(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 March 2019 (14.03.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/048404 A1

(51) International Patent Classification:
B01J 23/34 (2006.01) *B01J 37/08* (2006.01)
B01J 35/08 (2006.01) *C07C 1/00* (2006.01)
B01J 21/08 (2006.01) *C07C 11/04* (2006.01)
B01J 37/02 (2006.01)

(21) International Application Number:
PCT/EP2018/073680

(22) International Filing Date:
04 September 2018 (04.09.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
17189863.8 07 September 2017 (07.09.2017) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:
— *with international search report (Art. 21(3))*

WO 2019/048404 A1

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

(57) **Abstract:** The invention relates to a catalyst composition comprising spherical particles, wherein said spherical catalyst particles comprise a carrier material and a catalytically active material, wherein the carrier material comprises silica and wherein the catalytically active material comprises manganese, one or more alkali metals and tungsten, as well as to a process for preparing such particles; and to a process for the oxidative coupling of methane using said catalyst composition.

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

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 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 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 extensive academic and industrial research, as this 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 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), which is the preferred product. 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 (CO_2), or jointly "CO_x". Ethane and ethylene may further react into saturated and unsaturated hydrocarbons having 3 or more carbon atoms (C_{3+}), such as propane, propylene, butane and butene, etc.

A disadvantage of the OCM process is that it shows a characteristic performance of high selectivity towards C_2 products (ethane and ethylene) at relatively low conversion of methane, and vice versa. Moreover, the very high reaction exothermicity means that operation of OCM in fixed bed mode is challenging due to difficulties in removal of the large amount of heat generated, with increased chance of thermal runaway. While the latter problem could at least partially be solved by the use of fluidized catalyst beds, a particular drawback associated with performing OCM under fluidized bed conditions is the relatively low ratio of ethylene to ethane produced. In addition, especially under fluidized bed conditions, OCM catalysts have shown to suffer from poor physical strength leading to catalyst particle degradation and formation of fines. Moreover, agglomeration of catalyst particles has been demonstrated to defluidization and an increase in local catalyst temperature, resulting in further deterioration of catalyst performance.

It is therefore highly desirable to provide a catalyst and a process for the oxidative coupling of methane, wherein the catalyst shows improved stability, and wherein high C_2 - especially ethylene - selectivities and yields are obtained in an effective and economically attractive manner.

Summary of the Invention

The present inventors have found that catalyst compositions comprising spherical particles comprising a

silica carrier material and a catalytically active material comprising manganese, one or more alkali metals and tungsten, show advantageous C_{2+} selectivity and ethane to ethylene ($C_2/C_{2=}$) ratios and improved resistance against attrition and loss of catalytically active components under fluidized bed conditions.

Accordingly, in a first aspect of the present invention there is provided a catalyst composition comprising spherical particles, wherein said spherical catalyst particles comprise a carrier material and a catalytically active material, wherein the carrier material comprises silica and wherein the catalytically active material comprises manganese, one or more alkali metals and tungsten.

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 C_{2+} hydrocarbons, wherein said process comprises contacting a catalyst bed in a fluidized-bed reactor with a reactor feed comprising methane and oxygen under oxidative methane conversion (OCM) conditions,
wherein the catalyst bed comprises spherical particles of a catalyst composition as disclosed herein.

In a further aspect there is provided a method of preparing a catalyst composition, said process comprising

- providing a carrier material comprising spherical silica particles;
- optionally reducing the particle size distribution of the spherical silica particles;
- one or more impregnation steps, said impregnation steps comprising applying a solution of the catalytically active composition or one or more precursor thereof onto the

spherical silica particles, optionally followed by a drying step; and

- calcining the impregnated particles to obtain spherical catalyst particles.

As demonstrated herein, it was surprisingly found that under fluidized bed conditions, the use of spherical catalyst particles as disclosed herein results in a markedly higher selectivity towards C_{2+} products, higher yields of C_{2+} products and a lower ethane to ethylene ($C_2/C_{2=}$) ratio, as compared to using granular catalyst particles under the same conditions. It was further found that these spherical particles have a higher physical strength, thus preventing particle degradation and reducing the unwanted formation of fines during fluidization. In addition, it was found that the spherical particles display lower agglomeration behavior, resulting in preservation of fluidization and improved isothermal conditions within the fluidized bed.

Furthermore, when applied under fluidized bed conditions, the novel catalyst as disclosed herein exhibits higher stability than under fixed bed conditions, with reduced loss of catalytically active components with time on stream.

Brief description of the Figure.

Figure 1 shows optical micrographs of a granular catalyst composition A (top) and spherical catalyst composition B (bottom). Also shown are the hand-drawn perimeters of 10 randomly selected catalyst particles.

