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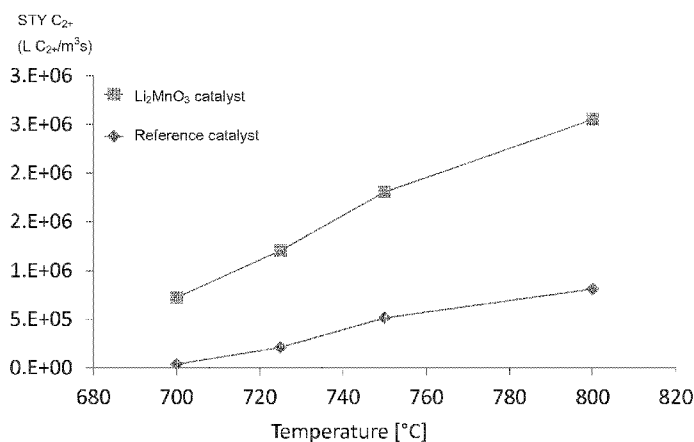
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(54) Title: CATALYST AND PROCESS FOR THE OXIDATIVE COUPLING OF METHANE

Figure 4



(57) Abstract: The invention relates to a catalyst composition comprising a ternary oxide compound, said ternary oxide compound comprising one or more alkali metals and manganese and having been prepared by reacting one or more alkali metal compounds selected from alkali metal hydroxide, alkali metal carbonate and alkali metal oxide with one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate; and a process for the oxidative coupling of methane using said catalyst composition.

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CATALYST AND PROCESS FOR THE OXIDATIVE COUPLING OF
METHANE

Field of the Invention

The present invention relates to a catalyst and a process for the oxidative coupling of methane.

Background of the Invention

5 Methane is a valuable resource which is used not only as a fuel, but is also used in the synthesis of chemical compounds such as higher hydrocarbons.

The conversion of methane to other chemical compounds can take place via indirect conversion wherein methane is reformed to synthesis gas (hydrogen and carbon
10 monoxide), followed by reaction of the synthesis gas in a Fischer-Tropsch process. However, such indirect conversion is costly and consumes a lot of energy.

Consequently, it is desirable for industry to be able to convert methane directly to other chemical
15 compounds without requiring the formation of intermediates such as synthesis gas. To this end, there has been increasing focus in recent years on the development of processes for the oxidative coupling of methane (OCM).
20

The oxidative coupling of methane converts methane into saturated and unsaturated, non-aromatic hydrocarbons having 2 or more carbon atoms, including ethylene. In this process, a gas stream comprising methane is
25 contacted with an OCM catalyst and with an oxidant, such as oxygen or air. In such a process, two methane molecules are first coupled into one ethane molecule, which is then dehydrogenated into ethylene. Said ethane and ethylene may further react into saturated and

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unsaturated hydrocarbons having 3 or more carbon atoms, including propane, propylene, butane, butene, etc. Therefore,—usually, the gas stream leaving an OCM process contains a mixture of water, hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, propane, propylene, butane, butene and saturated and unsaturated hydrocarbons having 5 or more carbon atoms.

In general, the conversion that can be achieved in an OCM process is relatively low. Besides, at a higher conversion, the selectivity decreases so that it is generally desired to keep the conversion low. As a result, a relatively large amount of unconverted methane leaves the OCM process. The proportion of unconverted methane in the OCM product gas stream may be as high as 50 to 60 mol% based on the total molar amount of the gas stream. This unconverted methane has to be recovered from the desired products, such as ethylene and other saturated and unsaturated hydrocarbons having 2 or more carbon atoms, which are also present in such gas streams.

A further difficulty with OCM processes is that a competing reaction that takes place is the oxidation of methane to carbon dioxide and water.

In view of the afore-mentioned issues, there has been a great deal of attention focussed on developing catalysts for use in OCM processes which are capable of increasing selectivity to C₂+ hydrocarbons at lower reaction temperatures.

In this regard, one of the best-performing catalysts that has 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

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(2012) 53-61, Fuel 106 (2013) 851-857, US 2014/0080699 A1 and US 6596912 B1.

Work in the OCM field has focussed on further improving the performance of catalyst compositions in the oxidative coupling of methane, for example, by changing the dopants and carrier supports therein and modifying the way in which the catalyst compositions are prepared.

In ChemCatChem 2011, 3, 1935-1947, Zavyalova et al. conduct statistical analysis of past catalytic data on oxidative methane coupling for new insights into the composition of high-performance catalysts.

US 2013/0023709 A describes the high throughput screening of catalyst libraries for the oxidative coupling of methane and tests various catalysts including catalysts comprising sodium, manganese and tungsten on silica and zirconia carriers.

US 2014/0080699 A1 describes a specific method for the preparation of catalysts such as $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst which is said to provide an improved catalyst material.

US 4499322 A discloses catalyst compositions comprising (a) at least one reducible oxide of at least one metal selected from the group consisting of Mn, Sn, In, Ge, Pb, Sb and Bi; and (b) a promoting amount of at least one promoter selected from the group consisting of alkali metals and compounds thereof. In a preferred embodiment in US 4499322 A, the stability of said catalyst compositions is further enhanced by incorporating a stabilising amount of phosphorus therein. The support in said catalyst compositions may either be a conventional support material such as silica, alumina, titania or zirconia, or it may be the alkali promoter such as Na_2O or K_2O .

