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54 **Process for upgrading synthesis gas and catalysts therefor.**

57 A process of upgrading synthesis gas to hydrocarbons and oxygenated hydrocarbons, particularly olefins and carboxylic acids, comprises contacting synthesis gas with catalysts comprising the mixed oxides of ruthenium, copper, an alkali or alkaline earth metal, and optionally a metal selected from Ca, Cr, Fe, Mn, Mo, Th, Zn or mixtures thereof. The synthesis gas upgrading product may be contacted with a hydrogenation catalyst to provide alkanes, alcohols and esters, useful for fuels.

Catalysts comprising the mixed oxides of ruthenium, copper, at least one alkali metal and at least one of rhodium, iridium, palladium, and platinum are further disclosed which are useful in the upgrading of synthesis gas, particularly for obtaining alkanes and alcohols.

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Process for Upgrading Synthesis Gas
and Catalysts Therefor

5 The present invention is directed to the upgrading of synthesis gas to produce mixtures of hydrocarbons and to catalysts of use in such process.

10 In particular, the present invention is directed to a vapour phase reaction of synthesis gas comprising carbon monoxide and hydrogen in the presence of a catalyst to produce mixtures of hydrocarbon and oxygenated hydrocarbons. It also relates to catalysts of use in such process.

15 U.S. Patent No. 2,476,788 discloses the synthesis of hydrocarbons, including oxygenates such as aldehydes, ketones and alcohols from carbon monoxide and hydrogen in the presence of metals or metal oxides selected from nickel, iron or cobalt, optionally with promoter metals or metal compounds of aluminium, cerium, magnesium, manganese, thorium, titanium, uranium, zinc, and zirconium. The catalyst could be supported on suitable carriers such as clay, silica gel, and alumina.

25 U.S. Patent Nos. 2,535,060 and 2,549,470 disclose the preparation of straight-chain primary hydroxyalkanes by introducing hydrogen, carbon monoxide and a hydroxylated solvent into a reaction vessel and heating the mixture in the presence of a ruthenium-containing catalyst (particularly ruthenium metal, oxide, carbonyl, or salts of carboxylic acids which give rise to formation of the carbonyl) and in Patent 2,549,470 in the presence of an alkaline reagent by maintaining pH in the range of 7.0 to 11.5. Both Patents teach that it is essential that the reaction take place in the liquid phase.

35 U.S. Patent No. 3,941,819 describes the production of ethane, ethylene and dimethyl ether by passing a carbon monoxide and hydrogen mixture over platinum supported on alumina.

U.S. Patent No. 4,014,913 discloses the preparation of acetic acid, ethanol and acetaldehyde by contacting H_2 and CO with a rhodium-manganese catalyst.

5 U.S. Patent No. 4,086,262 describes the production of hydrocarbon mixtures by contacting a mixture of carbon monoxide and hydrogen with a carbon monoxide reduction catalyst and an acidic crystalline aluminosilicate (zeolite). Chang-et al. teach that prominent
10 types of catalysts include metals or oxides of Zn, Fe, Co, Ni, Ru, Th, Rh, and Os, and that "with the exception of ruthenium, all practical art recognized synthesis catalysts contain chemical and structural promoters".

15 U.S. Patent No. 4,096,164 discloses the production of oxygenated 2 carbon atom hydrocarbons by reacting CO and H_2 in the presence of catalysts comprising Rh, Mo and W.

20 U.S. Patent No. 4,101,460 and U.S. Patent No. 4,136,104 disclose the conversion of synthesis gas to acetic acid and related 2 carbon atom oxygenated derivatives in the presence of a rhodium metal/ruthenium metal catalyst.

25 U.S. Patent No. 4,116,994 discloses the selective production of olefinic hydrocarbons from carbon monoxide and hydrogen using a catalyst comprising rhodium deposited on titanium containing oxides.

30 U.S. Patent No. 4,119,656 describes the production of one to 2 carbon atom oxygenated hydrocarbons by contacting synthesis gas with a catalyst consisting essentially of palladium.

35 U.S. Patent No. 4,122,110 discloses the manufacture of linear saturated primary alcohols from synthesis gas using a catalyst comprising copper, cobalt, a third metal selected from chromium, iron, vanadium and manganese, at least one alkali metal and optionally zinc.

U.S. Patent No. 4,162,262 discloses the production

of 2 carbon atom oxygenated hydrocarbons while minimizing co-production of methanol by reacting H_2 and CO with a catalyst containing rhodium metal, uranium or thorium and optionally iron, molybdenum or tungsten.

5 U.S. Patent No. 4,171,320 discloses the selective production of olefins from carbon monoxide and hydrogen using as a catalyst ruthenium on a support comprising at least one refractory Group VB metal oxide.

10 U.S. Patent No. 4,199,522 discloses the preparation of olefins of 2 to 4 carbon atoms from carbon monoxide and hydrogen using catalysts comprising a sulfide, oxide or metal of Mo, W, Re, Ru, Ni, Pd, Rh, Os, Ir or Pt and a hydroxide, oxide or salt of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba or Th.

15 U.S. Patent No. 4,201,597 discloses the preparation of oxygenated hydrocarbons by reacting carbon monoxide and hydrogen in the presence of a catalyst containing rhodium, tungsten and an alkali metal.

20 U.S. Patent No. 4,206,134 discloses the selective preparation of low weight olefins from carbon monoxide and hydrogen using as a catalyst ruthenium on a support consisting of a manganese-containing oxide.

25 U.S. Patent No. 4,235,801 discloses the preparation of ethanol by contacting a synthesis gas mixture containing CO and H_2 with a rhodium-iron catalyst.

30 U.S. Patent No. 4,246,186 discloses the preparation of two carbon atom oxygenated hydrocarbons from hydrogen and carbon monoxide by reaction with a rhodium metal catalyst, as compared to other single element Group VIII metal and copper catalysts.

35 European Patent Appln. No. 18,763 describes the production of oxygenated hydrocarbons having 1 to 4 carbon atoms by reaction of CO and H_2 in the presence of a catalyst comprising rhodium, chromium and optionally Fe, Mn, Mo, W or Ru. The catalyst may be prepared upon a support which has been formerly activated by the addition

of metals or non-metals such as alkalis, Th, Mn, Rh, Fe, Cr, Mo, B, and P.