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).

"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 constituents, "weight percent" (wt%) refers to the ratio of the total weight of the carrier, the metal-containing component or the metal in the dopant to the total weight of the catalyst composition. 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 four hours at temperatures of at least 120, preferably at least 150 °C, more preferably at least 300 °C.

Percentages of metals from the metal-containing constituents in the catalyst composition may be determined by X-ray fluorescence (XRF), or by dissolution followed by

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), all techniques being known in the art. The metals content of the 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 adding up to 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 indirectly to an oxygen either in the substrate or the surface.

The catalyst composition according to the present disclosure comprises spherical particles. The term "spherical" as used herein is intended to distinguish the catalyst particles from irregularly shaped, "granular" catalyst particles commonly known in the art. Such "granular" catalyst particles are typically obtained by pulverizing, grinding, crushing or otherwise reducing the size of bulk particles by mechanical means; this also includes size reduction of a carrier material, in order to provide a "granular" carrier material, onto which a catalytically active material is applied. Thus, the term "spherical" as used herein should be understood to exclude catalyst particles obtained by a process involving a mechanical size reduction step, such as pulverizing, grinding or crushing the carrier material or the entire catalyst particle comprising carrier material and catalytically active material. However, the step of sieving of spherical particles for the mere purpose of influencing the size distribution is not to be excluded.

As a measure of the spherical shape of the catalyst particles of the present disclosure, the circularity C of the projected (two-dimensional) area of the individual particles may be used. Suitably, the circularity C may be determined from a planar (2D) image of the catalyst particles observed using, e.g., a light microscope or a scanning electron microscope (SEM) and suitable image processing tools to determine the circumferential length (perimeter), area, as well as (mean) diameter, etc. of the particles. Per ISO standard 9276-6 the circularity C of a particle is related to the ratio between the circumference of a perfect circle of the same area as the projected (i.e., 2D image) surface area

of the particle and the actual perimeter of the projected area to the equation

$$C = (4*\pi*A/P^2)^{0.5}$$

Herein, A is the area of the imaged particle and P is the perimeter of the imaged particle. By formula inspection it can be deduced that for a perfect sphere (projected as a perfect circle) C equals 1; for a regular octagon C equals 0.97; for a semicircle C equals 0.86, for a rectangle having a long side of 2 and a short side of 1 C equals 0.84. It can further be seen that C provides a measurement of both the particle shape and its roughness; i.e., a rougher ("more granular") particle will have a larger actual circumference as compared to the circumference of the corresponding perfect circle with the same area, resulting in a reduced value for C.

Ideally, the sample number, i.e., the number of particles on the image with which the average value of circularity C is calculated is as large as possible; typically, at least 10 particles randomly are selected to determine the average circularity C as defined above.

The number-averaged circularity C of the catalyst particles of the present invention is preferably at least 0.9, more preferably at least 0.93, even more preferably at least 0.95, yet even more preferably at least 0.97, most preferably at least 0.98.

It is preferred that the spherical catalyst particles have a narrow size distribution, as it is expected that this will have a beneficial effect on fluidization properties, as

well as on heat exchange and temperature control in the reactor.

Preferably, the catalyst particles have a particle size distribution 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.

The spherical catalyst particles typically have a diameter in the range of 50 to 2000 micron. Preferably, the spherical catalyst particles have a volume mean diameter in the range of 100 to 1000 micron, more preferably in the range of 200 to 800 micron, most preferably in the range of 300 to 600 micron. Preferably, at least 90 % of the catalyst particles have a diameter between 100 and 800 micron, more preferably between 100 and 400 micron. Preferably, at most 10 % of the catalyst particles have a diameter smaller than 120 micron. Preferably, at most 10 % of the catalyst particles have a diameter larger than 500 micron.

Typically, the catalyst particles of the present invention comprise manganese in an amount of in the range of from 1 to 10 % by weight, preferably in the range of from 1 to 5 % by weight, more preferably in the range of from 1.3 to 3 % by weight and most preferably in the range of from 1.7 to 2.5 % by weight, relative to the total weight of the catalyst composition.

In some embodiments of the present invention, manganese is present in the catalyst particles in the form of one or more manganese-containing dopants such as one or more manganese-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 particles comprise at least one reducible oxide of manganese. Such reducible oxides include compounds of the 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 MnO_2, Mn_2O_3, Mn_3O_4 and mixtures thereof.

The catalyst composition of the present invention comprises one or more (Group 1) alkali metals. Said alkali metals are typically one or more of lithium, sodium, potassium, rubidium and cesium. In some embodiments the alkali metals are sodium and/or lithium. In a preferred embodiment, the catalyst composition comprises sodium.

