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(54) Process for the production of a catalyst composition for use in the conversion of synthesis gas to hydrocarbons

(57) 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 is represented by the formula:-

Ru_aCeO_x

wherein

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

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

is prepared by impregnating ceria with a non-aqueous organic impregnation solution, for example an acetone solution, of a soluble thermally decomposable ruthenium compound other than a carbonyl.

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SPECIFICATION

Process for the production of a catalyst composition for use in the conversion of synthesis gas to hydrocarbons

The present invention relates to a process for the production of a 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.

USP 4,477,595 describes a process for the selective production of C_5-C_{40} hydrocarbons containing C_5-C_{20} hydrocarbons having a high paraffins content by contacting H_2/CO mixtures with a ruthenium catalyst on a support containing titanium oxide, niobium oxide, vanadium oxide or tantalum oxide. A process is described for preparing the catalyst wherein ruthenium was impregnated onto the meshed TiO_2 by means of depositing a ruthenium salt, eg $RuCl_3$ or $Ru(NO_3)_3$, by stirring the TiO_2 particles in excess acetone containing dissolved ruthenium salt.

US Patent No. 4,171,320 describes a process for the synthesis of olefins of from C_2 to C_6 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 nonaquaeous, 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_6-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. It is stated that the ruthenium carbonyl compound is believed to be decomposed on the ceric oxide-containing support under the process conditions to give a highly dispersed ruthenium metal catalyst. By way of comparison a catalyst prepared by impregnating ceric oxide with an aqueous solution of $RuCl_3 \cdot 3H_2O$ (ruthenium content 0.62% w/w) is tested in Run 9 for the conversion of synthesis gas. The methane yield was 35.7% with a low olefin selectivity of 1.6%, the selectivity toward the formation of oxygenated products was 41.8% including 1.1% dimethyl ether and 1.1% propanol. Such methane yields are undesirably high and selectivity to olefins undesirably low.

We have now found that the disadvantages associated with the aforesaid impregnation method of preparing ruthenium/ceria synthesis gas conversion catalysts can be to a greater or lesser extent overcome.

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 is represented by the formula:

$$Ru_aCeO_x \quad (I)$$

wherein a is greater than zero and less than 1% w/w, based on the total weight of the composition, and x is a number such that the valence requirements of the other elements for oxygen is satisfied, which process comprises impregnating ceria with a nonaqueous, organic impregnation solution of a soluble, thermally decomposable ruthenium compound other than a carbonyl.

It has been observed that catalysts differing only from catalysts of the invention in the respect that their ruthenium content is greater than 1% w/w tend to produce large quantities of methane, the actual proportion of methane increasing with increasing ruthenium content, whereas catalysts according to the present invention in which the ruthenium content is less than 1% w/w, preferably less than 0.5% w/w, are at the same time both active and selective to hydrocarbons other than methane, and in particular to aliphatic hydrocarbons of carbon number greater than 2, of which C_5^+ hydrocarbons form a major proportion. Moreover the selectivity to unwanted carbon dioxide can be maintained within acceptable limits, unlike catalysts containing higher ruthenium loadings.

Any suitable impregnation technique including the incipient wetness technique or the excess solution technique, both of which are well-known in the art, may be employed for depositing the nonaqueous, organic solution of ruthenium on to the ceria support. The incipient wetness technique is so-called because it requires that the volume of impregnating solution be predetermined so as to provide the minimum volume of solution necessary to just wet the entire surface of the support, with no excess liquid. The excess solution technique, as the name implies, requires an excess of the impregnating solution, the solvent thereafter being removed, usually by evaporation.

As regards the nonaqueous organic solvent, a variety of solvents may be employed. These include ketones, such as acetone, methyl ethyl ketone, and the like; alcohols, such as methanol, ethanol, propanol and the like; liquid paraffinic hydrocarbons such as pentane, hexane and the like; amides such as dimethyl formamide, and the like; amines such as propylamine, and the like and ethers, such as diethylether, tetrahydrofuran and the like. A preferred solvent is acetone.

Any soluble ruthenium compound other than a carbonyl may be employed, for example a ruthenium salt or a ruthenium complex. Suitable ruthenium salts include the nitrate, chloride and acetate. A preferred ruthenium compound is the acetylacetonate.

