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(54) Title: EXTRUDED TITANIA-BASED MATERIALS COMPRISING QUATERNARY AMMONIUM COMPOUNDS AND/OR PREPARED USING QUATERNARY AMMONIUM COMPOUNDS

(57) Abstract: Porous, extruded titania-based materials further comprising one or more quaternary ammonium compounds and/or prepared using one or more quaternary ammonium compounds, Fischer-tropsch catalysts comprising them, uses of the foregoing, processes for making and using the same and products obtained from such processes.

EXTRUDED TITANIA-BASED MATERIALS COMPRISING QUATERNARY AMMONIUM COMPOUNDS AND/OR PREPARED USING QUATERNARY AMMONIUM COMPOUNDS

The present invention relates to a porous, extruded titania-based material further comprising one or more quaternary ammonium compounds and/or prepared using one or more quaternary ammonium compounds, particularly a porous, extruded titania-based material having improved crush strength and being suitable for use as a catalyst support, more particularly a Fischer-Tropsch catalyst support. The invention also relates to a porous, extruded titania-based material further comprising one or more quaternary ammonium compounds and/or prepared using one or more quaternary ammonium compounds, and comprising mesopores and macropores. The invention further relates to processes for the preparation of a porous, extruded titania-based material further comprising one or more quaternary ammonium compounds and/or prepared using one or more quaternary ammonium compounds, and processes for the production of Fisher-Tropsch synthesis catalysts comprising such material.

The conversion of synthesis gas into hydrocarbons by the Fischer-Tropsch process has been known for many years. The growing importance of alternative energy sources has seen renewed interest in the Fischer-Tropsch process as one of the more attractive direct and environmentally acceptable routes to high quality transportation fuels.

Many metals, for example cobalt, nickel, iron, molybdenum, tungsten, thorium, ruthenium, rhenium and platinum are known to be catalytically active, either alone or in combination, in the conversion of synthesis gas into hydrocarbons and oxygenated derivatives thereof. Of the aforesaid metals, cobalt, nickel and iron have been studied most extensively. Generally, the metals are used in combination with a support material, of which the most common are alumina, silica and carbon.

In the preparation of metal-containing Fischer-Tropsch catalyst, a solid support is typically impregnated with a metal-containing compound, such as a cobalt-containing compound, which may for instance be an organometallic or inorganic compound (e.g. $Co(NO_3)_2.6H_2O$), by contacting with a solution of the compound. The particular form of metal-containing compound is generally selected for its ability to form an appropriate oxide (for example Co_3O_4) following a subsequent calcination/oxidation step. Following

generation of the supported metal oxide, a reduction step is necessary in order to form the pure metal as the active catalytic species. Thus, the reduction step is also commonly referred to as an activation step.

It is known to be beneficial to perform Fischer-Tropsch catalysis with an extrudate, particularly in the case of fixed catalyst bed reactor systems. It is, for instance, known that for a given shape of catalyst particles, a reduction in the size of the catalyst particles in a fixed bed gives rise to a corresponding increase in pressure drop through the bed. Thus, the relatively large extrudate particles cause less of a pressure drop through the catalyst bed in the reactor compared to the corresponding powdered or granulated supported catalyst. It has also been found that extrudate particles generally have greater strength and experience less attrition, which is a particular value in fixed bed arrangements where bulk crush strength may be very high.

An impregnated extrudate may be formed by mixing a solution of a metal-compound with a support material particulate, mulling, and extruding to form an extrudate before drying and calcining. Alternatively, an extrudate of a support material is directly impregnated, for instance by incipient wetness, before drying and calcining.

Commonly used support materials for Fischer-Tropsch catalysts include alumina, silica and carbon; however, a particularly useful material is extruded titania (titanium dioxide). Extruded titania support materials typically have a mesoporous structure, i.e. the extruded material comprises pores having a pore size of 2 to 50 nm.

Titania is also extensively used as a catalyst in the Claus process that converts gaseous sulphur compositions into sulphur.

Although titania-based extrudates have been produced on a commercial scale, they generally suffer from poor mechanical (crush) strength, which makes the manufacturing, handling and loading of the catalyst into a reactor difficult. Moreover, in a fixed reactor, extrudates are subject to demanding conditions and have to tolerate stress from axial pressure difference, pressure oscillation in the process, surge of liquid flow, and the weight of catalyst in the upper bed, to list a few. Fracture failure of weak extrudates could cause catastrophic pressure drop in the process, and the particulates generated from crumbled extrudates could cause dysfunction or malfunction of downstream devices and equipment. This problem is worsened in extrudates having increased porosity, as the introduction of additional pores, particularly macropores, further reduces the crush strength of the

extrudates.

Various inorganic binders have been investigated to reinforce the structure of titania-based extrudates, and these include alumina and alumina-based composites, clays, boric acid, and activated titania and titania-based composites.

WO 2007/068731 discloses a process for the preparation of a catalyst or catalyst precursor, comprising the steps of: (a) admixing: (i) a catalytically active metal or metal compound, (ii) a carrier material, (iii) a gluing agent, and (iv) optionally one or more promoters, and/or one or more co-catalysts; (b) forming the mixture of step (a); and drying the product of step (b) for more than 5 hours at a temperature up to 100°C to form the catalyst or catalyst precursor. The catalytically active metal may comprise cobalt, iron or ruthenium, the carrier material may comprise titanium, and the forming step may comprise extrusion. The gluing agent may be selected from a wide range of materials, including quaternary ammonium hydroxides, although no examples of these materials are given. The process specifically excludes a calcining step.

There therefore remains a need for porous, extruded titania-based material having improved crush strength, particularly a porous, extruded titania-based material comprising mesopores and macropores and having improved crush strength.

It has now surprisingly been found that incorporating one or more quaternary ammonium compounds, particularly aqueous solutions thereof, during the extrusion of a titania-based material improves the crush strength of the porous, extruded titania-based material. Surprisingly, the incorporation of one or more quaternary ammonium compounds in the extrusion process has little impact on the porosity of the finished support, and even when macropores are introduced into the extrudates the use of one or more quaternary ammonium compounds increases the crush strength of the macroporous supports.

Thus, in a first aspect the present invention provides a porous, extruded titania-based material further comprising one or more quaternary ammonium compounds, particularly a porous, extruded titania-based material comprising mesopores and macropores and further comprising one or more quaternary ammonium compounds.