The one or more alkali metals are typically each present in an amount of in the range of from 0.1 to 2.0 % by weight, more preferably in the range of from 0.25 to 1.5 % by weight, and most preferably in the range of from 0.25 to 1.2 % by weight, relative to the total weight of the catalyst composition.

The catalyst composition of the present invention further comprises tungsten. Said tungsten may be present in a preferred amount of in the range of from 1 to 4.5 % by weight, more preferably in the range of from 1.5 to 3.5 % by weight, relative to the total weight of the catalyst composition.

In one embodiment, the catalyst composition comprises manganese, tungsten and sodium, generally denoted in the field as Mn/Na_2WO_4 or $Mn:Na_2WO_4$. In one embodiment, the catalyst composition comprises manganese in an amount of from 1 to 10 % by weight, preferably from 1 to 5 % by weight, more

preferably from 1.3 to 3 % by weight and most preferably in the range of from 1.7 to 2.5 % by weight and sodium tungstate (Na_2WO_4) in an amount of from 1 to 10 % by weight, preferably from 1 to 5 % by weight, more preferably from 1.3 to 3 % by weight and most preferably in the range of from 1.7 to 2.5 % by weight, all based on total weight of the catalyst composition.

In the preparation of the catalyst composition of the present invention, the one or more alkali metals and tungsten may be doped as separate metals and/or metal-containing compounds into said composition. In some embodiments, the one 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.

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

Thus, when sodium, tungsten and manganese are present in combination in the catalyst composition, they may be preferably present as one or more of Na_2WO_4, $Na_2W_2O_7$, Mn_2O_3 and $MnWO_4$. Preferably, the catalyst composition of the present invention comprises one or more of Na_2WO_4, $Na_2W_2O_7$, Mn_2O_3 and $MnWO_4$.

Catalyst particles for use in the process of the present invention may in principle be prepared by a variety of techniques known in the art for preparing catalyst compositions, such methods including impregnation, spray-drying, fluid bed coating or combinations thereof, on a

silica carrier material. Preferably, the silica carrier material comprises or consists of spherical particles, with the term "spherical" having the meaning as described above.

In one embodiment, the catalyst particles are prepared by one or more impregnation steps of spherical silica particles, said impregnation steps comprising applying a solution of the catalytically active composition or of one or more precursors thereof onto the spherical silica particles, optionally followed by a drying step, such as an intermediate drying step in case multiple solutions are applied consecutively.

A preferred method for providing catalyst particles according to the present disclosure is by incipient wetness impregnation (IWI) of porous silica particles with a solution of the catalytically active composition or one or more precursors thereof. Herein, typically the metal and alkali metal (or precursors thereof) are dissolved in one or more aqueous or organic solutions. Subsequently, the one or more solutions are added to the carrier particles either collectively or consecutively, while capillary action draws the solution into the pores of the carrier. Then, the particles may be dried and calcined in order to drive off the volatile components within the solution and to deposit the catalytically active materials on the catalyst surface.

Accordingly, in one aspect the present disclosure pertains to a process of preparing a catalyst composition as disclosed herein, said process comprising

- providing a carrier material comprising spherical silica particles;
- optionally reducing the particle size distribution of the spherical silica particles;

- one or more impregnation steps, said impregnation steps comprising applying a solution of the catalytically active composition or one or more precursor thereof onto the spherical silica particles, optionally followed by a drying step; and
- calcining the impregnated particles to obtain spherical catalyst particles.

Hence, according to this embodiment, in a first step a carrier material comprising spherical silica particles is provided. Preferably, the carrier material comprises at least 90 wt%, more preferably at least 95 wt% of spherical silica particles, or essentially consists of spherical silica particles. As for the eventual catalyst composition, it is preferred that the silica carrier particles have a number-average circularity C determined as described above, of at least 0.9, more preferably at least 0.93, even more preferably at least 0.95, yet even more preferably at least 0.97, most preferably at least 0.98. Examples of suitable spherical silica carrier particles are those commercially available under the trade name "CARiACT Q30 SiO_2" from Fuji Silysia Chemical Ltd.

It is preferred that the spherical silica carrier particles used for impregnation with the catalytically active material have a narrow size distribution, as it is expected that this will result in a narrow size distribution of the catalyst particles thus prepared.

Hence, in one embodiment the spherical silica carrier particles have a particle size distribution 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.

