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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [4] **:** **B01J 23/58, C07C 1/04**	**A1**	**(11) International Publication Number:** **WO 87/ 04085** **(43) International Publication Date:** 16 July 1987 (16.07.87)

(21) International Application Number: PCT/GB87/00007

(22) International Filing Date: 8 January 1987 (08.01.87)

(31) Priority Application Number: 8600445

(32) Priority Date: 9 January 1986 (09.01.86)

(33) Priority Country: GB

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(81) Designated States: AU, JP, NO, US.

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: IMPROVED SYNGAS CONVERSION CATALYST, PRODUCTION AND USE THEREOF

(57) Abstract

A composition for use after reductive activation as a catalyst in the conversion of synthesis gas to hydrocarbons, the composition having formula: $Ru_aA_bCeO_x$, wherein A is an alkali metal, x is a number such that the valence requirements of the other elements for oxygen is satisfied, a is greater than zero and less than 5% w/w, based on the total weight of the composition, b is in the range from zero to 10% w/w, based on the total weight of the composition, and Ce and O constitute the remainder of the composition, is produced by the steps of: (A) adding a solution or solutions of soluble compounds of the metals ruthenium and cerium, and optionally also an alkali metal compound, to a solution of a precipitant comprising a carbonate and/or a bicarbonate and/or a hydroxide of an alkali metal or ammonium under conditions whereby there is formed a precipitate comprising ruthenium and cerium, and optionally also an alkali metal, in the form of compounds thermally decomposable to the metals and/or their oxides, and (B) recovering the precipitate obtained in step (A).

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IMPROVED SYNGAS CONVERSION CATALYST, PRODUCTION AND USE THEREOF

The present invention relates to a process for the production of an improved catalyst for use in the conversion of gaseous mixtures principally comprising carbon monoxide and hydrogen, hereinafter referred to as synthesis gas, to hydrocarbons of carbon number greater than one, in particular to aliphatic hydrocarbons in the gasoline boiling range, and to the use of the catalyst so-produced in the conversion of synthesis gas to the aforesaid hydrocarbons.

The conversion of synthesis gas to hydrocarbons by the Fischer-Tropsch process has been known for many years but the process has only achieved commercial significance in countries such as South Africa where unique economic factors prevail. The growing importance of alternative energy sources such as coal and natural gas has focussed renewed interest in the Fischer-Tropsch process as one of the more attractive direct and environmentally acceptable routes to high quality transportation fuels.

Of the Group VIII metals, ruthenium has long been known to be one of the most active catalysts in the conversion of synthesis gas, the product, at moderate pressures and above, being high molecular weight paraffin waxes and, at low pressures, principally methane. Several recent patent publications, for example US Patents Nos. 4,042,614; 4,171,320; 4,206,134; 4,413,064 and 4,410,637 and GB-A-2119277, describe and claim the formation of different products from synthesis gas using catalysts containing ruthenium as an active component.

US Patent No. 4,042,614 describes a process for the selective synthesis of olefins from C_2 to C_{10} chain length inclusive from synthesis gas using as catalyst ruthenium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, rare earth titanates and mixtures thereof.

US Patent No. 4,171,320 describes a process for the synthesis of olefins of from C_2 to C_5 chain length inclusive from synthesis gas using as catalyst ruthenium on a support selected from the group consisting of V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-Nb_2O_5, SiO_2-Ta_2O_5, V_2O_3-carbon, Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth-group VB oxides, alkali metal-Group VB oxides, Group IVB-Group VB oxides and mixtures thereof.

USP 4,206,134 describes a process for the enhanced synthesis of C_2-C_4 olefins with reduced production of methane from synthesis gas using as catalyst ruthenium on a managanese-containing oxide support, wherein said manganese-containing oxide support is selected from the group consisting of MnO, Al_2O_3-MnO, SiO_2-MnO, MnO-carbon, Group IVB-manganese oxide, Group VB-manganese oxides, rare earth-manganese oxides and mixtures thereof.

USP 4,413,064 describes a process for the conversion of synthesis gas to a product high in straight chain paraffins in the diesel fuel boiling range from synthesis gas utilising a catalyst consisting essentially of cobalt, thoria or lanthana and ruthenium on an alumina support wherein said alumina is gamma-alumina, eta-alumina or a mixture thereof, said catalyst being prepared by contacting finely divided alumina with

(A) an aqueous impregnation solution of a cobalt salt, and

(B) a nonaqueous, organic impregnation solution of a ruthenium salt and a salt of thorium or lanthanum.

USP 4,410,637 describes a process for the preparation of a hydrocarbon mixture consisting substantially of C_5-C_{12} hydrocarbons from synthesis gas using a catalyst containing one or more of iron, nickel, cobalt, chromium and/or ruthenium and, as a carrier, magadite, a laminar crystalline silicate compound capable of absorbing metal ions or metal salts by intercalation.

The reaction of carbon monoxide and hydrogen on rare earth metal oxide catalysts is described in Chemical Communications, 1983, page 763/764 by Kieffer et al. Catalysts studied were Pd - La_2O_3 and Pd - Dy_2O_3, both of which were prepared by impregnation.

Finally, GB-A-2,119,277 describes a catalyst for the selective synthesis of olefins from a mixture of hydrogen and carbon monoxide or hydrogen and carbon dioxide comprising a ruthenium carbonyl compound deposited on a ceric oxide-containing support. In Example 3 there is disclosed a catalyst prepared by impregnating ceric oxide with an aqeous solution of $RuCl_3.3H_2O$ (ruthenium content 0.62% w/w). The impregnated catalyst when used in the conversion of synthesis gas (Run 9) produces an undesirably high methane yield (35.7%) and a low selectivity (1.6%) to desirable olefins.