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Examples 4, 5 and Comparative Example B in US 4499322 A test certain unsupported bulk oxides in the conversion of methane. The unsupported bulk oxides which were tested as catalysts in said Examples were prepared by calcination of certain precursor materials.

Specifically, Example 4 tests a bulk oxide designated as "NaMn oxide" which comprises NaMnO_2 and NaO.7MnO_2 and which was made by calcining sodium permanganate in air at 800 °C for several hours; Example 5 tests a bulk oxide designated as "LiMn oxide" which was prepared from Li_2MnO_3 as precursor by calcining under similar conditions to those in Example 4; and Comparative Example B tests a bulk manganese oxide designated as "Mn oxide" which comprises Mn_2O_3 and which was prepared by calcining manganese acetate under similar conditions to those in Example 4.

The results in Table II of US 4499322 A demonstrate relatively low C2-7 selectivities. For example, at 800 °C, the "LiMn oxide" shows 44.6 C₂-C₇ selectivity at 25.7 % CH₄ conversion.

However, whilst US 4499322 A demonstrates some of its highest C2-7 selectivities in Examples 6, 7, 8 and 15 therein, the associated methane conversions are often low.

US 4,758,484 describes a positive-electrode material for a rechargeable battery prepared by heat treatment of a mixture of manganese dioxide and lithium salt in the temperature range of 300 °C-430 °C.

Similarly, US 2012/0321954 and US 2013/0171525 describe a positive-electrode material for a rechargeable battery prepared by a molten salt method.

It is highly desirable in the OCM field to develop further catalysts for the oxidative coupling of methane

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which not only exhibit the selectivity benefits of catalysts comprising manganese, tungsten and sodium on a silica carrier, but which also show other improvements in performance, for example, with improved performance at lower reactor temperatures.

Summary of the Invention

The present invention has surprisingly found that certain catalyst compositions display advantageous performance in the oxidative coupling of methane.

Accordingly, in one aspect of the present invention there is provided a catalyst composition comprising a ternary oxide compound, said ternary oxide compound comprising one or more alkali metals and manganese and having been prepared by reacting one or more alkali metal compounds selected from alkali metal hydroxide, alkali metal carbonate and alkali oxide with one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate.

In another aspect of the present disclosure there is provided a method for preparing a ternary oxide compound comprising one or more alkali metals and manganese, said method comprising

i. providing a mixture of

- one or more alkali metal compounds selected from alkali metal hydroxide, alkali metal carbonate and alkali oxide, and
- one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate

ii. calcining the mixture in air at a temperature in the range of from 700 to 1000 °C.

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In a further aspect of the present invention, there is provided a process for the oxidative coupling of methane comprising converting methane to one or more C₂+ hydrocarbons, wherein said process comprises contacting a reactor feed comprising methane and oxygen with the afore-mentioned catalyst composition.

Brief Description of the Drawings

Figure 1 is a schematic diagram showing a typical reactor set-up for oxidative coupling of methane.

Figures 2 to 4 show the results obtained for the various catalysts tested.

Figure 5 shows an X-ray diffraction (XRD) pattern of a Li₂MnO₃ catalyst composition according to the present disclosure.

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Detailed Description of the Invention

To facilitate an understanding of the present invention, it is useful to define certain terms relating to the oxidative coupling of methane and the associated catalyst performance.

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

"Cx selectivity" refers to the percentage of converted reactants that went to product(s) having carbon number x and "Cx+ selectivity" refers to the percentage of converted reactants that went to the specified product(s) having a carbon number x or more. Thus, "C2 selectivity" refers to the percentage of converted methane that formed ethane and ethylene. Similarly, "C2+ selectivity" means the percentage of converted methane that formed compounds having carbon numbers of 2 or more.

"Cx yield" is used to define the percentage of products obtained with carbon number x relative to the theoretical maximum product obtainable. The Cx 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. "C2 yield" refers to the total combined yield of ethane and ethylene. The Cx yield may be calculated by multiplying the methane conversion by the Cx selectivity.

"Space time yield Cx" refers to the volume of products having carbon number x formed per volume of the reactor and time.

As used herein in the context of catalyst dopants, "weight percent" refers to the ratio of the total weight of the carrier, the metal-containing dopant or the metal in the dopant to the total weight of the catalyst composition the catalyst.

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Percentages of metals from the metal-containing dopants in the catalyst composition may be determined by XRF, 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-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, carboxylates, carbonates, bicarbonates, oxyhalides, etc. as well as surface species wherein the element in question is bound directly or

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indirectly to an oxygen either in the substrate or the surface.

The one or more alkali metals present in the catalyst composition of the present invention are preferably selected from lithium, sodium and potassium.