The present invention further provides a process for the preparation of a porous, extruded titania-based material having a crush strength greater than 3.0 lbf, said process comprising:

a) mixing titanium dioxide and a solution of one or more quaternary ammonium compounds to form a homogenous paste;

b) extruding the paste to form an extrudate; and

c) drying and/or calcining the extrudate.

The present invention further provides a process for the preparation of a porous, extruded titania-based material comprising mesopores and macropores and having a crush strength greater than 3.0 lbf, said process comprising:

a) mixing titanium dioxide and one or more porogens to form a homogenous mixture;

b) adding a solution of one or more quaternary ammonium compounds to the homogenous mixture, and mixing to form a homogenous paste;

c) extruding the paste to form an extrudate; and

d) drying and/or calcining the extrudate at a temperature sufficient to decompose the one or more porogens.

The present invention yet further provides a porous, extruded titania-based material obtainable by a process according to the invention.

The present invention further provides a Fischer-Tropsch synthesis catalyst comprising a porous, extruded titania-based material according to the invention, and further comprising at least one metal selected from cobalt, iron, nickel, ruthenium or rhodium, particularly a Fischer-Tropsch synthesis catalyst comprising a porous, extruded titania-based material according to the invention comprising mesopores and macropores, and further comprising at least one metal selected from cobalt, iron, nickel, ruthenium or rhodium.

The present invention yet further provides a process for the preparation of a Fischer-Tropsch synthesis catalyst according to the invention, said process comprising:

a) mixing titanium dioxide, a solution of one or more quaternary ammonium compounds and a solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound, to form a homogenous paste;

b) extruding the paste to form an extrudate;

c) drying and/or calcining the extrudate at a temperature sufficient to convert the one or more thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to an oxide thereof; or to the metal form; and, where an oxide is formed, optionally

d) heating the dried and/or calcined extrudate under reducing conditions to convert the one or more cobalt, iron, nickel, ruthenium or rhodium oxide to the metal form.

The present invention further provides a process for the preparation of a Fischer-Tropsch synthesis catalyst comprising a porous, extruded titania-based material comprising mesopores and macropores according to the invention, said process comprising:

a) mixing titanium dioxide and one or more porogens to form a homogenous mixture;

b) adding a solution of one or more quaternary ammonium compounds and a solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to the mixture, and mixing to form a homogenous paste;

c) extruding the paste to form an extrudate;

d) drying and/or calcining the extrudate at a temperature sufficient to decompose the one or more porogens and to convert the at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to an oxide thereof, or to the metal form; and, where an oxide is formed, optionally

e) heating the dried and/or calcined extrudate under reducing conditions to convert the one or more cobalt, iron, nickel, ruthenium or rhodium oxide to the metal form.

The present invention yet further provides a process for the preparation of a Fischer-Tropsch synthesis catalyst according to the invention, said process comprising:

a) impregnating a porous, extruded titania-based material according to the invention with a solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound;

b) drying and/or calcining the impregnated porous, extruded titania-based material at a temperature sufficient to convert the at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to an oxide thereof or to the metal form; and where an oxide is formed, optionally

c) heating the dried and/or calcined porous, extruded titania-based material under reducing conditions to convert the at least one cobalt, iron, nickel, ruthenium or rhodium oxide to the metal form.

There is yet further provided a Fischer-Tropsch synthesis catalyst obtainable by a process according to the invention, preferably having a crush strength of greater than 5.0 lbf.

There is yet further provided the use of a quaternary ammonium compound to prepare a porous, extruded titania-based material, preferably comprising mesopores and macropores, having a crush strength of greater than 3.0 lbf, and also the use of a quaternary ammonium compound to prepare a porous, extruded titania-based Fischer-Tropsch synthesis catalyst, preferably comprising mesopores and macropores, having a crush strength of greater than 5.0 lbf.

In a further aspect, the present invention provides a process for converting a mixture of hydrogen and carbon monoxide gases to hydrocarbons, which process comprises contacting a mixture of hydrogen and carbon monoxide with a Fischer-Tropsch synthesis catalyst according to the invention or a Fischer-Tropsch synthesis catalyst obtainable by a process according to the invention.

In a further aspect, the present invention provides a composition, preferably a fuel composition, comprising hydrocarbons obtained by a process according to the invention.

In a further aspect, the present invention provides a process for producing a fuel composition, said process comprising blending hydrocarbons obtained by a process according to the invention with one or more fuel components to form the fuel composition.

The porous, extruded titania-based material according to the present invention may be prepared using any quaternary ammonium compound capable of increasing the strength of titania-based extrudates. Without wishing to be bound by theory, it is believed that when titania nanocrystals, particularly anatase and/or rutile polymorphs thereof, are extruded, the particles formed generally lack cross-linkages based on chemical bond interactions, and that the forces that hold these particles together when they are formulated with water are mainly van der Waals forces, but that activation of the titania particles with one or more quaternary ammonium compounds generates chemical bonding interactions between these crystallites, and accordingly substantially improves mechanical strength of the extrudates, even if all of the quaternary ammonium compounds are removed during and after extrusion.

Suitable quaternary ammonium compounds for use in the present invention include, but are not limited to, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide and cetyltrimethylammonium hydroxide; particularly tetramethylammonium hydroxide.

As noted above, the improvement in crush strength provided by mixing one or more quaternary ammonium compounds with titanium dioxide before extrusion remains following extrusion, even if the one or more quaternary ammonium compounds is partially or even entirely removed during and/or after extrusion. Thus, porous, extruded titania-based materials according to the present invention may further comprise one or more quaternary ammonium compounds, or may be entirely free of such compounds. Preferably, the total amount of one or more quaternary ammonium compounds is at least partially reduced in the porous, extruded titania-based material of the present invention compared to the amount present during the formation of the material, and more preferably the porous, extruded titania-based material is substantially or entirely free of quaternary ammonium compounds.

The one or more quaternary ammonium compounds used in the preparation of porous, extruded titania-based materials according to the present invention may be removed therefrom in any suitable manner, such as by thermal decomposition or oxidation, for example by heating the extrudates to 430°C or higher, preferably 500°C or higher.

The total amount of one or more quaternary ammonium compounds used in the preparation of porous, extruded titania-based materials according to the present invention may be any amount sufficient to provide improvements in the crush strength of the finished extrudates, but a preferred range of amounts is from 0.1 to 1.0 mol per gram of titanium oxide.