In our European patent application publication No. 10169743 (BP Case No. 5890) there is described a process for the production of a composition for use after reductive activation as a catalyst in the conversion of synthesis gas to hydrocarbons of carbon number greater than one, which composition has the formula:

$$Ru_aA_bCeO_x \qquad (I)$$

wherein A is an alkali metal,

x is a number such that the valence requirements of the other elements for oxygen is satisfied,

a is greater than zero and less than 1% w/w, based on the total weight of the composition,

b is in the range from zero to 10% w/w. based on the total weight of the composition, and

Ce and O constitute the remainder of the composition,

which process comprises the steps of:

(A) bringing together in solution soluble salts of the metals ruthenium and cerium and a precipitant comprising a carbonate and/or a bicarbonate and/or a hydroxide of an alkali metal or ammonium under conditions whereby there is formed a precipitate comprising ruthenium and cerium in the form of compounds thermally decomposable to their oxides, and

(B) recovering the precipitate obtained in step (A).

In the embodiment of the invention specifically described therein, an aqueous solution of the precipitant is added to an aqueous solution of water soluble salts of the metals.

We have now surprisingly found that very active and long-lived catalysts are obtained when a solution or solutions of compounds of ruthenium and cerium, and optionally also an alkali metal compound, are added to a solution of the precipitant, which order of addition is the reverse of that previously described.

Accordingly, the present invention provides a process for the production of a composition for use after reductive activation as a catalyst in the conversion of synthesis gas to hydrocarbons of carbon number greater than one, which composition has the formula:

$$Ru_aA_bCeO_x \qquad (I)$$

wherein A is an alkali metal,

x is a number such that the valence requirement of the other elements for oxygen is satisfied,

a is greater than zero and less than 5% w/w, based on the total weight of the composition,

b is in the range from zero to 10% w/w, based on the total weight of the composition, and

Ce and O constitute the remainder of the composition,

which comprises the steps of:

(A) adding a solution or solutions of soluble compounds of the metals ruthenium and cerium, and optionally also an alkali metal compound, to a solution of a precipitant comprising a carbonate and/or a bicarbonate and/or a hydroxide of an alkali metal or ammonium under conditions whereby there is formed a precipitate comprising ruthenium and cerium, and optionally also an alkali metal, in the form of compounds thermally decomposable to the metals and/or their oxides, and

(B) recovering the precipitate obtained in step (A).

Preferably a in the formula (1) is less than 1% w/w.

In the formula (I) A is an alkali metal, which is preferably potassium. Preferably the amount b of alkali metal is greater than zero and up to 5% w/w, even more preferably up to 2% w/w.

As regards step (A) of the process, a solution or solutions of soluble compounds of the metals ruthenium and cerium, and optionally also an alkali metal, is added to a solution of a precipitant comprising a carbonate and/or a bicarbonate and/or a hydroxide of an alkali metal or ammonium under conditions whereby there is formed a precipitate comprising ruthenium and cerium, and optionally also an alkali metal, in the form of compounds thermally decomposable to the metals and/or their oxides.

In a preferred embodiment of the process step (A) may be operated continuously by feeding simultaneously to a precipitation zone and mixing therein a solution or solutions of soluble compounds of the metals ruthenium and cerium, and optionally also an alkali metal, and a solution of the precipitant under conditions whereby there is formed a precipitate comprising ruthenium and cerium, and optionally also an alkali metal, in the form of compounds thermally decomposable to their oxides. The precipitation zone may suitably take the form of a vessel provided with means for separately introducing a solution of soluble compounds of ruthenium and cerium, and optionally also alkali metal, and a solution of the precipitant, the means for separately introducing the solutions being so arranged as to achieve mixing of the solutions, agitation means, pH measuring means and means for continuously withdrawing the suspended precipitate, for example an overflow pipe.

Suitably the solution or solutions employed may be aqueous solutions. The compounds of ruthenium and cerium, and optionally also the alkali metal compound, may be contained in separate solutions and added to the precipitant solution in any order or they may be contained in a single solution and thereby added together to the precipitant.

Whilst any soluble compound of ruthenium and cerium may be employed, it will usually be found convenient to use ruthenium in the form of the chloride because this is a commercially available form and cerium in the form of the nitrate, for example cerous nitrate. Commercially available cerous nitrate, which contains rare earth metals other than cerium, may be employed if desired.

The precipitant in step (A) may be a carbonate and/or a bicarbonate and/or a hydroxide of an alkali metal. Instead of using a pre-formed carbonate or bicarbonate it is possible to use the precursors of these salts, for example a water soluble salt and carbon dioxide. Alternatively, urea, which is thermally decomposable to carbon dioxide and ammonia, may be used. In any event, b in the aforesaid formula (I) will have a value greater than zero, which value may be adjusted if desired by washing or addition of further alkali metal compound. Alternatively, ammonium carbonate and/or bicarbonate and/or hydroxide may be employed as the precipitant, in which case the value of b in the catalyst asinitially produced will be zero, though this value may subsequently be adjusted if desired by addition of alkali metal. Preferably ammonium bicarbonate, optionally mixed with an alkali metal bicarbonate, for example potassium bicarbonate, is used as the precipitant.

Suitably the soluble compounds of the metals ruthenium and cerium may be brought together at a temperature in the range from 0 to 100°C. In one preferred embodiment of the invention the temperature is suitably in the range from 60 to 100°C, preferably from 80 to 100°C. In another preferred embodiment the temperature is suitably below 50°C, preferably below 30°C, for example ambient temperature.

Precipitation may suitably be effected at a pH greater than about 6, preferably in the range from 6 to 10. Preferably the pH is substantially constant within the aforesaid range throughout the precipitation step. A substantially constant pH may suitably be achieved by using a large excess of the precipitant, for example about seven times the theoretical stoichiometric amount required for complete precipitation. Alternatively, a suitable buffer may be employed.

