A PROCESS FOR PRODUCING HYDROCARBONS, AND A CATALYST SUITABLE FOR USE IN THE PROCESS

The present invention relates to a process for producing hydrocarbons from synthesis gas, and to a catalyst which is suitable for use in the process.

The catalytic preparation of hydrocarbons from synthesis gas, i.e. a mixture of carbon monoxide and hydrogen, is well known in the art and is commonly referred to as Fischer-Tropsch synthesis.

Supported catalysts suitable for use in a Fischer-Tropsch synthesis process typically contain a catalytically active metal of Group VIII of the Periodic Table of the Elements (Handbook of Chemistry and Physics, 68th edition, CRC Press, 1987-1988). In particular, iron, nickel, cobalt and ruthenium are well known catalytically active metals for such catalysts. Reference may be made to EP-A-398420, EP-A-178008, EP-A-167215, EP-A-168894, EP-A-363537, EP-A-498976 and EP-A-71770.

There is a continuous interest in finding catalysts which provide an improved selectivity in the conversion of carbon monoxide into valuable hydrocarbons, in particular hydrocarbons containing 5 or more carbon atoms ("C_5+ hydrocarbons" hereinafter), and which minimise the formation of carbon dioxide, which is a carbon containing by-product of low value.

It has now surprisingly been found that when in the Fischer-Tropsch synthesis a catalyst is used which contains inorganic phosphate more hydrocarbon, in particular more C_5+ hydrocarbons, and less carbon dioxide are produced. Further, there is less decline of the catalyst activity so that the catalysts may be used for a

more prolonged period of time without the need for replacement or re-activation.

Accordingly, the present invention provides a process for producing hydrocarbons, which process comprises contacting a mixture of carbon monoxide and hydrogen at elevated temperature and pressure with a catalyst comprising a Group VIII metal supported on a carrier, which Group VIII metal is present at least partly in metallic form, and which catalyst further comprises inorganic phosphate in a quantity of at least 0.05 %w, calculated as elemental phosphorus relative to the weight of the catalyst.

The Group VIII metal is preferably one or more selected from iron, nickel, cobalt and ruthenium. More preferably, cobalt or ruthenium is selected as the Group VIII metal, because cobalt based catalysts and ruthenium based catalysts give a relatively high yield of C_5+ hydrocarbons. Most preferably, cobalt is selected as the Group VIII metal.

A further metal may be present in order to improve the activity of the catalyst or the selectivity of the conversion of synthesis gas into hydrocarbons. Suitable further metals may be selected from manganese, vanadium, zirconium, rhenium and ruthenium. A preferred further metal is manganese or vanadium, in particular manganese.

Catalysts which comprise, supported on a carrier, a Group VIII metal selected from nickel, cobalt, iron and ruthenium, and a further metal selected from manganese, vanadium, zirconium and rhenium, which catalyst further comprises inorganic phosphate in a quantity of at least 0.05 %w, calculated as elemental phosphorus relative to the weight of the catalyst, are novel. In a second aspect the present invention also provides these novel catalysts.

The amount of Group VIII metal present in the catalyst may vary widely. Typically, the catalyst comprises from 1 to 50 %w Group VIII metal, based on the weight of the metal relative to the weight of catalyst, preferably 3 to 40 %w, more preferably 5 to 30 %w on the same basis.

The amount of the further metal, if present, is typically from 0.05 and 60 %w, more typically from 0.1 to 25 %w, based on the weight of the metal relative to the weight of the catalyst.

The atomic ratio of the Group VIII metal to the further metal, as present in the catalyst, is typically at least 5:1 and it is typically at most 200:1.

The inorganic phosphate may be present in the catalyst in any amount of at least 0.05 %w, calculated as elemental phosphorus, relative to the weight of the catalyst. Typically the inorganic phosphate will be present in an amount of less than 5 %w and a preferred amount is in the range of from 0.1 to 2.5 %w, for example 0.5 %w, on the same basis.

Generally a porous inorganic carrier may be found adequate for use in the present invention. In a preferred embodiment, the carrier is a refractory oxide carrier. Examples of suitable refractory oxide carriers include alumina, silica, titania, zirconia or mixtures thereof, such as silica-alumina or physical mixtures such as silica and titania. Preferably, the carrier comprises titania, alumina, zirconia or mixtures thereof, in particular titania or alumina.

