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| (54) Title: PRODUCTION OF SYNTHESIS GAS FROM HYDROCARBONACEOUS FEEDSTOCK (57) Abstract A method for producing synthesis gas (essentially a mixture of hydrogen and carbon monoxide) from a mixture of methane and oxygen comprising partially oxidising the methane by bringing the reactant gas mixture at a relatively low temperature (100 °C to 950 °C) and at a pressure of up to 15 bar into contact with a defined nickel - aluminium Feitknecht compound/alumino-silicate clay mineral based catalyst. Resulting synthesis gas may be mixed with further oxygen and be further partially oxidised without being subjected to an intermediate compression stage to produce a second synthesis gas suitable for direct use in a high pressure downstream process for producing a chemical product, such as methanol. | | |

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PRODUCTION OF SYNTHESIS GAS FROM HYDROCARBONACEOUS FEEDSTOCK

This invention relates to the production of synthesis gas from hydrocarbonaceous feedstock, more particularly from methane-containing feedstock, such as natural gas. The invention also relates to the synthesis of products, such as methanol, hydrogen, synthetic crude oil and ammonia from the synthesis gas.

In this specification the term 'synthesis gas' means a mixture essentially of hydrogen and carbon monoxide, which may also contain carbon dioxide and/or steam and/or methane.

One known method of producing synthesis gas comprises passing a mixture of steam and a methane-containing feedstock over a catalyst under conditions to cause steam reformation and the production of synthesis gas.

An object of the present invention is to employ partial oxidation of methane at relatively low temperatures to produce synthesis gas.

Accordingly, the invention provides a method of producing synthesis gas from a reactant gas mixture comprising methane, oxygen and optionally, steam and/or carbon dioxide, wherein the method comprises partially oxidising the methane by

bringing the reactant gas mixture at a temperature in the range from 100°C to 950°C and at a pressure of up to 150 bar into contact with a first solid catalyst, which initiates the reaction, and conducting the reaction under substantially adiabatic conditions to produce the synthesis gas, the catalyst having been made by a method comprising intimately mixing a Feitknecht compound having the general formula:

$\text{Me}_x^{2+} \text{Me}_y^{3+} (\text{OH})_{2x+3y+2z} (\text{A}^{2-})_z \cdot n\text{H}_2\text{O}$ wherein

Me^{2+} is substantially completely Ni^{2+} ,

Me^{3+} is substantially completely Al^{3+} or substantially Al^{3+} and Cr^{3+} ,

A^{2-} is either a single divalent anion or two monovalent anions.

x/y lies between 1.5/1 and 4/1,

$z/(x+y)$ lies in the range 0.05 to 0.2, and

$n/(x+y)$ lies in the range 0.25 to 1.0,

with a non-calcined alumino-silicate clay mineral and, at the same time and/or subsequently but prior to calcination, with at least one added stabilising additive for reducing silicon-species loss comprising an alkaline earth and/or rare earth metal compound, and, optionally, an alkali metal compound, and thereafter calcining the resulting mixture and subjecting the catalyst material to a reducing process to activate the catalyst.

The Feitnecht compound is formed by a co-precipitation comprising the bringing together of a mixed solution of water soluble salts of nickel and aluminium, and optionally

chromium, and a precipitant solution. The mixed salt solution may, for example, be a mixed nitrate solution. The precipitant solution may be an alkaline solution such as sodium carbonate, bicarbonate or hydroxide; or potassium carbonate bicarbonate or hydroxide; or ammonium hydroxide or bicarbonate; or urea.

The Feitnecht compound may be co-precipitated in the presence of the clay mineral and the stabilising additive mixed in subsequent to the co-precipitation. Alternatively the Feitnecht compound may be co-precipitated in the absence of the clay mineral and the clay mineral and stabilising additive mixed in subsequent to the co-precipitation.

The resulting intimate mixture may be mixed with a cement binder prior to calcination of the mixture. Alternatively a cement binder may be added to the mixture after calcination. The cement binder may be a high alumina cement binder. The presence of the cement binder further strengthens and gives stability to the catalyst.

The clay mineral may be a layer-structured phyllosilicate and/or pseudo-layer-structured, such as a smectite - for example, bentonite. The bentonite, for example, also further strengthens and gives stability to the catalyst.

Applicants UK patent specification no. 2222963 is directed to catalysts and catalyst precursors, and the method of preparing

catalysts and catalyst precursors, employed in the present invention.

The synthesis gas may be produced at a temperature in the range from 500°C to 1000°C and at a pressure in the range from 1 to 40 bar.

The synthesis gas may, for example, be produced at a temperature in the range from about 500°C to about 900°C and at a pressure in the range from about 1 to about 10 bar. At these temperatures and pressures relatively good methane conversion occurs, i.e. there is relatively low methane slippage, and the resulting synthesis gas would, typically be used in fuel cells in which the resulting synthesis gas so produced, for example, would proceed to a shift reactor and then on for further processing without further reforming or compression of the synthesis gas being required. Such further processing may involve one or more techniques which are familiar to persons skilled in the art and are designed to remove carbon monoxide from the gas, such techniques, for example, including membrane separation, reverse methanation and selective oxidation.

The synthesis gas may instead, for example, be produced at a temperature in the range from about 700°C to about 1000°C and at a pressure in the range from about 5 to about 40 bar. Again, at these temperatures and pressures relatively good methane conversion occurs and the synthesis gas can be fed

straight to a process operating at a medium pressure to produce a chemical product from such synthesis gas, without the synthesis gas being further reformed or compressed.

