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(54) Catalytic process involving carbon monoxide and hydrogen

(57) Hydrogen containing gas is produced by reacting a hydrocarbon, hydrocarbon derivative with steam and/or, where appropriate, carbon dioxide, in the presence of a catalyst supported on a metal or alloy resistant to the conditions in which the reaction is carried out. Synthesis of methanol or purification of hydrogen by methanation of carbon oxides contained in it can also be carried out using such a catalyst. The support is suitably a chromium steel, of a grade depending on process temperature. Preferably the metal or alloy carries also an oxidic secondary support layer such as alumina. The catalyst is preferably in the form of small, random-packed, honeycombs.

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SPECIFICATION

Catalytic process involving carbon monoxide and hydrogen

This invention relates to a catalyst and catalytic process, particularly for the production of hydrogen by gaseous phase reaction of a carbonaceous feedstock with steam or, where appropriate, carbon dioxide.

Catalysts for such reactions have most commonly been supported on a refractory material such as alumina or hydraulic cement. A few proposals have been made to use a metal or alloy as the catalyst support, but these have not gained industrial acceptance and there has in effect been no alternative to refractory-support catalysts despite their drawbacks such as brittleness and generally complicated production methods.

It has been proposed, for example in UK 1471138, to use an alloy as support for metallic platinum as a catalyst for engine exhaust gas treatment. In UK 1492929 this type of catalyst is proposed for exhaust gas treatment and also for oxidation of ammonia to nitrogen oxides, oxidation of hydrocarbons or carbon monoxide or reduction of nitrogen oxides. In UK application 12934/77, published as German application 2813329, this type of catalyst is proposed for methanation of synthesis gas containing carbon monoxide, carbon dioxide and hydrogen.

According to the invention a gas containing hydrogen is produced by reacting in the gaseous phase a hydrocarbon, hydrocarbon derivative or carbon monoxide with steam and/or, where appropriate, carbon dioxide, in the presence of a catalyst supported on a metal or alloy resistant to the conditions in which the reaction is carried out.

In this specification the term "RTM" will be used to indicate the name of a product is proprietary and possibly registered in at least one of the countries in which applications are filed. Percentages are by weight unless otherwise indicated.

The reactions for which the catalyst is especially suitable are:

1. of a hydrocarbon

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$"CH_2" + H_2O \rightarrow CO + 2H_2$$

("CH_2" represents hydrocarbons higher than methane, for example normally gaseous hydrocarbons and normally liquid hydrocarbons boiling at up to 200°C). The analogous reactions with carbon dioxide

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

$$"CH_2" + CO_2 \rightarrow 2CO + H_2$$

can be carried out separately or with the steam reaction.

These reactions are strongly endothermic and can be carried out with external heating or else as a hybrid process in which oxygen is a reactant, so that heat evolved in oxidation is absorbed by the endothermic reactions. Commonly these reactions accompanied by the shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2;$$

If the starting hydrocarbon is CH_2 and the temperature is relatively low, the methanation reaction may also occur. However, the hydrogen containing gas with which the invention is concerned contains at least 30% v/v of hydrogen on a dry basis. Preferably it contains less than 30, especially less than 10% v/v of methane on a dry basis. For the production of hydrogen-containing synthesis gas, the catalyst preferably is active at temperatures in the range 350—600°C, but the outlet temperature is preferably at least 600°C to ensure low methane content. The range 750—900°C is of general application for making synthesis gas for ammonia or methanol production. As extremes, the support must withstand temperatures normally up to 950°C, but possibly up to 1100°C for the production of metallurgical reducing gas or, at the other extreme, to 700°C for the production of town gas. For the hybrid process using oxygen the temperature may be as high as 1300°C. It is however, within the invention to use a catalyst supported on a metal or alloy in lower-temperature regions of such processes and refractory ceramic catalysts in high temperature regions.

For these reactions the catalyst usually comprises metallic nickel and/or cobalt. The pressure is typically in the range 1—50 atm abs. but pressures up to 120 atm abs. are proposed.

2. Of a hydrocarbon derivative: the most important reaction is methanol decomposition

$$CH_3OH \rightarrow CO + 2H_2$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

(or analogously with CO_2)

The reaction of ethanol or isobutyraldehyde with steam to produce a hydrogen-containing gas has been proposed for industrial operation. Usually the hydrocarbon derivative is an aliphatic alcohol, ether, ester or amine, since then there is little if any catalyst poisoning, and its boiling point is not over 200°C. The catalyst is for example zinc oxide/chromium oxide or metallic copper on a support such as zinc oxide with possibly a difficult reducible oxide, if a gas of low methane content is required. The reaction may be accompanied by methanation of the carbon oxides and hydrogen, especially when a town gas or substitute natural gas is to be produced, in which an iron oxide/chromium oxide catalyst or a nickel and/or cobalt catalyst is used.

