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(54) Methanol synthesis and catalyst therefor.

(57) Methanol synthesis over a catalyst derived from an alloy of copper and/or a platinum group metal and a highly oxidisable metal such as a rare earth metal can be carried out at unusually low temperatures such as 70°C and using synthesis gas deficient in hydroben. The process life of the catalyst is longer if the starting alloy contains a further metal such as aluminium or manganese. The synthesis gas should preferably be very pure and substantially free of carbon dioxide and water vapour. The process can be advantageously carried out using the catalyst suspended in an inert liquid.

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Catalytic process and catalysts

This invention relates to a catalytic process, particularly methanol synthesis, and to catalysts therefor.

It has been recently proposed, for example by Wallace et
5   al (15th Rare earth research conference, Rolla-Missouri 1981) and
in US 4181630 to synthesise methanol over a catalyst made by form-
ing an alloy of an active metal such as copper with a metal having
a high affinity for oxygen such as a rare earth metal, Group IV A
metal or actinide and oxidising the alloy in controlled conditions.
10 Such catalysts were reported to be active at temperatures of the
same order as those used in conventional copper catalysed methanol
synthesis, with maximum activity at for example 270, 290, 320 or
340°C depending on the composition of the catalyst.

We have now found that an alloy-derived catalyst can be
15 usefully active in methanol synthesis at temperatures substantially
lower than those so far specifically disclosed, can be treated and/
or modified so as to lengthen their process life and can operate
efficiently in synthesis gas of unconventional composition.

In this specification the Groups of the Periodic Table
20 are those set out in "Abridgments of Specifications" published by
the UK Patent Office.

According to the invention in its first aspect methanol
synthesis by reacting carbon monoxide with hydrogen over a
catalyst comprising at least one active metal and/or oxide and a
25 difficultly reducible oxidic support material made by oxidation
(as hereinafter defined) of at least one element is characterised

by a catalyst temperature under 240°C.

"Oxidation" means bringing to at least that state of oxidation assumed by the element when in contact with methanol synthesis gas. As will be seen, the extent of oxidation may be
5   relatively small, especially when the synthesis gas contains only carbon monoxide and hydrogen.

The invention in its second aspect relates to the composition of the synthesis gas. In industrial methanol synthesis it is customary to use a synthesis gas containing hydrogen in
10 excess of what is required to react with all the carbon oxides present. Proposals have been made, for example in UK 1435253 (Karavaev et al), to use a synthesis gas deficient in hydrogen, but there has been no disclosure which of the usual methanol synthesis catalysts is satisfactory in such conditions.

15   According to the invention a process of methanol synthesis by reacting carbon monoxide with hydrogen over a catalyst comprising a metal and/or oxide having catalytic activity for methanol synthesis and a difficultly reducible oxidic support material made by oxidation (as herein defined) of at least one element is
20 characterised in that the composition of the gas mixture passed over the catalyst corresponds to

$$R = \frac{H_2 - CO_2}{CO + CO_2} = 0.5 \text{ to } 2.0$$

Further details of synthesis gas composition will be
25 given below.

The invention in its third aspect provides a process of methanol synthesis over a catalyst comprising at least one active metal and/or oxide and a difficultly reducible oxidic support material made by oxidation (as herein defined) of at least one
30 element, characterised in that the catalyst is contained in a body of liquid substantially inert in the conditions of cynthesis.

The detailed conditions and advantages of this aspect will be described below.

In making the catalyst to be used in the process the
35 oxidation is carried out preferably in the presence of the metal

which will as such or as its oxide be the active material of the
catalyst. (Such metal will be referred to herein as "activatable
metal"). Preferably oxidation is applied to a catalyst precursor
which is a compound of one or more such activatable metals with
5   the element. The compound can include non-metals but preferably
the elements present are metals and the precursor is an alloy.
The term "alloy" includes all types of microscopically homogeneous
metal combinations whether containing or consisting of intermetal-
lic compounds, interstitial compounds, single or mixed crystallo-
10 graphic phases or amorphous material.

The active or activatable metal preferably is or includes
copper and/or one or more platinum group metals having methanol
synthesis activity, for example ruthenium or rhodium but especially
palladium. The upper limit of the content of activatable metal is
15 set by the need to permit oxidation of other components at a
convenient rate. The content of copper is typically up to 80,
preferably up to 70 and at least 5%, for example in the range 30 -
60 for example 40 - 50%, calculated by weight on the precursor
from which the catalyst has been obtained. The content of the
20 platinum group metal in the catalyst precursor is typically in the
range 0.1 - 20, for example 1 - 10, % calculated as mentioned above.