In continuous operation of step (A) the solutions are preferably fed at a relative rate such as to achieve a substantially constant pH within the aforesaid ranges. In order to achieve a substantially constant pH it may be desirable to further feed a solution of an inorganic base, for example aqueous ammonia.

In order to improve the homogeneity of the catalyst it is preferred to agitate the mixture during precipitation, suitably by mechanical stirring.

The amounts of the ruthenium and cerium compounds and precipitant employed should be such as to satisfy the stoichiometric relationships in the formula (I). Alternatively, the alkali metal content of the composition may be supplemented by further addition thereof, or reduced, for example by washing, at any subsequent point in the preparative process.

In step (B) the precipitate obtained in step (A) is recovered. This may suitably be accomplished by filtration but other methods for separating solids from liquids, for example centrifugation, may be employed. After recovery it is preferred to wash the precipitate, suitably with water, so as to remove unwanted residual soluble matter. It is also preferred to dry the precipitate, suitably at a temperature below 180°C, for example about 100 to 150°C. It is possible that some thermal decomposition may occur in the drying step.

Thermally decomposable compounds comprised in the precipitate recovered in step (B) are preferably further thermally decomposed in a discrete step (C). This may suitably be accomplished by heating the precipitate, suitably in a non-reducing atmosphere, for example a stream of inert gas, such as nitrogen, at a temperature suitably in the range from 150 to 600°C.

In order to convert the composition of formula (I) into a catalyst for use in the conversion of syngas to hydrocarbons having a carbon number greater than 1, it is generally necessary to reductively activate the composition, suitably by contact at elevated temperature with a reducing gas, for example hydrogen, carbon monoxide or mixtures thereof. A suitable reducing gas is for example hydrogen which may be diluted with an inert gas such as argon. Typically, the conditions employed may suitably be a pressure in the range from 1 to 100 bar and a temperature in the range from 150 to 600°C for a period of up to 24 hours or longer. Reductive activation may be effected as a discrete step prior to use as a catalyst for the conversion of synthesis gas or it may be incorporated as a preliminary step into the synthesis gas conversion process, preferably the latter.

Those skilled in the art will readily appreciate that it may be possible to combine the thermal decomposition step and the reductive activation step into a single step under certain circumstances.

It is believed that coprecipitated catalysts differ fundamentally from impregnated catalysts and that this difference is reflected in their catalytic performance.

The present invention also provides a process for the production of hydrocarbons having a carbon number greater than one from synthesis gas which process comprises contacting synthesis gas with a catalyst comprising a reductively activated composition having the formula (I) produced by the process of claim 1 at a temperature in the range from 190 to 400°C and a pressure in the range from about 1 bar to 100 bar.

Reductive activation of the composition of formula (I) may be conducted either as a separate step outside the syngas conversion reactor, as a discrete step within the syngas conversion reactor prior to syngas conversion or within the syngas conversion reactor under syngas conversion conditions.

We have noted that benefits can arise from periodically treating the catalyst with hydrogen. This may suitably be accomplished by shutting off the carbon monoxide feed from time to time during the process.

As is well known in the art synthesis gas principally comprises carbon monoxide and hydrogen and possibly also minor amounts of carbon dioxide, nitrogen and other inert gases depending upon its origin and degree of purity. Methods for preparing synthesis gas are established in the art and usually involve the partial oxidation of a carbonaceous substance, e.g. coal. Alternatively, synthesis gas may be prepared, for example by the catalytic steam reforming of methane. For the purpose of the present invention the carbon monoxide to hydrogen ratio may suitably be in the range from 2:1 to 1:6. Whilst the ratio of the carbon monoxide to hydrogen in the synthesis gas produced by the aforesaid processes may differ from these ranges, it may be altered appropriately by the addition of either carbon monoxide or hydrogen, or may be adjusted by the so-called shift reaction well known to those skilled in the art.

In a modification of the process for the production of hydrocarbons, there may be combined with the catalyst an inert material, for example silica.

In a preferred embodiment, the catalyst may be combined with an acidic component, for example either a zeolite or a pillared clay.

The zeolite or pillared clay may be either physically admixed with the composition to form an intimately mixed bed or may be separate therefrom, for example in the form of a split bed, the zeolite or pillared clay forming one portion of the bed and the catalyst another. In the case of a physical admixture, the zeolite or pillared clay may be mixed with the composition either before or after reductive activation. Alternatively, the coprecipitation (step A) in the process for producing the composition of formula (I) may be performed in the presence of the zeolite or pillared clay, particularly when the precipitant is ammonium carbonate and/or bicarbonate and/or hydroxide.

A suitable zeolite is an MFI-type zeolite, for example ZSM-5 as described in US Patent No. 3,702,886, though other suitable high silica crystalline alumino- or gallo-silicate zeolites may be employed.

Suitable pillared clays are described for example in GB-A-2,059,408, USP-A-4,216,188, USP-A-4,248,739, USP-A-4,515,901 and USP-A-4,367,163. A particularly suitable pillared clay is the silylated pillared clay described in our copending EP-A-0150898 (BP Case No. 6035). The aforesaid patent publications are incorporated by reference herein.

The temperature is preferably in the range from 250 to 350°C and the pressure is preferably in the range from 10 to 50 bars. The GHSV may suitably be in the range from 100 to 20,000h^{-1}.

The process may be carried out batchwise or continuously in a fixed bed, fluidised bed, moving bed or slurry phase reactor.

In addition to their high activities and long lifetimes, catalysts produced by the process of the present invention provide low selectivities to methane and carbon dioxide, thereby minimising carbon wastage in the form of undesirable by-products.

