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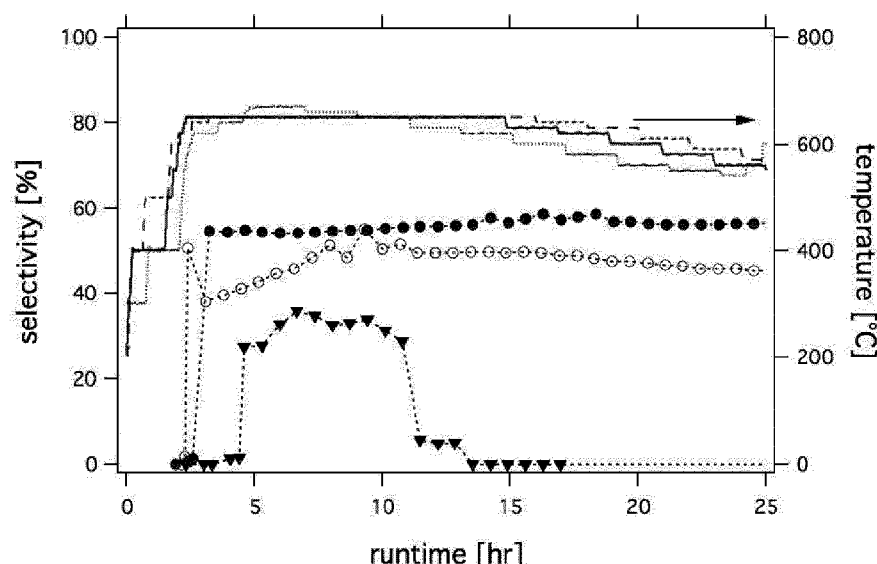
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(54) Title: PROCESS FOR OXIDATIVELY CONVERTING METHANE TO HIGHER HYDROCARBON PRODUCTS

FIG. 1



(57) Abstract: The present invention relates to a process for the oxidative coupling of methane to one or more C₂₊ hydrocarbons, wherein said process comprises contacting a catalyst bed comprising a catalyst composition comprising manganese, one or more alkali metals and tungsten on a silica carrier in a fixed-bed reactor with a reactor feed comprising methane and oxygen under oxidative methane coupling (OCM) conditions, wherein the ratio L/D of catalyst bed length L to catalyst bed diameter D is smaller than 10.

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PROCESS FOR OXIDATIVELY CONVERTING METHANE TO HIGHER
HYDROCARBON PRODUCTS

Field of the Invention

The present invention relates to a process and a reactor design for oxidatively converting methane to higher carbon products, in particular ethylene and ethane.

5 Background of the Invention

Methane (CH_4), the principal component of natural gas, is an abundant and readily usable energy resource that is considered cleaner than petroleum and coal. Moreover, being a C_1 compound, methane is also a versatile feedstock for the
10 production of chemical building blocks and value-added chemical products. Due to the inconvenient location of most of the world's natural gas resources and the relatively high transportation costs of natural gas, the conversion of methane to more energy-dense derivatives or value-added
15 product would significantly increase the world-wide economic potential of methane.

Amongst the potential routes for methane upgrading, oxidative coupling of methane ("OCM") has been the subject of comprehensive academic and industrial research, as this
20 process offers the prospect of a single integrated process for the direct conversion of methane to C_{2+} compounds, notably ethylene.

In the OCM process, a gas stream comprising methane is contacted with an oxidant, such as oxygen or air, in the
25 presence of a suitable metal oxide catalyst, whereby two methane molecules are first coupled into one ethane (C_2H_6) molecule, which is dehydrogenated to yield ethylene (C_2H_4).

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The reaction is exothermic, with a ΔH of about -70 kcal/mole. While thermodynamically more favourable, less preferred side reactions, both in terms of economic viability and environmental sustainability, are the partial or full combustion of methane to produce carbon oxide (CO) and carbon dioxide (CO₂). Ethane and ethylene may further react into saturated and unsaturated hydrocarbons having 3 or more carbon atoms (C₃+), such as propane, propylene, butane and butene, etc.

Academic and industrial research into the OCM process has consistently shown a characteristic performance of high selectivity at relatively low conversion of methane, and vice versa. Extensive efforts have been directed towards the development of novel catalysts that display improved stability at high temperatures while maintaining acceptable C₂ (ethane and ethylene) selectivities and yields. In this regard, one of the best-performing catalysts that have been found to date in the OCM field comprises manganese, tungsten and sodium on a silica carrier. The oxidative coupling of methane in the presence of said catalyst is studied in Applied Catalysis A: General 343 (2008) 142-148, Applied Catalysis A: General 425-426 (2012) 53-61, Fuel 106 (2013) 851-857, US 2014/0080699 A1 and US 6596912 B1. Typically, for small 2 w% Mn/2.2 % Na₂WO₄/SiO₂ catalyst particles (40-80 mesh = 0.18-0.42 mm), in the temperature range of 750 °C to about 950 °C C₂ yields of about 15%-25% and C₂ selectivities in the range of 55-85% can be obtained. However, at these temperatures, the high reaction exothermicity may cause steep adiabatic temperature rises, resulting in progressive catalyst degradation and severe selectivity losses.

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Conversely, at reactor temperatures below 650 °C the catalyst typically does not show any activity.

Since the OCM reaction involves a complex (and hitherto not completely elucidated) reaction mechanism, it is expected
5 that C₂ selectivity and yield do not only depend on catalyst chemical composition but also on catalyst morphology, reactor design and process conditions. It is therefore highly desirable to provide a process for the oxidative coupling of methane, which process is performed such that high C₂
10 selectivity and/or yields are obtained in an effective and economically attractive manner.

Summary of the Invention

The present inventors have found that the use of a relatively
15 flat catalyst bed in an OCM process has several advantages over the use of more elongated catalyst beds. Accordingly, in a first aspect the invention relates to a process for the oxidative coupling of methane to one or more C₂₊

hydrocarbons, wherein said process comprises
20 contacting in a fixed-bed reactor a catalyst bed comprising a catalyst composition comprising manganese, one or more alkali metals and tungsten on a silica carrier, with a reactor feed comprising methane and oxygen under oxidative methane coupling (OCM) conditions,

25 wherein the ratio L/D of catalyst bed length L to catalyst bed diameter D is smaller than 10, and wherein the process comprises heating the reactor to a first reactor temperature T₁ that is sufficient to ignite the catalyst composition, and

30 subsequently reducing the reactor temperature to a second temperature T₂ that is sufficient to maintain

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catalytic activity of the catalyst composition.

For example, the use of a relatively flat catalyst bed (small L/D ratio) results in improved stability at or above the ignition temperature as compared to more elongated catalyst beds. It was further found that conducting the OCM reaction in a relatively flat catalyst bed results in faster stabilization of the selectivity to C₂₊ compounds after ignition of the catalyst as compared to more elongated catalyst beds (larger L/D ratio). Additionally, it was found that the use of a catalyst bed with dimensions as defined herein allows the OCM process, once the exothermic methane coupling reaction has started, to be run at much reduced feed gas inlet temperatures, yet preserving satisfactory C₂₊ selectivities and yields. Since the OCM process can be sustained at much lower feed gas inlet temperatures, the risk of overheating of the catalyst due to adiabatic temperature rises of the exothermic OCM reaction is strongly reduced. This allows the use of reactor designs that do not require direct cooling of the reactor for preventing catalyst decay and selectivity loss. Another advantage of a lower feed temperature is that ignition phenomena in the gas phase, leading to more non-selective combustion reactions, can be avoided. Also from a process safety point of view the use of lower feed gas temperatures is favourable, as it decreases the risk of thermal runaways, detonations, explosions and other heat-induced adverse effects. Yet another advantage of the catalyst bed design as disclosed herein is its much lower pressure drop. This allows OCM reactors of the fixed-bed type to become feasible, thus avoiding the operation and design problems associated with high-temperature fluid-bed reactors. In general, the process as described herein allows the

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oxidative coupling of methane to be carried out in a more effective and economic manner.