The crush strength of the porous, extruded titania-based material according to the present invention may be measured by any suitable method known to those skilled in the art, for example using equipment designed to comply with ASTM D4179-01 standards, such as a Varian Benchsaver™ V200 Tablet Hardness Tester. Alternatively, crush strength may be measured using equipment designed to comply with ASTM D6175-03 standards.

The porous, extruded titania-based material according to the present invention suitably has a crush strength of greater than 3.0 lbf, preferably greater than 5.0 lbf, more preferably greater than 8.0 lbf. The upper limit of the crush strength is not critical; however, a suitable maximum crush strength may be 20 lbf. A particularly preferred range of crush strength for a porous, extruded titania-based material according to the present invention is 3.0 lbf to 20.0 lbf, such as 5.0 lbf to 15.0 lbf, 5.0 lbf to 12.0 lbf or 8.0 lbf to 12.0 lbf.

The porous, extruded titania-based material according to the present invention generally has a symmetrical geometry that includes, but is not limited to, cylinders, spheres, spheroids, pastilles, dilobes, such as cylindrical dilobes, trilobes, such as cylindrical trilobes, quadralobes, such as cylindrical quadralobes, and hollow cylinders.

The pore diameter of the porous, extruded titania-based material according to the present invention may be measured by any suitable method known to those skilled in the art, for example scanning electron microscopy or mercury porosimetry based on mercury intrusion using the Washburn equation with a mercury contacting angle of 130° and a mercury surface tension of 485 dynes/cm. As used herein, the term "pore diameter" equates with "pore size" and consequently refers to the average cross-sectional dimension of the pore, understanding, as the skilled person does, that a determination of pore size typically models pores as having circular cross-sections.

Preferably, the porous, extruded titania-based material comprising mesopores and macropores according to the present invention, comprises a multi-modal distribution of pores, i.e. the material comprises a range of pore sizes/pore diameters with two or more modes, such as two, three, four or more modes. Particularly suitable materials comprise a bi-modal distribution of pore sizes/pore diameters, i.e. a range of pore sizes/pore diameters comprising two modes, the first mode representing mesopores and the second mode representing macropores.

The porous, extruded titania-based material comprising mesopores and macropores according to the present invention suitably comprises mesopores having a pore diameter of 2 to 50 nm, for example 5 to 50 nm, preferably 15 to 45 nm or 20 to 45 nm, more preferably 25 to 40 nm or 30 to 40 nm.

The porous, extruded titania-based material comprising mesopores and macropores according to the present invention suitably comprises macropores having a pore diameter of greater than 50 nm, preferably 60 to 1000 nm, more preferably 100 to 850 nm.

The pore volume of a porous, extruded titania-based material comprising mesopores and macropores according to the present invention may be measured by any suitable method known to those skilled in the art, for example using mercury porosimetry.

Suitably, the porous, extruded titania-based material according to the present invention has a total pore volume of at least 0.30 ml/g, preferably at least 0.40 ml/g, more preferably at least 0.50 ml/g. The upper limit of the total pore volume is not critical, so

long as the material remains sufficiently robust to function as a catalyst support; however, a suitable maximum pore volume may be 1.00 ml/g, preferably 0.90 ml/g. Particularly preferred ranges of total pore volume for a porous, extruded titania-based material comprising mesopores and macropores further comprising zirconium oxide according to the present invention are 0.30 to 1.00 ml/g, such as 0.40 to 1.00 ml/g, 0.40 to 0.90 ml/g or 0.50 to 0.90 ml/g.

The surface area of the porous, extruded titania-based material comprising mesopores and macropores according to the present invention may be measured in any suitable way known to those skilled in the art, such as by nitrogen porosimetry using the BET model to the nitrogen adsorption isotherm collected at 77K on a Quadrasorb SI unit (Quantachrome).

Suitably, the porous, extruded titania-based material comprising mesopores and macropores according to the present invention has a surface area of at least 30 m^2/g, preferably at least 40 m^2/g. The upper limit of the surface area is not critical, so long as the material is suitable for the intended use, such as a catalyst support; however, a suitable maximum surface area may be 60 m^2/g or 55 m^2/g. A particularly suitable range of surface area for a porous, extruded titania-based material comprising mesopores and macropores of the present invention is 30 to 60 m^2/g, preferably 40 to 55 m^2/g.

The BET surface area, pore volume, pore size distribution and average pore radius of a porous, extruded titania-based material comprising mesopores and macropores may additionally be determined from the nitrogen adsorption isotherm determined at 77K using a Micromeritics TRISTAR 3000 static volumetric adsorption analyser. A procedure which may be used is an application of British Standard method BS4359: Part 1: 1984, "Recommendations for gas adsorption (BET) methods" and BS7591: Part 2: 1992, "Porosity and pore size distribution of materials" – Method of evaluation by gas adsorption. The resulting data may be reduced using the BET method (over the relative pressure range 0.05 – 0.20 P/P_0) and the Barrett, Joyner & Halenda (BJH) method (for pore diameters of 2 to 100 nm) to yield the surface area and pore size distribution respectively. Nitrogen porosimetry, such as described above, is the preferred method for determining the surface areas of the extruded titania-based materials according to the present invention.

Suitable references for the above data reduction methods are Brunaeur, S, Emmett,

P H, and Teller, E; J. Amer. Chem. Soc. 60, 309, (1938) and Barrett, E P, Joyner, L G and Halenda, P P; J Am. Chem. Soc., 1951, 73, 375 to 380.

As a further alternative, pore volume may be estimated through mercury porosimetry by use of an AutoPore IV (Micromeritics) instrument, and pore diameter may be measured from the mercury intrusion branch using the Washburn equation with a mercury contacting angle at 130° and a mercury surface tension of 485 dynes/cm. Further details are provided in ASTM D4284-12 Standard Test Method for Determining Pore Volume Distribution of Catalysts and Catalyst Carriers by Mercury Intrusion Porosimetry; and Washburn, E.W; The Dynamics of Capillary Flow (1921); Physical Review 1921, 17(3), 273. Mercury porosimetry, such as described above, is the preferred method for determining the pore volumes and pore diameters of the extruded titania-based materials according to the present invention.