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

A. CATALYST PREPARATION

Example 1

$RuCl_3(H_2O)_x$(0.3974g; 1.52 mmoles) dissolved in distilled water ($100cm^3$) was added dropwise to a vigorously stirred solution of $Ce(NO_3)_3.(H_2O)_6$(75.40g; 173.64 mmoles) made up to $750cm^3$ with distilled water. A solution of KNO_3(1.1421g; 11.30 mmoles) in distilled water ($50cm^3$) was then added dropwise to the aqueous ruthenium chloride/cerous nitrate with stirring. The solution containing ruthenium/cerium and potassium was added to freshly prepared aqueous NH_4HCO_3(299.7g; 3.79 mmoles) made up to $2500cm^3$ with distilled water over ca. 1 hour. The pH of the alkali was constant at 8.7 - 8.8 throughout the precipitation. Stirring was continued for 0.25h after all of the reagents were added and the mixture was vacuum filtered to yield a light grey sludge and a light yellow filtrate. The sludge was vigorously stirred with distilled water ($3000cm^3$) for 0.25h and then vacuum filtered. This procedure was repeated three times and the grey solid was partially dried on the vacuum filter before final drying in a vacuum oven (116°C, 17mm Hg, ca 24h). The dried solid (ca 25g) was ground to a fine powder and then pressed in a 3.5cm die at 10-11 tons. The pressed solid was crushed and sieved to 500-1400 μm. A portion (ca 20g) was given the following heat treatments:

(a) Flowing N_2(ca $50cm^3min^{-1}$): $20°C \xrightarrow{10°Cmin^{-1}} 450°C/3h \xrightarrow{10°Cmin^{-1}} 20°C$

(b) Flowing H_2(ca $50cm^3min^{-1}$: $20°C \xrightarrow{2°Cmin^{-1}} 225°C/8h \xrightarrow{2°Cmin^{-1}} 320°C/6h \rightarrow 20°C$

The heat-treated catalyst was exposed to air and stored in air in screw-top jars.

Example 2

The procedure of Example 1 was repeated except that the pH control during precipitation was inferior to that of Example 1, the pH varying from 8.40 - 8.65.

Example 3

A similar procedure to that of Example 1 was used except that approx. three times the quantity of reagents was used to yield 64.70g of product gel. The $RuCl_3/Ce(NO_3)_3$ solution was added to the aqueous NH_4HCO_3 solution at the rate of $50cm^3min^{-1}$. The addition of reagents was therefore completed in approx. the same time period (69 minutes) as the smaller scale preparations of Examples 1 and 2. The pH of the aqueous NH_4HCO_3 rose from 8.16 to 8.68 during the preparation.

Example 4

Continuous precipitation with NH_4HCO_3

In this Example the apparatus illustrated in Figure 1 was employed. With reference to the Figure, 1 is a stainless steel constant head mixing vessel, 2 is a precipitant delivery ring, 3 is a pipe for delivery of solution containing metals to be precipitated, 4 is a paddle stirrer, 5 is a pH electrode and 6 is an overflow pipe.

Solution A

$RuCl_3(H_2O)_3$ (12.085g; 46.23 mmoles) was dissolved in distilled water (0.40 litre) and added dropwise to a vigorously stirred solution of $Ce(NO_3)_3(H_2O)_6$ (303g; 0.698 moles) made up to 3 litres with distilled water. A solution of KNO_3 (4.700g; 46.24 mmoles) in distilled water (0.20 l) was then added dropwise to the aqueous ruthenium chloride/cerous nitrate solution with stirring. This solution is hereinafter referred to as solution A.

Solution B

NH_4HCO_3 (1.20 kg; 15.18 moles) was dissolved in 10 litres of distilled water. This solution is hereinafter referred to as solution B.

Method

With reference to Figure 1, solution A was fed through pipe 3 and solution B was fed simultaneously through the precipitant delivery ring 2 to the constant head mixing vessel 1 via peristatic pumps (not shown) at a flow rate ratio sufficient to control the pH in the mixing vessel 1 as measured by the pH electrode 5 between 8.0 and 8.7. Efficient mixing of the solutions A and B was received by rapid rotation of the paddle stirrer 4. The suspended precipitate was constantly bled off via the overflow pipe 6 and filtered on three 5 litre Buchner Funnel/Flasks to yield a light grey solid and a light yellow filtrate. The individual solids were sucked dry on the filter over ca. 2 hours and were left for 17 hours in air. The solids showed some signs of darkening during drying. The solids from the three Buchner Funnels were combined to yield 916.3g in total.

The damp cake was split into two portions C(279.3g) and D(630g).

Portion D was vigorously stirred with distilled water (2 litres) and filtered. This washing procedure was repeated twice more and finally the solid was vacuum dried (100°C, 17 mm Hg, 17 h) to yield 60.75g of dried gel.

The dried gel was then pressed and heat treated in an identical manner to that described in Example 1.

Example 5

Continuous precipitation with $KHCO_3$

The procedure described in Example 4 was repeated except that NH_4HCO_3 was replaced by $KHCO_3$ and the following quantitites of reagents were used:

Solution A

(i) $RuCl_3(H_2O)_3$ [155g; 5.93 moles in distilled water (0.0401)],

(ii) KNO_3 [4.667g; 46.17 mmoles in distilled water (0.201)],

(iii) $Ce(NO_3)_3(H_2O)_6$ [302.86g; 0.697 mole in distilled water (101)].

Solution (i) was added to solution (iii). Solution (ii) was added to the mixed solution (i) and (iii).

Solution B

$KHCO_3$ [1520.9g; 15.19 moles in distilled water (101)].

The co-precipitation was effected at a pH between 7.70 and 7.90.

The precipitated solid was vacuum filtered to yield a dense metallic silver sludge.

The dried solid was washed with (i) 101, (ii) 121 and (iii) 101 of distilled water before drying at 110°C in air for 17 hours.