Brief description of the drawings

5 Figure 1 displays the selectivity of CH₄ conversion as a function of OCM reaction runtime for a catalyst bed with L/D=1.6, L/D=3.2 and L/D=15.

10 Figure 2 displays the CH₄ conversion as a function of OCM reactor temperature upon heating until ignition and subsequent reduction of reactor temperature.

Detailed description

15 Implementations of the disclosed subject matter provide a process wherein a fixed catalyst bed comprising a catalyst composition comprising manganese, one or more alkali metals and tungsten on a silica carrier, wherein the ratio L/D of the length L of said catalyst bed to the diameter D of said catalyst bed is less than 10, is contacted in a reactor with a reactor feed comprising methane and oxygen under oxidative
20 methane coupling conditions.

25 Reactors typically used in laboratory set-up and in industrial practice for the oxidative coupling of methane comprise one or more reactor tubes, wherein the reactor tubes are not completely filled with catalyst; rather, the catalyst bed is located at some intermediate point in the catalyst tube. The reactor feed enters the reactor, either in up-flow or down-flow direction, at a point upstream of the catalyst bed and passes through a region upstream of the catalyst bed before passing through the catalyst bed.

30 In the start-up phase, heat can be supplied to the system by heating the catalyst tube containing the catalyst

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bed, by heating the feed gas stream entering the reactor, or by a combination of both. In a lab-scale setting, heating of the catalyst bed and the feed gas is typically accomplished by means of one or more heating devices or elements (such as a cylindrical tubular furnace) at least partially covering the catalyst tube, while on industrial scale, this may be achieved by a variety of fuel-based, electric-based or steam-based heating systems. After ignition of the catalyst, typically only heating of the gaseous feed stream entering the reactor bed would be required to maintain the reaction.

Typically, the OCM reactor and associated equipment are equipped with thermocouples for monitoring the temperature of the reactor and its inlet/outlet lines and contents, at one or more points selected from the temperature of the feed gas upstream of the catalyst bed, at the entrance of the catalyst bed (i.e., of the reactor feed gas just before entering the catalyst bed), of the catalyst bed itself, at the exit of the reactor, in the heat source adjacent to the catalyst bed (at the height corresponding to the feed gas entrance of the catalyst bed) and of the effluent gases. As used herein, unless indicated otherwise, wherever reference is made to a "reactor temperature" (or "temperature of the reactor"), or temperatures T_1 , T_i and T_2 as described in more detail below, this should be interpreted to refer to the temperature as measured at the entrance of the catalyst bed, i.e. the temperature of the reactor feed gas just before entering the catalyst bed. Due to the presence of heating elements in the region upstream of the catalyst bed and/or radiative heat transfer from the catalyst bed, the temperature of the reactor feed gas just before entering the catalyst bed is not necessarily the same as the temperature of the feed gas at

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the inlet of the reactor, i.e., it may for example be somewhat or substantially higher.

As used herein, the length L of the catalyst bed refers to the distance from the top to bottom of the bed in the flow-direction of the catalyst bed, also referred to as the "height" of the catalyst bed. As used herein, the diameter D of the catalyst bed refers to the diameter of the largest circular cross-section (perpendicular to the flow-direction) of the catalyst bed. In some embodiments, this cross-section may not be perfectly circular (for example, ellipsoidal); in such case, the diameter D is considered to be the major (largest) diameter passing through the center of said cross-section.

As used herein, the term "oxidative methane coupling conditions" refers to the temperature, pressure, gas velocity, and gas ratios that are suitable for oxidatively converting a gaseous feed stream comprising methane to C_{2+} products in desirable yields and selectivities. Typical suitable conditions for carrying out OCM reaction are known to the person of ordinary skill in the art and are disclosed in detail in the following sections.

The reactor feed comprising methane and oxygen is contacted with the catalyst bed at a first temperature T_1 that is sufficient to ignite the catalyst. The phenomenon of catalytic ignition is known in the field of gas-phase catalytic reactions, and refers to the rapid transition from a state controlled primarily by surface reaction kinetics to a primarily mass transport controlled, exothermic catalytic reaction state (see e.g., Frank-Kamenetskii DA. Diffusion and heat transfer in chemical kinetics. 2. New York: Plenum; 1969).

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As used herein, the term "temperature that is sufficient to ignite the catalyst" refers to the temperature as measured at the level of entry of the feed gas to the catalyst bed at which, under the prevailing process conditions, catalytic oxidative conversion of methane to C₂ (ethane and ethylene) products is observed. As used herein, the term "catalyst ignition temperature" T_i refers to the minimum temperature at which, under the selected process conditions (such as reactor pressure, gas velocity and feed gas ratios), catalytic oxidative conversion of methane to C₂ (ethane and ethylene) products is observed. This conversion may be observed as a suddenly increased and sustained consumption (conversion) of oxygen (O₂) and/or methane (CH₄) from the feed gas, and/or a suddenly increased and sustained production of C₂ compounds and optionally other products in the reactor effluent. As used herein, the ignition temperature T_i is understood to refer to the temperature at which O₂ conversion exceeds 80 %. Typically, the catalytic conversion of methane and oxygen to C₂₊ products is routinely measured by on-line quantitative analysis, e.g. by gas chromatography (GC), of oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, as well as C₃, C₄ and C₅ hydrocarbons concentrations.

Thus, the first temperature T₁ that is sufficient to ignite the catalyst may be equal to or higher than the catalyst ignition temperature T_i (T₁ ≥ T_i), and selection of this first temperature T₁ may, besides the aforementioned reaction conditions, further depend on factors including desired C₂ selectivity and/or C₂ yieldage of the catalyst, and reactor geometry.

In some embodiments the first temperature T₁ is at least

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500 °C, preferably at least 550 °C, more preferably at least 580 °C, even more preferably at least 600°C, yet even more preferably at least 620 °C, yet even more preferably at least 640 °C, yet even more preferably at least 660 °C, most
5 preferably at least 680 °C. In some embodiments the first temperature T_1 is at most 800 °C, preferably at most 780 °C, more preferably at most 760 °C, even more preferably at most 740 °C, most preferably at most 720 °C.

As mentioned previously, the catalytic oxidative
10 coupling of methane is exothermic with a ΔH of about -70 kcal/mole. Without wishing to be bound to theory, it is believed that by using a relatively flat catalyst bed as disclosed herein, heat transfer within the catalyst bed is impaired, causing a substantially adiabatic temperature rise
15 of the catalyst bed relative to the incoming feed gas stream. Additionally or alternatively, it has been proposed that local catalyst exothermic effects are moderated in a relatively flat catalyst bed, resulting in more rapid establishment of apparent stable selectivity and less rapid deactivation. It
20 has been found that the catalyst bed as defined herein will remain ignited, and thus catalytically active, even if the reactor temperature is subsequently reduced to temperatures below the minimum temperature required for ignition of the catalyst. As will be explained in more detail below, this may
25 suitably be achieved by decreasing the amount of external heat supplied to the catalyst bed, by decreasing the temperature of the feed gas entering the reactor, or both.

Thus, in accordance with the present disclosure, the reactor temperature is reduced to a second temperature T_2
30 that is sufficient to maintain catalyst activity. As for the catalyst ignition phase, maintaining catalytic activity for

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the oxidative conversion of methane can be observed as a sustained conversion (consumption) of oxygen (O_2) and/or methane (CH_4) from the feed gas, and/or a sustained production of C_2 products and optionally other products in the reactor effluent.