The synthesis gas may alternatively, for example, be produced at a temperature in the range from about 700°C to 1000°C and at a pressure in the range from about 25 to about 100 bar. Synthesis gas obtained at these temperatures and pressures may be employed in a process to obtain a second synthesis gas in order to overcome the problem described below.

In the past, prior to using synthesis gas which had been obtained by a steam reformation route in some relatively high pressure processes for producing further products, such synthesis gas has had to be compressed to a sufficiently higher pressure by, for example, a make-up compressor. For example, if methanol was to be produced in a process from synthesis gas, the process might require the input synthesis gas to be at a relatively high pressure to comply with desired reaction conditions. However, in order for the steam reformation reaction to produce synthesis gas with desired low methane content, i.e. with low methane slippage relatively low pressure conditions are required. If relatively high pressures were to be used for the steam reformation, not only would there be unwanted high methane content in the synthesis gas, i.e. increased methane slippage, but there would be metallurgical or constructional problems.

Another object of the present invention is to produce synthesis gas at a relatively high temperature and pressure without the assistance of a make-up compressor or like gas compressing means, suitable for direct use in a high pressure downstream synthesis process.

Accordingly, the invention also provides a method of producing a second synthesis gas at relatively high temperature and pressure, the method comprising utilising as feed gas a first synthesis gas produced by the method as defined above at a temperature in the range from 700°C to 1000°C and at a pressure in the range from 25 to 100 bar, and comprising carbon monoxide, carbon dioxide, hydrogen, steam and unreacted methane, and without having been subjected to a compression stage subsequent to its production, the present method comprising adding oxygen to the first synthesis gas and causing partial oxidation of hitherto unreacted methane, by passing the reactant mixture of first synthesis gas and oxygen at a temperature in the range from 600°C to 900°C and at a pressure in the range from 25 to 100 bar over a solid catalyst, and conducting the further partial oxidation under substantially adiabatic conditions to produce the second synthesis gas at a relatively high temperature and pressure.

The above method thus involves two stages; the first being an initial partial oxidation stage, and the second being a further partial oxidation stage.

It is envisaged that both stages in the above defined two stage or two step partial oxidation process can be carried out in adiabatic reactors which are of relatively simple design and relatively inexpensive to build and operate. In addition, metallurgical problems which constrain, for example, conventional fired tubular reformers can be removed and so the outlet temperature of the reactor can be increased substantially. This means that the pressure within the reactor can be increased without increasing methane slippage.

In the present two stage method the resulting synthesis gas can be produced at high pressures to match those used in various current commercial processes, e.g. methanol manufacture and ammonia production, avoiding the use of expensive and energy intensive make-up gas compressors.

Previous proposals by others have included two stages for producing synthesis gas or make-up gas as part of a single pressure process for the production of methanol in a synthesis loop - see European patent application EP 0329292 A2. In that application it is disclosed that the synthesis gas or make-up gas as produced is added to the synthesis loop without further compression. The process is based on the combination of a high pressure steam reformer and a catalytic partial oxidation reactor. Although the process removes the requirement for a make-up gas compressor, the need for a large, complex and expensive gas heated reformer remains.

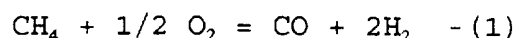
In the present first defined method and in the first stage of the present second defined method, prior to the reactant gas mixture being brought into contact with the partial oxidation catalyst, individual streams of each of the methane-containing gas e.g. natural gas, the oxygen-containing gas (e.g. air) and, optionally, steam and/or carbon dioxide may pass to a mixer whereafter the gas mixture is passed to and heated in a common pre-heater. Alternatively, the individual feed streams may pass to individual pre-heaters before being passed to a mixer to produce a mixture which ensures that the different gases are co-fed to the reactor. It will be appreciated that the residence time in the pre-heater must be kept shorter than the time which would result in auto-ignition of the reactant gas mixture. The pre-heat temperature may be in the range from 100°C to 500°C, typically 200°C to 300°C. Advantages stem from being able to employ such low pre-heat temperatures. On the one hand the required size of the pre-heater can be reduced with an accompanying reduction in cost. At the same time, the time required for auto-ignition of the reactant mixture is increased. Applicants investigations have shown that highly active and very robust steam reforming catalysts have to be used in order for the reaction to be initiated and sustained at these low temperatures. Examples of suitable catalysts are set out below.

By way of illustration, the 'cold' feed streams may be at ambient temperature and at a pressure of approximately 83 bar, whilst the heated gas mixture about to be passed over the

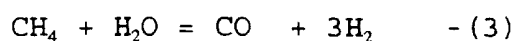
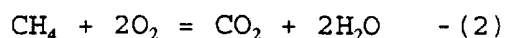
catalyst may be at about 300°C and at a pressure of about 82 bar. In such instances the product gas or synthesis gas emerging from the reaction zone containing the catalyst may be at a temperature of about 800°C and at a pressure of approximately 80.5 bar.

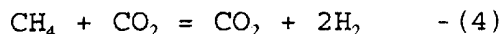
It is envisaged that high space velocities will be employed - in the order of 50,000hr⁻¹ (GHSV) - to give residence times of 0.1 to 10 seconds in the reactor containing the catalyst and 0.2 to 60 seconds for the passage through mixer, pre-heater(s) and reactor. The residence time is such that the reactant gases are contacted with the catalyst for sufficient time to be brought to thermodynamic equilibrium at the outlet temperature or temperature of the synthesis gas emerging from the reaction zone.