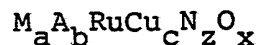
European Patent Appln. Nos. 4,653 and 4,656 describe the production of acetic acid, ethanol and acetaldehyde by reacting CO and H₂ with a catalyst containing rhodium, magnesium and a halide.

We have found that catalyst comprising the mixed oxides of ruthenium, copper and an alkali metal, optionally promoted with an oxide of at least one of Ce, Cr, Fe, Mn, Mo, Th, Zn or mixtures thereof, said catalysts being optionally nitrided, are useful for the upgrading of synthesis gas to hydrocarbons, particularly olefins, and oxygenated hydrocarbon products, particularly carboxylic acids, with high selectivity.

We have also found that catalysts comprising the mixed metal oxides of ruthenium, copper, at least one alkali metal, and at least one rhodium, iridium, palladium or platinum are useful for the upgrading of synthesis gas to hydrocarbons, exhibiting good selectivity to alkanes and oxygenated hydrocarbon products, particularly alcohols, with high selectivity.

The invention provides such catalysts and processes for upgrading synthesis gas utilizing such catalysts.

In one embodiment, the process of the present invention includes the upgrading of synthesis gas to obtain selectivity to olefins and carboxylic acids comprising contacting carbon monoxide and hydrogen in the vapour phase at a reaction temperature of at least 250°C and a reaction pressure of at least 500 psi (35 kg/cm²) with a catalyst of the formula



wherein A is an alkali metal or an alkaline earth metal or mixtures thereof,

wherein M is Ce, Cr, Fe, Mn, Mo, Th, Zn or mixtures thereof, and

wherein a is 0 to about 0.5

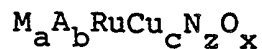
b is about 0.002 to about 2,

5 c is about 0.5 to about 3,

z is 0 to about 1 weight percent and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

The present invention further includes novel
10 catalysts of the composition



wherein A is an alkali metal or an alkaline earth metal
15 or mixtures thereof,

wherein M is Ce, Cr, Fe, Mn, Mo, Th, Zn or mixtures thereof, and

wherein a is 0 to about 0.5

b is about 0.002 to about 2,

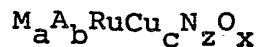
20 c is about 0.5 to about 3,

z is 0 to about 1 weight percent and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

The present invention further includes the upgrading
25 of synthesis gas to yield hydrocarbons, namely alkanes, alcohols and esters useful for fuels, comprising:

contacting carbon monoxide and hydrogen in the vapour phase at a temperature of at least 250°C and a pressure of at least 500 psi (35 kg/cm²) in the presence
30 of a catalyst of the formula



wherein A is an alkali metal or an alkaline earth metal
35 or mixtures thereof,

wherein M is Ce, Cr, Fe, Mn, Mo, Th, Zn or mixtures thereof, and

wherein a is 0 to about 0.5

b is about 0.002 to about 2,

5 c is about 0.5 to about 3,

z is 0 to about 1 weight percent and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

10 recovering the hydrocarbon and oxygenated hydrocarbon products;

contacting said products with hydrogen at elevated temperature and pressure in the presence of a hydrogenation catalyst.

15 In another embodiment, the process of the present invention includes the upgrading of synthesis gas to obtain selectivity to alkanes and alcohols comprising contacting carbon monoxide and hydrogen in the vapour phase at a reaction temperature of at least 250°C and a reaction pressure of at least 500 psi (35 kg/cm²) with a

20 catalyst of the formula



wherein A is an alkali metal,

25 M is Rh, Ir, Pd, Pt or mixtures thereof, and

wherein a is about 0.002 to about 0.5,

b is about 0.5 to about 3,

c is about 0.5 to about 3,

d is about 0.05 to about 0.5,

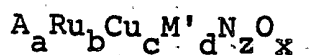
30 z is a level of 0 to about 1 weight % and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

In a further embodiment of the invention, the products of the synthesis gas upgrading process are

35 contacted with hydrogen at elevated temperature and pressure in the presence of a hydrogenation catalyst.

The present invention further includes novel catalysts of the composition



5

wherein A is an alkali metal,

M' is Rh, Ir, Pd, Pt or mixtures thereof, and wherein a is about 0.002 to about 0.5,

b is about 0.5 to about 3,

10

c is about 0.5 to about 3,

d is about 0.05 to about 0.5,

z is a level of 0 to about 1 weight % and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

15

Thus, in the process of the present invention, synthesis gas, or a mixture of carbon monoxide and hydrogen, is reacted in the presence of a carbon monoxide hydrogenation catalyst in the vapour phase to form hydrocarbons, and in particular, olefins and carboxylic acids in one embodiment of the invention, and alkanes and alcohols in another embodiment of the invention.

20

Synthesis gas may be produced by means known in the art and practiced commercially, including providing synthesis gas as a product of the partial combustion of coal, natural gas, petroleum bottoms or other carbonaceous materials. One method of derivation is the heating of coke in the presence of air and then steam. The ratio of carbon monoxide to hydrogen in the synthesis gas mixture to be upgraded may vary from about 1:10 to 10:1 and is preferably in the range of about 1:3 to about 3:1. The synthesis gas may contain a very low amount of sulfur compounds, and may also contain small amounts of carbon dioxide, nitrogen and other inerts.

25

30

35

Although synthesis gas is a preferred reactant, any other gas composed primarily of hydrogen and carbon monoxide and having CO:H₂ ratio of 1:10 to 10:1 may be

employed. Preferably the gaseous reactant is essentially sulfur free.

Process Conditions

5 The process of the present invention is carried out by contacting the gaseous reactants containing carbon monoxide and hydrogen, with the novel catalyst described below in a suitable fluid bed or fixed bed reactor. The reaction can be conducted continuously or in a batch-type operation. The reaction temperature should be
10 maintained between about 250°C to about 400°C, preferably 275°C to about 375°C.

The reaction pressure should normally be maintained between about 500 psi (35 kg/cm²) to about 5000 psi (350 kg/cm²) preferably 500 psi (35 kg/cm²) to about 1500 psi
15 (105 kg/cm²). The reactant gases may be fed to the reactor utilized at a space velocity (litres gaseous reactants fed per litre of catalyst per hour) of about 100 per hour to about 10,000 per hour, preferably about 500 per hour to 6,000 per hour.

20 The contact time of the reactants with the catalyst is generally between about 10 seconds to about 200 seconds, and is preferably about 15 seconds to about 100 seconds.