Thus, in the process as disclosed herein, heat produced by the oxidative conversion of methane is effectively transferred to and conserved in the catalyst bed as defined herein, thereby allowing the catalyst bed to provide its own heat source whilst the reactor temperature, by means of reducing the amount of external thermal energy supplied to the reactor, is reduced. In some embodiments, the first temperature T_1 is maintained for at least 30 minutes, more preferably at least 60 minutes, most preferably at least 120 minutes.

Thus, in some embodiments, the reactor temperature, i.e. the temperature at the entry of the catalyst bed, is reduced to a second temperature T_2 that is sufficient to maintain catalytic activity of the hot catalyst bed. It is within the ability of one skilled in the art to determine a suitable temperature T_2 that is sufficient to maintain catalytic activity, taking into consideration, for example, the overall composition of the reactor feed, along with other operating conditions, as well as the desired balance of product yields and selectivities. For example, by, starting from T_1 , reducing the reactor temperature in a controlled stepwise manner and monitoring oxygen (O_2) and/or methane (CH_4) conversion and/or C_2 product formation as described above, it is possible to determine the second temperature T_2 that provides optimum results for the oxidative methane coupling process in terms of, for example, C_{2+} yields and selectivity.

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In some embodiments, this process of finding the second temperature T_2 that provides optimum results OCM results included reducing the reactor temperature until extinction of the catalyst occurs. As used herein, catalyst extinction is considered to have happened if oxygen conversion drops below 80% of its initial (after ignition) rate.

In some embodiments, the second reactor temperature T_2 , defined previously as the temperature of the gas phase just before entry of the catalyst bed, is at least 20 °C lower, more preferably at least 40 °C lower, even more preferably at least 60 °C lower, even more preferably at least 80 °C lower, yet even more preferably at least 100 °C, most preferably at least 200 °C lower than the first temperature T_1 . Typically, in industrial reactors, this second temperature T_2 may be at least 120 °C lower, more preferably at least 160 °C lower, even more preferably at least 200 °C lower, yet even more preferably at least 300 °C lower, most preferably at least 400 °C, 500 °C, 600 °C or 700 °C lower than the first temperature T_1 .

In some embodiments the second temperature T_2 is at most 700 °C, preferably at most 650 °C, more preferably at most 600 °C, even more preferably at most 550 °C, yet even more preferably at most 500 °C, yet even more preferably at most 450 °C, yet even more preferably at most 400 °C, yet even more preferably at most 350 °C, yet even more preferably at most 300 °C, yet even more preferably at most 250 °C, yet even more preferably at most 200 °C, yet even more preferably at most 150 °C, most preferably at most 100 °C. In some embodiments, the second reactor temperature T_2 is at least ambient temperature, for example at least 15 °C or 20 °C, preferably at least 50 °C, more preferably at least 100 °C,

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more preferably at least 100 °C, more preferably at least 150 °C, more preferably at least 200 °C, more preferably at least 250 °C, even more preferably at least 300 °C, more preferably at least 350 °C, even more preferably at least 400 °C, more preferably at least 450 °C, even more preferably at least 500 °C, yet even more preferably at least 550 °C, most preferably at least 600 °C.

Typically, in OCM reactors using conventional, relatively long catalyst beds, at such a reduced temperature T_2 with respect to the temperature T_1 equal to or larger than the catalyst ignition temperature, no or little conversion of methane to desired products would be obtained, due to extinction of the catalyst or otherwise unfavorable reaction thermodynamics at these reduced temperatures. Conversely, the flat catalyst bed as disclosed herein allows the OCM process, after catalyst ignition, to be run at lower feed gas temperatures, thus enabling the process to be conducted in a more economic manner and preventing any adverse side effects of high feed gas temperatures.

In one embodiment, the ratio L/D of catalyst bed length L to catalyst bed diameter D is smaller than 5, preferably smaller than 3, more preferably smaller than 2, even more preferably smaller than 1, yet even more preferably smaller than 0.5, yet even more preferably smaller than 0.1, yet even more preferably smaller than 0.05, yet even more preferably smaller than 0.01, most preferably smaller than 0.005.

According to an advantageous aspect of the present disclosure, after catalyst ignition, the inlet temperature of the feed gas stream can be kept relatively cold. As used herein, the "inlet temperature of the feed gas stream" or "reactor feed inlet temperature" should be understood to

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refer to the temperature of the feed gases or the mixture of feed gases as measured at or near the inlet of the reactor, i.e. substantially upstream of the catalyst bed. In some embodiments, this point corresponds to the point at which feed gases are mixed.

As mentioned above, reduction of the reactor temperature after ignition can be achieved by decreasing the amount of external heat supplied to the catalyst bed, by decreasing the inlet temperature of the feed gas entering the reactor, or both. Accordingly, in one embodiment of the present disclosure, after catalyst ignition, the reactor temperature is reduced to a second temperature T_2 that is sufficient to maintain catalytic activity of the catalyst composition, by decreasing the amount of external heat supplied to the catalyst bed. Suitably, this is achieved by decreasing the temperature of the heating source of the catalyst bed, or by partially or entirely removing the heat source. In another embodiment, after catalyst ignition, the reactor temperature is reduced to a second temperature T_2 that is sufficient to maintain catalytic activity of the catalyst composition, by decreasing the temperature of the feed gas stream entering the reactor. In some embodiments, after catalyst ignition, the reactor temperature is reduced to a second temperature T_2 that is sufficient to maintain catalytic activity of the catalyst composition, by decreasing the amount of external heat supplied to the catalyst bed and by decreasing the temperature of the feed gas stream entering the reactor.

Accordingly, in some embodiments, the inlet temperature of the feed gas stream after catalyst ignition is at most 750°C, preferably at most 700 °C, more preferably at most 650 °C, even more preferably at most 600 °C, yet even more

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preferably at most 550 °C, yet even more preferably at most 500 °C, yet even more preferably at most 450 °C, yet even more preferably at most 400 °C, yet even more preferably at most 350 °C, yet even more preferably at most 300 °C, yet
5 even more preferably at most 250 °C, most preferably at most 200°C, 100 °C or at most 50 °C. In one embodiment, the feed gas stream supplied to the reactor inlet after catalyst ignition is not heated. Typically, in such case the temperature of the feed gas stream entering the reactor after
10 ignition will be at or close to the ambient temperature. In some embodiments, the temperature of the feed gas stream entering the reactor after ignition is at least 15 °C or at least 20 °C, preferably at least 50 °C, more preferably at least 80 °C, even more preferably at least 120 °C, even more
15 preferably at least 150 °C, yet even more preferably at least 200 °C, yet even more preferably at least 250°C, yet even more preferably at least 300°C, yet even more preferably at least 350 °C, most preferably at least 400 °C.

As used herein, the term "reactor feed" is understood to
20 refer to the totality of the gaseous stream at the inlet of the reactor. Thus, as will be appreciated by one skilled in the art, the reactor feed is often comprised of a combination of one or more gaseous stream(s), such as a methane stream, an oxygen stream, a recycle gas stream, a diluent stream,
25 etc.

In some embodiments of the present invention, methane and oxygen are added to the reactor as a mixed feed, that is to say, a feed wherein a methane and an oxygen stream, or an oxygen-containing stream such as air, have been mixed
30 together prior to addition to reactor. In such case, the reactor feed inlet temperature simply refers to the

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temperature of the total gas mixture.

In some embodiments of the present invention, there is so-called "distributed delivery" of reactants, whereby oxygen is added, for example, at multiple points in the reactor upstream of or in the catalyst bed to ensure low oxygen concentrations in the reactor. In such case, the inlet temperature of only one, or of more than one of the gaseous feed streams may be reduced such that the second temperature T_2 is reduced with respect to the first temperature T_1 .

As used herein, "methane (CH_4) conversion" and "oxygen (O_2) conversion" means the mole fraction of methane and oxygen converted to product(s), respectively.