3. Of carbon monoxide by the so-call "shift" reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Besides accompanying reaction 1 or 2 above, this can be carried out as a separate operation applied to a starting stream rich in carbon monoxide or to the product of reaction 1 or 2. For a separate operation the temperature is commonly in the range 200—300°C over a metallic copper containing catalyst or 300—450°C over an iron oxide-chromium oxide catalyst. If sulphur is present in the gas the catalyst can comprise sulphide of cobalt and/or nickel in combination with a sulphide of molybdenum and/or tungsten and possibly contains also an alkali metal hydroxide or weak acid salt. The steam partial pressure is commonly up to 70 bar, but of course below the level of saturation at the operating temperature.

The invention in a second aspect provides a process of methanol synthesis in the presence of a catalyst supported on a metal or alloy resistant to the conditions in which the reaction is carried out. This is process 2 in reverse:

$$CO + 2H_2 \rightarrow CH_3OH$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

These reactions are carried out commonly at 300—400°C over a zinc-chromium oxide catalyst or at 190—280°C over the more recently developed copper metal-containing catalysts. The pressure is typically in the range 200—500 bar for the high temperature process but only 30—150 bar for the low temperature process. The steam content of the gas in contact with the catalyst is typically under 2% v/v.

The invention in a third aspect provides a process of purifying a hydrogen stream of carbon oxides by conversion of such oxides to methane. The carbon oxides content is commonly up to 5, usually under 1.5% v/v initially. The catalyst is nickel and/or cobalt and/or (less preferably) a platinum group metal. The temperature is typically in the range 300—450°C and the pressure the same as for synthesis gas generation.

In general, owing to their possibly high geometric surface but low pressure drop, the catalysts are especially useful in reaction conditions in which the rate is limited by diffusion.

The metal or alloy catalyst support preferably is capable of forming an outer layer of water-soluble difficultly reducible oxide: "difficultly reducible" oxides include chromium and elements above chromium in the electromotive force series of the elements, a selection from which is set out on page 1521—3 of Handbook of Chemistry and Physics 32nd Edition.

Thus the supports that may be used can be for example titanium, zirconium and their alloys containing up to 10% other metals.

Preferably the support comprises iron and at least one other metal capable of forming an oxide layer effective to inhibit corrosion of iron. For processes at temperatures up to 750°C stainless steels, including ferritic steels, containing at least 12% of chromium (such as defined in ASTM specification 430) are generally suitable. For processes at up to 850°C it is preferred to use an austenitic stainless steel containing 16—20% of chromium, 6—10% of nickel and also minor constituents such as titanium or molybdenum, for example as defined in ASTM specifications 304, 316 and 321. For the generality of processes, including especially the steam hydrocarbon reaction at up to 1000°C, the preferred catalyst support is a high temperature alloy containing 20—30% of chromium, 15—40% of nickel, balance minor constituents and iron. Such alloys commonly have an austenitic structure. One example of such a preferred catalyst support is "alloy 800H", also known as INCOLOY (RTM) 800H and as UNS N—08810, as defined in ASTM specification 8407—77, the composition % of which is

Ni	30—35
Cr	19—23
Fe	at least 39.5 (by difference)
Mn	not over 1.5
C	0.05—0.10
Cu	not over 0.75
Si	1.0
S	not over 0.015
Al	0.15—0.60
Ti	0.15—0.60

Another is alloy 800 (UNS N—08810), defined in the same specification, which may contain less carbon. Yet another is "INCLOLOY DS" (RTM) which has the % composition 18 Cr, 37 Ni, 1.5—2.5 Si, not over 0.15 C.

If desired, an alloy of still higher nickel content, including those containing over 70% of Ni, balance minor constituents and chromium, such as NICHROME or INCONEL (RTMs) can be used, but for most purposes are considered too expensive.

Further alloys that can be used, but which show somewhat inferior mechanical strength in the most severe conditions encountered in the process of the invention, are those containing 0.5 to 12% of aluminium and 0.01 to 3% of yttrium, and possibly up to 25% of chromium. These alloys include those developed for oxidative conditions at high temperature encountered in the nuclear power industry.

Examples of useful alloys are the following:

TABLE 1

Aluminium	Chromium	Yttrium	Others	Iron
0.5 to 12	up to 20	0.1 to 3	—	balance
0.5 to 12	5 to 15	0.1 to 3	—	balance
4 to 6	5 to 15	0.1 to 3	—	balance
4 to 12	20 to 25	0.1 to 3	—	balance
4 to 5.5	20 to 25	0.1 to 0.5	—	balance
2 to 12	10 to 25	0.01 to 0.1	—	balance
4 to 5.5	15 to 22	0.01 to 0.1	—	balance
4.5	22.5	—	2.0 Co 0.1 C	balance

The support alloy may contain, in substitution for part of the iron balance up to 5.0, for example up to 3.0% of nickel and/or cobalt. Although such nickel and/or cobalt may exert some catalytic effect, the nickel and/or cobalt specified in the definition of the invention is additional thereto.