The dried solid was pressed and heat treated in a manner identical to that described in Example 1.

Example 6

Larger scale continuous precipitation with NH_4HCO_3

The procedure described in Example 4 was repeated using the following quantities of reagents:

Solution A

(i) $RuCl_3(H_2O)_3$ [43.46g; 166.24 mmoles in distilled water (11.21)],

(ii) KNO_3 [130.66g; 1292.47 mmoles in distilled water (5.61)],

(iii) $Ce(NO_3)_3(H_2O)_6$ [8.48 kg; 19.53 moles in distilled water (841)].

Solution (i) was added to solution (iii). Solution (ii) was added to the mixed solution (i) and (iii).

Solution B

NH_4HCO_3 (4.80kg; 60.72 moles in distilled water (401)]. The pH of the coprecipitation was adjusted to 8.50 using 0.880 aqueous ammonia.

The light grey precipitate produced by the coprecipitation was vacuum filtered and washed three times with 50-551 distilled water. The damp cake so-produced was dried at 110°C in air for 30 hours.

The dried gel was sieved to less than 1 cm and roasted in nitrogen using the following procedure.

$$\text{Flowing } N_2 \text{ (31 min}^{-1}\text{)/20°C} \xrightarrow{3h} \text{450°C/6h} \xrightarrow{14h} \text{20°C}$$

7 kg gel

The nitrogen-roasted gel was then mixed with distilled water (0.61 kg^{-1}) in a 'Z' blade mixer. Finally, it was dried at 30°C in air for 30h.

The powder was crushed and sieved to less than 1 mm and was then dry mixed with stearic acid (2g acid to 100g dry gel).

The mixture was then pelleted using a Manesty B3B 16 station mulitple punch tablet maker to yield 4.8 mm diameter x 4.0 mm long cylindrical pellets. These pellets were crushed and sieved to 250-500 um before testing.

B. CATALYST TESTING

Example 7

(i) Procedure

4 cm^3 of catalyst prepared in Example 1 were mixed with 6 cm^3 of crushed ceramic beads of the same particle size and charged to a fixed bed reactor. It was reduced for 16 h at 225°C under 75 cm^3 min^{-1} H_2 at atmospheric pressure. It was then pressurised under syngas (2:1 H_2:CO) to 30 barg and heated to 305-315°C (bed) over 2h. At this point the CO flow was stopped for 2h. CO was then readmitted and the wall temperature reduced to give a bed temperature of 295-300°C. Conditions were then kept constant until a steady state was achieved, after which process parameters were altered as desired.

(ii) Results

Data obtained at various times on stream and at different temperatures are given in Table 1. The run was continued for 2200 hours during which time the bed temperature was varied between 300 and 314°C corresponding to CO conversions ranging between 37% and 88%. The data derived in terms of CO conversion, CH_4 selectivity and CO_2 selectivity over the initial 350 hours of the test are plotted in Figure 2.

It can be seen from the Figure that the catalyst stabilised after about 100 HOS and CO_2 selectivity was uniformly low throughout the test. Methane selectivity was uniformly low at constant conversion. Moreover, the catalyst was reproducible in the sense that similar conversions were obtained at similar temperatures at different times on stream with intervening temperature changes.

The catalyst maintained its performance during the period 350 HOS to 2200 HOS.

Example 8

(i) Procedure

Using the catalyst produced in Example 4 in place of the catalyst produced in Example 1 the procedure of Example 7 was repeated except that the catalyst was reduced for 6h at 305°C (30 bar H_2, 111 cm^3 min^{-1}). At 47 HOS the catalyst was given a hydrogen treatment by stopping the CO flow for one hour.

(ii) Results

The results are presented in Table 2.

It can be seen from the Table that at similar CO conversions the treatment with hydrogen after 47 HOS leads to very much lower methane selectivity and a reduced CO_2 selectivity.

Example 9

(i) Procedure

Using the catalyst produced in Example 5 in place of the catalyst produced in Example 1 the procedure of Example 7 was repeated except that the catalyst was reduced for 6h at 305°C (30 bar H_2, 111 cm^3 min^{-1}).

(ii) Results

The results are presented in Table 3.

It can be seen from Table 3 that the methane selectivity is very low. A particularly attractive result is that obtained at 81.47% conversion (17 HOS) with a methane selectivity of only 10.66% and a CO_2 selectivity of only 3.59%.

Example 10

(i) Procedure

2 cm3 of the catalyst produced in Example 6 was reduced in flowing hydrogen (83.4 cm^3 min^{-1}) using the following temperature

regimes:

100°C for 1 hour, followed by 200°C for 1 hour and then 300°C for 16 hours followed by cooling to 200°C.

The catalyst was then exposed to synthesis gas (H_2:CO = 2:1) (83.4 cm^3 min^{-1} total flow) and equilibrated for 1 hour. The temperature was adjusted to 250°C for ca. 0.5h and then increased to 270°C before increasing to 290°C in 10°C steps and finally to the operating temperature (ca. 300°C) in 1°C steps.

The results are presented in Table 4.

The results presented in the Table demonstrate the flexibility of the catalyst and in particular that high CO conversions are achieved at low CH_4 and CO_2 selectivities over 500 HOS.