The porous, extruded titania-based material according to the present invention may be prepared by any suitable extrusion process known to those skilled in the art, but modified so that one or more quaternary ammonium compounds, preferably an aqueous solution thereof, is mixed with titanium dioxide before the extrusion step, and, preferably, so that, after extrusion at least a portion of the one or more quaternary ammonium compounds is removed. Where the porous, extruded titania-based material according to the present invention comprises mesopores and macropores, the process is also modified so that one or more porogens are included in the titania-based material during extrusion, and are subsequently removed by thermal or oxidative decomposition.

The porous, extruded titania-based material according to the present invention may be prepared using any suitable form of titanium oxide, such as titanium dioxide (CAS No: 13463-67-7), titanium dioxide anatase (CAS No: 1317-70-0), titanium dioxide rutile (CAS No: 1317-80-2), titanium dioxide brookite (CAS No: 98084-96-9), and admixtures or composites thereof.

Where the porous, extruded titania-based material according to the present invention is to be used as a catalyst support, it is preferably substantially free of extraneous metals or elements which might adversely affect the catalytic activity of the system. Thus, preferred porous, extruded titania-based materials according to the present invention are preferably at least 95% w/w pure, more preferably at least 99% w/w pure. Impurities preferably amount to less than 1% w/w, more preferably less than 0.6% w/w and most preferably less

than 0.3% w/w. The titanium oxide from which the porous, extruded titania-based material is formed is preferably of suitable purity to achieve the above preferred purity in the finished extruded product.

In the processes for the preparation of a porous, extruded titania-based material according to the present invention, titanium dioxide and one or more quaternary ammonium compounds are mixed to form a homogenous paste. Preferably the one or more quaternary ammonium compounds are mixed with the titanium dioxide as a solution, most preferably as an aqueous solution, which may be formed either before the mixing takes places (i.e. by dissolving the one or more quaternary ammonium compounds before mixing with the titanium dioxide) or during the mixing stage (i.e. by mixing titanium dioxide and one or more quaternary ammonium compounds and adding a suitable solvent, preferably water). The titanium dioxide and one or more quaternary ammonium compounds may be mixed using any suitable technique to form a homogenous mixture, such as by mixing in a mechanical mixer. If necessary, the wetness of the mixture of titanium dioxide and one or more quaternary ammonium compounds may be adjusted to form an extrudable paste by adding a liquid extrusion medium. Any suitable liquid extrusion medium may be used, i.e. any liquid capable of causing the titanium dioxide and one or more quaternary ammonium compounds to form a homogenous paste suitable for extrusion. Water is an example of a suitable liquid extrusion medium.

Where the one or more quaternary ammonium compounds is dissolved prior to mixing with titanium dioxide, it may be dissolved at any suitable concentration, preferably so that all of the one or more quaternary ammonium compounds is dissolved and/or so that when an amount of the one or more dissolved quaternary ammonium compounds sufficient to provide the required final amount of quaternary ammonium compound is mixed with the titanium dioxide the mixture will not be too wet to form a homogenous paste suitable for extrusion. Suitably the one or more quaternary ammonium compounds may be used at a concentration of 0.1 mol/litre or above, such as from 0.1 mol/L to 2.0 mol/L, or 0.2 mol/L to 1.0 mol/L, preferably 0.5 mol/litre or above.

The porous, extruded titania-based material comprising mesopores and macropores according to the present invention may be prepared using any suitable porogen, i.e. a material capable of enabling the formation of macropores in an extruded titania-based material once it has been removed therefrom, for example by thermal or oxidative

decomposition.

Suitable porogens for use in the processes for the production of a porous, extruded titania-based material comprising mesopores and macropores according to the present invention comprise cellulose or derivatives thereof, such as methyl cellulose (CAS No: 9004-67-5), ethyl cellulose (CAS No: 9004-57-3) and ethyl methyl cellulose (CAS No: 9004-69-7); alginic acid (CAS No: 9005-32-7) or derivatives thereof, such as ammonium alginate (CAS No: 9005-34-9), sodium alginate (CAS No: 9005-38-3) and calcium alginate (CAS No: 9005-35-0); latex, such as polystyrene latex (CAS No: 26628-22-8) or polyvinylchloride (CAS No: 9002-86-2).

The proportion of total porogen to titanium dioxide used in the processes of the present invention may be selected so as to provide a suitable proportion of macropores in the porous, extruded titania-based material. However, a preferred weight ratio of titanium dioxide to total porogen is from 1:0.1 to 1:1.0, preferably 1:0.1 to 1:0.8, more preferably 1:0.15 to 1:0.6.

Where a process of the present invention includes mixing one or more porogens with titanium dioxide to form a homogenous mixture, the porogen may be mixed with titanium dioxide either before or after mixing with the one or more quaternary ammonium compounds, or at the same time as the addition of the one or more quaternary ammonium compounds. Preferably, the titanium dioxide and one or more porogens are mixed to form a homogenous mixture before the addition of the one or more quaternary ammonium compounds to the homogenous mixture. Mixing of the titanium dioxide and one or more porogens may be carried out in the same apparatus as the mixing with one or more quaternary ammonium compounds or in different equipment, as required.

A process for the production of a porous, extruded titania-based material, according to the present invention may optionally further comprise a mulling step to reduce the presence of larger particles that may not be readily extruded, or the presence of which would otherwise compromise the physical properties of the resulting extrudate. Any suitable mulling or kneading apparatus of which a skilled person is aware may be used for mulling in the context of the present invention. For example, a pestle and mortar may be suitably used in some applications or a Simpson Muller may suitably be employed. Mulling is typically undertaken for a period of from 3 to 90 minutes, preferably for a period of 5 minutes to 30 minutes. Mulling may suitably be undertaken over a range of

temperatures, including ambient temperatures. A preferred temperature range for mulling is from 15°C to 50°C. Mulling may suitably be undertaken at ambient pressures.

The homogenous paste formed in a process for the production of a porous, extruded titania-based material according to the present invention may be extruded to form an extrudate using any suitable extruding methods and apparatus of which the skilled person is aware. For example, the homogenous paste may be extruded in a mechanical extruder (such as a Vinci VTE 1) through a die with an array of suitable diameter orifices, such as 1/16 inch diameter, to obtain extrudates with cylindrical geometry.

The extrudate formed in a process for the production of a porous, extruded titania-based material according to the present invention may be dried and/or calcined at any suitable temperature. Where the process includes the incorporation of a porogen before the extrusion step, the drying and/or calcining is preferably carried out at temperatures sufficient to decompose the one or more porogens.