Among the usable alloys are the steels available under the trade names FECRALLOY and KANTHAL (both RTM).

The presence of chromium, aluminium or silicon or more than one of these is believed to account for their property of bonding oxidic catalyst support material, especially alumina, at their surface. In addition they are characterised by high creep strength and high resistance to oxidation and carburisation, both of which properties are very desirable in a material intended to withstand the conditions prevailing in the steam/hydrocarbon reaction.

It will be appreciated that, since a catalyst support must have a relatively high geometric surface area and must thus be fabricated from metal or alloy of thin gauge, the alloys to be used are those within the above definitions that are available in wrought form.

It is also possible to use a metal or alloy that is not itself resistant to the reaction conditions but has been rendered resistant by a coating, for example of an oxide such as ceria. Suitable alloys are low chromium steels (up to 11% Cr), possibly containing a molybdenum (0.5 to 1.5% w/w).

The catalyst can be in the form of a monolith, that is, a honeycomb filling the cross-section of the reactor in which it is to be used and providing gas flow channels in one or more parallel sets. This arrangement is mainly suitable for reactions in which heat is not added or withdrawn by indirect heat exchange, such as through the wall of a reactor. More conveniently the catalyst is in the form of units each of which is small compared with the dimensions of the catalyst bed to be charged therewith. (By "small" we mean having at least one dimension less than 0.25, especially less than 0.15, of the catalyst bed average width). Since the units can have an open structure they can, if desired, be of a size between "small" and sufficient to fill the cross-section. The units can be for example small honeycombs, which may suitably be of the same order of size, or rather larger, than random-pack oxidic catalyst pieces. A suitable unit has one dimension in the range 5—20 mm, with the largest dimension not less than 0.2 or more than 5 times the smallest. Suitably such units are made by spirally winding a corrugatd or embossed strip of sheet or gauze. For this purpose windings of corrugated or embossed material can alternate with flat material or the corrugation or bosses can be spaced or angled to avoid nesting. together of successive corrugations. The thickness of the metal or alloy is suitably in the range 0.03 to 0.5 mm. A typical geometric surface to volume ratio is in the range 10 to 80, especially 20—50 cm^{-1}.

Alternative catalyst units are in wire or strip form fabricated into open three dimensional configuration, especially of the kind dimensioned to avoid contact between adjacent wires within the units. Examples of these are described more fully UK published application 2000045.

If the catalyst is in honeycomb form it is composed preferably of perforated, e.g. expanded strip, with 0.2 to 2 mm apertures.

Whichever form the catalyst is in, the units can be brought together into assemblies, for example by joining them together or enclosing them in cages. The assemblies can be supported separately within a reactor, and thus the weight carried by the lower layers of catalyst can be limited.

In regard to the active material of the catalyst, whereas the use of non-noble metals and their compounds has been emphasised, in a catalyst comprising nickel and/or cobalt there may also be present one or more platinum group metals, which are capable of increasing the activity of the nickel and/or cobalt and of decreasing the tendency to carbon lay-down when reacting steam with hydrocarbons higher than methane. Likewise palladium, alone or with copper can be used in the synthesis or decomposition of methanol. Further, the catalyst, especially in preferred forms, can contain a platinum group metal but no non-noble catalytic component. Such a catalyst is more suitable for the steam/hydrocarbon reaction than one containing a platinum group metal on the conventional oxidic support because a greater fraction of the active metal is accessible to the reacting gas.

The catalyst preferably includes a "secondary support" material, that is, a layer of a refractory oxidic material adhering to the surface of the metal or alloy, which then is referred to as the "primary support". The secondary support may consist of the oxide layer present on the surface of the primary support as the result of reaction with atmospheric oxygen or hot steam or of a deliberate oxidation treatment by an oxidising agent or electrolytic anodisation. Such an oxide layer tends to be thin and to have limited capacity for active metal, and accordingly it is preferred to have present at least one layer of refractory oxidic material externally applied. Preferably this is additional to the layer resulting from oxidation of primary support metal. It preferably does not bridge apertures in the primary support.

The externally applied layer or layers can comprise any oxidic material already known as a support for a catalyst for the reation to be carried out. Typically it comprises alumina and this is especially preferred when the primary support alloy comprises chromium, silicon or aluminium, so that it carries an oxide layer due to superficial oxidation. Other sesquioxides, for example, chromia and rare earth oxides may make up at least part of the applied layer. Other useful secondary support oxides are titania, zirconia, hafnia, thoria, vanadia, urania and those of manganese, molybdenum and tungsten. A very suitable secondary support layer comprises such oxides applied in two ways, namely in highly dispersed colloidal form and in flocculated powder form. The oxides can be the same or different: in particular colloidal alumina can be present along with a different alumina or with one or more different oxides. The ratio of colloidal material to such other material is suitably in the range 0.05 to 5.0.