That is to say, when the alkali metal in the catalyst composition is lithium, then said catalyst composition is prepared by reacting one or more lithium compounds selected from lithium hydroxide, lithium carbonate and/or lithium oxide with one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate. Similarly, when the alkali metal in the catalyst composition is sodium, then said catalyst composition is prepared by reacting one or more sodium compounds selected from sodium hydroxide, sodium carbonate and sodium oxide with one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate. Furthermore, when the alkali metal in the catalyst composition is potassium, then said catalyst composition is prepared by reacting one or more potassium compounds selected from potassium hydroxide, potassium carbonate and potassium oxide with one or more manganese compounds selected from manganese oxides, manganese hydroxide, and manganese acetate.

In a particularly preferred embodiment of the present invention, the alkali metal in the catalyst composition is lithium.

The catalyst composition of the present invention may be conveniently used without the need for a separate carrier. That is to say, in a preferred embodiment of the

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present invention, there is no separate carrier present in said composition.

However, in another embodiment of the present invention, the catalyst composition comprises a carrier. Said carrier is not particularly limited and any carrier commonly used in the formulation of catalyst compositions for use in the oxidative coupling of methane may be used. Examples of suitable carriers include silica, titania, zirconia and alumina.

When used in the catalyst composition of the present invention, the carrier may be present therein in an amount in the range of from 0 to 50 % by weight, relative to the total weight of the catalyst composition.

In one embodiment of the present invention, the ternary oxide compound has the composition $M^1M^2MnO_3$, wherein M^1 and M^2 are the same or different and are alkali metals selected from lithium, sodium and potassium.

In a preferred embodiment of the present invention, the ternary oxide compound has the composition M_2MnO_3 , wherein M is an alkali metal selected from lithium, sodium and potassium. Preferably, M is lithium.

The manganese compound that is used in the preparation of the ternary oxide compound is preferably selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate. More preferably, said manganese compound is manganese (III) oxide (Mn_2O_3).

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

In a preferred embodiment, the ternary oxide compound in the catalyst composition of the present

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invention is prepared by reacting one or more alkali metal compounds selected from alkali metal hydroxide, alkali metal carbonate and alkali metal oxide with one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate at a reaction temperature in the range of from 700 to 1000 °C. Typically, there is provided a mixture of one or more alkali metal compounds selected from alkali metal hydroxide, alkali metal carbonate and alkali oxide, and one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate. Preferably, the mixture is a slurry comprising a suitable solvent, preferably an organic solvent, such as acetone, methanol, or ethanol.

In one embodiment, the mixture or slurry is then calcined in air at a temperature in the range of from 700 to 1000 °C, in order to obtain the ternary oxide compound for use as a catalyst as disclosed herein. Preferably, the calcination temperature is at least 720 °C, more preferably at least 730 °C, even more preferably at least 740 °C, most preferably at least 750 °C. Preferably, the calcination temperature is at most 900 °C, more preferably at most 850 °C, more preferably at most 800 °C.

In one embodiment, the catalyst composition comprises at least 50 wt%, preferably at least 60 wt%, more preferably at least 70 wt%, even more preferably at least 80 wt%, even more preferably at least 90 wt%, most preferably at least 95 wt%, based on total weight of the catalyst composition, of a ternary oxide compound as disclosed herein. In one embodiment, the catalyst composition consists essentially of a ternary oxide compound as disclosed herein.

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In one embodiment, the ternary oxide compound has a single phase crystalline structure. Typically, said ternary oxide compound has a monoclinic structure.

5 In a preferred embodiment, the ternary oxide compound is single-phase monoclinic Li_2MnO_3 .

Optionally, the catalyst composition of the present invention may further comprise one or more co-promoters and/or additional metal-containing dopants.

10 In the event that the catalyst composition of the present invention comprises a carrier in addition to the ternary oxide compound, then the catalyst composition may, in principle, be prepared by any suitable technique known in the art for supported catalyst compositions.

15 Such "supported" catalyst compositions may be prepared by methods such as adsorption, impregnation, precipitation, co-precipitation, granulation, spray drying, or dry mixing.

20 After preparation of the catalyst composition of the present invention, calcination may take place at a temperature in the range of from 700 to 1000 °C.

The process of the present invention comprises utilising the catalyst composition as hereinbefore described in a reactor suitable for the oxidative coupling of methane.

25 The reactor may be any suitable reactor, such as a fixed bed reactor with axial or radial flow and with inter-stage cooling or a fluidized bed reactor equipped with internal and external heat exchangers.

30 In one embodiment of the present invention, the catalyst composition may be packed along with an inert packing material, such as quartz, into a fixed bed reactor having an appropriate inner diameter and length.

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Optionally, the catalyst composition may be pretreated in the reactor to remove moisture and impurities at a temperature in the range of from 100 to 300 °C for about one hour in the presence of an inert gas such as nitrogen, helium or argon.

Various processes and 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 such processes in conjunction with the catalyst composition as hereinbefore described.

Suitable processes include those described in EP 0206042 A1, US 4443649 A, CA 2016675 A, US 6596912 B1, US 2013/0023709 A1, WO 2008/134484 A2 and WO 2013/106771 A2.