Where the process of the present invention includes both drying and calcining, the drying step is preferably carried out before the calcining step.

Drying in accordance with the present invention is suitably conducted at temperatures of from 50°C to 150°C, preferably 75°C to 125°C. Suitable drying times are from 5 minutes to 24 hours. Drying may suitably be conducted in a drying oven or in a box furnace, for example, under the flow of an inert gas at elevated temperatures.

Preferably, a calcining step is incorporated in the processes of the present invention, to ensure that at least a portion, preferably a significant portion, more preferably substantially all, of the one or more quaternary ammonium compounds is removed from the finished extrudates.

Calcination may be performed by any method known to those of skill in the art, for example in a fluidized bed or a rotary kiln, suitably at a temperature of at least 400°C, such as at least 420°C, more preferably at least 500°C, and yet more preferably at 500-700°C.

The Fischer-Tropsch synthesis catalyst according to the present invention comprises a porous, extruded titania-based material, preferably comprising mesopores and macropores, according to the present invention, or obtainable by a process according to the present invention, and further comprises at least one metal selected from cobalt, iron, nickel, ruthenium or rhodium, preferably cobalt. The amount of metal, on an elemental basis, present in the Fischer-Tropsch synthesis catalyst according to the present invention

is suitably from 5.0 wt% to 30.0 wt%, preferably 7.0 wt% to 25.0 wt%, more preferably 10 wt% to 20 wt%, based on the total weight of the catalyst. As will be appreciated by the skilled person, the amount of metal, on an elemental basis, present in the Fischer-Tropsch synthesis catalyst may be readily determined by X-ray fluorescence (XRF) techniques.

The Fischer-Tropsch synthesis catalyst according to the present invention may additionally comprise one or more promoters, dispersion aids, binders or strengthening agents. Promoters are typically added to promote reduction of an oxide of metal to pure metal; for example cobalt to cobalt metal, preferably at lower temperatures. Preferably, the one or more promoters are selected from rhenium, ruthenium, platinum, palladium, molybdenum, tungsten, boron, zirconium, gallium, thorium, manganese, lanthanum, cerium or mixtures thereof. The promoter is typically used in a metal to promoter atomic ratio of up to 250:1, and more preferably up to 125:1, still more preferably up to 25:1, and most preferably 10:1.

The Fischer-Tropsch synthesis catalyst according to the present invention may be prepared by incorporating a solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound into a process for the production of a porous, extruded titania-based material according to the present invention, i.e. by adding the solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound at any stage before extrusion of the homogenous paste. Preferably, the solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound is added following mixing of the titanium oxide and one or more quaternary ammonium compounds.

Alternatively, a Fischer-Tropsch synthesis catalyst according to the present invention may be prepared by impregnating a porous, extruded titania-based material, preferably comprising mesopores and macropores, according to the present invention with a solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound. Impregnation of the porous, extruded titania-based material with the solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound in accordance with the present invention may be achieved by any suitable method of which the skilled person is aware, for instance by vacuum impregnation, incipient wetness or immersion in excess liquid. The impregnating solution may suitably be either an aqueous solution or a non-aqueous, organic solution of the thermally

decomposable metal compound. Suitable non-aqueous organic solvents include, for example, alcohols, ketones, liquid paraffinic hydrocarbons and ethers. Alternatively, aqueous organic solutions, for example an aqueous alcoholic solution, of the thermally decomposable metal-containing compound may be employed. Preferably, the solution of the thermally decomposable metal-containing compound is an aqueous solution.

Suitable metal-containing compounds are those which are thermally decomposable to an oxide of the metal following calcination, or which may be reduced directly to the metal form following drying and/or calcination, and which are completely soluble in the impregnating solution. Preferred metal-containing compounds are the nitrate, acetate or acetyl acetonate salts of cobalt, iron, nickel, ruthenium or rhodium, most preferably the nitrate, for example cobalt nitrate hexahydrate.

Following extrusion, the extrudate may be dried and/or calcined at a temperature sufficient to convert the at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to an oxide thereof or to the metal form.

Following impregnation, the impregnated extrudate may be dried and/or calcined at a temperature sufficient to convert the at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium containing compound to an oxide thereof or to the metal form.

The drying and calcining temperatures and conditions suitable for producing a porous, extruded titania-based material according to the present invention are also suitable for use in the processes for preparing Fischer-Tropsch synthesis catalysts according to the present invention.

Where an oxide of cobalt, iron, nickel, ruthenium or rhodium is formed during a process for the preparation of a Fischer-Tropsch synthesis catalyst according to the present invention, the material may be used as a catalyst in a Fischer-Tropsch reaction without further processing, and the oxide of cobalt, iron, nickel, ruthenium or rhodium will be converted to the metal form during such use. Alternatively, the material comprising an oxide of cobalt, iron, nickel, ruthenium or rhodium may optionally be heated under reducing conditions to convert the at least one cobalt, iron, nickel, ruthenium or rhodium oxide to the metal form before use as a Fischer-Tropsch synthesis catalyst. Any suitable means for converting the oxide of cobalt, iron, nickel, ruthenium or rhodium to the metal form known to those skilled in the art may be used.

Where promoters, dispersion aids, binders and/or strengthening aids are incorporated in the Fischer-Tropsch synthesis catalyst according to the present invention, the addition of these materials may be integrated at several stages of the process according to the present invention. Preferably, the promoter, dispersion aids, binder or strengthening aids are admixed during any stage prior to extrusion, or during the impregnation step.

The Fischer-Tropsch synthesis catalyst comprising a porous, extruded titania-based material according to the present invention or a Fischer-Tropsch synthesis catalyst obtainable by a process according to the present invention will preferably have a crush strength of greater than 5.0 lbf, more preferably greater than 7.0 lbf, and even more preferably greater than 10.0 lbf. The upper limit of the crush strength of the Fischer-Tropsch synthesis catalyst according to the present invention is not particularly critical, but a suitable upper crush strength is 25.0 lbf. Particularly preferred ranges of crush strength for Fischer-Tropsch synthesis catalysts according to the present invention are 5.0 lbf to 25.0 lbf, preferably 7.0 lbf to 20.0 lbf, more preferably 10.0 lbf to 17.0 lbf.