TABLE 1

HOS	Bed Temperature (°C)	CO Conversion (%)	Carbon Molar Selectivity (%)							Productivity (g/1/h)	
			C_1	C_2	C_3	C_4	C_5^+	CO_2	Oxygenates	C_2^+	C_5^+
197	300	37.1	8.3	3.2	11.2	12.5	62.2	2.3	0.3	166	120
330	305	56.6	10.7	2.8	8.9	10.0	64.5	2.1	1.0	233	180*
320	309	74.9	14.5	3.0	7.0	6.3	66.2	2.2	0.8	292	242*
343	314	88.0	17.0	2.8	11.9	11.7	53.8	2.4	0.4	373	259

* - Suspected loss of C_3 and C_4 hydrocarbons from liquid product

TABLE 2

HOS	Bed Temperature (°C)	CO Conversion (%)	Carbon Molar Selectivity (%)							Productivity (g/catalyst/h)	
			C_1	C_2	C_3	C_4	C_5^+	CO_2	Oxygenates	C_3^+	C_5^+
8.5	307	79.9	11.7	2.7	6.2	6.0	67.0	4.8	1.6	295	250
14.5	307	79.7	12.8	3.0	6.5	6.3	65.3	4.7	1.5	300	251
20.5	307	79.5	14.9	3.4	6.1	6.3	63.5	4.5	1.5	302	252
27.0	306	75.6	14.7	3.3	6.5	6.6	63.3	4.2	1.4	289	239
39.0	306	74.7	15.0	3.4	7.2	6.9	62.1	4.0	1.4	291	237
	H_2 TREATMENT										
121.0	303	73.2	7.7	2.5	7.2	7.1	70.8	3.4	1.3	315	262
134.0	300	60.3	7.4	2.4	9.8	10.5	65.4	3.2	1.3	263	201
143.0	300	60.1	7.4	2.7	9.3	10.7	65.5	2.9	1.6	261	200

TABLE 3

HOS	Bed Temperature (°C)	CO Conversion (%)	Carbon Molar Selectivity (%)							Productivity (g/1/h)	
			C_1	C_2	C_3	C_4	C_5^+	CO_2	Oxygenates	C_3^+	C_5^+
29	305	51.0	5.6	2.6	8.8	9.6	68.9	3.1	1.4	237	187
38	305	44.9	5.5	3.0	9.7	12.2	66.2	2.5	0.9	211	158
59	305	43.2	6.0	3.0	9.8	12.2	65.4	2.6	1.0	201	150
77	305	43.2	6.2	3.1	9.9	12.2	65.2	2.4	1.0	200	150
79	310	53.6	6.1	3.1	9.0	10.2	67.7	2.9	1.0	248	193
87	310	49.0	6.6	3.2	9.9	11.4	65.0	2.9	1.0	225	169
99	310	52.3	6.6	3.1	9.2	10.5	66.9	2.7	1.0	241	186
107	310	49.8	6.8	3.1	9.5	10.8	65.9	2.9	1.1	228	175
110	310	47.0	7.6	3.0	9.2	9.1	67.3	2.9	1.2	214	168
120	310	54.4	7.1	3.1	9.9	10.5	65.6	2.8	1.0	249	190
131	310	53.3	7.2	3.2	9.5	10.3	66.2	2.7	1.0	244	188
135	315	72.4	11.5	3.0	5.3	3.6	71.9	3.9	0.9	311	277
140	315	65.2	8.6	3.1	8.3	7.8	68.1	3.2	0.9	292	236
146	315	66.4	7.8	2.7	8.1	8.6	69.0	2.9	0.9	302	244
159	315	69.4	7.3	2.9	7.7	8.2	71.1	2.7	0.3	321	262
172	315	67.4	7.8	2.8	7.9	8.6	70.0	2.6	0.3	310	251
183	320	81.5	10.7	3.6	7.1	6.8	68.0	3.6	0.3	355	295
196	320	78.4	12.0	2.8	6.0	6.2	69.4	3.3	0.3	340	289
202	320	75.1	12.7	2.8	6.4	6.0	68.4	3.4	0.3	323	273
210	320	75.9	12.6	3.0	6.4	5.8	68.5	3.4	0.2	326	277
222	320	69.1	13.5	3.2	7.5	7.2	64.9	3.5	0.2	293	239
240	320	64.6	14.2	3.2	7.4	7.2	64.0	3.6	0.3	271	220
274	320	49.1	13.6	3.9	10.4	12.4	54.7	4.8	0.3	202	143
304	320	79.6	14.4								
308	320	83.7	12.5								
314	320	76.8	11.4								
320	320	74.1	11.7								
325	320	71.8	12.0								

TABLE 4

HOS	GHSV (h^{-1})	Dilution (Cat:Diluent	Temp (°C)	CO Conversion (%)	Carbon Molar Selectivity (%)						Productivity (kgm^{-3} $cat.h^{-1}$)	
					CH_4	CO_2	C_2	C_3^+	C_5+	Oxygenates	C_3^+	C_5^+
23	2500	-	295	52.5	9.7	3.4	2.7	84.2	64.3	-	240.7	183.8
65	2500	-	294	53.0	10.4	3.1	3.1	83.4	62.0	-	240.3	178.8
76	2500	-	296	65.2	6.9	2.4	2.0	88.7	72.9	-	314.5	258.5
88	2500	-	293	56.2	7.8	2.3	2.3	87.6	69.7	-	268.1	213.4
94	2500	-	297	65.5	8.0	2.3	1.7	87.9	70.2	-	313.2	250.2
112	2500	-	296	63.3	8.7	2.5	2.5	86.2	67.5	-	297.7	232.7
136	2500	-	296	60.5	8.0	2.3	2.4	87.4	68.9	-	287.9	227.0
162	2500	-	304	83.7	7.9	2.3	2.0	87.8	75.3	-	400.0	343.3
185.8	2500	-	304	82.0	8.3	2.2	2.1	87.4	73.7	-	390.1	328.7
211.8	2500	-	304	79.4	8.6	2.6	2.2	86.5	72.9	-	373.8	315.2
233.8	2500	-	304	79.9	8.1	2.4	2.1	87.5	73.1	-	380.5	318.0
256	2500	-	303	76.4	8.2	2.4	2.2	87.2	72.3	-	362.7	300.5
280	2500	-	305	79.5	8.9	2.6	2.3	86.3	72.5	-	373.7	313.6
3044	2500	-	305	81.1	7.4	2.1	1.9	88.6	75.0	-	391.3	331.3
330	2500	-	306	79.3	7.6	2.1	2.0	88.3	74.8	-	380.7	322.5
361	2500	-	306	78.0	7.5	2.3	1.9	88.3	73.9	-	374.6	313.6
401	2500	-	304	76.8	7.5	2.1	2.0	88.3	73.4	-	368.9	306.5
425	2500	-	304	74.4	7.4	2.1	1.9	88.6	73.6	-	358.7	298.1
449	2500	-	306	74.6	7.7	2.2	2.0	88.1	73.3	-	357.7	297.5
472	2500	-	310	79.8	8.5	2.4	2.1	86.9	72.8	-	377.3	316.1
499	2500	-	309	78.8	8.7	2.5	2.1	86.7	72.0	-	371.7	308.8