Preferably the secondary support includes a grain growth inhibitor, for example 0.1 to 3.0% of an oxide of a rare earth metal or mixture thereof, especially cerium or yttrium.

If alumina is present, it is preferably in one or more of the gamma, delta, theta and alpha forms.

When nickel and/or cobalt are present in the catalyst, it is expected that a sesquioxide layer will include, at least after a period of process operation, some nickel and/or cobalt spinel. It is within the invention to have the secondary support material at least partly in the form of spinel, whether of nickel and/or cobalt or of a divalent metal having a difficultly reducible oxide, especially magnesium or manganese or, less preferably, zinc. Some nickel and/or cobalt present as spinel is in a reduction-resistant oxidic form, it does not contribute significantly to the activity of the catalyst: active nickel

and/or cobalt are additional thereto. Other useful secondary support oxides are titania, zirconia, hafnia and thoria.

The specific surface of the externally applied support is suitably in the range 0.5 to 250, especially 100—200 m^2/g.

When the catalytic metal is to be copper, the secondary support preferably includes zinc oxide and preferably also one or more of boria, alumina, chromia, rare earth oxides, vanadia and manganese oxide.

The total content of catalytically available metal in the catalyst is suitably in the range 0.2 to 25.0%, especially 5 to 25%, calculated on the constituents non-volatile in air at 900°C of the catalyst precursor in which the catalytic metals are present as monoxides. The secondary support preferably constitutes 3 to 30% of the catalyst, calculated in the same way.

The specific surface of the catalytic metal is suitably in the range 0.1 to 50 m^2/g of catalyst. Within these ranges the larger areas are preferred for reactions under 600°C.

The catalyst can be made by applying a compound of the active metal and the secondary support (if present) or a precursor thereof to the primary support. In a preferred method the secondary support is applied first and a solution containing a thermally decomposable compound of active material is applied thereafter. In order to obtain enough content of active material, several applications of such a solution, each followed by drying and thermal decomposition, may be made. Oxides of metals such as aluminium can be produced *in situ* by including powdered metal in the composition. If desired a compound of the active metal can be applied along with the secondary support. Other methods, such as deposition from the vapour phase can be used.

The preferred method of making the catalyst comprises forming a collodial dispersion of support material, for example by acid-peptisation and preferably also de-ionisation, suspending further support material in the dispersion, applying the suspension to the metal or alloy support and calcining it to effect adhesion and adjust the surface area of the support material. Any grain growth inhibitor is preferably added with the dispersion or suspension. The suspension can be caused to gel before calcination.

EXAMPLE 1.

Processes using catalysts of low nickel content

Preparation of catalysts A and B

The primary catalyst support was FECRALLOY (RTM) steel having the following properties:

Chemical composition %

Fe 70.6
Cr 15.2
Al 4.8
Y 0.4

Catalyst units:

shape: helices of diameter 3 mm and height 5 mm
weight about 0.067 g
wire diameter 0.5 mm
space between turns of helix 0.5 to 1.0 mm

Catalyst bed properties:

bulk density about 1 g ml^{-1}
exposed surface about 11.9 cm^2 per ml of bed volume

Initially this support carried a very thin film of alumina as a result of heating in air Catalyst precursors were made from this support by applying nickel nitrate/alumina sol compositions as follows.

TABLE 2

	$NiO/(NiO + Al_2O_3)$ in sol %	NiO on Catalyst %	Al_2O_3 on Catalyst %
A	15	0.49	3.25
B	30	0.87	2.90

The product is a catalyst precursor and requires reduction to produce active catalyst.

Tests of catalyst A in purifying a hydrogen stream by methanation

This catalyst was reduced by pure hydrogen at 350°C, atmospheric pressure and then tested by passing over an impure ammonia synthesis gas in the following conditions:

Catalyst bed: 5 ml catalyst diluted with 70 ml of 5 mm alumina chips
Gas composition % v/v

CO	0.2
CO_2	0.2
H_2	75
N_2	25

Inlet Temperature: various levels between 250and 350°
Space velocity: 60000 h^{-1} volumes per unit of catalyst

The outlet gas was analysed and the percentage conversion of the carbon monoxide and dioxide impurities to methane was calculated for each temperature:

Temperature °C	250	270	290	294	306	322	338	349
% v/v CO to CH_4	5.1	7.7	23.1	25.6	33.9	41.0	50.0	52.7
% v/v CO_2 to CH_4	—	—	1.1	2.5	—	9.0	19.5	20.5

These catalysts thus have a level of activity that is to be regarded as substantial in view of their low nickel content.