It was found by the inventors that impregnation and subsequent calcination of the silica carrier particles results in a moderate reduction of particle size of the resulting catalyst particles relative to the untreated carrier particle size, typically not exceeding 20 %. Accordingly, the spherical silica particles used as carrier particles prior to impregnation and calcination typically have a diameter that is up to 25% larger than the diameter of the eventual catalyst particles.

Preferably, the spherical silica carrier particles used in the preparation of the spherical catalyst particles as disclosed herein have a diameter in the range of 100 to 2000 micron, more preferably in the range of 100 to 1000 micron. Preferably, at least 90 % of the carrier particles have diameter between 200 and 800 micron. Preferably, at most 10 % of the carrier particles have a diameter smaller than 150 micron. Preferably, at most 10 % of the carrier particles have a diameter larger than 900 micron.

The carrier particles size and catalyst particle size and its specific distribution can be determined by various techniques known in the art, including Scanning Electron Microscopy, sieving analysis, optical absorption, laser diffraction, dynamic light scattering and (automated) image analysis, and combinations thereof. As used herein, the carrier particles size and catalyst particle size and size distribution are determined using laser diffraction governed by ISO standard 13320.

The process of the present invention further comprises utilizing the catalyst composition as hereinbefore described in a fluidized bed suitable for the oxidative coupling of

methane. Accordingly, in one aspect the invention relates to a process for the oxidative coupling of methane to one or more C_{2+} hydrocarbons, wherein said process comprises contacting a catalyst bed in a fluidized bed reactor with a reactor feed comprising methane and oxygen under oxidative methane conversion (OCM) conditions, wherein the catalyst bed comprises spherical particles of a catalyst composition as defined herein.

Various processes and fluidized-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 such processes in conjunction with the catalyst composition as hereinbefore described. Suitable processes include those described in US5866737, EP 0206042 A1, US 4443649 A, and WO 2008/134484 A2.

The reactor may be any suitable fluidized-bed reactor, and may be equipped with internal and external heat exchangers, or a combination thereof. The fluidization technique is well known in the art and the term fluidized bed as employed herein is understood to mean a mass of finely divided solid particles, in the instant case catalyst particles which have the appearance of a powder, wherein said mass is contacted with a rising stream of a gas (in the instant case comprising a methane-oxygen mixture), such that the catalyst particles are lifted and agitated. This results in the medium then having many properties and characteristics of normal fluids, such as the ability to free-flow under gravity. A discussion of fluidization and the variables and relationships therein can be found in Avidan, A. A., King, D. F., Knowlton, T. M. and Pell, M. 2000. Fluidization. Kirk-Othmer Encyclopedia of Chemical Technology.

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

As used herein, the term "reactor feed" is understood to 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, etc.

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 and H2O). The diluent represents the balance of the feed gas and is an inert gas. Examples of suitable inert gases are nitrogen, argon and helium.

In some embodiments, the methane and oxygen are added to the reactor as mixed feed, optionally comprising further components therein, at the same reactor inlet. However, in some embodiments 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 at 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 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 most 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 some embodiments, the methane:oxygen volume ratio in the process of the present invention is preferably 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 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 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.

Typically, the reactor temperature is in the range of from 500 to 1000 °C. Preferably, said conversion is effected

at a reactor temperature in the range of from 650 to 1000 °C, more preferably in the range of from 700 to 950 °C, even more preferably in the range of from 750 to 900 °C and most preferably in the range of from 800 to 850 °C.

In some embodiments of the present invention, the conversion of methane to one or more C_{2+} 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 1 to 10 MPa.

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 1,000 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).

The invention is further illustrated by the following Examples.

EXAMPLES

Example 1: Preparation of Catalyst A (comparative)[2% Mn/2% Na_2WO_4 on granular SiO_2]

Catalyst A was prepared by impregnation of granular silica carrier particles. The carrier material was commercial grade granular silica (PD 11044 ex. PQ Corporation, USA; particle size 100 - 700 µm).

1.6 kg of the dry granular silica particles was introduced into a rotating impregnation drum. 142.37 g $Mn(NO_3)_2.4H_2O$ was dissolved in 2 L of demineralized) water and 13.3 mL of concentrated nitric acid (HNO_3) (65 %) was added to this solution. Water was added to provide a total volume of 2960 ml. This solution was added into a rotating drum (120 rpm) containing the granular silica particles by a gear pump with a nozzle (nozzle distance 12cm; Schlick-nozzle type 5, 2000 rpm gear pump speed). After addition of the solution, the drum was allowed to rotate for an additional 30 min at 20 rpm. The sample was then indirectly dried with a Leister fan for 45 minutes to a drying grade of more than 99.5 % as determined by weighing.