During the oxidative coupling of methane, a reactor feed comprising methane and oxygen is introduced into the reactor. Optionally, the reactor feed may further comprise one or more of a diluent gas, together with minor components of the methane feed (ethane, propane etc.) or the methane recycle stream (e.g. ethane, ethylene, propane, propylene, CO, CO₂, H₂, H₂O). The diluent represents the balance of the feed gas and is an inert gas. Examples of suitable inert gases are nitrogen, argon or helium.

As used herein, the term "reactor feed" is understood to refer to the totality of the gaseous stream at the inlet or inlets 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, etc.

In a preferred embodiment, the methane and oxygen added to the reactor as mixed feed, optionally comprising

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further components therein, at the same reactor inlet. However, in another embodiment of the present invention, the methane and oxygen may be added in separate feeds, optionally comprising further components therein, to the reactor at separate inlets.

Methane may be present in the reactor feed in a concentration of at least 35 mole-%, and most 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-%, and most preferably at most 85 mole-%, relative to the total reactor feed.

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

In addition to methane, the reactor feed further comprises oxygen, which may be provided either as pure oxygen or air. In an oxygen-based process, high-purity (at least 95 mole-%) oxygen or very high purity (at least 99.5 mole-%) oxygen is employed.

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 under the prevailing operating conditions. Often, in practice, the oxygen concentration in the reactor feed may be no greater than a pre-defined percentage (e.g., 95%, 90%, 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 may vary over a wide range, the oxygen concentration

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in the reactor feed is typically at least 7 mole-%, or at least 10 mole-%, relative to the total reactor feed. Similarly, the oxygen concentration of the reactor feed is typically at most 25 mole-%, or at most 20 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-%, and preferably in the range of from 10 to 20 mole-%, relative to the total reactor feed.

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.

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, and more preferably in the range of from 3/1 to 6/1.

The reactor feed optionally may further comprise a diluent gas, such as helium, argon, nitrogen or a combination thereof.

The order and manner in which the components of the reactor feed are combined prior to contacting the catalyst composition is not limited, and they may be combined simultaneously or sequentially. However, as will be 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 understood by one of skill in the art, the concentration of various feed components present in the

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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 the widest possible variations in the composition of the reactor feed during normal operation.

Figure 1 is a schematic representation showing a typical reactor and product separation set-up for the oxidative coupling of methane.

Feed gas comprising methane and oxygen (or air) is introduced into the OCM reactor 101, via lines 107 and 108, respectively. The methane may consist of fresh feed and recycled methane (derived from the separation stage of the process). The product mixture exiting the OCM reactor is passed to condensation vessel 102, where the majority of the water by-product of OCM is removed. The product from 102 is then sent to the separation section 103, wherein the desired C₂+ hydrocarbons are separated (stream 104), either as a mixed hydrocarbon stream or as separated streams of ethylene, ethane, propylene and other hydrocarbons. Unreacted methane separated from the OCM product mixture in 103 may optionally be recycled, as stream 106, which is combined with fresh feed stream 107, before entering the reactor. Undesired products of OCM, such as CO and CO₂, as well as N₂ in the case of OCM with air feed, are also separated from the product mixture in 103 and leave the process as stream 105. The separation section may also include a section for conversion of alkanes to olefins (e.g. ethane cracker).

The process of the present invention is not limited to any particular reactor or flow configurations, and those depicted in Figure 1 are merely exemplary. Furthermore, the sequence in which various feed

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components are introduced into the process and their respective points of introduction, as well as the flow connections, may be varied from that depicted in Figure 1.

5 In the process of the present invention, the reactor feed comprising methane and oxygen may be conveniently contacted with a catalyst composition as hereinbefore described in order to effect the conversion of methane to one or more C₂+ hydrocarbons at a reactor temperature in
10 the range of from 500 to 1000 °C. Preferably, said conversion is effected at a reactor temperature in the range of from 650 to 900 °C. In particular, it is preferred that the conversion is effected at a reactor temperature of less than 850 °C. More preferably, the
15 reactor temperature is preferably in the range of from 650 to 850 °C, even more preferably in the range of from 650 to 800 °C and most preferably in the range of from 700 to 775 °C.

 In a preferred embodiment of the present invention,
20 the conversion of methane to one or more C₂+ hydrocarbons is effected at a reactor pressure in the range of from 1 to 25 MPa. More preferably, said reactor pressure is in the range of from 2 to 10 MPa.

 The gas hourly space velocity (GHSV) in the process
25 of the present invention is the entering volumetric flow rate of the reactor feed divided by the catalyst bed volume at standard conditions. Preferably, said gas hourly space velocity is in the range of from 10000 to 300000 h⁻¹, and most preferably in the range of from
30 20000 to 70000 h⁻¹.

 In a preferred embodiment, the process of the present invention has a C₂+ hydrocarbon selectivity of greater than 40 %, and more preferably greater than 60 %.

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In a preferred embodiment, the process of the present invention results in an ethane:ethene weight ratio of less than 1.6, and more preferably less than 0.6.

5 Preferably, the afore-mentioned C2+ hydrocarbon selectivity, C2 hydrocarbon selectivity and ethane:ethene ratio values are determined at a reactor temperature of less than 850 °C, more preferably at a reactor temperature in the range of from 650 to 850 °C, even more
10 preferably at a reactor temperature in the range of from 650 to 800 °C and most preferably at a reactor temperature in the range of from 700 to 775 °C.