In the reaction zone over the partial oxidation catalyst it is considered that methane reacts with oxygen to produce synthesis gas in accordance with the overall reaction:



It is believed that the reaction comprises the following three steps which may or may not happen simultaneously:





Unless precautions are taken, a further, undesirable reaction may also occur:



which would result in solid carbon deposition in the reaction zone and this should be avoided or minimised at all times.

It will be appreciated that the steam/methane and/or carbon dioxide/methane and oxygen/methane ratios can be varied within wide limits depending on the synthesis gas composition required at the outlet from the reaction zone.

The steam to methane and/or CO_2 to methane ratio can be varied from 0 to 10 depending on the outlet composition required. The oxygen to methane ratio can be varied from 1 to 0.2.

The invention will now be further described by way of illustration with reference to the following experiments and investigations.

PREPARATION OF CATALYST 1

A catalyst used in a method according to the invention.

To prepare the catalyst precursor a solution containing 25.4kg of anhydrous sodium carbonate in 80 litres of deionised water

was heated to 75°C. 35.2kg of nickel nitrate hexahydrate, 13.6kg of aluminium nitrate nonahydrate and 1.6kg of chromium nitrate hexahydrate were dissolved in 80 litres of deionised water and heated to 75°C. The precursor was precipitated by slow addition of the carbonates solution to the nitrates solution at a constant temperature of 75°C, both solutions being vigorously stirred throughout. After precipitation an aqueous slurry containing 1.7kg of kaolin and 0.8kg of magnesium oxide was added to the solution with stirring. The slurry was filtered and the filter cake reslurried with 140 litres of deionised water at 60°C. The process of reslurrying followed by filtration was continued until the filtrate contained less than 100ppm by weight of sodium. The resulting material was dried at 125°C and then calcined at 450°C for two hours to give the calcined precursor. The calcined precursor was ground to pass a 850 micron sieve, then mixed with 4.95kg of Secar 71 high alumina cement, supplied by Larfarge, as a binder to improve strength. This powder was further blended with 2% by weight of graphite and then pelleted. The pelleted catalyst was steamed at atmospheric pressure at 240°C for 16 hours and then soaked at room temperature in deionised water for over 12 hours. The pellets were dried at 125°C and then dipped in a solution containing 2% by weight of potassium hydroxide. The composition of the final catalyst precursor is given in Table 1.

Experiment 1

A feed gas containing by volume 20% CO₂, 60% N₂, 11.4% CH₄ and 8.5% O₂ was passed over a 70g bed of catalyst 1 at 15 bar (GHSV 35,000). The temperature of the feed gas was 300°C and the temperature of the gaseous mixture emerging from the bed (i.e. outlet temperature) was 750°C. The composition by volume of the emerging gas mixture was H₂ - 10.3%, CO₂ - 17.7%, N₂ - 58.4%, CO - 13.0% and CH₄ - 0.8%. No oxygen was observed in the outlet gas. This was calculated to be at thermodynamic equilibrium with the 'outlet' temperature. The run lasted more than 500 hours. At the end of the run, the catalyst was found to be in good physical condition with little dusting and no carbon laydown, and there was no significant deactivation of the catalyst.

This experiment demonstrated that the catalyst can initiate the reaction and bring it to equilibrium under simulated commercial conditions of inlet composition, pressure, space velocity and temperature. It further demonstrated that the catalyst is active at relatively low temperatures and maintains its activity and physical integrity through the relatively high temperature part of the bed (hot spot). Thus, the single catalyst was used both to initiate the reaction and maintain it through the catalyst bed. Consequently, the reactor can be adiabatic with a single catalyst charge. As a result, the reactor is simple to construct and inexpensive to operate.

A further series of experiments were conducted in which each of the following catalysts were tested for their suitability for catalytic partial oxidation of methane to synthesis gas using 1 gram of catalyst material to form 4cm length beds in 0.21 inch (0.535cm) internal diameter stainless steel tubes.

Preparation or identification of Catalysts

CATALYST 1 - see above.

CATALYST 2 - To prepare the catalyst precursor 5.1kg of bentonite clay was placed in a solution containing 2.9kg of anhydrous sodium carbonate in deionised water. The clay was allowed to swell in this solution overnight. This was then added to a solution containing a further 58kg of anhydrous sodium carbonate in 100 litres of deionised water and heated to 95°C. 84.4kg of nickel nitrate hexahydrate and 36.3kg of aluminium nitrate nonahydrate dissolved in 100 litres of deionised water and heated to 95°C. The precursor was precipitated by slow addition of the carbonates solution to the nitrates solution at a constant temperature of 95°C. Both solutions were vigorously stirred throughout. When precipitation was complete, an aqueous slurry containing 2.9kg of magnesium oxide was added to the mixture and the resulting slurry was maintained at 95°C for 20 minutes with constant stirring. The slurry was filtered and the filter cake reslurried with 140 litres of deionised water at 60°C. The process of reslurrying followed by filtration was continued

until the filtrate contained less than 100 ppm by weight of sodium. The wet mud was then placed in a blender and an aqueous solution of 160g of anhydrous potassium carbonate was added to it with stirring. The resulting material was dried at 125°C and then calcined at 450°C for two hours to give the calcined precursor. The calcined precursor was ground to pass a 850 micron sieve, blended with 2% by weight of graphite and then pelleted. The composition of the final catalyst precursor is given in Table 1.