Catalyst

25 The novel catalyst provided in one embodiment of the present invention is believed to be an oxide complex and comprises the composition described by the empirical formula



30 wherein A is an alkali metal or an alkaline earth metal or mixtures thereof,

wherein M is Ce, Cr, Fe, Mn, Mo, Th, Zn or mixtures thereof, and

wherein a is 0 to about 0.5,

35 b is about 0.002 to about 2,

c is about 0.5 to about 3,

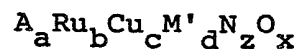
z is about 1 weight percent and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

A may be selected from Na, Li, K, Rb, Cs, Be, Ms, Ca, Sr and Ba although Na, Li, Rb, Cs and Mg are preferred.

The ratio of ruthenium to copper is preferably about 0.5:1 to about 2:1. An oxide of alkali metal or an alkaline earth metal, preferably an alkali metal, is required in the present catalyst. Mixed oxide catalysts of ruthenium and copper which are alkali metal and alkaline earth metal free produce essentially all methane. The alkali metal or alkaline earth metal may be present in the catalyst at a level of about 0.002 to about 2 moles per mole of ruthenium oxide, most preferably about 0.02 to about 0.4. Preferred is a level of about 0.02 to about 1 mole alkali metal per mole of ruthenium oxide. The level of alkaline earth metal, if present, to ruthenium oxide is preferably 0.02 to about 0.5 moles per moles of ruthenium oxide. Preferably the M promoter is present in a level of 0.1 to 0.5 moles per mole of ruthenium oxide.

The novel catalyst provided in another embodiment of the present invention is believed to be an oxide complex and comprises the composition described by the empirical formula



wherein A is an alkali metal,

M' is Rh, Ir, Pd, Pt or mixtures thereof, and

wherein a is about 0.002 to about 0.5,

b is about 0.5 to about 3,

c is about 0.5 to about 3,

d is about 0.05 to about 0.5,

z is a level of 0 to about 1 weight % and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

M' is preferably rhodium, iridium or palladium, and A may be selected from Na, Li, K, Rb and Cs, although Na, K, and Rb are preferred.

5 The Ru to Cu ratio is preferably about 1:0.75 to about 1:1.5. The ratio of ruthenium to the promoter metal (M') is generally about 1:0.05 to about 1:0.5 and is preferably about 1:0.1 to about 1:0.5. Alkali metal is required in the catalyst of the present invention. Mixed oxide catalysts of ruthenium and copper which are
10 alkali free produce essentially all methane, at low conversion. The alkali metal may be present in the catalyst at a level of about 0.002 to about 0.5 moles alkali metal per mole of ruthenium. A level of about 0.02 to about 0.4 moles alkali metal per mole of ruthenium is
15 preferred.

The catalyst of the present invention is a mixed metal oxide. In the process of the present invention, the catalyst is preferably utilized in a partially reduced state, however, the catalyst is not totally reduced to
20 elemental metal and thus retains its oxide character.

The catalyst may be prepared by conventional means, such as mixing compounds containing the catalyst components in a liquid solution or slurry, such as a water solution or slurry and heating, recovering the catalyst precursor
25 from the liquid, drying and calcining. Suitable catalyst component containing compounds may include but are not limited to oxides, hydroxides, inorganic salts such as nitrates, phosphates, halides, carbonates, silicates, aluminates, and salts of organic acids such as
30 acetates, formates, butyrates, propionates, benzylates, and the like. Preferred catalysts of the present invention, containing the alkali metal component are prepared by recovering the catalyst precursor by adding to the aqueous solution of ruthenium, copper and promoter (if any)
35 components, an alkali metal hydroxide to cause precipitation of the catalyst precursor, heating in the presence

of the alkali metal, and thereafter filtering the precipitate.

The catalyst may be formed in a conventional manner, such as tableting, pelleting, or supporting the active catalyst material on a carrier. The carrier is preferably inert, and may include silica, alumina, Alundum, clay, alumina-silica, silicon carbide and the like. The active catalytic material may be coated on the carrier by the method described in U.S. Patent No. 4,077,912 or may be impregnated on the carrier such as by depositing a solution of the catalyst component containing compounds onto a carrier, drying and calcining. Catalyst components may be added to the carrier separately, if desired.

Products

Products of the synthesis gas upgrading process of the present invention in which the M promoter metal is utilized in the catalyst include methane, gaseous alkanes, having more than one carbon atom and olefins having from 2 carbon atoms to about 4 carbon atoms; alcohols, carboxylic acids and aldehydes having from one to 5 carbon atoms present in an aqueous product phase; and olefins, carboxylic acids, esters, aldehydes and alcohols in an organic or oil product phase. Generally, very low amounts of higher weight paraffins are produced. The predominant products, however, are olefins and carboxylic acids.

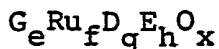
Products of the synthesis gas upgrading process include, among others, methane, ethane, propane, butane, ethylene, propylene, butylene, methanol, ethanol, propanol, butanol, pentanol, acetic acid, propanoic acid, butyric acid, valeric acid, and low amounts of aldehydes and esters including acetaldehyde and methyl butyrate. These products are useful as chemical feedstocks, or as fuels, such as in gasoline mixtures. Where conversion is maintained at a moderate or low level, these products can be recovered from the reactor effluent, and the remaining synthesis gas recycled to the reaction.

Products of the upgrading of synthesis gas process of the present invention in which the M' promoter metal is utilized in the catalyst include, among others, propane, ethylene, methanol, ethanol, propanol, butanol, pentanol, acetic acid, propanoic acid, butyric acid, valeric acid. Small amounts of other alkanes, olefins and aldehydes are present in the products of the inventive process in some embodiments. These products are useful as chemical feedstocks, or as fuels, such as in gasoline mixtures.

Where conversion is maintained at a moderate or low level, these products can be recovered from the reactor effluent, and the remaining synthesis gas recycled to the reaction.

Alkanes, esters and alcohols are most suitable for use as fuels, such as in gasoline mixtures. Therefore, in one embodiment of the invention, the liquid product mixture obtained from the synthesis gas upgrading process (containing in addition to alcohols and esters, the non-fuel components such as olefins, aldehydes and carboxylic acids) is contacted with hydrogen at elevated temperature and pressure in the presence of a hydrogenation catalyst. The resulting hydrogenation products, alkanes, alcohols and esters are suitable for use as fuel components.