" C_x selectivity" refers to the percentage of converted reactants that went to product(s) having carbon number x and " C_{x+} selectivity" refers to the percentage of converted reactants that went to the specified product(s) having a carbon number x and higher. Thus, " C_2 selectivity" refers to the percentage of converted methane that formed ethane and ethylene. Similarly, " C_{2+} selectivity" means the percentage of converted methane that formed compounds having carbon numbers of 2 and higher.

" C_x yield" is used to define the percentage of products obtained with carbon number x relative to the theoretical maximum product obtainable. The C_x yield is calculated by dividing the amount of obtained product having carbon number x in moles by the theoretical yield in moles and multiplying the result by 100. " C_2 yield" refers to the total combined yield of ethane and ethylene. The C_x yield may be calculated by multiplying the methane conversion by the C_x selectivity.

As used herein in the context of catalyst dopants, "weight percent" refers to the ratio of the total weight of

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the carrier, the metal-containing dopant or the metal in the dopant to the total weight of the catalyst composition the catalyst. Said percentages are determined with respect to the weight of the total dry catalyst composition. Suitably, the weight of the total dry catalyst composition may be measured following drying for at least one hour at 300 °C, or at least four hours at 120 to 150 °C.

Percentages of metals from the metal-containing dopants in the catalyst composition may be determined by XRF or ICP as is known in the art. The metals content of catalyst composition may also be inferred or controlled via its synthesis.

The components of the catalyst composition are to be selected in an overall amount not to exceed 100 wt%.

As used herein, the term "compound" refers to the combination of a particular element with one or more different elements by surface and/or chemical bonding, such as ionic and/or covalent and/or coordinate bonding.

The term "ion" or "ionic" refers to an electrically chemical charged moiety; "cation" or "cationic" being positive, "anion" or "anionic" being negative, and "oxyanion" or "oxyanionic" being a negatively charged moiety containing at least one oxygen atom in combination with another element (i.e., an oxygen-containing anion). It is understood that ions do not exist in vacuo, but are found in combination with charge-balancing counter ions when added.

The term "oxidic" refers to a charged or neutral species wherein an element in question is bound to oxygen and possibly one or more different elements by surface and/or chemical bonding, such as ionic and/or covalent and/or coordinate bonding. Thus, an oxidic compound is an oxygen-

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containing compound which also may be a mixed, double or complex surface oxide. Illustrative oxidic compounds include, but are not limited to, oxides (containing only oxygen as the second element), hydroxides, nitrates, sulfates,

5 carboxylates, carbonates, bicarbonates, oxyhalides, etc. as well as surface species wherein the element in question is bound directly or indirectly to an oxygen either in the substrate or the surface.

10 In one embodiment of the present disclosure, unreacted methane is separated from the reactor product stream and is recycled to the reactor. Preferably, said recycled methane gas stream is combined with the main methane and oxygen streams as part of the reactor feed prior to entry into the reactor.

15 In some embodiments of the present disclosure, methane may be present in the reactor feed in a concentration of at least 35 mole-% and preferably at least 40 mole-%, relative to the total reactor feed. Similarly, methane may be present in the reactor feed in a concentration of at most 90 mole-%, 20 preferably at most 85 mole-%, relative to the total reactor feed.

In some embodiments of the present disclosure, methane may be present in the reactor feed in a concentration in the range of from 35 to 90 mole-%, preferably in the range of 25 from 40 to 85 mole-%, relative to the total reactor feed.

In general, the oxygen concentration in the reactor feed should be less than the concentration of oxygen that would form a flammable mixture at either the reactor inlet or the reactor outlet at the prevailing operating conditions. Often, 30 in practice, the oxygen concentration in the reactor feed may be no greater than a pre-defined percentage (e.g., 95%, 90%,

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etc.) of oxygen that would form a flammable mixture at either the reactor inlet or the reactor outlet at the prevailing operating conditions.

Although the oxygen concentration in the reactor feed
5 may vary over a wide range, the oxygen concentration in the reactor feed is preferably at least 7 mole-%, more preferably at least 10 mole-%, relative to the total reactor feed. Similarly, the oxygen concentration of the reactor feed is preferably at most 25 mole-%, more preferably at most 20
10 mole-%, relative to the total reactor feed.

In some embodiments, oxygen may be present in the reactor feed in a concentration in the range of from 7 to 25 mole-%, preferably in the range of from 10 to 20 mole-%, relative to the total reactor feed.

15 It is within the ability of one skilled in the art to determine a suitable concentration of oxygen to be included in the reactor feed, taking into consideration, for example, the overall composition of the reactor feed, along with the other operating conditions, such as pressure and temperature.

20 However, in a preferred embodiment, the methane:oxygen volume ratio in the process of the present invention is in the range of from 2:1 to 10:1, more preferably in the range of from 3:1 to 6:1.

The reactor feed may further comprise one or more of a
25 diluent gas, minor components typically present in the methane feed stream (e.g. ethane, propane etc.) or the methane recycle stream (e.g. ethane, ethylene, acetylene, propane, propylene, carbon monoxide, carbon dioxide, hydrogen and water). The diluent represents the balance of the feed
30 gas and is an inert gas. Examples of suitable inert gases are nitrogen, argon or helium.

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The order and manner in which the components of the reactor feed are combined prior to contacting with the catalyst composition is not limited, and they may be combined simultaneously or sequentially. However, as will be
5 recognized by one skilled in the art, it may be desirable to combine certain components of the inlet feed gas in a specified order for safety reasons. For example, oxygen may be added to the inlet feed gas after the addition of a dilution gas for safety reasons. Similarly, as will be
10 understood by one of skill in the art, the concentration of various feed components present in the inlet feed gas may be adjusted throughout the process, for example, to maintain a desired productivity, optimize the process, etc. Accordingly, the above-defined concentration ranges were selected to cover
15 the widest possible variations in the composition of the reactor feed during normal operation.

Thus, in one embodiment of the present invention, one reactor feed gas stream comprising methane and oxygen may be fed to the reactor. Alternatively, in other embodiments of
20 the present invention, two or more reactor feed gas streams may be fed to the reactor, which gas streams form a combined reactor feed gas stream inside the reactor. For example, one reactor feed gas stream comprising methane and another reactor feed gas stream comprising oxygen may be fed to the
25 reactor separately. Said one reactor feed gas stream or multiple reactor feed gas streams may additionally comprise an inert gas, as further described below.

The process of the present invention comprises utilising the catalyst composition in a reactor suitable for the
30 oxidative coupling of methane. In view of the reduced need for direct cooling of the reactor, the catalyst design as

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defined herein is particularly suitable for use in a fixed-bed reactor. Typically, such reactor would be a fixed bed reactor with axial or radial flow and with inter-stage cooling. Various fixed-bed reactor set-ups are described in the OCM field and the process of the present invention is not limited in that regard. The person skilled in the art may conveniently employ any of said reactor set-ups in conjunction with the process of the present invention. Accordingly, reactor set-ups as described in EP 0206042 A1, US 4443649 A, CA 2016675 A, and/or WO 2013/106771 A2 may be conveniently employed.

The gas hourly space velocity (GHSV) in the process of the present invention is the entering volumetric flow rate (m^3/s) of the reactor feed (at standard conditions) divided by the catalyst bed volume. Preferably, said gas hourly space velocity is in the range of from 3,000 to 1,000,000 h^{-1} . It should be noted that suitable and favorable space velocities differ markedly between laboratory test reactors and industrial reactors. For the latter, the GHSV is typically in the range of 10,000 to 300,000 h^{-1} , preferably in the range of from 20,000 to 150,000 h^{-1} . Said GHSV is measured at standard temperature and pressure, namely 0 °C and 1 bara (100 kPa).

In general, the product stream comprises water in addition to the desired product. Water may easily be separated from said product stream, for example by cooling down the product stream from the reaction temperature to a lower temperature, for example room temperature, so that the water condenses and can then be separated from the product stream.