TABLE 1

CATALYST
PRECURSOR

COMPOSITION

| | Ni wt% | Al wt% | Si wt% | Mg wt% | La wt% | C wt% | Cr wt% | K wt% | Nominal Clay Mineral Content wt% |
|---|-----------|-----------|-----------|-----------|-----------|----------|-----------|----------|--|
| 1 | 36.1 | 18.6 | 1.9 | 2.3 | - | - | 1.0 | 0.5 | 10.0 |
| 2 | 49.9 | 9.2 | 3.8 | 4.8 | - | 3.9 | - | 0.4 | 17.0 |

Compositions analysed by inductively coupled plasma emission spectroscopy. Error in silicon content + or - 0.1 wt%.

CATALYST 3 - ICI Methane steam reforming catalyst 57/3.

CATALYST 4 - As CATALYST 1 above.

In preparation for use in the experiments, catalysts 1, 2 and 3 were reduced in flowing hydrogen at 500°C for 1 hour. Catalyst 4 was left unreduced.

Experiment 2

After cooling to about 100°C the reaction feed (10% methane, 49% carbon dioxide and 41% air GHSV 9,500) was introduced into the tube and the temperature raised incrementally to 300°C. Catalysts 1 and 2 were able to initiate and maintain the reaction when the temperature reached 150°C. Catalyst 3 did not initiate the reaction until the temperature reached 380°C. The unreduced version of catalyst 1, i.e. catalyst 4 did not initiate the reaction below 400°C.

This experiment demonstrated that catalysts 1 and 2 can initiate the reaction at very low temperatures, even with very dilute feed gas compositions. This enables reduction in the size of the feed gas pre-heater and the start-up heaters as the catalyst bed need only reach a relatively low temperature for the reaction to be initiated. This in turn would reduce start up times and capital and operational costs. The lower pre-heat temperature would also increase the safety of the system because the reactant mixture would be below its auto-ignition temperature and therefore residence times within the pre-heater and reactor inlet manifolds would not be so critical. This in turn increases the flexibility of any plant by increasing the operational turn-down ratio.

As catalyst 4 was unable to initiate the reaction at low temperatures, this indicates that the catalysts are best used in the reduced form.

Experiment 3

To check for the stability of the catalysts at high temperature, the four catalysts were loaded into the reactors in a similar fashion to that in experiment 2. Catalysts 1, 2 and 3 were reduced in hydrogen at 500°C for 1 hour. Catalyst 4 was left unreduced. The reactor temperature was then raised to 850°C. During the 250+ hour test the outlet gas composition for all four reactors was very similar (approximately 5% hydrogen, 43% carbon dioxide, 34% nitrogen and 17% carbon monoxide). This was calculated to be very close to the thermodynamic equilibrium.

Experiment 4

The temperature stability tests (Experiment 3) were repeated using 0.05g of catalyst so that the GHSV was increased to 51,000/hr in this experiment. Catalyst 4 was not included. At 850°C the selectivity over catalysts 1 and 2 i.e. the outlet gas compositions were very similar to experiment 3 ($H_2 \approx 5\%$, $CO \approx 16\%$, $CO_2 \approx 43\%$), with substantially complete methane conversion. Increasing methane slippage was observed over catalyst 3, indicating deactivation of the catalyst, during the 150+ hours on stream at 850°C and H_2 , CO and CO_2 outlet compositions changed from 5.1, 14.3 and 44% to 3.6, 8.6 and 48.9% respectively.

Experiments 3 and 4 demonstrated that catalysts 1 and 2 can bring the reaction to equilibrium at very high space velocities. This means that these catalysts are stable and active for extended periods of time under the most arduous conditions. As catalyst 3 is deactivated under these conditions, this demonstrated that catalysts 1 and 2 would be the preferred catalysts as a commercial reactor utilising these two of the four catalysts tested could be smaller and cheaper for the same duty. Experiment 4 also demonstrated that the process is catalysed heterogeneously and that 'empty tube' gas phase reactions are not solely responsible for the occurrence of the reactions under these conditions.

Experiments 1 to 4 also demonstrate that catalysts 1, 2 and 3 can carry out catalytic partial oxidation in the presence of CO₂. This is commercially useful in the exploitation of CO₂ containing feed gas. The CO₂ could be present in the feed natural gas or as part of a recycle stream.

Experiment 5

A feed gas containing by mole 31.3% steam, 60% N₂, 11.4% CH₄ and 8.5% O₂ was passed over a 70g bed of catalyst 1 at 20 bar (GHSV 30,000 dry). The temperature of the feed gas was 300°C and the temperature of the gaseous mixture emerging from the bed (i.e. outlet temperature) was 750°C. The composition by mole of the emerging gas mixture was: H₂ 27.6%, CO₂ 8.2%, N₂ 51.6%, CO 4.48% and CH₄ 7.59%. This was calculated to be at

the thermodynamic equilibrium with the 'outlet' temperature. The run lasted more than 200 hours with no significant deactivation of the catalyst.

Experiment 5 demonstrated that catalyst 1 can carry out catalytic partial oxidation in the presence of steam, that the increase in partial pressure of steam (and the decrease in partial pressure of CO_2) does not cause deactivation problems or physical collapse of the catalyst, and that the catalyst can bring the reactant gases to equilibrium under these conditions.