The carrier comprising titania, alumina, zirconia or ~~mixtures thereof, may further comprise up to 50 %w of~~ another refractory oxide, typically silica, based on the total weight of the carrier. More preferably, the additional refractory oxide, if present, comprises up to

20 %w, even more preferably up to 10 %w, on the same basis.

The carrier most preferably comprises titania, in particular titania which has been prepared in the absence of sulphur-containing compounds. An example of such preparation method involves flame hydrolysis of titanium tetrachloride. It will be appreciated that the titania powder derived from such preparation method may not be of the desired size and shape. Thus, usually a shaping step is applied to prepare the carrier. Shaping techniques are well known to the skilled person and include palletising, extrusion, spray-drying and hot oil dropping methods.

The catalyst may suitably be prepared by methods known to the skilled person, such as by precipitating the catalytically active components or precursors onto the carrier; spray-coating, kneading, mulling and/or impregnating the catalytically active components or precursors onto the carrier; and/or extruding one or more catalytically active components or precursors together with carrier material to prepare catalyst extrudates. The term "catalytically active components" includes the Group VIII metal, any further metal and the inorganic phosphate, as present in the catalyst. It is not excluded that, in addition to the catalytically active components and the carrier, the catalyst comprises further components.

It will be appreciated that the method of preparation may vary, depending e.g. on the desired size of the catalyst particles. It belongs to the skill of the skilled person to select the most suitable method for a ~~given set of circumstances and requirements.~~

A preferred method of preparing the catalyst is by preparing a mixture of the carrier, the catalytically active components and/or precursors and a liquid, for example by kneading or mulling, shaping and drying the

mixture thus obtained and subsequently calcining, such as disclosed in WO 99/34917.

A suitable liquid is water, ammonia, alcohols such as methanol and ethanol, ketones such as acetone, aldehydes such as propanal, and aromatic solvents such as toluene. Water is a preferred liquid.

The Group VIII metal and the further metal may be employed in the form of the metal itself, or as an oxide, a hydroxide, or a salt such as a nitrate or an acetate, or mixtures thereof.

Suitable precursors of the phosphate as present in the catalyst are, for example, phosphorus compounds comprising an acid of phosphorus, such as metaphosphoric acid, pyrophosphoric acid, phosphorous acid, but preferably orthophospposphoric acid (H_3PO_4), or precursors of an acid of phosphorus, that is, a phosphorus containing compound capable of forming a compound containing at least one acidic hydrogen atom under circumstances where water is present or under such circumstances as applied in the preparation of the catalyst and/or in the activation of the catalyst, as set out hereinafter. A precursor of an acid of phosphorus is for example phosphorus pentoxide, phosphorus pentachloride or ammonium phosphates.

Calcination is typically carried out at a temperature between 200 and 900 °C, preferably, between 250 and 600 °C. The duration of the calcination treatment is typically from 0.5 to 24 hours, preferably from 1 to 4 hours. Suitably, the calcination treatment is carried out in an oxygen-containing atmosphere, preferably air. It will be appreciated that the average temperature during the calcination treatment will normally be higher than the average temperature during the drying treatment.

The catalyst is typically used to catalyse a process for the preparation of hydrocarbons from synthesis gas.

Typically, when in use in that process, at least part of the Group VIII metal is present in its metallic state. Preferably between 50 and 100 %w of the Group VIII metal is present in its metallic state, especially between 60 and 98 %w.

Therefore, it is normally advantageous to activate the catalyst prior to use by a reduction treatment, in the presence of hydrogen at elevated temperature. Typically, the reduction treatment involves treating the catalyst at a temperature in the range from 100 to 450 °C, at elevated pressure, typically from 1 to 200 bar abs, frequently for 1 to 200 hours. Pure hydrogen may be used in the reduction treatment, but it is usually preferred to apply a mixture of hydrogen and an inert gas, like nitrogen. The relative amount of hydrogen present in the mixture may be in the range of from 0.1 to 100 %v.