The hydrogenation process may be conducted in the vapour phase, at a reaction temperature of about 150°C to about 450°C and a reaction pressure of about 250 psig (12.5 kg/cm² g) to about 5000 psig (350 kg/cm² g). Any suitable hydrogenation catalyst, such as nickel or copper chromite may be used, although catalysts such as those disclosed in USSN 264,744 are preferred. These catalysts may be represented by the formula



- wherein G = Zn, Cd and mixtures thereof;
- D = Co, Ni and mixtures thereof;
- E = Fe, Cu, Rh, Pd, Os, Ir, Pt and mixtures thereof;

and wherein $e = 0$ to 1 ,

$f = 0.01$ to 3 ,

$g = 0.01$ to 3 ,

$h = 0$ to 1 ,

5 $x =$ the number of oxygens determined by the valence requirements of the other elements.

The following Examples (1-37) are given by way of illustration only. In these Examples the following general procedures were followed:-

10 Catalyst Preparation

In the examples below, catalysts were prepared by the following method. An amount of ruthenium chloride and copper chloride required to give 0.03 moles of each metal were dissolved in 250 millilitres of water with
15 stirring for 30 minutes. Aqueous sodium hydroxide (50 % by weight) was added dropwise, with stirring, until the pH reached and remained at 8.3 to 8.5 (approximately 7 to 15 millilitres). The resulting slurry was heated near boiling for 30 minutes with
20 constant stirring, then cooled. The pH was adjusted if necessary to 7.5. The mixture was filtered, washed, and reslurried with subsequent filtering and washing steps until the molar ratio of sodium to ruthenium present was approximately 0.02 to 0.2:1. The solid mixed oxide
25 was dried at 125°C for about 16 hours, was calcined for three hours at about 350°C (in air) and was ground to pass 140 mesh (0.105 millimeters).

The catalysts were coated upon alumina-silica supports in the following manner. 25 grams of Norton SA
30 5223 Alundum, 10/30 mesh (0.595 millimeters-2.00 millimeters) were placed in a vessel. 1.25 g distilled water was sprayed onto the Alundum which was rolled for approximately 10 minutes and the procedure was repeated. The metal oxide catalysts, in an amount calculated to
35 give a total of 0.015 moles of active metal, was added in two equal portions with 15 minutes rolling after each.

The coated catalyst was dried for about 16 hours at 125°C and calcined three hours at 350°C. Catalysts prepared in this manner contain approximately 5 weight percent active metals, 0.01% to 0.1% by weight sodium and have surface areas of about 2 m²/g, with pore volumes of from about 0.06 to about 0.09 cc/g. Promoter elements were added either before precipitation of the RuCu precursor, or the RuCu oxide containing powder was impregnated with a solution of the promoter compound.

The catalysts were partially reduced in the following manner. A 20 cc stainless steel tube reactor was packed with catalyst, and hydrogen gas was introduced into the reactor at 150-200 cc/min. at atmospheric pressure. The electric block furnace placed around the reactor was increased in 50° increments stepwise until 500°C was reached. The final temperature was maintained for two hours, at which time the reactor was allowed to cool with hydrogen flow being continued.

Certain catalysts identified below were nitrided after reduction by contacting the catalyst with ammonia for several hours at atmospheric pressure and a temperature of about 400°C, with subsequent cooling under ammonia. The nitrided catalysts contained up to 1 weight % nitrogen, as is preferred. Between 0.5 and 1 weight percent nitrogen is most preferred.

Reaction Procedure

Following catalyst reduction (and nitriding if applicable) and subsequent cooling to room temperature, the reactor was charged to the desired pressure with hydrogen. The split block electric furnace surrounding the reactor was activated and set for run temperature. The system was allowed to equilibrate for at least 15 minutes at run temperature before carbon monoxide flow was started and both gases were adjusted to the desired flow rate. After about one to one and one-half hours of reaction, the off-gas (effluent) was sampled and analyzed and the

condensable product diverted from a pre-run receiver to a product collection receiver. A recovery run proceeded for one to three hours during which time the off-gas was analyzed by gas chromatography and its volume measured.

5 The liquid product also was weighed and analyzed.

In addition to gas chromatography analysis for the gas phase, hydrocarbons having more than three carbon atoms were determined by flame ionization detection.

10 Liquid phase hydrocarbons and oxygenated hydrocarbons were analyzed by gas chromatography. The results reported in the Tables below were calculated as follows.

$$\text{Selectivity} = \frac{\text{Moles Product} \times \text{number of carbon atoms in product} \times 100}{\text{Moles CO input} - \text{Moles CO effluent}}$$

15

$$\text{CO Conversion} = \frac{\text{Moles of CO input} - \text{moles CO effluent} \times 100}{\text{Moles of CO input}}$$

20 Selectivity to gas and aqueous phase products are reported as a percent of total products. Selectivity to oil phase products are reported as a percent of total oil phase product obtained, calculated as above. Weight percent hydrocarbons are reported as weight percent of total product weight. Carbon dioxide and water are not
25 considered in the calculations.

The catalysts identified in the examples below were prepared according to the catalyst preparation methods set forth above. The catalysts were reduced, and where identified were nitrated, and tested for synthesis gas
30 upgrading by the reaction procedure set forth above. Reaction conditions and test results are set forth in the Tables below.

Examples 1-2

35 Catalysts of the formula 5% Na_bRuCuO_x/95% Alundum were prepared according to the procedure first set forth above. Products of the synthesis gas upgrading reaction

utilizing these catalysts were predominantly olefins and carboxylic acids.

Examples 3-4

5 Catalysts of formula 5% $\text{Na}_b\text{RuCu}_2\text{O}_x$ /95% Alundum were prepared according to the procedure of Example 1 except that twice the level of copper chloride was utilized in the catalyst preparation. Product selectivity to olefins and paraffins increased, with good selectivity to carboxylic acids remaining.

10 Example 5

The catalyst 5% $\text{Na}_b\text{RuCuN}_2\text{O}_x$ /95% Alundum was prepared by nitriding the catalyst of Example 1 by the nitriding procedure set forth above. The catalyst continued to show selectivity to olefins and carboxylic acids, with an increase in alcohol production.

15 Example 6

A catalyst of the formula 5 % $\text{Na}_b\text{RuCuO}_x$ /95% Alundum was prepared according to the procedure of Example 1. The predominant products of synthesis gas upgrading using this catalyst were carboxylic acids and olefins.