This is commercially significant in that presence of the steam reduces the exotherm of the partial oxidation reaction whilst causing more methane to be converted by driving reaction (3) further to the right. This process is also known as autothermal reforming. The result is that the reactor and catalyst can operate at lower temperatures for the same methane conversion, and more hydrogen is produced. This is commercially useful for hydrogen production processes and fuel processing for fuel cells. It is also advantageous where the feed natural gas is relatively rich (i.e. there is a considerable amount of higher hydrocarbons present in the feed gas). This could be due, for example, to the composition of the feed gas from the reservoir or pipeline, or to recycling light hydrocarbons from a downstream process such as Fischer-Tropsch process.

During each of the longer term 'life' experiments, the reactor was shut down several times and each time the catalysts 1 and 2 were able to re-initiate the reaction without difficulty except for catalyst 3 in experiment 4. This indicates that although catalysts do deactivate to some extent under the demonstration conditions, there is sufficient residual activity for these catalysts to function, and that the catalysts are robust to pressure and temperature shocks.

In other processes where the fuel and oxidant streams are fed separately to the reactor and they pass through some sort of combustor before passing over the catalyst, the inadvertent production of flammable gas mixtures at above the auto-ignition temperature is avoided. Such gas mixtures would obviously ignite and could be extremely hazardous in the wrong places.

In the example method described here, the reactants are pre-mixed whilst cold and co-fed to the pre-heater, the temperature of which may be below or just above the adiabatic auto-ignition temperature. The adiabatic auto-ignition temperature is defined as the temperature at which in an adiabatic enclosure the self heating effect of the reaction mixture will eventually lead to ignition. Ignition is defined as thermal runaway. Reaction mixtures below the adiabatic auto-thermal ignition temperature may exhibit self heating, but this will never lead to ignition. It is therefore considered vitally important that the residence times through

the pre-heater and on to the catalyst bed are kept to a minimum. Studies indicate that times in the order of 1 to 10 seconds are safe depending on the gas mixture in use.

The effect of inert additives to the gas feed (such as N₂) is to increase delay times. The presence of carbon dioxide and/or steam significantly increase delay times, whilst the presence of higher hydrocarbons and especially hydrogen in natural gas feedstock will decrease delay times.

By varying the steam to methane and/or CO₂ to methane ratio, the outlet H₂ to CO ratio can be varied from 0.25:1 to 8:1. This can be achieved by varying the O₂ concentration in the feed gas mixture without either carbon deposition nor excessive outlet temperature. Typically 1.5-2:1 would be used for manufacturing, for example, synthetic fuels or methanol, whilst >6:1 could be used for fuel processing for fuel cells.

The reactant gases are contacted with the catalyst for sufficient time to be brought to thermodynamic equilibrium at the outlet temperature. Because the exothermic combustion reactions (grouped under reaction - equation (2) - see above) are faster than the reforming reactions (equations (3) and (4) above), the temperature profile in the reactor passes through a peak or hot spot. It is important that the reactor is engineered so that this hot spot is minimised and kept below 950°C (preferably 900°C). It is important that there is sufficient catalyst in the reactor to bring the gases to

equilibrium after the hot spot. Although it is possible to operate the reactor away from equilibrium i.e. have a short catalyst bed/very high flowrate and thus low residence times, in general, however, it is not advantageous to do this as methane slippage is increased and therefore conversion is reduced. Selectivity to CO is also impaired as the CO₂ reforming reaction is the slowest step.

Applicants believe that a number of advantages can be had from producing synthesis gas by these methods described above and in accordance with the invention since these methods allow

- (a) the use of low reactor inlet temperature (approximately 300°C) which means that small pre-heaters of simple designs can be used,
- (b) the use of low steam/carbon ratio in the feedstock (1:1 or less) which allows the operator greater flexibility over feedstock compositions (e.g. high levels of higher hydrocarbons or carbon dioxide can easily be utilised) and outlet compositions, without Boudouard carbon laydown, or coking, whilst the hydrogen to carbon monoxide ratio may be varied from 0.25:1 to 8:1,
- (c) the use of low reactor outlet temperatures, for example, as low as 600°C, the optimum outlet temperature being 700 to 800°C,

- (d) the use of simple reactor construction, as the reactor is adiabatic, with no cold shot or interstage cooling, or tubular internals being required. This means relatively low capital and maintenance costs and relatively easy start-up and operation.

The reactor could readily be constructed to operate over a wide range of pressures (1 to 100 bar or more) and could be fed with either oxygen or air as the oxidant.

In conducting experiments similar to experiment 1 but altering the pressure, Applicants observed that catalyst 1 was able to initiate and maintain the partial oxidation reaction at very low pressures (down to 1 bar), even though the residence time was greatly reduced.

In addition, Applicants have demonstrated that catalyst 1 was also effective at high pressures (up to 70 bar) in the presence of steam in initiating and maintaining reforming activity whilst retaining good physical condition.

It will be appreciated that although Applicants have observed in relation to the methods of the invention good catalytic activity, and good final condition of the catalyst over a wide range of pressures and temperatures in the experiments described above, various conditions which are detrimental to the catalyst, particularly at high temperatures and pressures or conditions and as are known to persons skilled in the art,

must still be avoided or be kept to a minimum. For example, the following should be avoided: (1) high concentrations of carbon monoxide at low temperatures 200 to 300°C such that Nickel carbonyl could be formed; (2) conditions under which methane or other hydrocarbons will crack; (3) conditions under which Boudouard carbon will be laid down; (4) and the introduction of sulphur or other catalyst poison. The conditions (1), (2) and (3) can readily be predicted and avoided by careful consideration of the feed composition and process conditions.