The invention is further illustrated by the following Examples.

15 Examples and Comparative Example
Catalyst Preparation Procedure

Li_2MnO_3 catalyst composition according to the present invention was prepared by conventional solid state reaction. 3.947 g of Mn_2O_3 was mixed with 4.197 g
20 of $\text{LiOH}\cdot\text{H}_2\text{O}$ in a mortar and pestle. The mixture was ground for 30 minutes. Acetone was added during the grinding to form a slurry. The final intimate mixture was transferred to an alumina boat or crucible. The calcination was carried out at 750 °C for 24 hours in air
25 inside a muffle furnace. During the calcination heating rate was 3 °C/minute and cooling rate was 2 °C/minute. The final product after calcination was brick red in colour and was ground before catalytic testing. Figure 5 displays an X-ray diffraction (XRD) pattern of the
30 catalyst composition, showing a monoclinic single phase of Li_2MnO_3 .

The reference catalyst used for comparison purposes in the testing was 2% Mn/2% $\text{Na}_2\text{WO}_4/\text{SiO}_2$ which is the best

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performing catalyst for oxidative coupling of methane (OCM) based on open literature publications.

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General Testing Procedure

Catalysts were tested in accordance with the following general testing procedure.

The active test was carried out in a quartz fixed-bed microreactor with an isothermal zone of 4 cm and internal diameter of 2 mm.

Typically, 50 g of the catalyst composition to be tested was loaded in the reactor filled with a solid quartz tube in rest space of the reactor to minimise the contribution from any gas-phase reactions.

The reagents of CH₄ (>99.9 %) and O₂ (99.9 %) were used without further purification. The reactor feed comprised methane and oxygen in a mole ratio of 4:1, with 5 mol. % nitrogen as inert gas.

The catalyst composition was evaluated at 700 °C, 725 °C, 750 °C and 800 °C, and 3.5 barg (350 kPa) pressure with a flow of 4.8 Nl/h.

The reaction products were then analysed with an on-line GC device equipped with a 2 TCD and 2 FID using different columns for the separation of CH₄, CO₂, C₂H_x, C₃H_x, C₄H_x, C₅H_x, O₂, N₂, CO.

The conversion, selectivities, yields and space time yields were all calculated for the products identified.

Results(I) Testing at 700 °CTable 1

Catalyst	XCH ₄ (%)	SC ₂ (%)	SC ₂₊ (%)	YC ₂ (%)	Y C ₂₊ (%)	STY C ₂₊ (L C ₂₊ /m ³ s)
Li ₂ MnO ₃ catalyst composition	15.9	26.6	28.0	4.3	4.5	722522.4
Reference catalyst	6.6	12.9	13.1	0.8	0.9	38762.7

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(II) Testing at 725 °CTable 2

Catalyst	XCH ₄ (%)	SC ₂ (%)	SC ₂₊ (%)	YC ₂ (%)	Y C ₂₊ (%)	STY C ₂₊ (L C ₂₊ /m ³ s)
Li ₂ MnO ₃ catalyst composition	18.5	37.5	40.6	6.9	7.5	1205915.4
Reference catalyst	14.6	30.4	32.2	4.4	4.7	211088.3

(III) Testing at 750 °CTable 3

Catalyst	XCH ₄ (%)	SC ₂ (%)	SC ₂₊ (%)	YC ₂ (%)	Y C ₂₊ (%)	STY C ₂₊ (L C ₂₊ /m ³ s)
Li ₂ MnO ₃ catalyst composition	22.7	44.6	49.4	10.1	11.2	1805473.6
Reference catalyst	23.0	44.7	49.7	10.3	11.4	513650.5

(IV) Testing at 800 °CTable 4

Catalyst	XCH ₄ (%)	SC ₂ (%)	SC ₂₊ (%)	YC ₂ (%)	Y C ₂₊ (%)	STY C ₂₊ (L C ₂₊ /m ³ s)
Li ₂ MnO ₃ catalyst composition	26.3	53.4	60.4	14.0	15.9	2550606.1
Reference catalyst	28.7	54.7	62.8	15.7	18.0	810941.2

Discussion

Tables 1-4 and Figures 2-4 summarize the results of the testing.

5

As seen from the results, the Li₂MnO₃ catalyst of the present invention displays advantageous activity for

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oxidative coupling of methane (OCM) at a lower temperature of 700 °C - showing 15.9 % methane conversion and 28% selectivity for C2+. Methane conversion and selectivity for C2+ are higher than the reference catalyst.

5

Also, at 800 °C - which a typical OCM test condition, the Li_2MnO_3 catalyst of the present invention displays very similar performance compared to reference catalyst - showing 26.3% methane conversion and 60.4% selectivity for C2+ under these test conditions.

10

As shown in Figure 4, the Li_2MnO_3 catalyst of the present invention shows remarkably higher space time yield (STY) compared to the reference catalyst.