34.97 g $Na_2WO_4.2H_2O$ was dissolved in 2 L of demineralized water, to which 44.55 g citric acid monohydrate was added. Water was added to provide a total volume of 2960 ml. This solution was added into the rotating drum (120 rpm) containing the afore-mentioned dried sample by a gear pump with a nozzle (nozzle distance 12 cm, Schlick nozzle type 5, 2000 rpm gear pump speed). After the addition, the drum was allowed to rotate for an additional 30 min at 20 rpm. The sample was then indirectly dried with a Leister fan for 45 minutes to a drying grade of 99.5 % (as determined by weighing) and subsequently calcined at 850°C for 5h while

applying a rate of increase of temperature of 3 °C/min. Impregnation and calcination was found to result in significant size reduction of the thus produced granular catalyst particles relative to the untreated granular carrier particles. A 300-425 micron sieving fraction of the thus prepared catalyst particles was used for further characterization and OCM performance testing.

Example 2: Preparation of Catalyst B [2% Mn/2% Na_2WO_4 on spherical SiO_2]

A catalyst composition comprising 2 wt% Mn and 2 wt% Na_2WO_4 on spherical silica carrier particles was prepared by an impregnation method identical to Example 1, except that the impregnation solution volumes were 1968 ml. The carrier material (CARiACT Q30 75-500 micron spherical silica particles) was purchased from Fuji Silysia Chemicals Ltd. No significant size reduction of the spherical particles after impregnation and annealing was observed. A 300-425 micron sieving fraction of these catalyst particles was used for further characterization and OCM performance testing.

Example 3: Preparation of Catalyst C (comparative) [2% Mn/5% Na_2WO_4 on granular SiO_2

Catalyst C was prepared by impregnation of granular silica carrier particles by a method identical to that described in Example 1, with the exception that in preparing the sodium tungstate solution 87.43 g $Na_2WO_4.2H_2O$ was dissolved in 2 L of demineralized water, to which 111.26 g citric acid monohydrate was added, and subsequently water was added to provide a total volume of 2960 ml. A 300-425 micron sieving fraction of the thus prepared catalyst particles was used for further characterization and OCM performance testing.

Example 4: Preparation of Catalyst D [2% Mn/5% Na_2WO_4 on spherical SiO_2

Catalyst D was prepared by impregnation of spherical silica carrier particles by a method identical to that described in Example 2, with the exception that in preparing the sodium tungstate solution 87.43 g $Na_2WO_4.2H_2O$ was dissolved in 2 L of demineralized water, to which 111.26 g citric acid monohydrate was added, and subsequently water was added to provide a total volume of 2960 ml. A 300-425 micron sieving fraction of the thus prepared catalyst particles was used for further characterization and OCM performance testing.

Example 5: Optical characterization of 2% Mn/2% Na_2WO_4/SiO_2 catalyst compositions

Figure 1 shows high-resolution photographs of fresh granular (Catalyst A; top) and spherical (Catalyst B; bottom) 2% Mn/2% Na_2WO_4/SiO_2 catalyst compositions, prepared using a Leica MZ125 high-performance stereomicroscope. Scale bars are included in both photographs. Also included are manually drawn outlines of 10 randomly selected particles per photograph. It can be seen that catalyst composition B (prepared using spherical silica carrier particles) predominantly contains highly spherical particles with smooth surfaces and having a narrow size distribution. Conversely, catalyst composition A (prepared using amorphous silica granules) contains irregularly shaped particles without discernible smooth areas.

Based on the dimensions of the drawn outlines of the particles, it is estimated that the circularity C of the particles of catalyst B is more than 0.9, while for the

particles of catalyst A the circularity C is estimated to be less than 0.75.

Example 6: Elemental analysis of catalyst compositions

Elemental analysis was performed by X-ray fluorescence (XRF) (analysis glass bead) of fresh catalyst compositions A–D and the respective spent versions after OCM fluidized bed testing with CH_4:O_2:N_2 ratio of 4:1:4, 80 hours operation in a 20 mm internal diameter (ID) quartz reactor. The results are presented in Table 1.

Table 1. Elemental analysis of catalyst compositions A–D before ("fresh") and after ("spent") testing in a fluidized bed OCM reactor.