When the active material comprises at least one platinum
group metal the catalyst and the precursor from which it is formed
are new compositions of matter, constituting a fourth aspect of
25 the invention.

Naturally the catalyst should be substantially free of
metals capable of catalysing unwanted side reactions.

The oxidic support of the catalyst and also any other
oxides introduced by the oxidation can be identified with known
30 oxides but, especially when such oxidation is by compounds of
very low oxidising power, can be incompletely oxidised as in some
lower valency state or contain other elements such as carbon.

The elements whose oxide is difficultly reducible to
elements are preferably metals having a standard electrode potential
35 (stable cation to metal) at least 0.8 volt negative with respect

to the standard hydrogen electrode. (A table of such potentials
is set out on pages D 145 - 6 of the CRC Handbook of Chemistry
and Physics 58th edition 1977 - 1978, published by CRC Press,
Cleveland, USA). A preferred catalyst is one obtained from a

5 precursor alloy containing, apart from activatable metal only
metals having a standard electrode potential at least 1.3 volt
negative with respect to the standard hydrogen electrode. Examples
of suitable metals are manganese (1.029 volts) and vanadium (1.2
volts) and, in a still preferred range above 1.8, rare earths

10 particularly those of atomic number 62 and below, such as cerium
2.335 volts, lanthanum 2.37 volts and praseodymium, neodymium and
samarium, other Group III A (including thorium), II A, IV A and
V A metals. If rare earth metal is present, preferably more than
one is used for example as in the available mixtures didymium or

15 mischmetall. Preferred metals other than rare earths are aluminium,
yttrium, and Group IV A metals.

A catalyst of usefully lengthened process life can be
derived from a combination comprising at least two such metals,
one of which is not a rare earth metal. Preferably at least one

20 of the metals has an electrode potential above 1.8 volt negative
with respect to the standard hydrogen electrode and at least one
has such a potential in the range 0.8 to 1.8 volt. In making the
active catalyst it is possible that the metals are oxidised to
different extents, those of lower potential being less oxidised

25 than those of higher potential. The active catalyst may contain
one or more intermetallic compounds of the active metal(s) with
one or more of the oxidisable metals. Typical combinations include
(a) one or more rare earth metals with (b) aluminium and/or
manganese. Rare earth and aluminium may be present for example

30 in the weight ratio range 10 to 0.2, especially between 6 and 1.
When manganese is a constituent of the alloy from which the
catalyst is made, a preferred alloy comprises copper and rare
earth metal in a weight ratio between 0.5 and 2.0 and manganese to
the extent of 0.5 to 15, especially 1 - 5% $^W/w$ of the total alloy.

35 Aluminium can also be present, to the extent of for example 1 - 20% $^W/w$

of the total alloy.

The above-mentioned catalysts containing two or more
oxidic support materials and the alloys from which they are made
by oxidation are believed to be new compositions of matter, and
5 constitute a fifth aspect of the invention.

A further interesting catalyst within the scope of the
invention is one containing as active material a platinum group
metal and an oxide having methanol synthesis activity. Such oxides
are usually reducible to metal with moderate difficulty, correspond-
10 ing to a standard electrode potential between 0.5 and 0.8. Specific
examples are palladium + zinc and/or chromium.

In addition to the active metal and/or oxide and the
oxidic support material made by oxidation, the catalyst can contain
one or more of such constituents not so obtained. These can be
15 introduced for example by adding one or more of them to the
catalyst after its formation from the precursor, or possibly by
incorporation into the alloy at the melting stage. Other con-
stituents optionally present in the catalyst are graphite (especially
as a shaping lubricant), active carbon, and refractory solids such
20 as silicon carbide or silicon nitride. An especially important
purpose of such additional components is to assist in bringing the
catalyst into a suitable mechanical form, for example by binding
the catalyst constituents together in random packable particles
(such as 2 - 20 mm cylinders, rings or spheres), or improving the
25 cohesion of fluidisable particles or the adhesion of a catalyst
layer to a structured ceramic or metal support or heat exchange
surface.

The catalyst precursor can be made by melting or sinter-
ing together the metal components of the alloy. The melting tech-
30 nique depends of the metals present, an electric arc being desir-
able when all of them melt at over 1000°C, for example those con-
taining zirconium or hafnium. Those containing Group II or Group
III metals, including some rare earth metals, can be made at lower
temperatures, for example under 1000°C. Usually it is preferred
35 to make a homogeneous melt, but useful catalysts can be made from

compositions in which alloying takes place at junctions between
metal or alloy particles but not within such particles. Very con-
venient melting or sintering method uses radio frequency induction
heating or an electron beam. Melting and subsequent solidification
5 should be carried out in a vacuum or inert atmosphere, preferably a
noble gas.