20 Examples 7-14

Catalysts of the formula 5% $\text{Na}_b\text{RuCuN}_2\text{O}_x$ /95 % Alundum were prepared according to the procedure of Example 5. Predominant products again were olefins and carboxylic acids.

25 Examples 15-23

The promoter metals listed below were added by coprecipitation or in the initial catalyst component slurry, or were added by impregnating the RuCuO_x containing powder to form 5% $\text{M}_a\text{Na}_{0.02-0.2}\text{RuCuN}_2\text{O}_x$ /95% Alundum catalysts by the method first set forth above, with nitriding. The catalysts were tested for synthesis gas upgrading under the conditions listed in Table III. These catalysts also exhibit good selectivity to olefins and carboxylic acids.

Example No.	Promoter (M_a)	Compound	Addition
15	Ce _{0.2}	cerium oxide	initial slurry
16	Cr _{0.2}	chromium chloride	coprecipitation
17	Fe _{0.1}	iron chloride	coprecipitation
5 18	Mn _{0.2}	manganese chloride	coprecipitation
19	Mn _{0.2}	manganese chloride	coprecipitation
20	Mo _{0.1}	ammonium heptamolybdate	coprecipitation
21	Mo _{0.1}	ammonium heptamolybdate	coprecipitation
22	Th _{0.2}	thorium nitrate	impregnation
10 23	Zn _{0.5}	zinc nitrate	impregnation

Comparative Examples 24-25

Alkali metal/alkaline earth metal-free catalysts of the formula 5% RuCuN_zO_x/95% Alundum were prepared from a solution of ruthenium nitrate and copper nitrate, with nitriding of the catalyst being conducted after partial reduction. The catalysts were tested for synthesis gas upgrading under the conditions listed in Table IV, resulting in predominantly methane production.

Examples 26-35

The alkali and alkaline earth metals listed below were added to form the catalysts listed in Table IV by impregnation of either RuCuO_x or RuCuNa_{0.3}O_x catalysts, prepared with nitriding. These catalysts exhibit good selectivity to olefins and carboxylic acids as reported in Table IV.

Example No.	Ab Promoter Added	Compound Added	Base catalyst
26	Na _{0.2}	sodium carbonate	RuCuNa _{0.3} O _x
30 27	Li _{0.2}	lithium hydroxide	RuCuNa _{0.3} O _x
28	Li _{0.2}	lithium hydroxide	RuCuNa _{0.3} O _x
29	Mg _{0.2}	magnesium hydroxide	RuCuNa _{0.3} O _x
30	Mg _{0.2}	magnesium hydroxide	RuCuNa _{0.3} O _x
31	Na _{0.2}	sodium carbonate	RuCuO _x
35 32	Na _{0.2}	sodium carbonate	RuCuNa _{0.3} O _x
33	Cs _{0.2}	cesium acetate	RuCuO _x

34	Li _{0.4}	lithium hydroxide	RuCuO _x
35	Li _{0.4}	lithium hydroxide	RuCuO _x

Example 36

5 A catalyst of the formula 5 % Na_{0.02-0.2}RuCuN_z/95% SiO₂ was prepared according to the method of Example 5 except that silica was substituted for the alumina silica-
 Alundum support. The catalyst was tested for synthesis
 10 gas upgrading at a temperature of 350°C, a pressure of 1300 psi, a space velocity of 330 per hour and a CO:H₂ ratio of 3:7. CO conversion was 31.2% and the product distribution was as follows:

	<u>Product</u>	<u>Wt. %</u>
	Alkanes	28.9
15	Olefins	30.5
	Carboxylic Acid	20.3
	Alcohols	13.0
	Aldehydes	1.8
	Esters	5.4

20 This catalyst exhibited good selectivity to olefins and carboxylic acids.

As an example of the product mixture produced by the inventive process, the products obtained by testing the catalyst of Example 34 are as follows.

	<u>Product</u>	<u>Wt. (g)</u>
25	Methane	0.2832
	Ethane	0.0500
	Propane	0.1393
	Ethylene	0.0681
30	Propylene	0.2850
	Methanol	0.0278
	Ethanol	0.0291
	Propanol	0.0093
	Butanol	0.0111
35	Pentanol	0.0043
	Acetic Acid	0.0585

	Propionic Acid	0.0369
	Butyric Acid	0.0202
	Valeric Acid	0.0097
	Higher Alkanes	0.0528
5	Higher Olefins	0.2097
	Higher Alcohols	0.1656
	Higher Acids	0.3635
	Aldehydes	0.0501
	Esters	0.0383

10

Example 37

A portion of the liquid products of the process of the present invention, comprising mainly carboxylic acids and olefins, with minor amounts of alcohols and aldehydes, was hydrogenated in the vapour phase at a reaction temperature of 200°C and a pressure of 1000 psi in the presence of a hydrogenation catalyst comprising 5% RuCoPdZn_{0.4}O_x on 95% Alundum. Hydrogen was introduced to the reaction at 300 cc/minute, and hydrocarbon liquid was introduced to the reaction at 5 cc/hr. Olefins and aldehydes were completely converted to alkanes and alcohols, and over 90 % of the acids were converted to either alcohols or esters. The hydrogenated products of the process of the present invention, alkanes, alcohols and esters, are useful for fuels.

30

35

TABLE I
 Synthesis Gas Upgrading Using Promoted 5% RuCuO_x/95% Alundum Catalysts

Ex. No.	Catalyst	Temp °C	Pressure (psi)	Space ₁ Vel. (hr ⁻¹)	CO:H ₂ Ratio	% CO Conversion	Gas	Product Phase, Wt% (a)	
							Aqueous	Organic	
1	Na _b RuCuO _x	350	1300	3300	3:7	42.2	45.5	17.8	36.7
2	Na _b RuCuO _x	350	600	510	1:1	71.4	18.7	12.9	68.4
3	Na _b RuCu ₂ O _x	350	1300	3300	3:7	79.4	41.8	9.6	48.7
4	Na _b RuCu ₂ O _x	350	600	510	1:1	98.1	30.1	2.3	67.5
5	Na _b RuCuN _z O _x	350	1300	3300	3:7	31.2	56.4	12.5	31.1
6	Na _b RuCuO _x	350	1300	3300	3:7	35.6	34.2	14.8	51.0
7	Na _b RuCuN _z O _x	350	1300	3300	3:7	34.9	38.0	19.9	42.1
8	Na _b RuCuN _z O _x	350	1300	3300	3:7	32.4	33.4	16.5	50.1
9	Na _b RuCuN _z O _x	350	1300	3300	3:7	59.1	43.7	9.5	46.8
10	Na _b RuCuN _z O _x	340	1300	3300	3:7	35.4	25.7	13.3	61.0
11	Na _b RuCuN _z O _x	340	1300	3300	3:7	35.6	33.8	14.2	52.0
12	Na _b RuCuN _z O _x	340	1300	3300	3:7	31.8	24.3	12.9	62.7
13	Na _b RuCuN _z O _x	320	1000	5500	3:7	4.0	18.9	24.3	56.8
14	Na _b RuCuN _z O _x	345	1300	3300	3:7	39.4	48.2	9.9	41.9