Catalyst composition		Element			
		Mn	Na	W	Si
A	2% Mn/2% Na_2WO_4/ granular SiO_2; fresh	1.86±0.06	0.28±0.05	1.17±0.04	44.9±1.3
	2% Mn/2% Na_2WO_4/ granular SiO_2; spent	1.73±0.05	0.27±0.05	1.11±0.03	45.2±1.4
B	2% Mn/2% Na_2WO_4/ spherical SiO_2; fresh	1.90±0.06	0.31±0.05	1.22±0.04	44.9±1.3
	2% Mn/2% Na_2WO_4/ spherical SiO_2; spent	1.90±0.06	0.29±0.05	1.12±0.03	45.1±1.4
C	2% Mn/5% Na_2WO_4/ granular SiO_2; fresh	1.97±0.06	0.77±0.05	3.09±0.09	43.5±1.3
	2% Mn/5% Na_2WO_4/ granular SiO_2; spent	1.97±0.06	0.74±0.05	2.65±0.09	43.9±1.3
D	2% Mn/5% Na_2WO_4/ spherical SiO_2; fresh	1.94±0.06	0.77±0.05	3.09±0.09	43.4±1.3
	2% Mn/5% Na_2WO_4/ spherical SiO_2; spent	1.85±0.06	0.77±0.05	2.88±0.09	44.0±1.3

As can be seen in Table 2, the total loss of catalytically active material after 7 hours of operation under fluidized bed conditions is reduced for spherical catalyst particles as compared to the granular particles known in the prior art.

Example 5: Oxidative coupling of methane (OCM) performance under bubbling bed conditions in a 20 mm ID quartz reactor

Testing of the OCM catalytic performance of catalyst compositions A-D under bubbling fluidized bed conditions was carried out in a quartz reactor with an internal diameter (ID) of 20 mm and height of 112 cm placed in a vertical tube furnace (Lab-Temp Split Tube Furnace, LSP-2.38-0-38-6C) with six successive heating zones, each controlled by a separate temperature controller. The length of the isothermal zone was 20 cm.

In a typical experiment, 7.5 g of catalyst particles, either having spherical (catalyst A/C) or granular (catalyst B/D, comparative) morphology, were placed in the reactor. On application of a cold nitrogen flow (50-100 Nl/h), the catalyst was observed to be in the bubbling fluidization regime. The nitrogen flow was then switched to a mixture of methane, nitrogen and oxygen before heating up the oven. The total feed flow rate applied in the experiments was 40 NL/h, while the CH_4:O_2:N_2 molar ratio was 4:1:4. The pressure was 1.3 bara and the gas hourly space velocity (GHSV) was in the range of 2100-2300 NL/L cat/h. The temperature of the hot zone of the furnace as 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]). Successful fluidization was confirmed by the observation of

the small and constant pressure drop over the reactor (i.e., <0.06 bar at 40 NL/h flow). The composition of the product stream was determined with an online micro-gas chromatography (GC) apparatus using a flame ionization detector (FID) with a molesieve column and 3 thermal conductivity detectors (TCD) with Hayesep Q, Al_2O3/Na_2SO_4 and Carbosphere 60-80 columns.

It was found that temperature control within the fluidized bed was enhanced for the fluidized catalyst particles based on a spherical support (catalysts B and D) as compared to particles based on a granular support (catalysts A and C), indicating that fluidization was improved and agglomeration was reduced for the spherical catalyst particles as disclosed herein.

For catalysts A and C, some amount of fines was found in the reactor's outlet connection at the end of the run (c. 80 hours), indicating attrition of the granular catalyst particles having occurred after ca. 80 h of operation under fluidized bed conditions. In contrast, in experiments with OCM catalyst B an D on a spherical support no evidence for attrition was found.

Table 2. OCM catalytic performance of catalyst compositions A-D under fluidized bed conditions: oxygen conversion (X O_2), methane conversion (X CH_4), selectivity to C_{2+} hydrocarbons (S C_{2+}), yield of C_{2+} hydrocarbons (Y C_{2+}), selectivity to ethylene (S C_2H_4), ethane to ethylene ratio (C_2H_6:C_2H_4).

Catalyst composition		T (°C)	X O_2 (%)	X CH_4 (%)	S C_2+ (%)	Y C_2+ (%)	S C_2H_4 (%) [C_2H_6:C_2H_4]
B	2% Mn/2% Na_2WO_4/ granular SiO_2	750	99.1	25.2	61.6	15.5	36.1 [0.47]
A	2% Mn/2% Na_2WO_4/ spherical SiO_2	744	99.3	26.0	64.8	17.4	39.2 [0.39]
D	2% Mn/5% Na_2WO_4/ granular SiO_2	715	99.8	26.3	62.8	16.5	36.7 [0.46]
C	2% Mn/5% Na_2WO_4/ spherical SiO_2	715	99.9	27.1	63.9	17.4	36.9 [0.44]

Discussion

As shown in the Table 2, under bubbling fluidized bed conditions, catalyst compositions A and C having spherical silica supports and overall spherical morphology exhibit increased oxygen and methane conversion, higher C_{2+} selectivity and yield than catalyst compositions B and D having a granular morphology. In addition, under bubbling fluidized bed conditions, catalyst compositions A and C produced C_2 products having a substantially lower C_2/C_2= molar ratio, i.e. producing more ethylene than ethane, which is favored.