After formation of the precursor, it or the catalyst
obtained from it has to be brought into a mechanical state suitable
for the process to be catalysed. If desired, the molten precursor
10 can be comminuted, for example by spraying, and may then be finely
enough dispersed to be used as a feed for shaping or in a fluidised
bed or in presence of a liquid. More conveniently, the solid pre-
cursor can be crushed and then, if it is to be used in a fixed
catalyst bed, shaped mechanically by, for example, compression alone
15 or with a binder or lubricant such as graphite or application to the
surface of a shaped support. Such comminution or crushing steps
are best carried out in an inert atmosphere, but the finely divided
material can be stabilised by superficial oxidation in cool oxygen,
whereafter it can be handled in air. Preferably the catalyst-form-
20 ing oxidation is carried out before shaping, as that any chemical
change resulting in a change in density takes place largely before
shaping and thus cannot damage the shaped pieces mechanically.
Especially if the precursor includes a hydride-forming metal, for
example rare earth or titanium, in addition to the activatable
25 metal and/or metal convertible to active oxide, it is preferably
hydrided before comminution, to make it more fragile.

The step of hydriding before comminution results in the
formation of a catalyst precursor having advantages over non-
hydrided precursor, in that the catalyst resulting from it in con-
30 tact with methanol synthesis gas may be found to maintain its
activity for longer periods. Hydriding can be, alternatively or
additionally, carried out after comminution.

Some at least of such hydrided catalyst precursors are
believed to be new compositions of matter, and thus they constitute
35 a sixth aspect of the invention. Their general formula is, by

atomic proportions
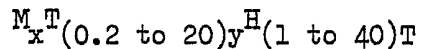
$$M_x T(0.2 \text{ to } 20)_y H(1 \text{ to } 40)T$$

where M is copper and/or at least one platinum group metal;

    T is selected from rare earth metals; yttrium, titanium,

5   zirconium, hafnium and thorium;

    x = y = 1 when M is copper, y = 20x when M is a platinum

    group metal.

More than one metal M or T can be present. In addition, minor

proportions of metals outside these classes can be present,

10 especially aluminium, manganese or alkaline earths.

    The preferred metal combinations are as described herein

for other aspects of the invention.

    If desired, the hydridation can be carried out in a

plurality of cycles of hydride formation followed by hydride de-

15 composition by change of pressure and/or temperature.

    Whether or not cyclic hydridation is used, hydridation

of the precursor is preferably to at least 50% of its capacity.

The hydrogen pressure is typically in the range 1 - 200 bar abs.

and the temperature under $50^{\circ}C$.

20   In making the catalyst the oxidation step is preferably

so as to oxidise the metal of high electrode potential, but not to

oxidise in bulk the active metal. There may be slight, mainly

superficial, oxidation of active metal, but this should be insuf-

ficient to produce an exotherm in subsequent reduction with hydrogen.

25 Oxidation can be by means of diluted oxygen, at for example 0.01

to 0.5% in methane, nitrogen or a noble gas, or by an oxygen com-

pound such as water vapour, CO_2 or N_2O, mixed if desired with an

inert or noble gas or with a reducing gas to give a balance of

oxidising and reducing power. When it is intended to oxidise only

30 the metal of electrode potential at least 0.8 volts, the oxidis-

ing agent can be carbon monoxide alone or with hydrogen: in this

event the controlled oxidation need not be a distinct step in making

the catalyst but takes place when the alloy is contacted with

methanol synthesis gas. If the oxidation is controlled so as to

35 oxidise active metal, a final reduction is carried out before

starting up methanol synthesis.

Whereas in the last decade there have been numerous reports that alloy-derived catalysts are highly active there has been no agreement as to how best to treat the alloy or to what

5 is present in the active catalyst. For example in US 4181630 treatments with air at room temperature, air at $400^{\circ}C$, $H_2 + H_2O$ at $400^{\circ}C$, or $CO + 3H_2$ at $400^{\circ}C$ are disclosed to produce a supported copper catalyst active in methanol synthesis. It has been suggested that tha element having the high affinity for oxygen is

10 converted to oxide or hydride or that at least one of the components is converted to carbide.