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In some embodiments, the process of the present invention has a C₂₊ hydrocarbon selectivity of at least 45 %, preferably at least 50 %, more preferably at least 55 %, even more preferably at least 60 %.

5 In some embodiments, the process of the present invention results in an ethane:ethene mole ratio of less than 1.0 , more preferably less than 0.5.

The catalyst composition for use in the process of the present invention comprises manganese, one or more alkali
10 metals and tungsten on a carrier. The carrier material is not limited and may be conveniently selected from one or more of silicon-, titanium-, zirconium- and aluminium-containing carriers such as silica (SiO₂), titania (TiO₂), zirconia (ZrO₂) and alumina (Al₂O₃). The catalyst material
15 can have any desirable monolithic (such as monolithic foams) or particular (pellet) shape, provided that the catalyst bed comprising the catalyst material has the length to diameter ratio L/D as defined herein.

Catalyst compositions for use in the process of the present invention may in principle be prepared by any
20 suitable technique known in the art for similar catalyst compositions.

Thus, methods such as precipitation, co-precipitation, coating (of monoliths), impregnation, granulation, spray-
25 drying or dry-mixing can be used.

Optionally, prior to use in the process of the present invention, the catalyst composition may be pretreated at high temperature to remove moisture and impurities therefrom. Said pretreatment may take place, for example, at
30 a temperature in the range of from 100-300 °C for about one hour in the presence of air or an inert gas such as helium.

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In one embodiment, the catalyst composition is in the form of catalyst particles. As used herein, the term "catalyst particles" refers to shaped particles wherein the individual particles contain a suitable carrier and a catalytically active composition comprising manganese, one or more alkali metals and tungsten, supported by (e.g., adsorbed or impregnated on) said carrier. In other words, individual carrier particles and individual particles of a composition comprising unsupported manganese, one or more alkali metals and tungsten do not fall under the present definition of "catalyst particles". Examples of suitable catalyst particle shapes are granules, spheres, ellipsoids, rods, cones etc. In one embodiment, the catalyst particles are granular catalyst particles. In some embodiments, the catalyst particle shape and dimension may be determined by particular choice of carrier material onto which the catalyst composition is attached, such as impregnation, ion exchange, equilibrium adsorption or spray-drying. For example, a catalyst composition comprising spherical catalyst particles may be prepared by impregnation of a catalytically active composition onto a spherical carrier (or "support") material of suitable dimensions. In some embodiments, the catalyst particle shape and dimension may be determined by sizing of a ready-made catalyst composition, such as by grinding and/or sieving.

The carrier may be present in the catalyst composition in an amount in the range of from 80-98 % by weight, and most preferably in the range of from 92-96 % by weight, relative to the total weight of the catalyst composition including the carrier.

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In some embodiments, the catalyst particles have a number-average particle size d_1 in at least one dimension of at least 1 mm, preferably at least 2 mm, more preferably at least 3 mm, most preferably at least 4 mm. Typically, this average dimension d_1 does not exceed 50 mm, preferably does not exceed 20 mm, more preferably does not exceed 15 mm, most preferably does not exceed 10 mm. Typically, in such case the size distribution of the number-average particle size d_1 in at least one dimension is narrow, with a span $(D90-D10)/D50$, wherein D10, D50 and D90 represent the value of the diameter where 10%, 50% and 90% of the population lies below this value, respectively, of smaller than 2, preferably smaller than 1.5, more preferably smaller than 1.0, even more preferably smaller than 0.5, most preferably smaller than 0.2.

In some embodiments, the catalyst particles are substantially spherical, with all of the particle's dimensions being substantially identical and thus corresponding to the diameter of said spherical particle. Accordingly, in some embodiments the catalyst particles are substantially spherical or spherical particles having a number-average diameter of at least 1 mm, preferably at least 2 mm, more preferably at least 3 mm, more preferably at least 3.5 mm, most preferably at least 4 mm. Typically, such spherical particles have a narrow size distribution, having a span $(D90-D10)/D50$, smaller than 2, preferably smaller than 1.5, more preferably smaller than 1.0, even more preferably smaller than 0.5, most preferably smaller than 0.2. The catalyst particle size and its specific distribution can be determined by various techniques known in the art, including sieving analysis, laser diffraction,

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dynamic light scattering and (automated) image analysis. Unless indicated otherwise, all particle sizes and particle size distributions disclosed herein are determined using dynamic image analysis according to ISO 13322-2.

5 A preferred method for providing catalyst particles is by incipient wetness impregnation (IWI) of a porous carrier material (such as silica) with one or more solutions of active metal precursor. Herein, typically the metal and alkali metal precursors are dissolved in an aqueous or
10 organic solution. Subsequently, the metal precursor-containing solution is added to a catalyst carrier, while capillary action draws the solution into the pores of the carrier. Then, the catalyst may be dried and calcined to drive off the volatile components within the solution,
15 depositing the metal and alkali metals on the catalyst surface.

 In one embodiment, the catalyst particles according to the present disclosure are core-shell particles comprising a core comprising a carrier material and a shell comprising
20 manganese, one or more alkali metals and tungsten. In a preferred embodiment, the carrier material is porous, typically comprising at least 20 wt%, preferably at least 50 wt% of the manganese, one or more alkali metals and tungsten, by total weight of the catalyst particle. Suitable
25 examples of porous catalyst supports may be commercially available carrier materials such as CARiACT silica catalyst supports manufactured by Fuji Silysia.

 The B.E.T. surface area, total pore volume, median pore diameter and pore size distribution of the carrier material
30 may be conveniently selected by the person skilled in the art.

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Typically, the B.E.T. surface area of the carrier is in the range of 50-400 m²/g; the total pore volume is typically in the range 0.5-2.0 mL/g; the average pore diameter is typically in the range 10-50 nm.

5 Typically, the catalyst composition comprises manganese in an amount of in the range of from 1.0 to 10.0 % by weight, preferably in the range of from 1.0 to 5.0 % by weight, more preferably in the range of from 1.3 to 3.0 % by weight and most preferably in the range of from 1.7 to 2.5 %
10 by weight, relative to the total weight of the catalyst composition.

 In a preferred embodiment, the manganese is present in the catalyst composition in the form of one or more manganese-containing dopants such as one or more manganese-
15 containing oxides. Said manganese-containing oxides may be reducible oxides of manganese and/or reduced oxides of manganese. However, in the active state, the catalyst composition comprises at least one reducible oxide of manganese. Such reducible oxides include compounds of the
20 general formula Mn_xO_y wherein x and y designate the relative atomic proportions of manganese and oxygen in the composition and one or more oxygen-containing Mn compounds which contain manganese, oxygen and additional elements. Particularly preferred reducible oxides of manganese include
25 MnO₂, Mn₂O₃, Mn₃O₄ and mixtures thereof.

 The preferred catalyst composition for use in the process of the present invention comprises one or more (Group 1) alkali metals. Said alkali metals are preferably from selected one or more of lithium, sodium, potassium,
30 rubidium and cesium. Particularly preferred alkali metals are lithium and sodium.

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The one or more alkali metals are preferably in a total amount of in the range of from 0.1 to 1.5 % by weight, more preferably in the range of from 0.3 to 0.9 % by weight, relative to the total weight of the catalyst composition.

5 Tungsten may be present in an amount of in the range of from 1 to 5 % by weight, more preferably in the range of from 1.2 to 4.0 % by weight, relative to the total weight of the catalyst composition.