According to a preferred embodiment, the catalyst is brought to the desired temperature and pressure level in a nitrogen gas atmosphere. Subsequently, the catalyst is contacted with a gas mixture containing only a small amount of hydrogen gas, the rest being nitrogen gas. During the reduction treatment, the relative amount of hydrogen gas in the gas mixture is gradually increased up to 50 %v or even 100 %v.

It may be preferred to activate the catalyst in-situ, that is inside the reactor for the preparation of hydrocarbons from synthesis gas. WO 97/17137 describes an in-situ catalyst activation process which comprises contacting the catalyst in the presence of hydrocarbon ~~liquid with a hydrogen-containing gas at a hydrogen~~ partial pressure of at least 15 bar abs., preferably at least 20 bar abs., more preferably at least 30 bar abs. Typically, in this process the hydrogen partial pressure is at most 200 bar abs.

The process for the preparation of hydrocarbons from synthesis gas is typically carried out at a temperature in the range of from 125 to 350 °C, preferably from 175 to 275 °C. The pressure is typically in the range of from 5 to 150 bar abs., preferably from 5 to 80 bar abs., in particular from 5 to 60 bar abs.

Hydrogen and carbon monoxide are typically fed to the process at a molar ratio in the range from 1 to 2.5. Low hydrogen to carbon monoxide molar ratios will increase the C_5+ selectivity, i.e. the selectivity of the formation of C_5+ hydrocarbons. The C_5+ selectivity of the process is preferably at least 90 %w based on the total amount of hydrocarbons produced, preferably 95%.

However, in the embodiment of the invention in which the Group VIII metal is cobalt and the further metal is manganese and/or vanadium, which are present in an atomic ratio of cobalt/(manganese + vanadium) of at least 12:1, the C_5+ selectivity of the catalyst is remarkably high, even when using synthesis gas having a high hydrogen to carbon monoxide atomic ratio. In this embodiment the hydrogen to carbon monoxide molar ratio is in the range from 1.5 to 2.5.

The gas hourly space velocity ("GHSV" hereinafter) may vary within wide ranges and is typically in the range from 400 to 10000 Nl/l/h, for example from 400 to 4000 Nl/l/h.

The term "GHSV" is well known in the art, and relates to the gas per hour space velocity, i.e. the volume of synthesis gas in Nl (i.e. at the standard temperature of 0 °C and the standard pressure of 1 bar (100,000 Pa)) which is contacted in one hour with one litre of catalyst particles, i.e. excluding interparticular void spaces. In the case of a fixed bed catalyst, the GHSV is usually expressed as per litre of catalyst bed, i.e. including interparticular void space. In that case a GHSV of

1600 Nl/l/h on catalyst particles corresponds to about 1000 Nl/l/h on catalyst bed.

The process for the preparation of hydrocarbons may be conducted using a variety of reactor types and reaction regimes, for example a fixed bed regime, a slurry phase regime or an ebullating bed regime. It will be appreciated that the size of the catalyst particles may vary depending on the reaction regime they are intended for. It belongs to the skill of the skilled person to select the most appropriate catalyst particle size for a given reaction regime.

Further, it will be understood that the skilled person is capable to select the most appropriate conditions for a specific reactor configuration, the reaction regime and a work-up scheme. For example, the preferred gas hourly space velocity may depend upon the type of reaction regime that is being applied. Thus, if it is desired to operate the hydrocarbon synthesis process with a fixed bed regime, preferably the gas hourly space velocity is chosen in the range from 500 to 2500 Nl/l/h. If it is desired to operate the hydrocarbon synthesis process with a slurry phase regime, preferably the gas hourly space velocity is chosen in the range from 1500 to 7500 Nl/l/h.

The invention will now be illustrated further by means of the following Examples.

Example I

A mixture was prepared containing 112.5 g commercially available titania powder (P25 ex. Degussa), 49.5 g commercially available $CO(OH)_2$ powder, 8.2 g $Mn(Ac)_2.4H_2O$ ("Ac" means acetate), 2.2 g phosphoric acid and 45 g water. The mixture was kneaded for 30 minutes. The mixture was shaped by means of an extruder. The extrudate were dried for 2 hours at 120 °C

and calcined for 2 hours at 500 °C. The catalyst contained 22 %w CO, 1.2 %w Mn and 0.7 %w P.