In investigating such catalysts containing copper we have found higher activity in methanol synthesis than has so far been published. We believe this is at least partly the result

15 of better activation conditions, especially avoiding excessive heating of the alloy during activation.

According to the invention in its seventh aspect an alloy of an activatable metal with an element having a high affinity for oxygen is converted to active catalyst by contacting it

20 with a reactive medium of oxidising power less than half that of air at a temperature not over $200^{\circ}C$.

The temperature of conversion to active catalyst is preferably below $150^{\circ}C$ and can be as low as $0^{\circ}C$ or less, provided the consequent lengthened process start-up time can be tolerated.

25 A very suitable temperature is in the range $40-120^{\circ}C$, especially for a catalyst preparation from an alloy comprising copper and one or more hydride-forming metals such as rare earth metals.

Control of temperature can be for example by means of diluent gas, heat exchange surfaces or presence of a liquid.

30 The oxidation activation preferably follows a pretreatment with hydrogen, suitably at a temperature in a range suitable for the activation.

Methanol synthesis according to the invention can be carried out in conventional conditions, for example a temperature

35 in the range $150 - 450^{\circ}C$, a pressure up to 400 bar abs. and a

space velocity such that the methanol output is in the range 0.1 to 2.0 kg per kg of catalyst per hour.

The synthesis is carried out preferably in these conditions:

5 Temperature : up to 220, especially up to 180°C, and offering a choice of 50 - 120 and 140 - 180°C to suit process design requirements;

10 Pressure : up to 400, especially 20 - 120 bar abs;

Space velocity : 1000-80,000, especially 5000-50,000 h^{-1}.

The ratio R of hydrogen to carbon oxides in the gas
15 entering the synthesis catalyst can have any convenient value for example up to 4 or even up to 12 or more, but can be sub-stoichiometric. Ratio R is expressed by the formula

$$R = \frac{H_2 - CO_2}{CO + CO_2}$$

20 Typically it is in the range 0.5 to 2.0, especially over 0.8 and very suitably in the range 1.0 to 1.8. Further, it is preferred to keep the $CO_2 + H_2O$ content of the synthesis gas below 0.2, especially below 0.05, bar and, indeed, as low as practicable; in particular below 0.1, especially below 0.01 bar: then R becomes
25 merely the H_2:CO ratio.

After leaving the synthesis catalyst the reacted synthesis gas is cooled and methanol is condensed out, if methanol is to be the product of the over-all process. In preferred operating conditions such condensed-out methanol is pure enough for many uses.
30 If greater purity is required, the condensed-out methanol need be subjected only to a simple distillation or to adsorptive purification. The synthesis process is thus very suitable for making fuel-grade methanol economically.

When the catalyst is formed from an alloy, particles of
35 it have essentially a metallic skeleton and thus, provided excessive

oxidation is avoided, can be highly resistant to attrition. Accordingly the catalysts, preferably in fine particle form, especially under 16 mesh ASTM (1000 microns) and more preferably in the range 0.1 to 100 microns, are highly suitable for use in

5   suspension in a liquid. At the same time, since the alloy-derived catalyst particles are generally denser than particles made by reducing oxides, they are less readily entrained in the flowing synthesis gas. Further, since the alloy-derived catalysts are active at temperatures lower than oxide-derived catalysts, the

10 liquid can have a lower boiling point than was previously thought desirable. An especially useful form of this process is operated at a temperature over $100°C$, for example in the range $140-180°C$, such that the rate of reaction in a fixed bed process would have been subject to pore-diffusion limitation and could not be

15 increased by the usual expedient of decreasing the catalyst particle size because that would result in excessive resistance to gas flow.

Such a process in which the catalyst is contained in a body of liquid substantially inert in the conditions of synthesis,

20 constitutes the third aspect of the invention, as mentioned above.

If methanol is to be the product of the process the liquid should be readily separable from methanol. Thus it preferably has a boiling point more than $5°C$ different from that of methanol and in any event should not form an azeotrope with

25 methanol. Alternatively, if the methanol is to be reacted further, for example by dehydration, conversion to hydrocarbon or etherification or esterification, the liquid should be readily separable from the products of those further reactions. Separability is of course not needed if the liquid chosen is to be a constituent of a

30 product mixture.

Examples of suitable liquids are aliphatic, cyclealiphatic and aromatic hydrocarbons, alcohols and esters, provided they are free of ethylenic or acetylenic unsaturation.

Suitable methanol synthesis processes in presence of

35 liquid are described in GB-A-1413929 and EP-A-34011.