Test of catalyst B in hydrogen steam production by the methane reaction

One sample of catalyst B was reduced in these conditions:
Catalyst bed: 40 ml catalyst + 520 ml
5.4 x 3.6 squat alumina cylinders
Temperature: 645°C
Pressure: 28 bar abs
Gas mixture % v/v H_2: 10
H_2O: 90
Time: 21 h
Total space velocity 50000 h^{-1} volumes per volume of catalyst.

Then a 1:3 v/v methane-steam mixture was passed over it at the same pressure and a 400°C inlet temperature but various outlet temperatures and space velocities. The outlet gas was analysed after establishing steady operation in each set of conditions, then adjustment was effected to the next set of conditions. The percentage methane conversion is set out in Table 3.

TABLE 3

Conditions (see below)	A	B	C	D	A	B
Hours after reduction	2	23	26	47	50	71
% methane conversion	0.1	0.7	33.9	17.3	0.0	0.7

Conditions	Outlet temp °C	Methane v/v space vel velocity
A	600	8550
B	600	21375
C	750	8550
D	750	21375

It is evident that the catalyst has useful activity at an outlet temperature of 750°C.

EXAMPLE 2

Hydrogen production using catalyst of higher nickel content

A FECRALLOY (RTM) steel support as described in Example 1 was dipped in a nickel nitrate solution containing 20 g Ni per 100 ml for 10 minutes, then drained, dried and calcined at 450°C for 8 hours. This operation was repeated and the resulting catalyst precursor contained 2.0% of NiO.

It was reduced and tested in the steam methane reaction as described above. The results are shown in Table 4.

TABLE 4

Day	% Methane Conversion			
	A	B	C	D
0	13.2			
1		9.4	43.1	
2	5.3			39.6
3		3.8		
4			46.4	41.1
7			52.5	41.1
8	1.4	1.3		31.2
10				38.2
11				32.3
16		0		39.0

Conditions:

A inlet = 400°C, exit = 600°C, CH_4 = 342 lh^{-1}, H_2O = 770 mlh^{-1}

B inlet = 400°C, exit = 600°C, CH_4 = 855 lh^{-1}, H_2O = 1924 mlh^{-1}

C inlet = 400°C, exit = 750°C, CH_4 = 342 lh^{-1}, H_2O = 770 mlh^{-1}

D inlet = 400°C, exit = 750°C, CH_4 = 855 lh^{-1}, H_2O = 1924 mlh^{-1}

EXAMPLE 3

Processes using catalyst of still higher nickel content

A catalyst precursor was made as in Example 2 but using a support having a heavier coating of alumina (14%) and thus a greater capacity for nickel. The NiO content was 14.0%.

It was tested in hydrogen purification by methanation as described in Example 1. The percentage conversions to methane were as follows.

Temperature °C	210	221	232	247	257	266	292	303	324
CO to CH_4%	54	62	68	63	67	65	68	71	83
CO_2 to CH_4%	1	5	9	15	26	35	59	68	77

Comparative results for a commercially available methanation catalyst containing 25% NiO on alumina and aluminous cement were:

Temperature °C	198	220	252	275	300	344
CO to CH_4%	8	30	45	65	70	76
CO_2 to CH_4%	1	6	19	40	53	71

This catalyst precursor was tested in hydrogen production by the steam/methane reaction as described in Example 1. The results were as shown in Table 5.

TABLE 5

Conditions	A	B	C	D	A	B
Hours after reduction	2	23	26	47	50	71
% methane conversion	15.2	5.8	58.4	50.8	14.9	7.1

EXAMPLE 4

Hydrogen production by steam/methane reaction over catalyst in form of small honeycombs

(a) Fabrication of honecomb catalyst support

For each honeycomb, expanded stainless steel strip (16.8% Cr, ASTM type 430) 17 mm wide, 0.125 mm thick, mesh openings 0.4—0.6 mm was cut into an 18 cm and a 23 cm length. The 23 cm length was corrugated with a wavelength of 2.8 mm and an amplitude of 1 mm by passing it between toothed rollers. The two strips were wound together and the resulting spiral honeycomb was bound together with NICHROME (RTM) wire. Its diameter was 20 mm and weight 3.7 g.

It was washed with acetone to remove grease, dried in air and calcined at 600°C for 6 hours in air to ensure formation of a layer containing chromium oxide.

(b) Application of alumina as secondary support

The alumina was derived from a dispersible alumina hydrate ("Cerasol"—RTM) having the following characteristics:

Composition %:

Al_2O_3	65
H_2O	35
Na_2O	0.02
SiO_2	0.01
Fe_2O_3	0.02

Crystallite size: about 70 Angstrom units
Crystal structure: böhmite
Helium density: 2.78 g ml^{-1}
Hg density: 1.56 g ml^{-1}
pore volume: 0.28 ml g^{-1}

Alumina hydrate (600 g) was added to dilute nitric acid (2200 ml of 0.14 M acid) and stirred vigorously for 4 hours at room temperature. The resulting sol was deionised by dialysis through the walls of a cellulose acetate container surrounded by deionised water. To a 150 ml sample of deionised sol was added 300 g of the same alumina. This was followed by 10 ml of non-ionic wetting agent and 2.25 g cerium nitrate in 10 ml of water, and then water was stirred in to bring the total volume to 1.2 litres, corresponding to about 30% of Al_2O_3.