C L A I M S

1. Method for preparing a ternary oxide compound comprising one or more alkali metals and manganese, said method comprising
 - i. providing a mixture of
 - 5 - one or more alkali metal compounds selected from alkali metal hydroxide, alkali metal carbonate and alkali oxide, and
 - one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate
 - 10 ii. calcining the mixture in air at a temperature in the range of from 700 to 1000 °C.
2. Method according to claim 1, wherein the mixture in step (i) is a slurry further comprising a solvent.
- 15 3. A catalyst composition comprising a ternary oxide compound, said ternary oxide compound comprising one or more alkali metals and manganese and having been prepared by reacting one or more alkali metal compounds selected from alkali metal hydroxide, alkali metal carbonate and alkali oxide with one or more manganese compounds selected from manganese oxides, manganese hydroxide, manganese acetate and manganese nitrate.
- 20 4. Catalyst composition according to Claim 3, comprising at least 50 wt%, based on total weight of the catalyst composition, of a ternary oxide compound obtainable by the method of Claim 1 or 2.
- 25 5. Catalyst composition according to Claim 3 or 4, wherein said ternary oxide compound has a single phase crystalline structure.
- 30 6. Catalyst composition according to Claim 5, wherein said ternary oxide compound has a monoclinic structure.

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7. Catalyst composition according to Claims 3 to 6,
wherein the ternary oxide compound has the composition
 $M^1M^2MnO_3$, wherein M^1 and M^2 are the same or different and
are alkali metals selected from lithium, sodium and
5 potassium.
8. Catalyst composition according to Claims 3 or 7,
wherein the ternary oxide compound has the composition
 M_2MnO_3 , wherein M is an alkali metal selected from
lithium, sodium and potassium.
- 10 9. Catalyst composition according to Claims 3 to 8,
wherein the alkali metal is lithium.
10. Catalyst composition according to Claims 3 to 9,
wherein the manganese compound is manganese (III) oxide
(Mn_2O_3).
- 15 11. Catalyst composition according to Claims 3 to 10,
wherein the ternary oxide compound is single-phase
monoclinic Li_2MnO_3 .
12. Catalyst composition according to Claims 3 to 11,
wherein said ternary oxide compound is not supported on a
20 carrier.
13. A process for the oxidative coupling of methane
comprising converting methane to one or more C2+
hydrocarbons, wherein said process comprises contacting a
reactor feed comprising methane and oxygen with a
25 catalyst composition according to Claims 3 to 12.
14. Process according to Claim 13, wherein the
conversion is carried out at a reactor temperature of
less than 850 °C.
15. Process according to Claim 14, wherein the
30 conversion is carried out at a reactor temperature in the
range of from 650 to 850 °C.