Claims:

1 A process for the production of a composition for use after reductive activation as a catalyst in the conversion of synthesis gas to hydrocarbons of carbon number greater than one, which composition has the formula:

$$Ru_aA_bCeO_x \qquad (I)$$

wherein A is an alkali metal,

x is a number such that the valence requirements of the other elements for oxygen is satisfied,

a is greater than zero and less than 5% w/w, based on the total weight of the composition,

b is in the range from zero to 10% w/w, based on the total weight of the composition, and

Ce and O constitute the remainder of the composition,

which comprises the steps of:

(A) adding a solution or solutions of soluble compounds of the metals ruthenium and cerium, and optionally also an alkali metal compound, to a solution of a precipitant comprising a carbonate and/or a bicarbonate and/or a hydroxide of an alkali metal or ammonium under conditions whereby there is formed a precipitate comprising ruthenium and cerium, and optionally also an alkali metal, in the form of compounds thermally decomposable to the metals and/or their oxides, and

(B) recovering the precipitate obtained in step (A).

2 A process according to claim 1 wherein a in the formula (I) has a value less than 1% w/w.

3 A process according to either claim 1 or claim 2 wherein step (A) is effected continuously by feeding simultaneously to a precipitation zone and mixing therein a solution or solutions of soluble compounds of the metals ruthenium and cerium, and optionally also an alkali metal, and a solution of the precipitant under conditions whereby there is formed a precipitate comprising ruthenium and cerium, and optionally also an alkali metal, in the form of compounds thermally decomposable to the metals and/or their oxides.

4 A process according to any one of the preceding claims wherein thermally decomposable compounds comprised in the precipitate recovered in step (B) are thermally decomposed in a discrete step (C).

5 A process according to any one of the preceding claims wherein precipitation is effected at a pH in the range from 6 to 10.

6 A process according to claim 5 wherein the pH is maintained substantially constant throughout the precipitation.

7 A process according to any one of the preceding claims wherein precipitation is effected at a temperature below 30°C.

8 A process for the production of hydrocarbons having a carbon number greater than one from synthesis gas which process comprises contacting synthesis gas with a catalyst comprising a reductively activated composition having the formula (I) produced by the process of claim 1 at a temperature in the range from 190 to 400°C and a pressure in the range from about 1 bar to 100 bar.

9 A process according to claim 8 wherein the composition having the formula (I) is reductively activated in a preliminary step in the synthesis gas conversion process.