The catalyst was tested in a process for the preparation of hydrocarbons. A micro-flow reactor containing 10 ml of the catalyst in the form of a fixed bed of catalyst particles was heated to a temperature of 260 °C, and pressurised with a continuous flow of nitrogen gas to a pressure of 2 bar abs. The catalyst was reduced in-situ for 24 hours with a mixture of nitrogen and hydrogen gas. During reduction the relative amount of hydrogen in the mixture was gradually increased from 0% to 100%. The water concentration in the off-gas was kept below 3000 ppmv.

Following reduction the pressure was increased to 31 bar abs. The preparation of hydrocarbons was carried out with a mixture of hydrogen and carbon monoxide at a H_2/CO ratio of 1.1:1. The GHSV amounted to about 930 Nl/l/h. The reaction temperature is expressed as the weighted average bed temperature was 205 °C. The space time yield, expressed as grams hydrocarbon product per litre catalyst particles (including the voids between the particles) per hour, was 100 g/l/h. The selectivity of CO_2, expressed in %mole CO_2 obtained relative to the number of moles CO converted; the selectivity of the hydrocarbons, expressed as %mole of carbon present in the hydrocarbons obtained relative to the number of moles CO converted; and the selectivity to hydrocarbons containing 5 or more carbon atoms (C_5+ selectivity), expressed as a weight percentage of the total hydrocarbon product, were determined after 30 hours of operation. The results are set out in Table I.

Example II (comparative)

Example I was substantially repeated but with the difference that no phosphoric acid was present in the mixture.

TABLE I

Example	I	II *)
Selectivity CO_2 (%mole)	0.9	1.3
Selectivity hydrocarbons (%mole)	99.1	98.7
C_5+ selectivity (%w)	94	92

*): Comparative

It will be appreciated that the catalyst of Example I, i.e. according to the invention, is much better than the catalyst of Example II, i.e. the comparative catalyst.

C L A I M S

1. A process for producing hydrocarbons, which process comprises contacting a mixture of carbon monoxide and hydrogen at elevated temperature and pressure with a catalyst comprising a Group VIII metal supported on a carrier, which Group VIII metal is present at least partly in metallic form, and which catalyst further comprises inorganic phosphate in a quantity of at least 0.05 %w, calculated as elemental phosphorus relative to the weight of the catalyst.

2. A process as claimed in claim 1, characterised in that the Group VIII metal is cobalt.

3. A process as claimed in claim 1 or 2, characterised in that a further metal is present which further metal is selected from manganese, vanadium, zirconium, rhenium and ruthenium.

4. A process as claimed in any of claims 1-3, characterised in that inorganic phosphate is present in a quantity in the range of from 0.1 to 2.5 %w, calculated as elemental phosphorus relative to the weight of the catalyst.

5. A process as claimed in any of claims 1-4, characterised in that the carrier comprises titania or alumina.

6. A catalysts which comprises, supported on a carrier, a Group VIII metal selected from nickel, cobalt, iron and ruthenium, and a further metal selected from manganese, ~~vanadium, zirconium and rhenium, which catalyst further~~ comprises inorganic phosphate in a quantity of at least 0.05 %w, calculated as elemental phosphorus relative to the weight of the catalyst.

7. A catalysts as claimed in claim 6, characterised in that at least part of the Group VIII metal is present in its metallic state.

8. A catalyst as claimed in claim 6 or 7, wherein the inorganic phosphate is present in a quantity in the range of from 0.1 to 2.5 %w, calculated as elemental phosphorus relative to the weight of the catalyst.

9. A process for preparing a catalyst as claimed in claim 6, comprising the steps of preparing a mixture of the Group VIII metal, the further metal and the inorganic phosphate and/or precursors thereof, the carrier and a liquid, shaping and drying the prepared mixture and subsequently calcining.

10. A process for the preparation of a catalyst as claimed in claim 7, which comprises subjecting a catalyst as claimed in claim 6 to a reduction treatment in the presence of hydrogen.