This suspension was circulated through a batch of honeycombs for 45 minutes. The honeycombs were allowed to drain, dried at room temperature overnight and calcined at 700°C for 1 hour. The coated honeycombs then carried 4.2% of alumina. To obtain a thicker coating this operation was repeated, giving 7.9% of alumina, calculated on alloy. The alumina was of gamma and eta type, with crystallite size about 60 Angstrom units, surface area 180 m^2/g, mercury density 1.53 g ml^{-2}.

(c) Production of catalyst precursor

A sample of alumina-coated honeycombs was immersed for 20 minutes in a nickel nitrate solution containing 20 g of nickel (as metal) per 100 ml. They were allowed to drain for 30 minutes, dried for 4 hours at 105—120°C and calcined at 450°C for 6 hours. This procedure was repeated. The resulting precursor contained 14.2% nickel oxide NiO and 6.3% of Al_2O_3.

(d) Steam/methane reaction: initial activity

A 500 ml charge (45 honeycombs) was placed in a 250 mm long 50 mm internal diameter tube equipped for external electric heating. A preheated (400°C) mixture of desulphurised natural gas (vol% 91 CH_4, 3.5 C_2H_6, 2N_2) and steam (ratio 1:3) was passed through the charge at a volume space velocity of 2000 h^{-1}, atmospheric pressure. The catalyst temperature was adjusted to successive levels between 350 and 754°C. Although the catalyst precursor was not reduced before feeding methane and steam to it, its activity developed rapidly and resulted in raw hydrogen streams whose contents of unreacted methane are shown in Table 6. (The remainder of the gas is hydrogen, carbon oxides and nitrogen).

TABLE 6

Activity of fresh catalyst

Temperature °C	CH_4, % v/v
350	67.9
373	53.7
390	51.9
408	43.1
430	38.7
453	36.6
501	26.4
556	14.3
576	7.3
620	3.7
660	2.9
686	2.9
715	2.9
728	2.9
754	2.9

(e) Steam/methane reaction: duration of catalyst activity

The following further operations were carried out using the same charge of catalyst:

13 hours run at 730°C;
2 hours steaming at 730°C, space velocity 1500 h^{-1};
activity test at temperatures in the range 411—745°C;
18 hours run at 730°C at halved space velocity;
activity test at temperatures in the range 368—775°C;
16 hours treatment with steam (3 volumes) and nitrogen (1 volume) at 730°C, space velocity 2000 h^{-1};
activity test at temperatures in the range 385—728°C.

The content of methane in the hydrogen streams obtained in the final activity test are shown in Table 7.

TABLE 7

Activity of catalyst after extended operation

Temperature °C	CH_4 % v/v
385	72.9
428	50.2
442	47.7
456	43.0
510	24.2
539	17.3
580	10.1
725	2.9
728	2.9

It is evident that the catalyst has lost some activity, especially at the lower end of the temperature range, but the loss is not serious at the higher end, which represents the temperatures in industrial use in hydrogen production. The catalyst was in excellent mechanical condition, with substantially no loss of coating and no distortion of shape.

EXAMPLE 5

Hydrogen production by steam/methane reaction over catalyst containing other oxides as secondary support

The catalyst preparation of Example 4 was repeated using the same metal honeycomb support, a dialysed alumina sol containing 20% of alumina, and coating mixtures having the following constituents:

5A 950ml sol, 390 g alumina trihydrate ("BACO FRF 80");
5B 1000 ml sol, 300 g titania (BTP pigment anatase);
5C 1000 ml sol, 300 g zirconia powder (BA-chemicals "s-grade");
5D 1000 ml sol, 300 g alpha alumina powder ("Universal Grade 12").

Each mixture also contained 1.5 g of cerium nitrate and 5 ml of non-ionic wetting agent.

The catalyst was tested as described in paragraph (d) of Example 4. The contents of support oxide and nickel oxide in the catalyst precursor before test are shown in Table 8. The percentages of methane in the raw hydrogen streams produced are shown in Table 9, in comparison with the calculated percentages at equilibrium.