In some embodiments the catalyst composition comprises
10 manganese, one or more alkali metals and tungsten on a silica carrier. In some embodiments the catalyst composition comprises manganese, one or more alkali metals and tungsten on a spherical silica carrier. In some embodiments the catalyst composition comprises manganese, sodium and
15 tungsten on a silica carrier. In some embodiments the catalyst composition comprises manganese and sodium tungstate (Na_2WO_4) on a silica carrier, preferably on spherical silica particles. In some embodiments the catalyst composition comprises manganese and sodium tungstate (Na_2WO_4)
20 supported on spherical silica carrier particles having a number-average diameter of at least 1 mm, preferably at least 2 mm, more preferably at least 3 mm, more preferably at least 3.5 mm, most preferably at least 4 mm. Typically, such catalyst particles are prepared by impregnation of
25 commercially available spherical silica beads with one or more solutions of the metals or metal-containing compounds. In one embodiment of the present disclosure, the catalyst composition is prepared by incipient wetness impregnation (IWI) of a porous silica carrier with one or more solutions
30 comprising manganese, one or more alkali metals and tungsten.

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In the preparation of the afore-mentioned catalyst composition, the one or more alkali metals and tungsten may be doped as separate metals and/or metal-containing compounds into said composition. However, typically, the one
5 or more alkali metals and tungsten may be doped into the catalyst composition in the form of one or more compounds comprising both alkali metal(s) and tungsten therein. Suitable examples of such compounds include sodium tungstate and lithium tungstate.

10 During the oxidative coupling of methane according to the process of the present invention, the specific form of the manganese, one or more alkali metals, tungsten and any optional co-promoters and/or additional metal-containing dopants in the catalyst composition may be unknown.

15 Thus, when sodium, tungsten and manganese are present in combination in the catalyst composition, they may present as Na_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$ and/or Mn_2WO_4 and Mn_2O_3 .

During the preparation of the afore-mentioned preferred catalyst composition, the specific form in which the
20 manganese-containing dopant, the alkali metal-containing dopants, the tungsten-containing dopant and any optional co-promoters and/or additional metal-containing dopants are provided is not limited, and may include any of the wide variety of forms known.

25 For example, a manganese-containing dopant, an alkali metal-containing dopant, a tungsten-containing dopant and an optional co-promoter and/or additional metal-containing dopant may suitably be provided as ions (e.g., cation, anion, oxyanion, etc.), or as compounds (e.g., alkali metal
30 salts, salts of a further co-promoter, etc.).

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Generally, suitable compounds are those which can be solubilized in an appropriate solvent, such as a water-containing solvent.

As will be appreciated by persons skilled in the art,
5 while specific forms of the afore-mentioned metal-containing dopants may be provided during catalyst preparation, it is possible that during the conditions of preparation of the catalyst composition and/or during use in oxidative coupling of methane, the particular forms initially present may be
10 converted to other forms. Furthermore, in many instances, analytical techniques may not be sufficient to precisely identify the forms that are present. Accordingly, the afore-mentioned disclosure is not intended to be limited by the exact form of the manganese-containing dopant, the alkali
15 metal-containing dopants, the tungsten-containing dopant and/or any optional co-promoters and/or additional metal-containing dopants that may ultimately exist on the catalyst composition during use.

Additionally, it should be understood that while a
20 particular compound may be used during catalyst preparation (e.g., in an impregnation solution), it is possible that the counter ion added during catalyst preparation may not be present in the finished catalyst composition.

As previously discussed, the specific form in which the
25 one or more alkali metals is provided is generally not limited, and may include any of the wide variety of forms known. For example, the one or more alkali metal-containing dopants may be provided as ions (e.g., cation), or as alkali metal compounds.

30 Examples of suitable alkali metal compounds include, but are not limited to, alkali metal salts and oxidic compounds

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of the alkali metals, such as the nitrates, nitrites, carbonates, bicarbonates, oxalates, carboxylic acid salts, hydroxides, halides, oxyhalides, borates, sulfates, sulfites, bisulfates, acetates, tartrates, lactates, oxides, peroxides, and iso-propoxides, etc.

As previously mentioned, the alkali metal-containing dopant may comprise a combination of two or more alkali metal dopants. Non-limiting examples include combinations of lithium and sodium, lithium and potassium, lithium and rubidium, lithium and cesium, sodium and potassium, sodium and rubidium, sodium and cesium, potassium and rubidium, potassium and cesium and rubidium and cesium.

Optionally, the preferred catalyst compositions for use in the process of the present invention may further comprise one or more co-promoters and/or additional metal-containing dopants.

Examples of co-promoters and metal-containing dopants that may be conveniently used therein include lanthanum, cerium, niobium and tin.

The catalyst composition may comprise said optional co-promoters and/or metal-containing dopants in a total amount of in the range of from 0.1 to 5 % by weight, relative to the total weight of the catalyst composition.

Detailed Description of the Figures

Figure 1 shows the selectivity of CH_4 conversion to C_{2+} products as a function of OCM reaction runtime for a catalyst bed with $\text{L/D} = 1.6$ (closed circles), $\text{L/D} = 3.2$ (open circles) and $\text{L/D} = 15$ (triangles), all comprising 200-300 μm spherical 2 wt% Mn/2 wt% $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst particles. Also provided on the right axis are the reactor temperature

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profiles as measured in the heating element adjacent to the entry of the feed gas to the catalyst bed, for catalyst beds with $L/D = 1.6$ (dashed line), $L/D = 3.2$ (solid line) and $L/D = 15$ (dotted line).

5 Figure 2 shows CH_4 conversion as a function of reactor temperature for a catalyst bed with $L/D = 1.5$ (sample F) upon heating until ignition (closed circles) and subsequent decrease of reactor temperature at a rate of 10°C/hr (open circles).

10

The invention is further illustrated by the following Examples.

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EXAMPLES

Effect of L/D ratio of catalyst bed:

5 Fixed bed OCM experiments have been performed to compare the performance at similar pressure, gas hourly space velocity (GHSV) and catalyst loading (weight) of small (200-300 microns) and large particles (3500-4000 microns) of a 2% Mn/2% Na₂WO₄/SiO₂ catalyst in fixed catalyst beds having
10 different L/D ratios.

Catalyst preparation

Small Catalyst Particles (2 wt% Mn/2 wt% Na₂WO₄/SiO₂)

A 300 gram batch of catalyst particles comprising 2% Mn/2% Na₂WO₄ supported by silica spheres (B.E.T. surface area 111 m²/g, water pore volume 1.23 mL/g) was made by incipient wetness impregnation. Manganese nitrate tetrahydrate and sodium tungstate dihydrate precursors were weighed to
15 achieve a target composition of 2wt%Mn and 2wt% Na₂WO₄. Ammonium oxalate monohydrate was dissolved in 350 mL demineralized water in a 2L glass vessel (2.77:1 ammonium oxalate vs. tungsten molar ratio). Sodium tungstate was added to the solution and stirred until dissolved. Citric acid monohydrate (1.23:1 citric acid vs. tungsten molar
20 ratio) was added to the solution. Manganese nitrate was added upon which precipitates were formed. 65% nitric acid was added drop wise to the mixture until the precipitates dissolved and the solution became clear orange. The solution was added to the silica carrier material (CARiACT 75-500 µm
25 spherical silica support, purchased from Fuji Silysia),
30 rolled for 17 hours, and subsequently transferred to a glass

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bowl for blow drying with air at 60 °C for 7 hours, until the mass became yellow. Thereafter the composition was transferred to a static oven (air atmosphere) for drying and calcination. The heating program was as follows: 2 °C/min to 120 °C, dwell 4 hours, 4.2 °C/min to 500°C, dwell for 6 hours, 2.9 °C/min to 850 °C, dwell for 8 hours, cool to room temperature. The resulting catalyst particles were sieved, and the 212-300 µm size fraction (herein referred to as "200-300 µm" particles) was used in this study. The frequency size distribution of the spherical catalyst particles was measured on a Horiba Laser Diffraction instrument. The particles had a mean particle size of 232 µm, with d_{10} = 165 µm, d_{50} = 225 µm, d_{90} = 312 µm.