The Fischer-Tropsch synthesis catalyst comprising a porous, extruded titania-based material according to the present invention or a Fischer-Tropsch synthesis catalyst obtainable by a process according to the present invention may be used as a catalyst in any conventional Fischer-Tropsch process for converting a mixture of hydrogen and carbon monoxide gases to hydrocarbons. The Fischer-Tropsch synthesis of hydrocarbons from a mixture of hydrogen and carbon monoxide, such as syngas, may be represented by Equation 1:

$$mCO + (2m+1)H_2 \rightarrow mH_2O + C_mH_{2m+2} \qquad \text{Equation 1}$$

As discussed hereinbefore, the Fischer-Tropsch synthesis catalysts according to the present invention or obtainable by the process of the present invention have improved crush strength and are therefore better suited for use in fixed-bed Fischer-Tropsch processes. Additionally, Fischer-Tropsch synthesis catalysts according to the present invention, or obtainable by a process of the present invention, and comprising mesopores and macropores have been surprisingly found to have improved catalyst activity and/or selectivity, particularly reduced selectivity for methane. The Fischer-Tropsch synthesis catalyst according to the present invention, or obtainable by a process according to the

present invention, therefore provides particularly useful ranges of hydrocarbons when used in a Fischer-Tropsch reaction.

A composition according to the present invention comprising hydrocarbons obtained by a process of the present invention is preferably a fuel composition, for example a gasoline, diesel or aviation fuel or precursor thereof.

The present invention will now be illustrated by way of the following Examples.

EXAMPLES

Comparative Example 1

Titania extrudate formed with distilled water

Titanium dioxide (BASF P25) was mixed in a mechanical mixer (Vinci MX 0.4) with sufficient distilled water to form an extrudable paste, for example at a water to titanium mass ratio of 0.66 g/g. The resultant paste was extruded through a die with an array of 1/16 inch circular orifices using a mechanical extruder (Vinci VTE1) to obtain extrudates with cylindrical shape.

The extrudates were air dried for one hour, then dried at a temperature of between 100 and 120°C overnight, followed by calcination in air flow at 500°C for four hours, via a ramp of 2°C/min.

The mechanical strength of the extrudates was analysed using a Varian Benchsaver™ V200 Tablet Hardness Tester. 50 particles were analysed in each test, and the mean value was calculated.

The surface area of the extrudates was estimated using the BET model to the nitrogen adsorption branch of the isotherms collected at 77K on a Quadrasorb SI unit (Quantachrome).

Pore size and pore volume were characterised using mercury porosimetry conducted on an AutoPore IV (Micromeritics) instrument.

Total pore volume was estimated from mercury intrusion volume at 7000 psia. Pore size distribution of the sample was calculated using the BJH model from desorption isotherms for pore diameters of less than 17 nm and the mercury intrusion profile using the Washburn equation with a contact angle of 130° and a surface tension of bulk mercury of 485 mN/m for pore diameters of greater than 17 nm.

The physical properties of the extrudates were as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: 4.7 lbf

BET surface area: 51 m^2/g

Pore volume: 0.36 ml/g

Mean pore diameter: 33nm

Example 1

Titania extrudate prepared using 0.2 mol/L tetramethylammonium hydroxide

The procedure of Comparative Example 1 was repeated, with the exception that the distilled water was replaced by a 0.2 mol/L aqueous solution of tetramethylammonium hydroxide (Aldrich).

The physical properties of the extrudates of Example 1 were determined as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: 10.2 lbf

BET surface area: 54 m^2/g

Pore volume: 0.30 ml/g

Mean pore diameter: 24 nm

Compared with the pure titania extrudates prepared in Comparative Example 1, the extrudates of Example 1 prepared using 0.2 mol/L tetramethylammonium hydroxide exhibited substantially higher mechanical strength.

Example 2

Titania extrudate prepared using 0.5 mol/L tetramethylammonium hydroxide

The procedure of Comparative Example 1 was repeated, with the exception that the distilled water was replaced by 0.5 mol/L aqueous solution of tetramethylammonium hydroxide.

The physical properties of the extrudates of Example 2 were determined as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: 11.8 lbf

BET surface area: 45 m^2/g

Pore volume: 0.26 ml/g

Mean pore diameter: 24 nm

Example 3

Titania extrudate prepared using 1.0 mol/L tetramethylammonium hydroxide

The procedure of Comparative Example 1 was repeated, with the exception that the distilled water was replaced by 1.0 mol/L aqueous solution of tetramethylammonium hydroxide.

The physical properties of the extrudates of Example 3 were determined as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: 30.2 lbf

BET surface area: 39 m^2/g

Pore volume: 0.19 ml/g

Mean pore diameter: 12.3 nm

A comparison of the results of Examples 1 to 3 with the results of Comparative Example 1 shows that the use of tetramethylammonium hydroxide to bind the particles of titanium dioxide before extrusion resulted in an increase in crush strength, with increases in the concentration of tetramethylammonium hydroxide increasing the crush strength.

Example 4

Titania extrudate prepared using 0.5 mol/L tetraethylammonium hydroxide

The procedure of Example 2 was repeated, with the exception that the 0.5 mol/L aqueous solution of tetramethylammonium hydroxide was replaced by a 0.5 mol/L aqueous solution of tetraethylammonium hydroxide (Aldrich).

The physical properties of the extrudates of Example 4 were determined as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: 15.9 lbf

BET surface area: 40.2 m^2/g

Pore volume: 0.14 ml/g

Mean pore diameter: 10.0 nm

Example 5

Titania extrudate prepared using 0.5 mol/L tetrapropylammonium hydroxide

The procedure of Example 2 was repeated, with the exception that the 0.5 mol/L

aqueous solution of tetramethylammonium hydroxide was replaced by a 0.5 mol/L aqueous solution of tetrapropylammonium hydroxide (Aldrich).

The physical properties of the extrudates of Example 5 were determined as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: 14.0 lbf

BET surface area: 42.1 m^2/g

Pore volume: 0.15 ml/g

Mean pore diameter: 13.1

Example 6

Titania extrudate prepared using 0.5 mol/L tetrabutylammonium hydroxide

The procedure of Example 2 was repeated, with the exception that the 0.5 mol/L aqueous solution of tetramethylammonium hydroxide was replaced by a 0.5 mol/L aqueous solution of tetrabutylammonium hydroxide (Aldrich).

