst, thereby forming regenerated dehydrogenation catalyst; and
returning regenerated dehydrogenation catalyst to the reaction zone where it is contacted with the feed stream.

14. A method for forming a dehydrogenation catalyst, the method comprising:
obtaining a zirconia support;
adding a chromium-containing precursor to the zirconia support to form a chromium-containing zirconia; and

calcining and drying the chromium-containing zirconia to form a dehydrogenation catalyst.

15. The method of claim 14, wherein adding the chromium-containing precursor to the zirconia support to form a chromium-containing zirconia is a process selected from the group consisting of:

adding the chromium-containing precursor to the zirconia support, wherein the zirconia support is a fluidizable zirconia support;

adding the chromium-containing precursor to the zirconia support by spray drying;

adding the chromium-containing precursor to the zirconia support by granulation; and combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/035550

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C07C5/32 C07C5/48 C07C11/04
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C07C
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO- Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	S. DE ROSSI, ET AL.: "Propane dehydrogenation on chromia/zirconia catalysts", APPLIED CATALYSIS A: GENERAL, vol. 81, no. 1, 30 January 1992 (1992-01-30), pages 113-132, XP093224267, Elsevier Science, Amsterdam, NL ISSN: 0926-860X, DOI: 10.1016/0926-860X(92)80264-D	1, 3, 4, 6, 7, 9, 14, 15
Y	Catalysts; pages 115-116; table 1 Procedure; pages 116-117 page 120; figure 2 The catalytic activity of samples heated in water vapour at 773 K; pages 121-122; figure 3 ----- - / - -	2, 5, 8, 10-13

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 20 November 2024	Date of mailing of the international search report 06/12/2024
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer English, Russell
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/035550

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 430 209 A (AGASKAR PRADYOT A [US] ET AL) 4 July 1995 (1995-07-04) cited in the application	2, 5, 10-13
A	claims 1,5,11,18 Scheme A; column 3, line 63 - column 4, line 40 column 8, line 23 - line 46 -----	1, 3, 4, 6-9, 14, 15
Y	A. ZUBKOV, ET AL.: "Influence of Cr/Zr ratio on activity of Cr-Zr oxide catalysts in non-oxidative propane dehydrogenation", CRYSTALS, vol. 11, no. 11, 1435, 22 November 2021 (2021-11-22), pages 1-12, XP093224490, MDPI, Basel, CH ISSN: 2073-4352, DOI: 10.3390/cryst11111435 -----	8
A	Catalytic Tests; page 3 page 5; table 1 page 8; figure 5 -----	1-7, 9-15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/035550

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims;; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-15

Method for converting alkanes to alkenes using a dehydrogenation catalyst comprising zirconia and chromium without a gaseous oxidant; method for preparing a dehydrogenation catalyst comprising zirconia and chromium

1.1. claims: 1-13

Method for converting alkanes to alkenes using a dehydrogenation catalyst comprising chromium and zirconia without a gaseous oxidant

1.2. claims: 14, 15

Method for preparing a dehydrogenation catalyst comprising chromium and zirconia

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/035550

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5430209	A	NONE	