10 A process according to either claim 8 or claim 9 wherein the catalyst is periodically treated with hydrogen.

FIG.1

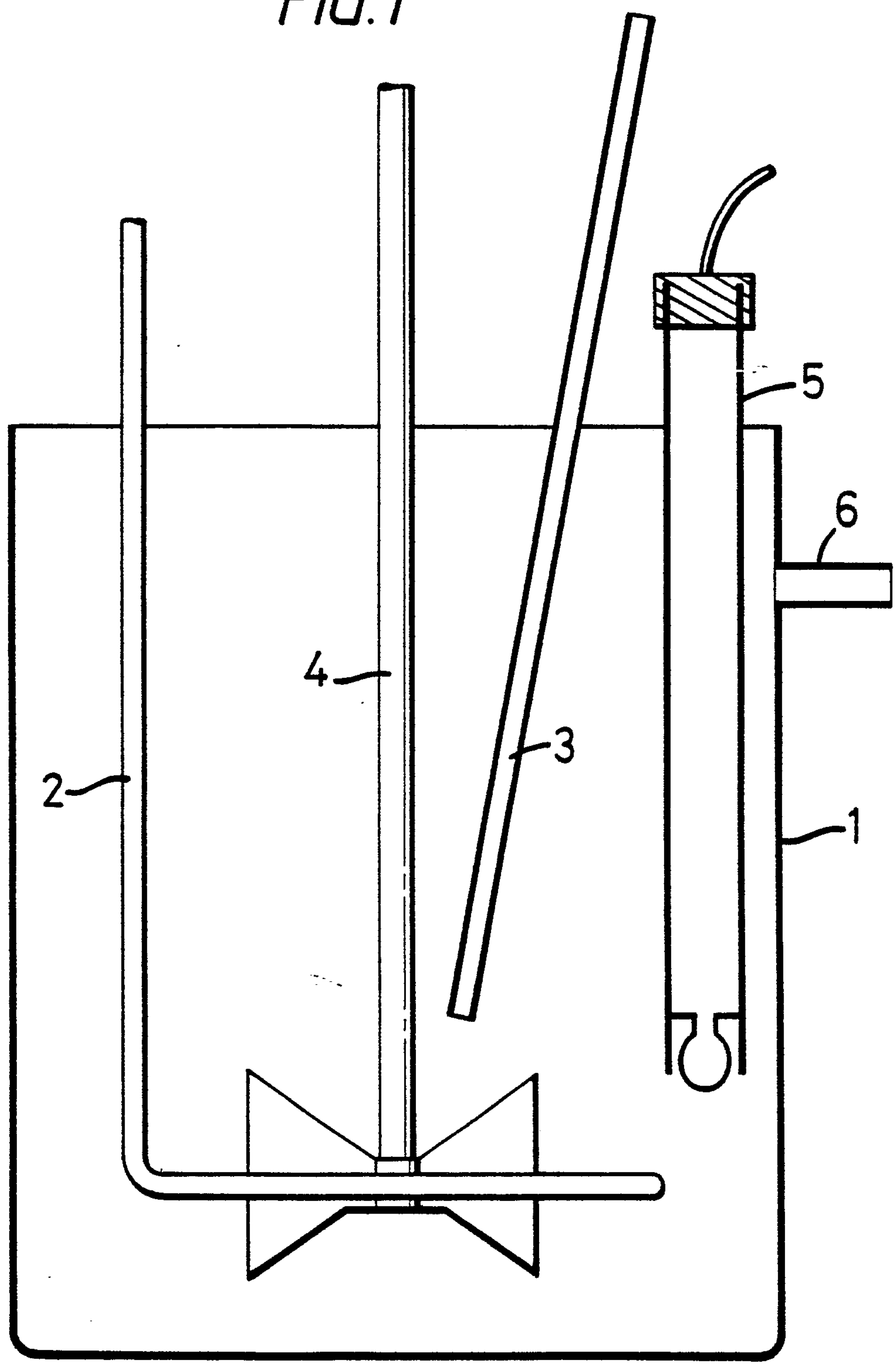
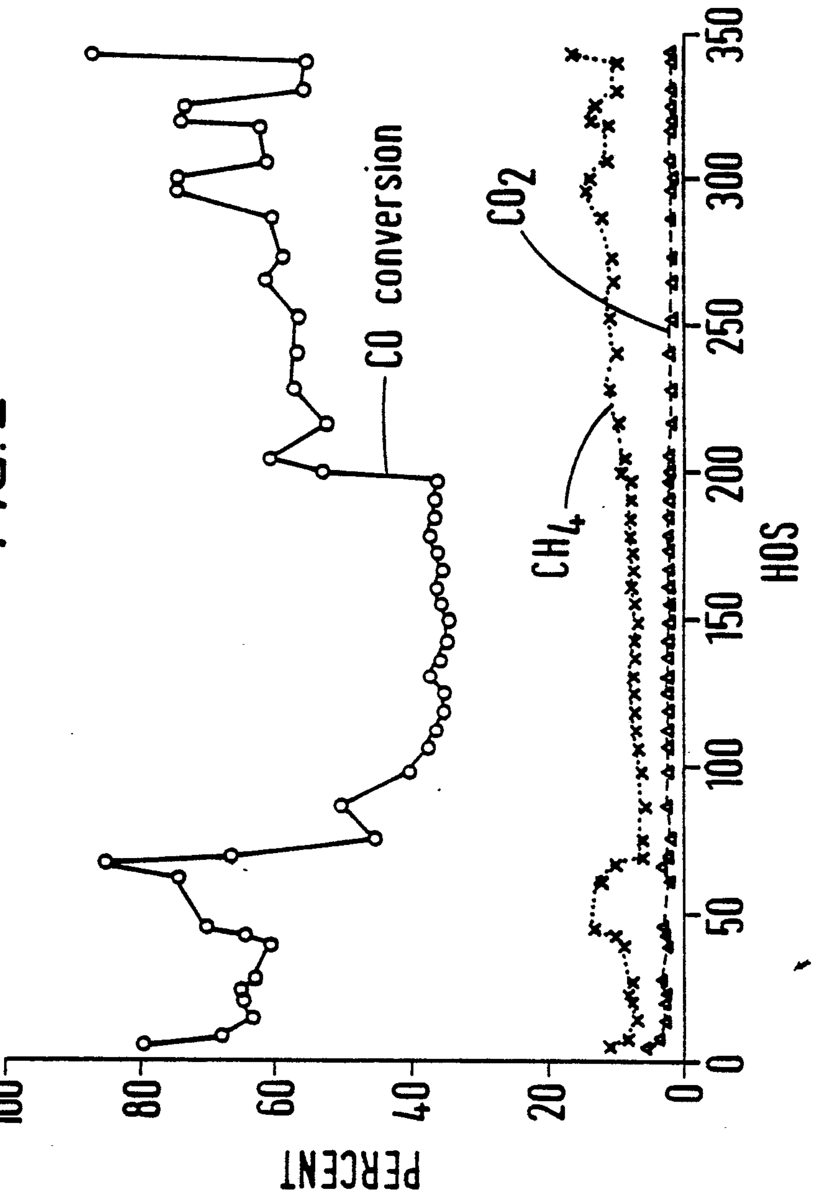


FIG. 2


CO conversion
CO_2
CH_4
HOS
PERCENT
0
20
40
60
80
100
0
50
100
150
200
250
300
350

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00007

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: B 01 J 23/58; C 07 C 1/04

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	B 01 J 23/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A,P	EP, A, 0169743 (BP) 29 January 1986 cited in the application & WO, A, 86/00885	
A	US, A, 4001143 (E.L. McCANN) 4 January 1977	
A	US, A, 4060500 (L.R. CLAVENNA) 29 November 1977	
A	US, A, 2358050 (G.L. BOULET) 12 September 1944	

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
22th April 1987	21 MAY 1987
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. VAN MOL

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 87/00007 (SA 15784)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/05/87

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		AU-A-	4672085	25/02/86
		JP-T-	61502948	18/12/86
US-A- 4001143	04/01/77	JP-A-	51123795	28/10/76
		CA-A-	1068250	18/12/79
US-A- 4060500	29/11/77	None		
US-A- 2358050		None		

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82