TABLE 8

Catalyst	Support oxide %	NiO %
5A	9.8	17.5
5B	10.1	17.4
5C	29.0	14.4
5D	13.0	17.6

TABLE 9

Methane contents of raw hydrogen streams

Temperature °C \ Catalyst	5A	5B	5C	5D	Equilibrium
550	15.8	16.3	15.0	18.5	12.3
600	9.3	9.2	10.2	11.9	6.0
650	5.1	4.7	5.9	7.5	2.2
700	2.8	2.8	3.1	4.8	0.7
750	1.8	2.2	3.0	2.4	0.2
760	1.6	2.0	2.8	2.2	0.1

It is evident that the catalysts have useful activity. The coatings adhered excellently to the alloy support.

EXAMPLE 6

Hydrogen production by steam/methane reaction over catalyst supported on chromium nickel stainless steel

The honeycomb catalyst support fabrication describd in paragraph (a) of Example 4 was repeated using ASTM 304 stainless steel having the following % composition:

Fe 69.6, Cr 18.3, Ni 9.3, Cu 0.2, Mo 0.4, Co 0.06, V 0.05

The resulting honeycombs were coated twice with a mixture as follows:

1.9 l dialysed alumina sol ("Cerasol", 30% Al_2O_3)
300 g powdered "Cerasol" (RTM) alumina hydrate
2.25 g cerium nitrate
10 ml non-ionic wetting agent.

After each coating the honeycombs were drained, dried overnight and calcined at 700°C for 1 hour. The coated honeycombs were twice immersed in nickel nitrate solution, dried and calcined, as described in Example 4, paragraph (c). The resulting catalyst precursor contained 6.6% of alumina and 16.8% of NiO.

It was tested in the steam/methane reaction as described in Example 4 paragraph (d). Table 10 shows the methane content of the raw product hydrogen streams, in comparison with calculated equilibrium values.

TABLE 10

Methane contents of raw hydrogen streams

Temperature °C	Methane content % v/ v	
	This catalyst	Equilibrium
500	21.6	20.8
550	14.4	12.3
600	7.6	6.0
650	4.9	2.2
700	3.2	0.7
725	2.7	0.5
750	2.2	0.2
760	1.8	0.2

EXAMPLE 7

Hydrogen production by steam/methane reaction over catalyst supported on chromium-aluminium-yttrium steel

The honeycomb catalyst support fabrication described in paragraph (a) of Example 4 was repeated using two unperforated strips of FECRALLOY (RTM) steel, one flat 25 cm long and one corrugated and 22 cm long after corrugation, each 0.002 inch (0.051 mm) in thickness. These were smaller overall than the Example 4 support, such that 70 honeycombs occupied 500 ml.

As a result of the heat treatment it carried a thin coating of alumina. Further alumina was applied from aqueous suspension, followed by two impregnations with nickel nitrate solution, as described in Example 4, paragraph (c). The resulting catalyst precursor contained 10.3% of Al_2O_3 and 20.4% of NiO.

The precursor was tested as described in Example 4, paragraph (d), then steamed at 750°C for 16 hours and re-tested, then cooled under nitrogen, re-heated and re-tested. Table 11 shows the methane contents of the resulting raw hydrogen streams, in comparison with the equilibrium values.

TABLE 11

Methane contents of raw hydrogen streams

Temperature °C	Methane % v/v			
	initial	after steaming	after nitrogen	equilibrium
400	46.6	56.7	62.1	44.5
450	–	38.1	30.3	31.6
500	21.4	–	17.9	20.8
550	8.2	17.9	11.9	12.3
600	2.5	7.8	6.9	6.0
650	1.1	2.9	7.9	2.0
700	0.7	2.2	1.1	0.7
750	0.5	0.5	0.5	0.2
760	0.4	0.4	0.5	–

EXAMPLE 8

Use of high temperature alloy as catalyst support

Sheets 0.015 inch (0.8 mm) thick of roughened flat unperforated INCOLOY 800H (RTM) steel were coated with a dispersion of 27 g böhmite (average particle size 2.5 microns) and 0.2 g mixed rare earth oxides (50% CeO_2) in 100 ml water, drained, dried and calcined at 1000°C for 6 hours. By X-ray diffraction the coating was shown to consist of delta and theta alumina. This operation was then repeated using a coating mixture made by dispersing 10 g of pseudoböhmite in 100 ml of 0.2% nitric acid and suspending 100 g of the böhmite therein. The total content of alumina was 2.8%. The major alumina phase present was alpha.

The coated support was impregnated twice with nickel nitrate solution, each time followed by calcination to nickel oxide. The total NiO content was 1.4%. (Since the alloy thickness was approximately double what would be used in practice, the Al_2O_3 and NiO contents appear to be low).

The resulting catalyst precursor was tested in the steam/methane reaction at 30 atm abs pressure, with various runs at 568—657°C outlet temperature, 2.2—3.8 volumes steam per volume of methane. After 216 hours there was no loss of coating and no distortion of the catalyst. The catalyst was at least as active as conventional ceramic-supported catalyst.