For OCM catalyst compositions B and D having granular morphology, a small amount of powder was found in the reactor's outlet connection at the end of the run, consistent with attrition having occurred after ca. 16 h operation. In contrast in experiments with the OCM catalyst on spherical support no evidence for attrition was found.

These results demonstrate that the use of spherical catalyst particles in an OCM process under fluidized bed conditions as disclosed herein results in increased conversion

of methane and oxygen to produce higher yields of C_2 products, a markedly higher selectivity towards C_2 (ethane an ethylene) products, and a lower ethane to ethylene (C2/C2=) ratio, as compared to using known granular catalyst particles under the same conditions. These spherical particles further exhibit a higher physical strength, thus preventing particle degradation (and loss of catalytically active components) and reducing the unwanted formation of fines during fluidization.

CLAIMS

1. A catalyst composition comprising spherical particles, wherein said spherical catalyst particles comprise a carrier material and a catalytically active material, wherein the carrier material comprises silica and wherein the catalytically active material comprises manganese, one or more alkali metals and tungsten.

2. Catalyst composition according to claim 1, wherein the carrier material comprises spherical silica particles.

3. Catalyst composition according to claim 1 or 2, wherein the spherical catalyst particles have a volume mean diameter in the range of 100 to 1000 micron, preferably in the range of 200 to 800 micron, most preferably in the range of 300 to 600 micron.

4. Catalyst composition according to claims 1-3, comprising manganese in an amount of 1 to 10 wt%, preferably in an amount of 1 to 5 wt%, based on total weight of the catalyst composition.

5. Catalyst composition according to claims 1-4, comprising tungsten in an amount of 1 to 4.5 wt%, preferably in an amount of 1.5 to 3.5 wt%, based on total weight of the catalyst composition.

6. Catalyst composition according to claims 1-5, comprising one or more alkali metals in an amount of 0.1 to 2.0 wt% per alkali metal, preferably in an amount of 0.25 to 1.5 % wt%, based on total weight of the catalyst composition.

7. Catalyst composition according to claims 1-6, comprising sodium in an amount of 0.1 to 2.0 wt%, based on total weight of the catalyst composition.

8. Catalyst composition according to claims 1-8, comprising manganese-sodium tungstate ($Mn:Na_2WO_4$) as the catalytically active material.

9. Catalyst composition to any of the preceding claims, wherein the spherical catalyst particles 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.

10. A process for the oxidative coupling of methane to one or more C_{2+} hydrocarbons, wherein said process comprises contacting a catalyst bed in a fluidized-bed reactor with a reactor feed comprising methane and oxygen under oxidative methane conversion (OCM) conditions,
wherein the catalyst bed comprises spherical particles of a catalyst composition according to any one of the preceding claims.

11. Process according to Claim 10, wherein the process is carried out at a reactor temperature of less than 850 °C.

12. A process for the preparation of a catalyst composition according to any one of claims 1-9, said process comprising

- providing a carrier material comprising spherical silica particles;
- optionally reducing the particle size distribution of the spherical silica particles;
- one or more impregnation steps, said impregnation steps comprising applying a solution of the catalytically active composition or one or more precursor thereof onto the spherical silica particles, optionally followed by a drying step; and
- calcining the impregnated particles to obtain spherical catalyst particles.