Large Catalyst Particles (2 wt% Mn/2 wt% Na₂WO₄/SiO₂)

A 130 gram batch of catalyst particles comprising 2% Mn/2% Na₂WO₄ supported by silica spheres (B.E.T. surface area = 112 m²/g, water pore volume = 0.98 mL/g) was made by incipient wetness impregnation. The silica carrier material (CARIACT 1.70-4.00 mm spherical silica support, purchased from Fuji Silysia) was pre-dried at 300 °C for 2.5 hours. Manganese nitrate tetrahydrate and sodium tungstate dihydrate precursors were weighed to achieve a target composition of 2wt% Mn and 2 wt% Na₂WO₄. Ammonium oxalate monohydrate was dissolved in 120 mL demineralized water in a 500 mL glass vessel (6.35:1 ammonium oxalate vs. tungsten molar ratio). Sodium tungstate was added to the solution and stirred until dissolved. Manganese nitrate was added upon which precipitates were formed. 65% nitric acid was added drop wise to the mixture until the precipitates dissolved and the solution became clear orange. The solution was added to the

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silica carrier, rolled for 18 hours, and subsequently transferred to a glass bowl for blow drying with air at 60 °C for 4 hours. Thereafter the composition was transferred to a static oven (air atmosphere) for drying and
5 calcination. The heating program was as follows: 2 °C/min to 120 °C, dwell 4 hours, 4.2 °C/min to 500 °C, dwell for 6 hours, 2.9 °C/min to 850°C, dwell for 8 hours, cool to room temperature. The resulting catalyst particles were sieved, and the 3500-4000 µm size fraction (herein referred to as
10 "3500-4000 µm" particles) was used in this study. The frequency size distribution of the spherical catalyst particles was measured on a Retsch Camsizer instrument. The particles had a mean particle size of 3.51 mm, with $d_{10} = 3.3$ mm, $d_{50} = 3.5$ mm, $d_{90} = 3.8$ mm.

Performance Testing

General procedure

Catalyst particles were loaded in a tubular quartz reactor
20 equipped with a six-zone tubular furnace providing an isothermal temperature profile exceeding the catalyst bed length, wherein the catalyst composition was situated at the top part of the isothermal temperature profile of the reactor. Typically, the catalyst bed length was in the range
25 of 3-15 cm. Immediately above and below the catalyst bed was a thin layer of quartz wool. The remainder of the reactor volume above and below the catalyst composition was filled up with solid quartz tubes having an outer diameter 2 mm smaller than the inner diameter of the tubular reactor.
30 Thermocouples were used for measuring the temperature of at least the feed gas entering the reactor, at the top of the

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reactor, and in the furnace adjacent to the reactor wall at the height corresponding to the entry of the catalyst bed.

A reactor feed comprising a mixture of methane, oxygen and nitrogen (4:1:4 molar ratio) having an initial
5 temperature of 100 °C was passed upflow over the catalyst bed being tested at a GHSV in the range of about 4000-7000 h⁻¹ and at a pressure in the range of 0.13-0.19 MPa (1.3-1.9 bara).

The temperature of the hot zone of the furnace as
10 measured adjacent to the entry of the catalyst bed, was gradually increased from about 400 °C until catalyst ignition was observed (as measured by oxygen conversion approaching 100% using gas chromatography [GC]). Conversion of methane and oxygen and product composition was, after
15 condensation of the water vapour in a separator, measured with an on-line GC (Thermoscientific GC, Breda) equipped with three TCD detectors and an FID detector for quantitative analyses of oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, C₃, C₄ and C₅
20 hydrocarbons.

The total off-gas flow of the micro flow unit was determined by the amount of nitrogen (in Nl/hr) in the reactor feed and in the off gas (determined from the results of the on-line GC analyses). From this total off-gas flow,
25 the individual component flows were calculated in Nl/hr. From these individual component flows, the total carbon balance was calculated, which in most experiments was between 98 and 102 %C. Besides the carbon balance, oxygen and methane conversions as well as C₂₊ selectivity and yields
30 were calculated. The results are summarized in Table 1.

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Examples

OCM performance was tested as described above for catalyst beds comprising large catalyst particles (3500-4000 micron) with L/D 5.5, 2.8 and 1.5 (Samples A, B and C) and catalyst
5 beds comprising small catalyst particles (200-300 micron) with L/D 15, 3.2, and 1.6 (Samples D, E and F). In these tests, 1-17 hrs after catalyst ignition the furnace hot zone temperature was decreased stepwise (10-20 °C steps) until oxygen conversion was zero. In Examples B, D, E and F, the
10 gas flow rate was subsequently increased and the temperature was increased until the catalyst was reignited.

Table 1.

Ex.	Outlet pressure (pressure drop over reactor) [bara]	Cat. Loading [g]	Cat. size [um]	GHSV [h ⁻¹]	Gas flow [NL/h]	L/D	First ignition temp.; Second ignition temp. [°C]	C ₂₊ Selectivity [%]	CO selectivity [%]
A	1.5 (0.18)	1.7	3500–4000	5625	24.3	5.5	710 (670); n.d.	58	11.6
B	1.6 (0.2)	7.5	3500–4000	4638 (11019)	80.1; 190.3	2.8	680 (550); 726	59	21.2
C	1.45 (0.15)	3.8	3500–4000	4251	40.1	1.5	670 (560); n.d.	60	17.8
D	1.9 (0.6)	4.8	200–300	6802 (16161)	80.1; 190.3	15	671 (620); 710	36**	42.8
E	1.3 (0.4)	7.5	200–300	4049 (9619)	80.1; 190.3	3.2	650 (540); 730	50	29.6
F	1.3 (0.2)	3.8	200–300	4114 (8228)	40.1, 80.1	1.6	650 (510); 670	58	23.3

** No stable selectivity reached

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Discussion

In industrial OCM processes, it is highly desirable to employ catalyst and reactor designs for which high C₂₊ selectivities and/or yields are obtained in an effective and economically attractive manner.

It is apparent from Table 1 and Figure 1 that after ignition and subsequent decrease of the reactor temperature, conversion and/or selectivity of the OCM reaction to C₂₊ products is improved (and more stable) for catalyst beds with smaller L/D ratios. It is further apparent from Table 1 and Figure 2 that after catalyst ignition, the reactor temperature can be decreased to substantially lower temperatures while maintaining catalytic conversion and selectivity, and that this effect is most pronounced for the catalyst beds with smaller L/D ratios.

These data also show that after extinction, for the catalyst bed having smaller L/D ratios, reignition of the catalyst requires relatively low temperatures.

Generally, the data show a lower pressure drop across the catalyst bed with smaller L/D ratio than for the catalyst bed with larger L/D ratio, allowing operation at lower average pressure.

CLAIMS

1. A process for the oxidative coupling of methane to one or more C₂₊ hydrocarbons, wherein said process comprises
5 contacting in a fixed-bed reactor a catalyst bed comprising a catalyst composition comprising manganese, one or more alkali metals and tungsten on a silica carrier, with a reactor feed comprising methane and oxygen under oxidative methane coupling (OCM)
10 conditions,
wherein the ratio L/D of catalyst bed length L to catalyst bed diameter D is smaller than 10, and
wherein the process comprises heating the reactor to a first reactor temperature T₁ that is sufficient to
15 ignite the catalyst composition, and
subsequently reducing the reactor temperature to a second temperature T₂ that is sufficient to maintain catalytic activity of the catalyst composition.
- 20 2. Process according to claim 1, wherein the ratio L/D of catalyst bed length L to catalyst bed diameter D is smaller than 5, preferably smaller than 3, more preferably smaller than 2, even more preferably smaller than 1, most preferably smaller than 0.5
- 25 3. Process according to any of the preceding claims, wherein after catalyst ignition, the reactor temperature is reduced to a second temperature T₂ that is sufficient to maintain catalytic activity of the catalyst
30 composition,
by decreasing the amount of external heat supplied to

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the catalyst bed,

by decreasing the temperature of the feed gas stream entering the reactor,

or by a combination thereof.