The physical properties of the extrudates of Example 6 were determined as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: 16.0 lbf

BET surface area: 40.6 m^2/g

Pore volume: 0.15 ml/g

Mean pore diameter: 13.1

A comparison of the results of Examples 4 to 6 with the results of Comparative Example 1 and the results of Examples 1 to 3 demonstrate that the mechanical strength of titania extrudates may be substantially improved by using alternative quaternary ammonium hydroxide compounds.

Comparative Example 2

Titania extrudate comprising mesopores and macropores prepared using a cellulose porogen and formed with distilled water

Titanium dioxide (Evonik P25) was mixed with cellulose fibre (CF, Aldrich) at a cellulose fibre:titanium dioxide ratio of 0.5 g/g and the mixture was homogenised using a 360° rotating mixer (Turbula). The mixture was then formulated in a pilot plant scale mechanical mixer (Simpson Muller) with sufficient deionised water to form an extrudable

paste. The resultant paste was extruded through a die with an array of 1/16 inch circular orifices using a pilot plant scale extruder (Bonnet) to obtain extrudates with cylindrical shape. The extrudates were dried and calcined as set out in Comparative Example 1.

The physical properties of the dried and calcined extrudates of Comparative Example 2 were determined as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: Less than 1.0 lbf (below the detection limit of the instrument)

BET surface area: 47.3 m^2/g

Pore volume: 0.52 ml/g

Mean pore diameter: bi-modal distribution, centred at 30.2 nm and 124.9 nm, respectively.

Example 7

Titania extrudate comprising mesopores and macropores prepared using a cellulose porogen and 0.5 mol/L tetramethylammonium hydroxide

The procedure of Comparative Example 2 was repeated, with the exception that the deionized water was replaced by a 0.5 mol/L aqueous solution of tetramethylammonium hydroxide. The extrudates of Example 7 were characterised as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter cylinder

Crush strength: 7.2 lbf

BET surface area: 46.5 m^2/g

Pore volume: 0.44 ml/g

Mean pore diameter/distribution: bi-modal distribution, centred at 19.1 nm and 60.3 nm, respectively.

Example 8

Titania extrudates prepared using 0.5 mol/L tetramethylammonium hydroxide

The procedure of Example 7 was repeated, with the exception that the homogenized paste was extruded through an array of 1/16 inch cylindrical trilobe orifices to obtain extrudates with cylindrical trilobe geometry. The extrudates were dried and calcined, and subsequently characterised, as set out in Comparative Example 1, and the results are as follows:

Geometry: 1/16 inch diameter trilobe

Crush strength: 9.7 lbf

BET surface area: 46.8 m^2/g

Pore volume: 0.44 ml/g

Mean pore diameter/distribution: bi-modal distribution, centred at 20.1 nm and 60.3 nm, respectively.

A comparison of the results of Comparative Example 2 and Examples 7 and 8 demonstrates that the mechanical strength (crush strength) of titania extrudates comprising micropores and macropores may also be substantially improved by using a quaternary ammonium hydroxide solution during the formulation of the homogeneous paste to be extruded, and also that the improved crush strength is maintained in different extrudate geometries.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope and spirit of this invention.

Claims

1. A porous, extruded titania-based material further comprising one or more quaternary ammonium compounds.

2. A porous, extruded titania-based material according to claim 1, in the form of symmetrical cylinders, dilobes, trilobes, quadralobes or hollow cylinders.

3. A porous, extruded titania-based material according to claim 1 or claim 2 having a crush strength of greater than 3.0 lbf, preferably greater than 5.0 lbf.

4. A porous, extruded titania-based material according to any preceding claim wherein the one or more quaternary ammonium compounds comprises tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or cetyltrimethylammonium hydroxide.

5. A porous, extruded titania-based material according to any preceding claim comprising mesopores and macropores.

6. A porous, extruded titania-based material according to claim 5, wherein the mesopores have a pore diameter of 2 to 50 nm, preferably 15 to 45 nm or 30 to 45 nm, more preferably 25 to 40 nm or 30 to 40 nm.

7. A porous, extruded titania-based material according to claim 5 or claim 6, wherein the macropores have a pore diameter of greater than 50 nm, preferably 60 to 1000 nm, more preferably 100 to 850 nm.

8. A porous, extruded titania-based material according to any of claims 5 to 7 wherein the total pore volume is at least 0.3 ml/g, preferably at least 0.40 ml/g.

9. A porous, extruded titania-based material according to any of claims 5 to 8 wherein the surface area is at least 30 m^2/g, preferably at least 40 m^2/g.

10. A process for the preparation of a porous, extruded titania-based material having a crush strength greater than 3.0 lbf, said process comprising:

a) mixing titanium dioxide and a solution of one or more quaternary ammonium compounds to form a homogenous paste;

b) extruding the paste to form an extrudate; and

c) drying and/or calcining the extrudate.

11. A process according to claim 10 wherein the solution of one or more quaternary ammonium compounds comprises tetramethylammonium hydroxide, tetraethylammonium

hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or cetyltrimethylammonium hydroxide.

12. A porous, extruded titania-based material obtainable by the process of claim 10 or claim 11.

13. A process for the preparation of a porous, extruded titania-based material comprising mesopores and macropores and having a crush strength greater than 3.0 lbf, said process comprising:

a) mixing titanium dioxide and one or more porogens to form a homogenous mixture;

b) adding a solution of one or more quaternary ammonium compounds to the homogenous mixture, and mixing to form a homogenous paste;

c) extruding the paste to form an extrudate; and

d) drying and/or calcining the extrudate at a temperature sufficient to decompose the one or more porogens.

14. A process according to claim 13, wherein the solution of one or more quaternary ammonium compounds comprises tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or cetyltrimethylammonium hydroxide.

15. A process according to claim 13 or claim 14, wherein the one or more porogen comprises cellulose or a derivative thereof, such as methyl cellulose, ethyl cellulose and ethyl methyl cellulose; alginic acid or a derivative thereof, such as ammonium alginate, sodium alginate and calcium alginate; latex or polyvinyl chloride.

16. A process according to any of claims 13 to 15, wherein the weight ratio of titanium dioxide to porogen is from 1:0.1 to 1:1.0, preferably 1:0.1 to 1:0.8, more preferably 1:0.15 to 1:0.6.