(a) excludes weight of H₂O and CO₂

b = 0.02 to 0.2

z = 0.5 - 1 wt % active catalyst

TABLE II

Synthesis Gas Upgrading

Ex NO.	% Selectivity (Total) Gas Phase		% Selectivity (Total) Aqueous Phase		% Selectivity Organic Phase		% Selectivity Ester		% Selectivity Aldehyde		% Selectivity Olefin		Wt % Paraffin
	CH ₄	>C ₂	Alkanes	Olefins	Alcohol	Alcohol	Carboxylic Acid	Carboxylic Acid	Alcohol	Alcohol	Aldehyde	Olefin	
1	9.9	5.4	16.4	1.3	5.6	17.1	42.2	-	15.6	25.0	tr		
2	1.8	0.8	3.3	0.4	1.8	20.1	48.5	-	5.3	26.1	-		
3	10.4	5.3	13.6	1.4	2.4	18.4	28.7	3.0	3.2	46.7	33		
4	4.3	4.2	14.4	0.6	0.3	20.1	25.0	9.6	2.1	43.2	28		
5	12.0	8.3	32.3	1.9	4.8	33.7	39.4	1.1	9.7	16.2	tr		
6	7.3	5.6	15.4	1.3	4.2	16.7	43.7	2.8	8.5	28.3	4		
7	4.4	5.9	9.9	1.0	3.6	15.9	52.5	1.3	3.6	26.7	5		
8	7.7	6.4	11.9	1.3	3.9	15.3	44.1	2.5	7.4	30.8	-		
9	11.1	6.4	13.3	1.3	4.8	17.9	35.2	2.3	7.1	37.5	5		
10	3.6	5.6	9.3	1.1	4.2	16.5	43.4	2.6	11.2	26.3	2		
11	7.2	4.4	8.2	0.9	3.7	13.1	44.1	2.1	12.0	28.8	2		
12	4.8	5.2	10.3	0.5	4.6	13.4	40.0	2.1	11.6	32.9	2		
13	8.2	-	3.2	0.5	7.5	7.7	69.3	4.0	10.8	8.2	-		
14	3.7	9.0	28.2	0.9	3.3	12.8	49.2	3.0	4.7	30.4	2		

* Trace aldehydes present

TABLE III
 Synthesis Gas Upgrading Using 5 & M_aNa_bCuRuN_zO_x/95% Alundum Catalysts

Ex No.	Ma Promoter	Temp (°C)	Pressure (psig)	Space Velocity (hr ⁻¹)	% CO Conv.	Weight & Useful Products					
						Alkanes	Olefins	Carboxylic Acids	Alcohols	Aldehydes	Esters
15	Ce _{0.2}	340	1300	3300	92.4	51.2	24.2	13.3	9.4	0.4	1.5
16	Cr _{0.2}	350	1300	3300	82.9	51.5	24.7	14.9	7.6	0.4	0.9
17	Fe _{0.1}	300	1000	5500	9.5	45.0	14.9	18.5	9.6	3.9	1.3
18	Mn _{0.2}	310	1000	5500	10.9	30.9	28.9	24.1	6.8	7.2	2.0
19	Mn _{0.2}	315	1300	3300	60.4	41.1	29.7	16.7	7.0	2.9	2.5
20	Mo _{0.1}	320	1000	5500	15.1	61.4	23.2	9.0	8.3	-	-
21	Mo _{0.1}	350	1000	5500	40.6	47.4	22.8	15.1	13.8	0.8	-
22	Th _{0.2}	340	1300	3300	38.3	29.1	34.0	21.8	10.1	2.9	2.2
23	Zn _{0.5}	340	1300	3300	4.4	48.7	34.7	4.3	12.3	-	-

b = 0.02 - 0.2

z = 0.5-1 wt % active catalyst

CO:H₂ ratio = 3:7

TABLE IV

Synthesis Gas Upgrading Using 5% A₁B₂RuCuN₂O_x/95% Alundum Catalysts

Ex No.	Ab Promoter	Temp (°C)	Pressure (psig)	Space Velocity (hr ⁻¹)	% CO Conversion	Weight % Useful Products				
						Alkanes	Olefins	Carboxylic Acids	Alcohols Aldehydes Esters	
C24	-	360	1300	3300	tr	100	-	-	-	
C25	-	320	1000	5500	tr	70.9	-	15	14.1	
26	Na _{0.5}	320	1000	5500	6.6	12.5	15.8	49.2	11.4	7.6
27	Li _{0.2} Na _{0.3}	320	1000	5500	13.8	20	22.3	46.0	9.2	7.1
28	Li _{0.2} Na _{0.3}	340	1300	3300	42.4	25.5	34.2	25.0	9.9	2.7
29	Mg _{0.2} Na _{0.3}	320	1000	5500	15.3	27.3	34.2	21.5	8.5	6.2
30	Mg _{0.2} Na _{0.3}	330	1300	3300	77.0	38.0	31.6	16.0	8.5	1.2
31	Na _{0.2}	350	1300	3300	35.5	29.4	29.2	25.0	11.2	3.0
32	Na _{0.5}	340	1300	3300	46.1	24.5	30.6	27.0	11.7	4.0
33	Cs _{0.2}	350	1300	3300	17.0	72.8	8.1	12.4	6.7	-
34	Li _{0.4}	320	1000	5500	13.2	27.5	29.4	25.6	12.9	2.6
35	Li _{0.4}	330	1300	3300	43.5	34.4	35.1	15.8	10.6	2.1

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The following Examples (38-47) are also given by way of illustration only. In these examples the following general procedures were adopted:

Specific Embodiments - Examples 38-47

5 Catalyst Preparation

In the examples below, catalysts were prepared by the following method. An amount of ruthenium chloride and copper chloride required to give 0.03 moles of each metal and an amount of promoter metal component sufficient to provide the desired mole ratio of promoter metal to ruthenium were dissolved in 250 millilitres of water with stirring for 30 minutes. Aqueous sodium hydroxide (50% by weight) was added dropwise, with stirring, until the pH reached and remained at 8.3 to 8.5 (approximately 7 to 15 millilitres). The resulting slurry was heated near boiling for 30 minutes with constant stirring, then cooled. The pH was adjusted if necessary to 7.5. The mixture was filtered, and washed, and reslurried with subsequent filtering and washing steps until the molar ratio of sodium to ruthenium present was approximately about 0.02 to about 0.2:1. The solid mixed oxide was dried at 125°C for about 16 hours, was calcined for three hours at about 350°C (in air) and was ground to pass 140 mesh (0.105 millimeters).