Applicants have submitted catalysts 1 and 2 to tests for many thousands of hours under reaction conditions where the partial pressure of super-heated steam was much higher than the highest pressure to be used in the partial oxidation process to which the present invention relates. These tests demonstrated that catalysts 1 and 2 are capable of performing the partial oxidation reaction at the highest pressures and temperatures claimed by the Applicants in relation to the present invention.

In tests, Catalysts 1 and 2 have shown:-

- (a) high activity for reforming at low light-off temperatures,
- (b) stability and activity at high operating temperatures; very good sinter resistance,

- (c) excellent strength and retention of this strength in operation,
- (d) no loss of strength or activity or leaching in steam environments, e.g. silica or potassium leaching.

These excellent qualities arise from the very particular nature of the catalyst formulation. The Applicants believe that the first two characteristics arise from the relatively high nickel content of both catalysts which is finely dispersed on the substrate. The substrate in turn is supported by high alumina cement in the case of Catalyst 1, and Bentonite in the case of Catalyst 2 which gives it added strength and stability.

As regards the method according to the invention of further partially oxidising the synthesis gas produced via the initial method as illustrated above, a simplified process flow sheet will now be described with reference to Figure 1.

Reference numeral 1 indicates a reactor in which 'low' temperature partial oxidation as illustrated above occurs. The synthesis gas emerging from reactor 1 passes to reactor 2 which is also fed with oxygen. Reactor 2 may be a known 'high' temperature partial oxidation reactor such as that, for example, described in European patent application no. 89300704.7 (published under the number EP 0329292 A2) and identified therein by the reference number 46. That reactor comprises a large refractory lined pressure vessel, a burner

and a high temperature reforming catalyst. The incoming partially reformed synthesis gas is combusted with the oxidising stream at the burner head and the resulting mixture is then passed over the catalyst (typically Chromium on alumina) which brings the reactants to thermodynamic equilibrium with respect to reaction equations (2), (3) and (4) above at a temperature higher than that in reactor 1. The methane slippage from this reactor is typically less than 5%.

Thus, having regard to Figure 1, the partially oxidised/reformed gases leaving reactor 1 are mixed with more oxygen in the burner assembly (not shown) in reactor 2. The further partially oxidised product gases which are now further reformed and comprise a mixture of carbon monoxide, carbon dioxide, hydrogen, steam and a reduced amount of unreacted methane. No higher hydrocarbons are present. These product gases emerge from reactor 2 and typically pass through a series of heat exchangers before passing, without being subjected to compression operations, to further reactors to undergo further processing to produce, for example, methanol.

It will be seen from the Figure that heat exchanger 3, which is one of the series mentioned above, is used to pre-heat the feed natural gas, oxygen and steam and/or carbon dioxide before they are introduced into the reactor 1.

Before the further partially oxidised product gases or the "fully reformed" gas, i.e. the further synthesis gas or make-up gas, reach the synthesis loop, they may pass through one or more purification/scrubbing stages. It may, for example, be desirable to remove some of the carbon dioxide present in the make-up gas, prior to the gas being passed to the synthesis loop. It is envisaged that such removed carbon dioxide could be recycled and used as part of the carbon dioxide feed to the reactor 1.

As a result of Applicants investigations it is envisaged that typical feed compositions, conditions and parameters for preparing synthesis gas or make-up gas, via the two stages discussed above, for use in methanol synthesis would be as follows.

The initial feed gas mixture supplied may be at a pressure of from 50 to 100 bar. The individual components prior to forming the feed gas mixture may be

Moles

| | |
|-----------|-----------------------------|
| 100 | - natural gas (90% methane) |
| 15 to 55 | - oxygen (99.5%) |
| 50 to 150 | - steam |

As regards the first partial oxidation stage typical operating conditions would be:

Pressure - 80 bar

Inlet temperature - 300°C

Outlet temperature - 800°C

| Inlet Composition | | Outlet Composition |
|--------------------------|-----------|--------------------|
| | Molar (%) | Molar (%) |
| CH ₄ | 50 | 28.6 |
| O ₂ | 12.5 | 0.0 |
| H ₂ O (steam) | 37.5 | 26.9 |
| CO ₂ | - | 7.0 |
| CO | - | 7.9 |
| H ₂ | - | 29.0 |
| N ₂ | - | 0.6 |

For the second partial oxidation stage typical operating conditions would be:

Pressure - 80 bar

Inlet temperature - 750°C

Outlet temperature - 1100°C

| Inlet Composition | | Outlet Composition |
|--------------------------|-----------|--------------------|
| | Molar (%) | Molar (%) |
| CH ₄ | 28.6 | 1.6 |
| O ₂ | 39.0 | - |
| H ₂ O (steam) | 26.9 | 22.0 |
| CO ₂ | 7.0 | 4.9 |
| CO | 7.9 | 22.3 |
| H ₂ | 29.0 | 48.6 |

N₂

0.6

0.5

It will be noted that the inlet composition at the second stage corresponds to the outlet composition at the first stage except that further oxygen is added.

Applicants believe that a number of advantages can be had from producing synthesis gas or make-up gas by using the two-stage method according to the invention, since in addition to the advantages referred to earlier specifically in relation to the first stage of the method, the method also allows

- (1) in both stages of the method the use of partial oxidation reactors which are adiabatic and auto-thermal and which do not require large heat transfer areas. Consequently, large, capital intensive, tubular steam reformers (which are required in known steam reforming processes) would not be required here, and
- (2) operation at relatively high pressures, thereby removing the need for a make-up gas compressor.