The composition of formula (I) may incorporate an alkali metal, which for reasons of availability and cost is suitably either sodium or potassium. The alkali metal may suitably be present in an amount up to 2% w/w, preferably up to 1% w/w, even more preferably up to 0.5% w/w, based on the total weight of the composition. The alkali metal may suitably be added by impregnation with either an aqueous or nonaqueous organic solution of a soluble compound, for example the carbonate, nitrate or chloride. Impregnation may be effected either before or after the addition of the ruthenium compound.

Impregnation may suitably be effected at room temperature, though elevated temperatures may be employed if so desired.

Following impregnation, any solvent remaining in the composition may suitably be evaporated off.

Thermally decomposable compounds comprised in the impregnated composition are preferably thermally decomposed in a discrete step. This may suitably be accomplished by heating the composition, suitably in a stream of a gas, such as nitrogen, or an oxygen-containing gas such as air, at a temperature suitably in the range from 250 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 nitrogen. 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 350°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 into the synthesis gas conversion process.

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.

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 at a temperature in the range from 190 to 400°C and a pressure in the range from 0 to 100 bar synthesis gas with a catalyst comprising the reductively activated composition having the formula (I) produced by the process as hereinbefore described.

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.

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 incorporated into the catalyst an inert material, for example silica. It is preferred, however, to incorporate a zeolite. A suitable zeolite is an MFI-type zeolite, for example ZSM-5 as described in US Patent No. 3,702,886. It is preferred to use the hydrogen form of the zeolite which may be obtained by acid exchange or by thermal decomposition of the ammonium-exchanged form of the zeolite. Preferably the alkali metal-free composition is modified by incorporation of the zeolite. Suitably from 1 to 5, preferably from 1 to 2 parts by volume of zeolite is incorporated per part by volume of the catalyst composition. Incorporation of a zeolite can improve the selectivity to paraffinic hydrocarbons.

The temperature is preferably in the range from 250 to 350°C and the pressure is preferably in the range from 10 to 50 bar. The GHSV may suitably be in the range from 100 to 5000h^{-1}.

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

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

CATALYST PREPARATION

Example 1 – Composition A (0.3% Ru/CeO_2)

Ruthenium chloride ($RuCl_3 \cdot 2H_2O$, 0.47 g) was dissolved in 30 cm^3 of AnalaR acetone. This solution was slowly added to CeO_2 (60g) with continuous stirring, until a consistent paste was formed. A further 10 cm^3 of acetone was used to ensure that all the ruthenium was washed onto the ceria. With continuous stirring/kneading, the paste was dried over a steam bath until a uniform powder was formed. The powder was stored in an oven at 150°C overnight prior to pretreatment.

Example 2 – Composition B (0.3% Ru/CeO_2)

The method described in Example 1 was used, except that [$Ru(acac)_3$] (0.71g) was used instead of the chloride.

Example 3 – Composition C (0.3% Ru/0.1% K/CeO_2)

K_2CO_3 (0.13g) was dissolved in 30 cm^3 of water. This solution was added to CeO_2 (60g) with continuous stirring. The resulting paste was dried over a steam bath with continuous stirring/kneading until a powder was formed. A second solution, containing ruthenium chloride ($RuCl_3 \cdot 2H_2O$, 0.46g) dissolved in 30 cm^3 of AnalaR acetone, was then slowly added to the 0.1% K/CeO_2 in a manner similar to that described in Example 1.

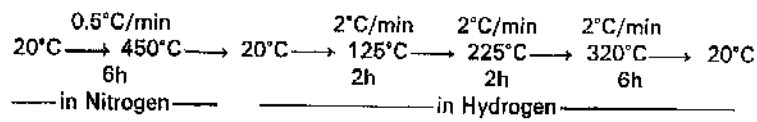
Example 4 – Composition D (0.5% Ru/CeO_2)

This catalyst was prepared in a manner similar to Example 1. Ruthenium chloride ($RuCl_3 \cdot 2H_2O$, 0.75g) was dissolved in 50 cm^3 of AnalaR acetone and impregnated onto CeO_2 (60g).