EXAMPLE 9

Hydrogen production by shift reaction

(a) Copper-containing catalyst

Honeycombs were made from expanded metal as described in Example 6 but made of chromium steel of the composition shown in Example 4. They were coated with alumina as described in Example 6, to apply 10.1% of Al_2O_3 calculated on metal.

Sample 8A was impregnated with copper oxide and zinc oxide by immersing three times in a solution of 241.6 g of cupric nitrate trihydrate and 297.5 zinc nitrate hexahydrate in 350 ml of solution, with operations of draining, drying and calcination (400°C, 4 hours) after each immersion. The total content of CuO and ZnO was 28.1%.

Sample 8B was impregnated with copper oxide (31.5%) by 4 such operations of immersion in cupric nitrate solution (705 g trihydrate in 500 ml of solution), draining, drying and calcination.

Each was tested by placing 5 of them in the 500 ml reactors described above, along with chips of fused alumina to fill the space, reducing at 230°C by means of 5% v/v H_2 in nitrogen at 210 1 h^{-1}, passing a reactant gas through and analysing the product gas. The pressure was 1 atm abs. The composition 1 h^{-1} of the reactant gas was:

CO 15, CO_2 45, H_2 240, steam 150.

Table 10 shows the percentage conversions of carbon monoxide to hydrogen at various times after starting the processes.

TABLE 12

Conversion of carbon monoxide to hydrogen by reaction with steam

Catalyst	Time h						
	2	21	72	91	96	117	166
8A	14.7	14.3	–	–	9.4	8.5	–
8B	–	–	12.2	18.9	–	–	11.1

The catalyst has evidently useful activity in the shift reaction, and considerable stability, especially in the absence of zinc oxide.

(b) Catalyst for sulphur-containing gas

Coated supports as described in Example 7 were impregnated twice with cobalt nitrate solution, each time followed by calcination to provide 4.0% of CoO. This product was impregnated twice with ammonium molybdate solution, each time followed by calcination at 550°C, to provide 16.0% of MoO_3. Part of the batch was then impregnated with potassium carbonate solution to provide 3.0% of K_2O. The two-part-batches can be used as catalysts for the shift reaction in the presence of sulphur compounds and may be sulphided by treatment with H_2S or by the sulphur compounds in the reactant gas.

EXAMPLE 10

Methanol synthesis

Catalyst preparation 8A was repeated with the following differences:

honeycombs 4 cm long, 0.5 cm outside diameter,
alumina content 10.5% before application of copper and zinc nitrates,
total CuO + ZnO content 14.7%

Methanol synthesis was carried out using a micro-reactor, catalyst weight 1.29 g. The catalyst precursor was reduced by a mixture of 5% H_2, 45% N_2 at 210°C, then pressurised to 50 atm abs and subjected to a synthesis gas of composition % v/v:

H_2 67, N_2 20, CO 10, CO_2 3

at a flow rate of 9 1 h^{-1}. The percentage v/v of methanol in the product gas was 0.7 after 8 hours (234°C) and 0.8 after 80 hours operation (250°C).

CLAIMS

1. A process for producing a gas containing hydrogen which comprises reacting in the gaseous phase a hydrocarbon, hydrocarbon derivative or carbon monoxide with steam and/or, where appropriate, carbon dioxide in the presence of a catalyst supported on a metal or alloy resistant to the conditions in which the reaction is carried out.

2. A process according to claim 1 in which natural gas or methanol is reacted with steam and/or carbon dioxide.

3. A process according to claim 1 in which carbon monoxide is reacted with steam at 200—300°C over a catalyst containing metallic copper or at 300—450°C over an iron oxide-chromium oxide catalyst or at 200—400°C over a catalyst comprising a sulphide of cobalt and/or nickel in combination with a sulphide or molybdenum and/or tungsten and possibly an alkali metal hydroxide or weak acid salt.

4. A process of methanol synthesis in the presence of a catalyst supported on a metal or alloy resistant to the conditions in which the reaction is carried out.

5. A process of purifying a hydrogen stream of carbon oxides by conversion of such oxides to methane in the presence of a catalyst supported on a metal or alloy resistant to the conditions in which the reaction is carried out.

6. A process according to any one of the preceding claims in which the catalyst support is an iron alloy containing one or more of aluminium, chromium or silicon.

7. A process according to claim 6 in which the alloy contains 20—30% of chromium, 15—40% of nickel, balance minor constituents and iron.

8. A process according to claim 6 in which the alloy contains 0.5—12% of aluminium and 0.01 to 3% of yttrium.

9. A process according to any one of the preceding claims in which the catalyst includes a secondary support layer of refractory oxidic material adhering to the surface of the metal or alloy.

10. A process according to any one of the preceding claims in which the catalyst is in the form of units of open three-dimensional configuration having one dimension in the range 5—20 mm, with the largest dimension not less than 0.2 nor more than 5 times the smallest.

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