Although the two stage process proposed above is to produce make-up gas for use in a synthesis loop for producing methanol, it will be apparent that the process could be used to produce make-up gas for use in other synthesis methods, such as Fischer Tropsch synthesis to produce higher hydrocarbons or alcohols.

N₂

0.6

0.5

It will be noted that the inlet composition at the second stage corresponds to the outlet composition at the first stage except that further oxygen is added.

Applicants believe that a number of advantages can be had from producing synthesis gas or make-up gas by using the two-stage method according to the invention, since in addition to the advantages referred to earlier specifically in relation to the first stage of the method, the method also allows

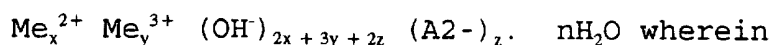
- (1) in both stages of the method the use of partial oxidation reactors which are adiabatic and auto-thermal and which do not require large heat transfer areas. Consequently, large, capital intensive, tubular steam reformers (which are required in known steam reforming processes) would not be required here, and
- (2) operation at relatively high pressures, thereby removing the need for a make-up gas compressor.

Although the two stage process proposed above is to produce make-up gas for use in a synthesis loop for producing methanol, it will be apparent that the process could be used to produce make-up gas for use in other synthesis methods, such as Fischer Tropsch synthesis to produce higher hydrocarbons or alcohols.

of the process equipment itself. In a remote location, the units or equipment can be substantially completed or assembled before shipping to the site as 'modules'. This greatly reduces the work which has to be done in the remote location and generally increases the ease with which the units and equipment can be transported both to and from the remote location.

CLAIMS

1. A method for producing synthesis gas from a reactant gas mixture comprising methane, oxygen and, optionally, steam and/or carbon dioxide, wherein the method comprises partially oxidising the methane by bringing the reactant gas mixture at a temperature in the range from 100°C to 950°C and at a pressure of up to 150 bar into contact with a first solid catalyst, which initiates the reaction, and conducting the reaction under substantially adiabatic conditions to produce the synthesis gas, the catalyst having been made by a method comprising intimately mixing a Feitknecht compound having the general formula:



Me^{2+} is substantially completely Ni^{2+} ,

Me^{3+} is substantially completely Al^{3+} or substantially Al^{3+} and Cr^{3+} ,

A^{2-} is either a single divalent anion or two monovalent anions.

x/y lies between 1.5/1 and 4/1,

$z/(x+y)$ lies in the range 0.05 to 0.2, and

$n/(x+y)$ lies in the range 0.25 to 1.0,

with a non-calcined alumino-silicate clay mineral and, at the same time and/or subsequently but prior to calcination, with at least one added stabilising additive for reducing silicon-species loss comprising an alkaline

earth and/or rare earth metal compound, and, optionally, an alkali metal compound, and thereafter calcining the resulting mixture and subjecting the catalyst material to a reducing process to activate the catalyst.

2. A method as claimed in claim 1, wherein the synthesis gas produced is at a temperature in the range from 500°C to 1000°C and at a pressure in the range from 1 to 40 bar.
3. A method as claimed in claim 1, wherein the synthesis gas produced is at a temperature in the range from 700°C to 1000°C and at a pressure in the range from 25 to 100 bar.
4. A method for producing a second synthesis gas at relatively high temperature and pressure, the method comprising utilising as feed gas a first synthesis gas produced by the method as claimed in claim 3, comprising carbon monoxide, carbon dioxide, hydrogen, steam and unreacted methane and without having been subjected to a compression stage subsequent to its production, the present method comprising adding oxygen to the first synthesis gas and causing partial oxidation of hitherto unreacted methane by passing the reactant mixture of first synthesis gas and oxygen at a temperature in the range from 600°C to 900°C and at a pressure in the range from 25 to 100 bar over a solid catalyst, and conducting the further partial oxidation under substantially

adiabatic conditions to produce the second synthesis gas at a relatively high temperature and pressure.