Thermal Decomposition/Reductive Activation to Produce the Catalyst

Catalysts A to D

The compositions were pretreated as follows:–



CATALYST TESTING

Example 5

Catalyst A was pressed to 4 tons and the resulting pellets crushed and sieved to BSS 8-20 mesh. The catalyst was then loaded into a fixed bed reactor and reduced in a slow stream of hydrogen with the following overnight programme:

Syngas (H_2:CO molar ratio = 2:1) was then introduced into the reactor, the pressure adjusted to 20 bar and the run started.

Example 6

Example 5 was repeated except that Catalyst A was replaced by Catalyst B.

Example 7

Example 5 was repeated except that Catalyst A was replaced by Catalyst C.

Example 8

Example 5 was repeated except that Catalyst A was replaced by Catalyst D.

Example 9

Example 8 was repeated except that Catalyst D was diluted with BSS 8-20 mesh granules of silica in the ratio 3 parts catalyst to 2 parts silica diluent. The catalyst may therefore be considered equivalent to a 0.3% Ru/CeO_2 catalyst.

Example 10

Example 6 was repeated except that the Catalyst B was diluted with BSS 8-20 mesh granules of hydrogen form of an MFI zeolite (silica:alumina molar ratio = 24.6) in the ratio of 7 parts catalyst to 5 parts zeolite.

The reaction conditions and the results obtained for Examples 5 to 10 are given in the Table.

TABLE

$CO:H_2$ molar ratio = 1:2
Pressure = 20 bar

Example	*Catalyst*	*T/°C*	*GHSV (h^{-1})*	*%CO Converted*	*Carbon Molar Selectivity (%)**					*C_3^+ Productivity Kg/m^3 cat/h*
					CO_2	*CH_4*	*C_2*	*C_3^+*	*C_5^+*	
5	A	305	2500	45	1.7	17.7	6.3	73.7	50.5	169
6	B	282	2500	44	2.1	13.5	4.0	79.6	62.0	183
7	C	297	2500	52	3.5	17.2	5.4	71.9	52.8	180
8	D	274	2500	28	1.3	19.3	6.1	71.8	42.0	102
9	D	291	2500	40	1.4	14.5	4.8	77.4	53.4	160
10	B	279	1250	42	3.0	11.7	2.5	82.8	66.5	96

* Oxygenates not included

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 is represented by the formula:–

$$Ru_aCeO_x \quad (I)$$

wherein a is greater than zero and less than 1% w/w, based on the total weight of the composition, and x is a number such that the valance requirements of the other elements for oxygen is satisfied, which process comprises impregnating ceria with a non-aqueous organic impregnation solution of a soluble, thermally decomposable ruthenium compound other than a carbonyl.

2. A process according to claim 1 wherein impregnation is effected by either the incipient wetness technique or the excess solution technique.

3. A process according to either claim 1 or claim 2 wherein the non-aqueous organic solvent is either a ketone, an alcohol, a liquid paraffinic hydrocarbon, an amide, an amine or an ether.

4. A process according to claim 3 wherein the non-aqueous organic solvent is acetone.

5. A process according to any one of the preceding claims wherein the ruthenium compound is the acetylacetonate.

6. A process according to any one of the preceding claims wherein the composition of formula (I) incorporates an alkali metal in an amount up to 2% w/w.

7. A process according to any one of the preceding claims wherein thermally decomposable compounds comprised in the impregnated composition are thermally decomposed by heating the composition at a temperature in the range from 250 to 600°C in a stream of gas which is either nitrogen or air.

8. A process according to any one of the preceding claims wherein the composition of formula (I) is reductively activated by contact at elevated temperature with a reducing gas.

9. A process according to claim 8 wherein the reducing gas is hydrogen diluted with nitrogen.

10. A process for the production of hydrocarbons having a carbon number greater than one which process comprises contacting at a temperature in the range from 190 to 400°C and a pressure in the range from 0 to 100 bar synthesis gas with a catalyst comprising the reductively activated composition having the formula (I) produced by the process as claimed in claims 1 to 9.

11. A process according to claim 10 wherein the catalyst incorporates a zeolite.
12. A process according to claim 11 wherein the zeolite is ZSM-5 in the hydrogen form.
13. A process according to any one of claims 10 to 12 wherein the temperature is in the range from 250 to 350°C and the pressure is in the range from 10 to 50 bar.

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