25 The catalysts were coated upon alumina-silica supports in the following manner. 25 grams of Norton SA 5223 Alundum, 10/30 mesh (0.595 millimeters-2.00 millimeters) were placed in a vessel. 1.25 grams distilled water was sprayed onto the Alundum which was rolled for approximately 10 minutes and the procedure was repeated. 30 The metal oxide catalysts, in an amount calculated to give a total of 0.015 moles of active metal, were added in two equal portions with 15 minutes rolling after each. The coated catalyst was dried for about 16 hours at 125°C and calcined three hours at 350°C. Catalysts prepared in 35 this manner contain approximately 5 weight percent active

metals, 0.01% to 0.1% by weight sodium and have surface areas of about 2 m²/g, with pore volumes of from about 0.06 to about 0.09 cc/g.

5 The catalysts were partially reduced in the following manner. A stainless steel tube reactor was packed with catalyst, and hydrogen gas was introduced into the reactor at 150-200 cc/min. at atmospheric pressure. The electric block furnace placed around the reactor was increased in 50° increments stepwise until 500°C was
10 reached. The final temperature was maintained for two hours, at which time the reactor was allowed to cool with hydrogen flow being continued.

In one embodiment of the invention, catalysts are nitrided after reduction by contacting the catalyst with
15 ammonia for several hours at atmospheric pressure and a temperature of about 400°C, with subsequent cooling under ammonia. The nitrided catalysts contain up to 1 weight percent nitrogen, as is preferred. Between 0.5 to 1 weight percent nitrogen is most preferred.

20 The reaction procedure for examples 38-47 was carried out as in examples 1-37. The results reported in Table V below were calculated as follows.

25
$$\text{CO Conversion} = \frac{\text{Moles of CO input} - \text{moles of CO effluent} \times 100}{\text{Moles of CO input}}$$

$$\text{Weight \%} = \frac{\text{Weight product identified} \times 100}{\text{Total product weight}}$$

Carbon dioxide and water were not considered in the calculations.

30 The catalysts identified in the examples below were prepared according to the catalyst preparation method set forth above. The catalysts were reduced, nitrided and tested for synthesis gas upgrading by the reaction procedure set forth above. Reaction and test results are
35 set forth in the Table below.

Examples 38-41

Catalysts of the formula $5\% \text{Na}_a \text{RuCuRh}_{0.5} \text{N}_z \text{O}_x / 95\%$ Alundum were prepared and tested according to the procedure set forth above. Rhodium chloride was utilized as the promoter element containing compound. Products of the synthesis gas upgrading reaction utilizing these catalysts were predominantly alkanes and alcohols.

Example 42

A catalyst of the formula $5\% \text{Na}_a \text{RuCuRh}_{0.1} \text{N}_z \text{O}_x / 95\%$ Alundum was prepared and tested according to the procedure of Examples 38-41 except that a lower level of rhodium was utilized in the catalyst preparation. The catalyst was selective to alkanes and alcohol production, with olefin and carboxylic acid production increasing.

Examples 43-44

Catalysts of the formula $5\% \text{Na}_a \text{RuCuIr}_{0.5} \text{N}_z \text{O}_x / 95\%$ Alundum were prepared and tested according to the procedure of Examples 38-41 except that iridium chloride was substituted for rhodium chloride. Products of the synthesis gas upgrading reaction utilizing these catalysts were predominantly alkanes and alcohols.

Examples 45-46

Catalysts of the formula $5\% \text{Na}_a \text{RuCuPd}_{0.5} \text{N}_z \text{O}_x / 95\%$ Alundum were prepared and tested according to the procedure of Examples 38-41 except that palladium acetate was substituted for rhodium chloride in the preparation. Products of the synthesis gas upgrading reaction utilizing these catalysts were predominantly alkanes and alcohols.

Comparative Example 47

A catalyst of the formula $5\% \text{Na}_a \text{RuCuN}_z \text{O}_x / 95\%$ Alundum was prepared and tested according to the procedure of Examples 38-41, except that no promoter metal (M') was added in the catalyst preparation. Products of the synthesis gas upgrading reaction utilizing this catalyst were predominantly carboxylic acids.

As an example of the product mixture produced by

the inventive process, the products obtained by testing the catalyst of Example 38 are as follows.

	<u>Product</u>	<u>Wt. (g)</u>
	Methane	0.0500
5	Ethylene	0.0123
	Methanol	0.1075
	Ethanol	0.0136
	Propanol	0.0027
	Butanol	0.0017
10	Pentanol	0.0022
	Acetic Acid	0.0043
	Propionic Acid	0.0055
	Butyric Acid	0.0051
	Valeric Acid	0.0096
15		
20		
25		

TABLE V
 SYNTHESIS GAS UPGRADING USING 5% M_dNa_aCuRuN_O/95% ALUNDUM CATALYSTS
 Weight & Useful Products

Ex. No.	M _d	CO:H ₂ Ratio	Temp °C	Pressure (psig)	Space Velocity Hr ⁻¹	% CO Conv.	Weight & Useful Products			
							Alkanes	Olefins	Carboxylic Acids	Alcohols
1	Rh _{0.5}	7:3	360	1300	2000	6.2	23.3	5.7	11.4	59.5
2	Rh _{0.5}	3:7	360	1300	3300	2.6	86.8	-	2.0	11.2
3	Rh _{0.5}	3:7	350	1300	2000	5.5	33.6	-	10.3	56.1
4	Rh _{0.5}	1:1	360	1300	2000	5.6	36.8	6.2	7.8	49.1
5	Rh _{0.1}	3:7	350	1300	3300	20.5	35.2	21.3	29.1	10.6 j
6	Ir _{0.5}	3:7	360	1300	2000	11.6	85.4	-	1.8	12.8
7	Ir _{0.5}	7:3	360	1300	2000	3.1	61.5	4.4	8.0	26.0
8	Pd _{0.5}	3:7	350	1300	3300	14.0	84.6	-	0.7	14.6
9	Pd _{0.5}	3:7	320	1000	5500	3.6	79.5	-	0.3	20.2
C10	-	3:7	320	1000	5500	4.0	14.3	8.3	63.0	5.2 k

a = 0.002 - 0.02

j = less than 4% aldehydes and esters (combined) also present.