17. A porous, extruded titania-based material obtainable by a process according to any of claims 13 to 16.

18. A Fischer-Tropsch synthesis catalyst comprising a porous, extruded titania-based material according to any of claims 1 to 4 or claim 12, and further comprising at least one metal selected from cobalt, iron, nickel, ruthenium or rhodium.

19. A Fischer-Tropsch synthesis catalyst comprising a porous, extruded titania-based material according to any of claims 5 to 9 or claim 17, and further comprising at least one metal selected from cobalt, iron, nickel, ruthenium or rhodium.

20. A Fischer-Tropsch synthesis catalyst according to claim 18 or claim 19, further comprising one or more promoters, preferably wherein the one or more promoters are selected from rhenium, ruthenium, platinum, palladium, molybdenum, tungsten, boron, zirconium, gallium, thorium, manganese, lanthanum, cerium or mixtures thereof.

21. A process for the preparation of a Fischer-Tropsch synthesis catalyst according to claim 18, said process comprising:

a) mixing titanium dioxide, a solution of one or more quaternary ammonium compounds and a solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound, to form a homogenous paste;

b) extruding the paste to form an extrudate;

c) drying and/or calcining the extrudate at a temperature sufficient to convert the one or more thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to an oxide thereof; or to the metal form; and, where an oxide is formed, optionally

d) heating the dried and/or calcined extrudate under reducing conditions to convert the one or more cobalt, iron, nickel, ruthenium or rhodium oxide to the metal form.

22. A process for the preparation of a Fischer-Tropsch synthesis catalyst according to claim 19, said process comprising:

a) mixing titanium dioxide and one or more porogens to form a homogenous mixture;

b) adding a solution of one or more quaternary ammonium compounds and a solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to the mixture, and mixing to form a homogenous paste;

c) extruding the paste to form an extrudate;

d) drying and/or calcining the extrudate at a temperature sufficient to decompose the one or more porogens and to convert the at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to an oxide thereof, or to the metal form; and, where an oxide is formed, optionally

e) heating the dried and/or calcined extrudate under reducing conditions to convert the one or more cobalt, iron, nickel, ruthenium or rhodium oxide to the metal form.

23. A process according to claim 21 or claim 22, wherein the solution of one or more quaternary ammonium compounds comprises tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or cetyltrimethylammonium hydroxide.

24. A process for the preparation of a Fischer-Tropsch synthesis catalyst according to claim 18 or claim 19, said process comprising:

a) impregnating a porous, extruded titania-based material according to any of claims 1 to 9, 12 or 17 with a solution of at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound;

b) drying and/or calcining the impregnated porous, extruded titania-based material at a temperature sufficient to convert the at least one thermally decomposable cobalt, iron, nickel, ruthenium or rhodium compound to an oxide thereof or to the metal form; and where an oxide is formed, optionally

c) heating the dried and/or calcined porous, extruded titania-based material under reducing conditions to convert the at least one cobalt, iron, nickel, ruthenium or rhodium oxide to the metal form.

25. A Fischer-Tropsch synthesis catalyst obtainable by the process of any of claims 21 to 24, preferably having a crush strength of greater than 5.0 lbf.

26. Use of a quaternary ammonium compound to prepare a porous, extruded titania-based material having a crush strength of greater than 3.0 lbf, preferably wherein the quaternary ammonium compound is tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or cetyltrimethylammonium hydroxide.

27. Use of a quaternary ammonium compound to prepare a porous, extruded titania-based Fischer-Tropsch synthesis catalyst having a crush strength of greater than 5.0 lbf, preferably wherein the quaternary ammonium compound is tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or cetyltrimethylammonium hydroxide.

28. Use of a quaternary ammonium compound and a porogen to prepare a porous, extruded titania-based material comprising mesopores and macropores and having a crush strength of greater than 3.0 lbf, preferably wherein the quaternary ammonium compound is tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or cetyltrimethylammonium hydroxide.

29. Use of a quaternary ammonium compound to prepare a porous, extruded titania-based Fischer-Tropsch synthesis catalyst comprising mesopores and macropores and having a crush strength of greater than 5.0 lbf, preferably wherein the quaternary

ammonium compound is tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or cetyltrimethylammonium hydroxide.

30. A process for converting a mixture of hydrogen and carbon monoxide gases to hydrocarbons, which process comprises contacting a mixture of hydrogen and carbon monoxide with a Fischer-Tropsch synthesis catalyst according to any of claims 18 to 20 or 25, or a Fischer-Tropsch synthesis catalyst obtainable by a process according to any of claims 21 to 24.

31. A composition, preferably a fuel composition, comprising hydrocarbons obtained by a process according to claim 30.

32. A process for producing a fuel composition, said process comprising blending hydrocarbons obtained by a process according to claim 30 with one or more fuel components to form the fuel composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/066805

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J21/06 B01J23/75 B01J35/10 B01J32/00 B01J35/02
B01J37/00 B01J37/02 B01J37/18 B01J37/08
ADD. C07C1/04 C10G2/00 C10L1/02
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 C10G C10L 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 Y	US 5 484 757 A (SZYMANSKI THOMAS [US] ET AL) 16 January 1996 (1996-01-16) column 1, lines 19-26, 31-33, 36-37, 49 column 1, line 51 - column 2, line 9 column 2, lines 49-69 column 3, line 43 - column 4, line 8 examples 1-3 claims 1-3, 6, 9, 12	3,5,6,8,9 1-6,8-17,26,28
X Y	US 2006/286026 A1 (DAHAR STEPHEN L [US]) 21 December 2006 (2006-12-21) example 1 paragraphs [0003], [0010], [0023] - [0024]	3,5-9 1-15,17,26,28

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

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search	Date of mailing of the international search report
23 September 2016	05/10/2016

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/306173 A1 (DOGTEROM RONALD JAN [NL] ET AL) 11 December 2008 (2008-12-11)	1-4,6, 9-12,18, 20,21, 23, 25-27, 29-32
Y	example experimental figures 1-2 pages 8-12 claim 1	1-17,26, 28

X	US 8 729 140 B2 (BEZEMER GERRIT LEENDERT [NL] ET AL) 20 May 2014 (2014-05-20)	19,22,24
Y	column 5, lines 3-7, 24-27 column 9, lines 17-23, 32-45, 52-67 column 10, lines 27-67	1-17,26, 28

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