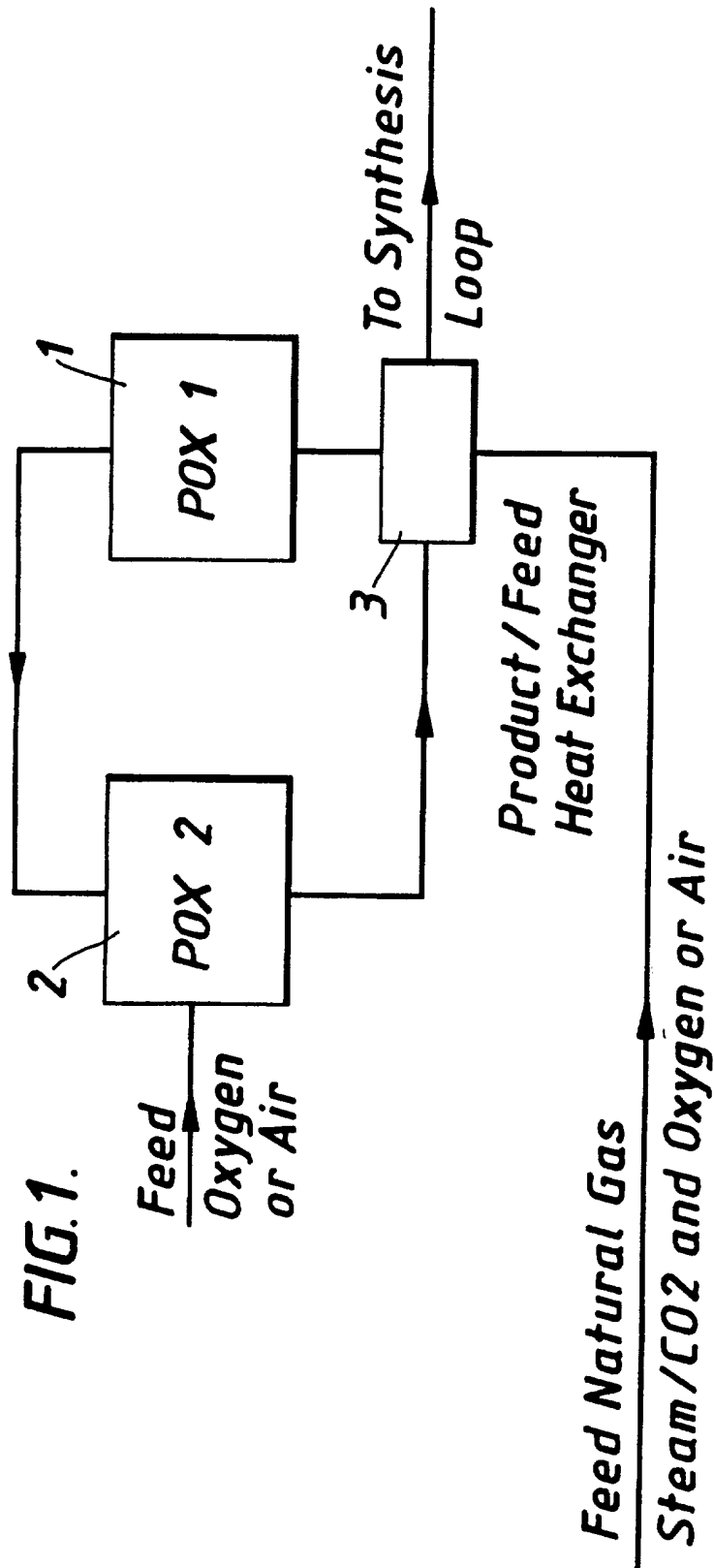
5. A method as claimed in claim 4, wherein the second synthesis gas as produced by the method is at a temperature in the range from 900°C to 1150°C.
6. A method as claimed in claim 5, wherein the temperature of the second synthesis gas as produced by the method is in the range from 1000°C to 1100°C.
7. A method as claimed in any of claims 3 to 6, wherein the hydrogen-to-carbon monoxide molar ratio in the second synthesis gas as produced by the method is from 0.25:1 to 8:1.
8. A method as claimed in any of the preceding claims, wherein the reactant gas mixture is at a temperature in the range from 150°C to 500°C when it is brought into contact with the first solid catalyst.
9. A method as claimed in claim 8, wherein the reactant gas mixture is at a temperature in the range from 250°C to 360°C when it is brought into contact with the first solid catalyst.
10. A method as claimed in any of the preceding claims, wherein the reactant gas mixture is brought into contact

with the first solid catalyst at a temperature not lower than 200°C below the auto-ignition temperature of the reactant gas mixture.

11. A method as claimed in any of the preceding claims, wherein the reactant gas mixture which is brought into contact with the first solid catalyst has a steam-to-methane molar ratio of from 0.0 to 6.0, a carbon dioxide-to-methane molar ratio of from 0 to 1.2, and a methane-to-oxygen molar ratio of from 0.1 to 0.75.
12. A method as claimed in any of the preceding claims, in which the first solid catalyst comprises a cement binder.
13. A method as claimed in claim 12, in which the cement binder is a high alumina cement binder.
14. A method as claimed in claim 13, in which the first solid catalyst is substantially the same as 'Catalyst 1' in reduced form as hereinbefore described with reference to the Examples.
15. A method as claimed in any of claims 1 to 11, in which the clay mineral is a layer-structured phyllosilicate and/or pseudo-layer-structured.
16. A method as claimed in claim 15, in which the layer-structured clay mineral is a smectite.

17. A method as claimed in claim 16, in which the smectite is bentonite.
18. A method as claimed in claim 17, in which the first solid catalyst is substantially the same as 'Catalyst 2' in reduced form as hereinbefore described with reference to the Examples.
19. A method of producing a chemical product utilising synthesis gas whenever incorporating a method as claimed in any of the preceding claims.
20. A method of producing a chemical product utilising second synthesis gas produced by the method of claim 4 or any of claims 5 to 18 as dependent on claim 4, without the said produced second synthesis gas being subjected to a compression stage subsequent to its production and prior to undergoing a reaction in the production of the chemical product.
21. Synthesis gas whenever obtained by a method as claimed in any of claims 1 to 18.

1/1



INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 97/00900

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/38 C01B3/40

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)
IPC 6 C01B

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| Y | WO 94 14700 A (AMOCO CORP) 7 July 1994 see page 3, line 24 - page 6, line 27 see page 8, line 23 - line 35 see page 9, line 20 - page 10, line 12 see page 13, line 26 - page 15, line 27 see examples 7-12,21 see tables 4-7 | 1-3,12, 13,15-21 |
| Y | GB 2 222 963 A (BRITISH GAS PLC) 28 March 1990 cited in the application see page 2, paragraph 2 - page 8, paragraph 1 see page 10, paragraph 4 --- -/-- | 1-3,12, 13,15-21 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "&" document member of the same patent family

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1 July 1997

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Van der Poel, W

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/00900

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