Fig.1A

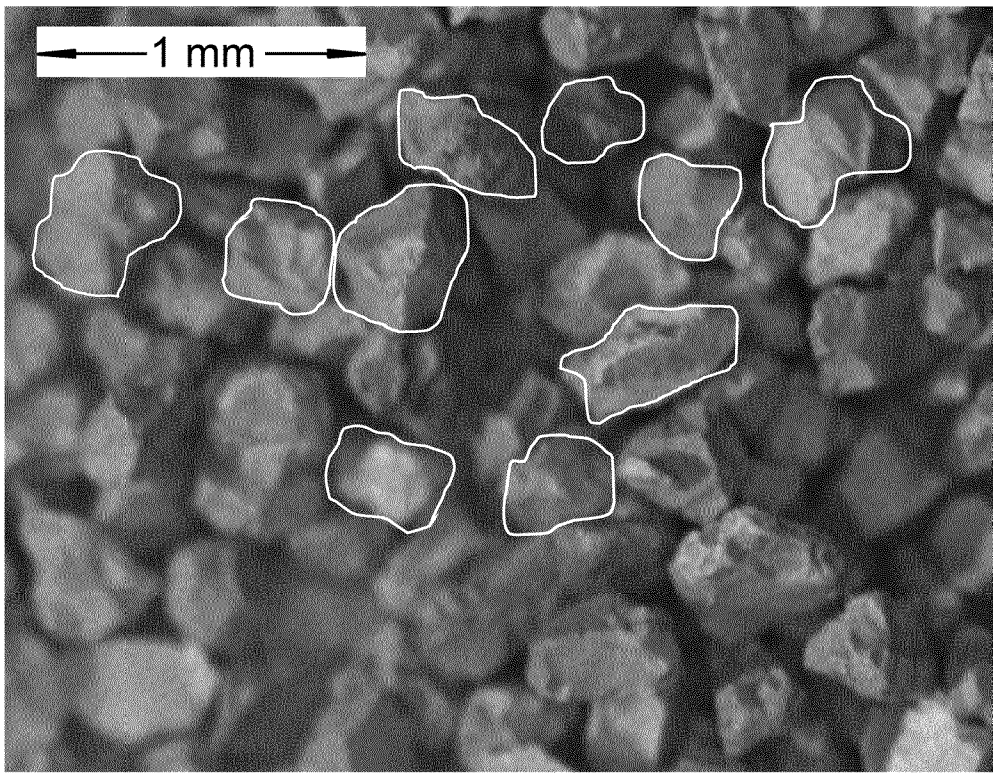
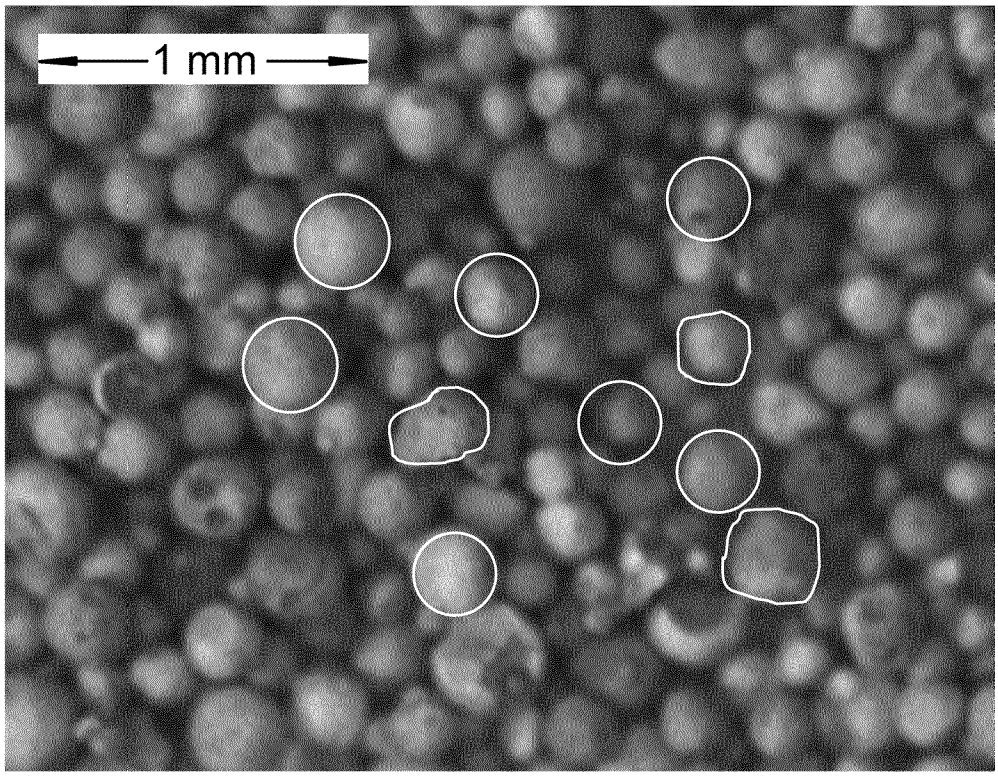


Fig.1B



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/073680

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/34 B01J35/08 B01J21/08 B01J37/02 B01J37/08
C07C1/00 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)
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.
X	CN 104 759 291 A (ECO ENVIRONMENTAL INVEST COMPANY LTD; ECO ENVIRONMENTAL ENERGY RES INS) 8 July 2015 (2015-07-08) abstract comp. ex. 2 -----	1,2,8-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 November 2018	13/11/2018

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/073680

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 104759291 A	08-07-2015	CN 104759291 A	08-07-2015
		WO 2015101345 A1	09-07-2015