5

4. Process according to any of the preceding claims, wherein the second temperature T_2 is at least 20 °C lower, more preferably at least 40 °C lower, even more preferably at least 60 °C lower, even more preferably at least 80 °C lower, most preferably at least 100 °C lower than the first temperature T_1 .

10

5. Process according to any of the preceding claims, wherein T_1 is at least 500 °C and wherein T_1 is at most 800 °C.

15

6. Process according to any of the preceding claims, wherein T_2 is at most 700 °C.

20

7. Process according to any of the preceding claims, wherein the inlet temperature of the feed gas stream after catalyst ignition is at most 50°C.

25

8. Process according to any of the preceding claims, wherein the catalyst composition is in the form of particles and wherein said particles have a number-average particle size d_1 in at least one dimension of at least 1 mm, preferably at least 2 mm, more preferably at least 3 mm.

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9. Process according to claim 8, wherein the particles of the catalyst composition are spherical particles comprising manganese, one or more alkali metals and tungsten on a spherical silica carrier, wherein the spherical silica carrier has a diameter of at least 1 mm, preferably at least 2 mm, more preferably at least 3 mm.
10. Process according to claim 8 or 9, wherein the particles of the catalyst composition are core-shell particles comprising a core comprising a carrier material and a shell comprising manganese, one or more alkali metals and tungsten.
11. Process according to any of claims 8-10, wherein the particles of the catalyst composition are obtained by incipient wetness impregnation (IWI) of a porous silica carrier with one or more solutions comprising manganese, one or more alkali metals and tungsten.

FIG. 1

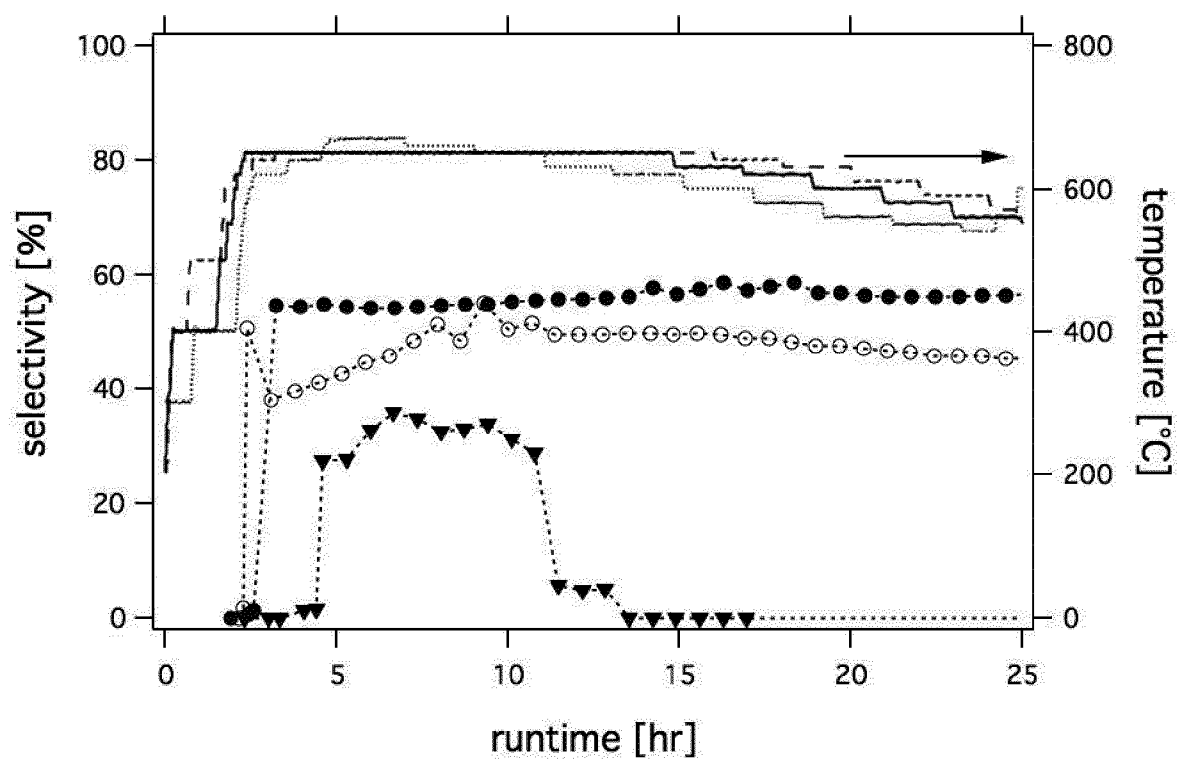
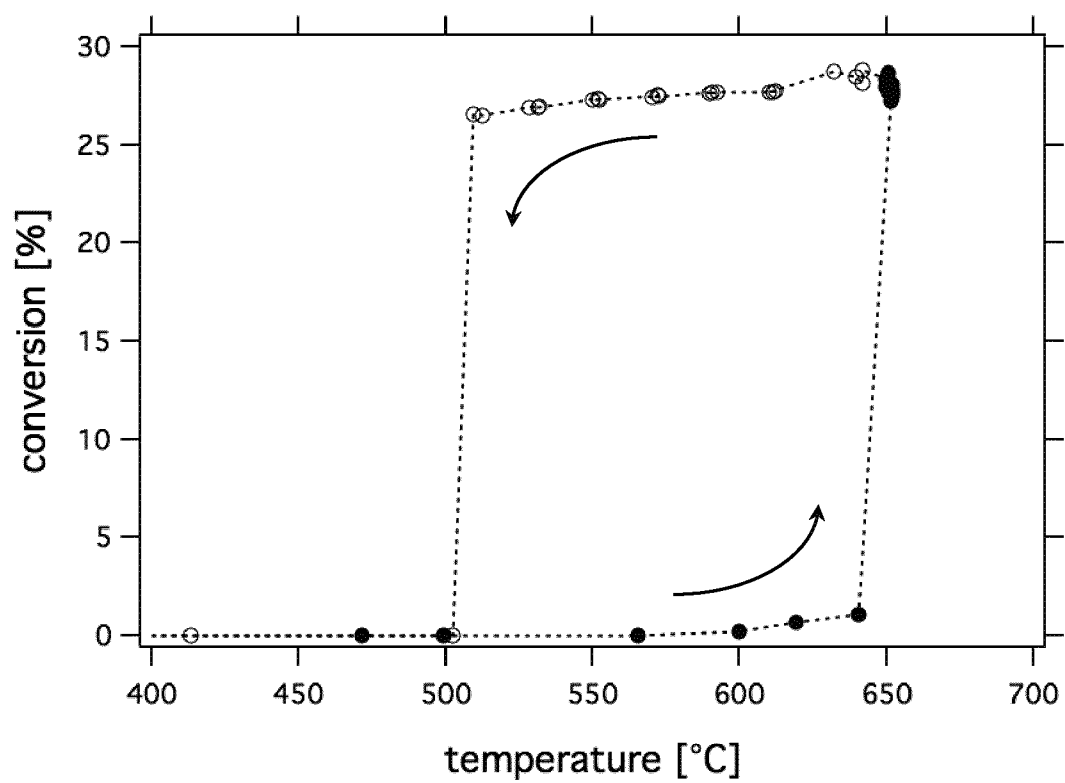


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/073697

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/84 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.
A	WO 2017/009449 A1 (SHELL INT RESEARCH [NL]; SHELL OIL CO [US]) 19 January 2017 (2017-01-19) the whole document -----	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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Date of the actual completion of the international search

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Date of mailing of the international search report

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/073697

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 2017009449	A1	19-01-2017	CN 107848906 A	27-03-2018
			US 2018208525 A1	26-07-2018
			WO 2017009449 A1	19-01-2017