k = 5.5% aldehydes, 3.8% esters

z = 0.5 - 1 weight % active catalyst

CLAIMS:-

1. A catalyst composition of the formula



wherein A is an alkali metal or an alkaline earth metal or a mixture thereof,

wherein M is Ce, Cr, Fe, Mn, Mo, Th, Zn or mixtures thereof, and

wherein a is 0 to 0.5,

b is 0.002 to 2,

c is 0.5 to 3,

z is 0 to 1 weight percent and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

2. A catalyst as claimed in claim 1 characterised in that A is selected from Na, Li, K, Rb, Cs, Mg or mixtures thereof.

3. A catalyst as claimed in claim 1 or claim 2 characterised in that a is 0.1 to 0.5.

4. A catalyst as claimed in any of claims 1 to 3 characterised in that b is 0.02 to 1.

5. A catalyst as claimed in any of claims 1 to 4 characterised in that c is 1.

6. A catalyst as claimed in any of claims 1 to 5 characterised in that the catalyst is partially reduced.

7. A catalyst as claimed in any of claims 1 to 6 characterised in that the catalyst is supported on an inert carrier, preferably alumina, silica, alumina-silica, Alundum, clay or silicon carbide.

8. A process for the upgrading of synthesis gas to obtain selectivity to olefins and carboxylic acids comprising contacting carbon monoxide and hydrogen in the vapour phase at a reaction temperature of at least 250°C and a reaction pressure of at least 500 psi (35 kg/cm²) with a catalyst as claimed in any of claims 1 to 7.

9. A process as claimed in claim 8 characterised in that the ratio of carbon monoxide to hydrogen is 10:1 to 1:10, preferably 3:1 to 1:3.

10. A process as claimed in claim 9 characterised in that the reaction temperature is from 275 to 375°C.

11. A process for the upgrading of synthesis gas to yield hydrocarbons, alcohols and esters useful for fuel, comprising contacting carbon monoxide and hydrogen in the vapour phase as claimed in any of claims 8 to 10;

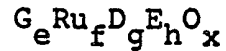
recovering the resulting hydrocarbon and oxygenated hydrocarbon products; and

contacting said products with hydrogen at elevated temperature and pressure in the presence of a hydrogenation catalyst.

12. A process as claimed in claim 11 characterised in that the products are contacted with hydrogen at a temperature of at least 200°C.

13. A process as claimed in claim 11 or claim 12 characterised in that the products are contacted with hydrogen at a pressure of 500 psi to 5,000 psi (35 to 350 kg/cm²).

14. A process as claimed in any of claims 11 to 13 characterised in that the hydrogenation catalyst is represented by the formula



wherein G = Zn, Cd and mixtures thereof;
 D = Co, Ni and mixtures thereof;
 E = Fe, Cu, Rh, Pd, Os, Ir, Pt and mixtures thereof;

and wherein e = 0 to 1;

f = 0.01 to 3,

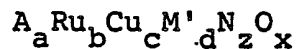
g = 0.01 to 3,

h = 0 to 1,

x = the number of oxygens determined by the valence requirements of the other elements.

15. A process as claimed in claim 14 characterised in that the hydrogenation catalyst has the formula $RuCoPdZn_{0.4}O_x$.

16. A catalyst of the composition



wherein A is an alkali metal,

wherein M' is Rh, Ir, Pd, Pt or mixtures thereof and

wherein a is 0.02 to 0.5,

b is 0.5 to 3,

c is 0.5 to 3,

d is 0.05 to 0.5,

z is a level of 0 to 1 weight % and

x is the number of oxygens needed to fulfill the valence requirements of the other elements.

17. A catalyst as claimed in claim 16 characterised in that A is selected from sodium, potassium and rubidium.

18. A catalyst as claimed in claim 16 or claim 17 characterised in that z is 0.02 to 0.4.

19. A catalyst as claimed in any of claims 16 to 18 characterised in that b and c are each 1.

20. A catalyst as claimed in any of claims 16 to 19 characterised in that d is 0.1 to 0.5.

21. A catalyst as claimed in any of claims 16 to 20 characterised in that the catalyst is partially reduced.

22. A catalyst as claimed in any of claims 16 to 21 characterised in that the catalyst is supported on an inert carrier preferably alumina, silica, alumina-silica, Alundum, clay or silicon carbide.

23. A process for the upgrading of synthesis gas to obtain selectivity to alkanes and alcohols comprising contacting carbon monoxide and hydrogen in the vapour phase at a reaction temperature of at least 250°C and a reaction pressure of at least 500 psi (35 kg/cm²) with a catalyst as claimed in any of claims 16 to 22.

24. A process as claimed in claim 23 characterised in that the ratio of carbon monoxide to hydrogen is 10:1 to 1:10, preferably 3:1 to 1:3.

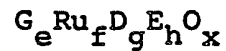
25. A process as claimed in claim 23 or claim 24 characterised in that the reaction temperature is 275°C to 375°C.

26. A process as claimed in any of claims 23 to 25 characterised in that the reaction pressure is 500 psi to 5000 psi (35 to 350 kg/cm²).

27. A process as claimed in any of claims 23 to 26 characterised in that it includes as a further step contacting the resulting products of the upgrading of:

synthesis gas with hydrogen at elevated temperature and pressure in the presence of a hydrogenation catalyst.

28. A process as claimed in claim 27 characterised in that the hydrogenation catalyst is represented by the formula



wherein G = Zn, Cd and mixtures thereof;

D = Co, Ni, and mixtures thereof;

E = Fe, Cu, Rh, Pd, Os, Ir, Pt and mixtures thereof;

and wherein e = 0 to 1

f = 0.01 to 3,

g = 0.01 to 3,

h = 0 to 1,

x = the number of oxygens determined by the valence requirements of the other elements.