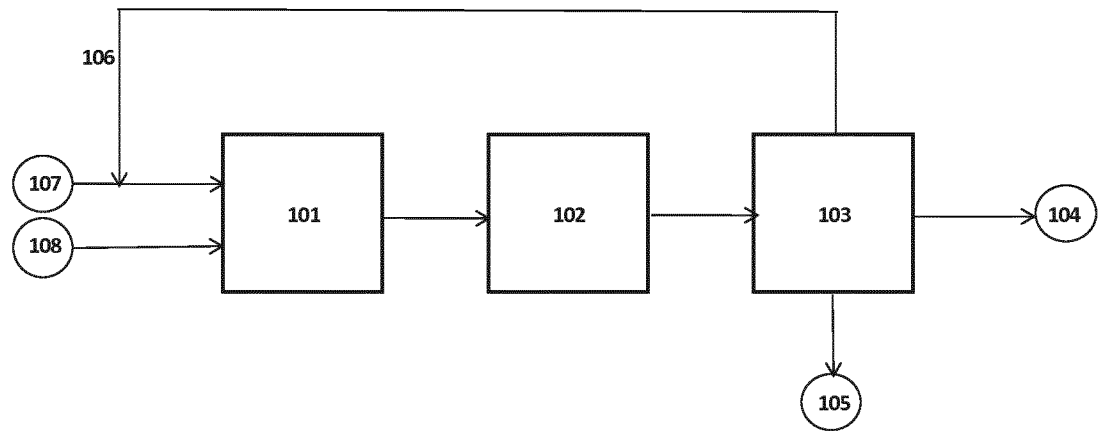
Figure 1

Figure 2

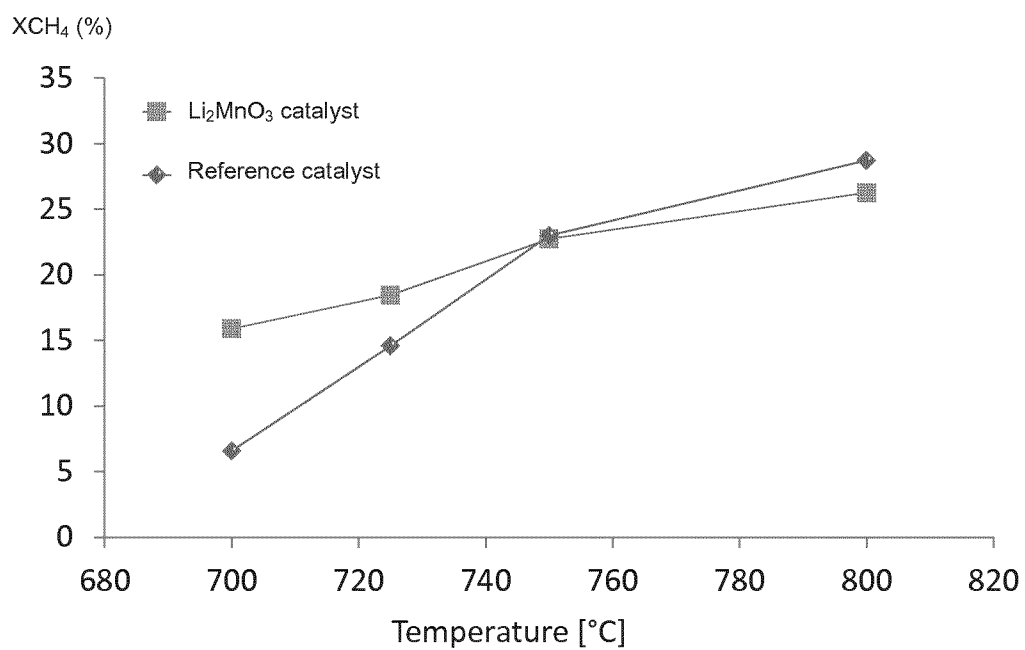


Figure 3

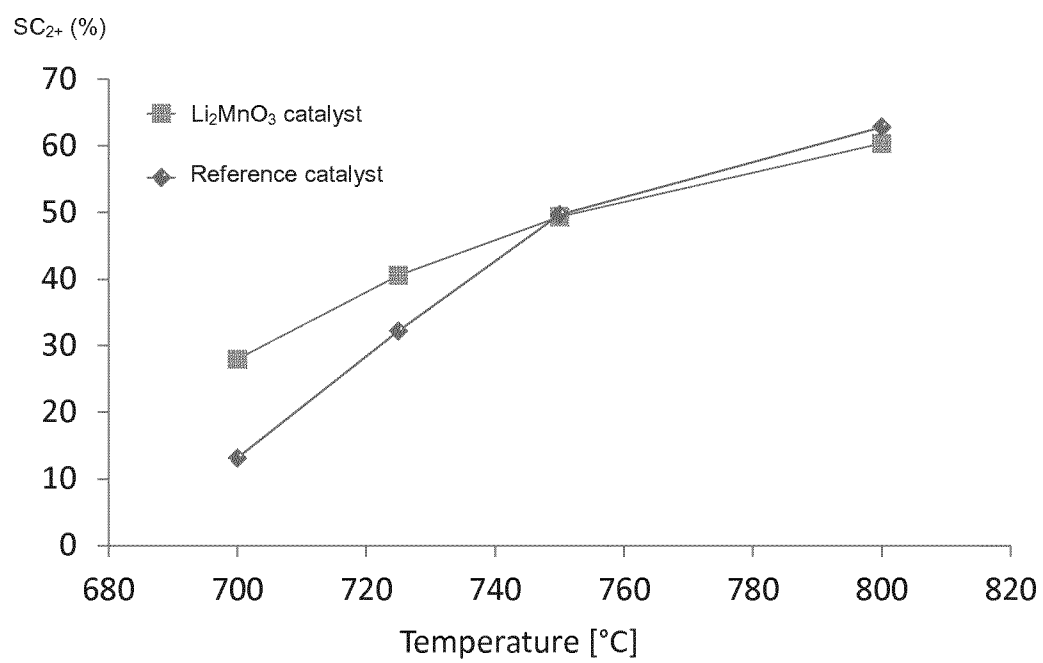


Figure 4

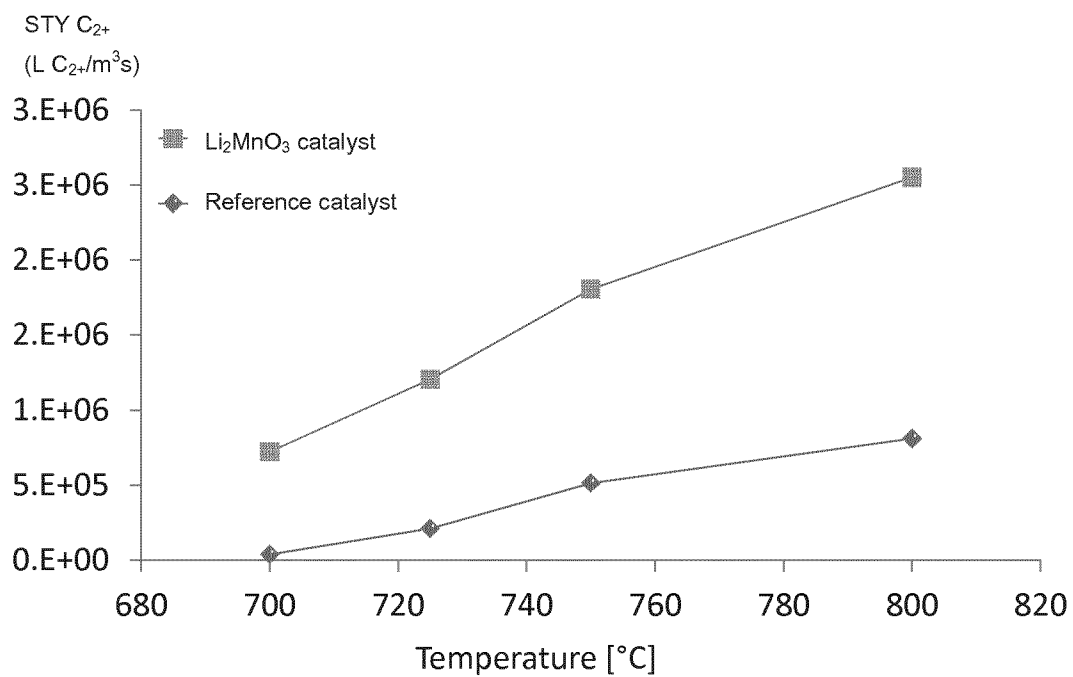
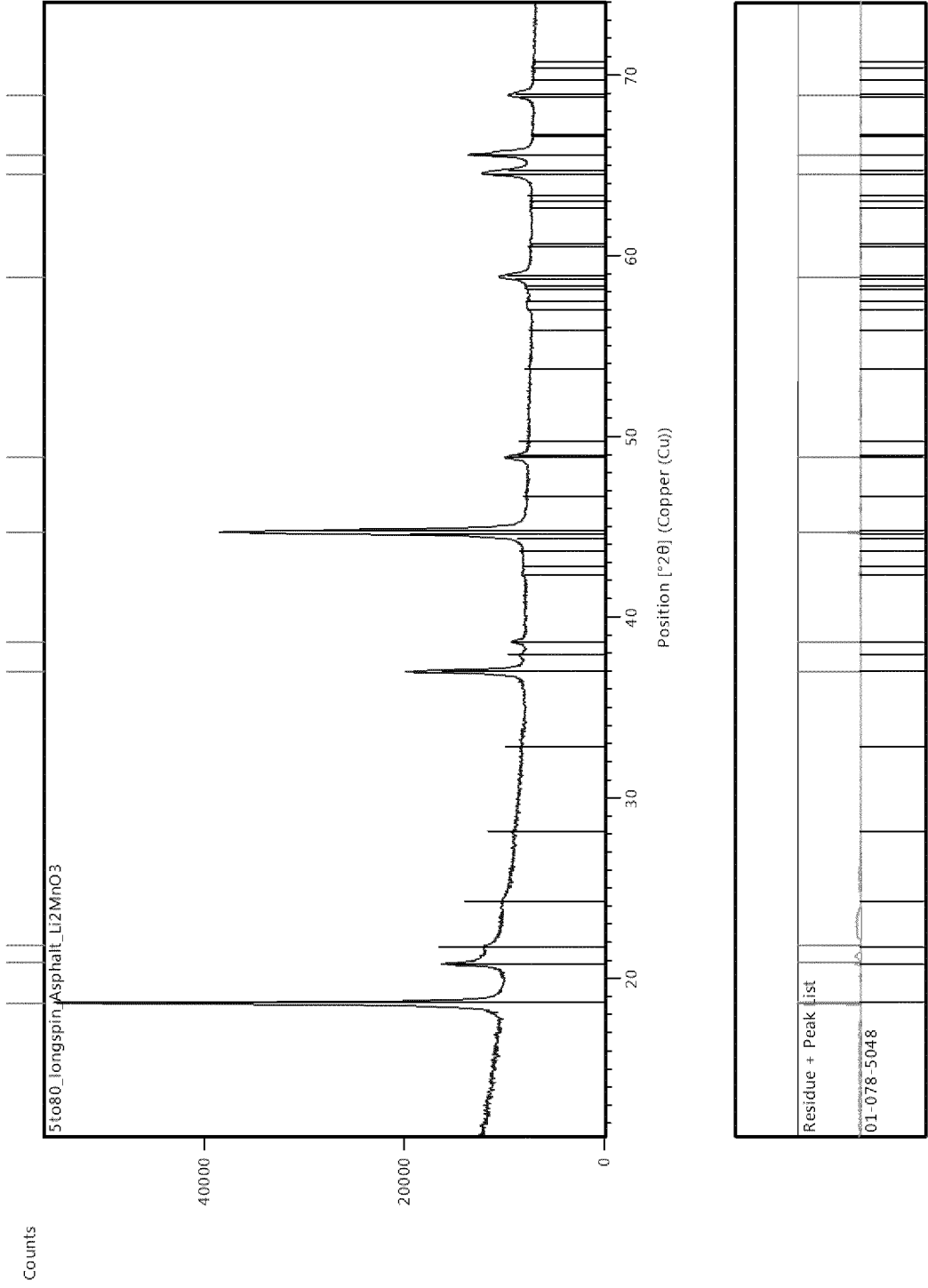


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/066386

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J37/04 B01J37/08 B01J23/34 C07C2/84
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)
B01J 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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2012/321954 A1 (ISOMURA RYOTA [JP] ET AL) 20 December 2012 (2012-12-20) paragraph [0077] ----- -/-	1-5,10, 12



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

16 September 2016

Date of mailing of the international search report

07/10/2016

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/066386

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

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International application No

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