The unpurified or purified methanol product or, more
preferably the reacted synthesis gas as a whole, can be passed
to further reactions, especially (a) dehydration of methanol to
dimethyl ether catalysed by alumina or silica-treated alumina
5 and (b) conversion of methanol and/or dimethyl ether to aromatics
catalysed by a zeolite of the ZSM-5 family or to olefins
catalysed by a zeolite of the FU-1, MCH or NU-3 type.

When the starting value of R is less than 2, the un-
reacted gas remaining after separation of methanol is rich in
10 carbon monoxide. This gas can be recycled to the synthesis
catalyst or passed to separate downstream stages of methanol
synthesis and separation, until the CO content has built up to a
level at which slower synthesis cannot be tolerated. Alternatively
the unreacted gas can be subjected to shift and CO_2 removal to
15 increase its H_2:CO ratio and then passed to methanol synthesis by
recycle or downstream separate stages.

Since the synthesis can operate efficiently at low H_2:CO
ratios it can be fed with partial oxidation gas that has been
purified of catalyst poisons but has not undergone shift or hydrogen
20 addition. Examples of gases that can be used are Koppers-Totzek
gas (R = 0.47), Texaco coal gas (R - 0.74) and Shell-Koppers gas
(R = 0.47). More conveniently the H_2:CO ratio can be increased by
adding hydrogen, especially as described in our published European
application 47596.

25 Despite the low temperatures at which the process can
be operated, rates of methanol production are comparable with
those reported to be obtained at temperatures of maximum activity
in the references. We believe an important factor leading to
relatively large rates of methanol formation is the purity of the
30 gas contacting the catalyst. Thus preferably that gas contains
less than 1 part in 10^6, especially less than 1 part in 10^9, by
weight of volatile metal compounds (these are chiefly carbonyls
of iron and/or nickel). Preferably the halogen content (which
apparently is in combined form as hydracid or organic compounds)
35 is less than 1 part in 10^6, especially less than 1 part in 10^9,

by volume as equivalent HCl. Preferably the sulphur content is less than 100 parts in 10^9 by volume as equivalent H_2S.

It appears to be desirable to keep the content of such impurities down to low limits during the preparation of the
5   catalyst.

A further important factor is the content of water and/or carbon dioxide in the synthesis gas passing over the catalyst. The partial pressure of such gases is preferably low, as described above. At the same time the process conditions
10 should be controlled to limit the access of any by-product water to the catalyst. Thus the space velocity is preferably kept high enough to limit the occurrence of water-forming reactions and/or to carry any water rapidly away from the catalyst. It appears that at the specified low temperature, and especially the preferred
15 upper limit $220^{\circ}C$ and range 140 to $180^{\circ}C$, especially $50-120^{\circ}C$, the formation of methanol is so much more rapid than that of dimethyl ether or higher oxygenated compounds that water-formation can be substantially avoided. As a result, the low temperature and high gas purity provide a "window" leading to high output of methanol
20 pure enough for some uses without distillation.

To provide the required level of purity the synthesis gas and any gas recycled to the synthesis is subjected preferably to at least one of the following treatments, namely a molecular sieve, cold methanol (under $-20^{\circ}C$) or a liquid absorber of CO_2
25 and H_2O such as a glycol, polyglycol or polyglycol dialkyl ether.

In the following Examples the synthesis gas was purified, before entering the synthesis reactor, by subjection to a mixture of 5A and 13X molecular sieves at room temperature to remove CO_2, H_2O, sulphur compounds and halogen compounds, then to
30 copper wool at $350^{\circ}C$ to decompose any metal carbonyls, than to a cooler to bring it to synthesis inlet temperature.

EXAMPLE 1

A mixture of small particles of cerium metal (50 parts) and copper metal (50 parts) all by weight was melted for 20 min
35 in vacuo (10^{-6} Torr) on a cooled copper hearth by means of an

(b)   A corresponding catalyst containing lanthanum in place of cerium was made and tested in the same way, but without the flow rate increase.

(c)   A catalyst as (a) but containing no aluminium was made and tested in the same way, except that the low temperature and high temperature test runs were carried out separately and that the flow rate was not increased.

(d)   Preparation (a) was repeated using mischmetall (mainly Ce and La, minor Nd and Pr, less than 0.1% other metals) instead of pure cerium, and tested in 60 CO:40 H_2 synthesis gas.

Table 1

Catalyst temp. °C	Methanol % ^{V}/v in reacted gas at various times, h										Non-MeOH organics % ^{w}/w
	0	10	40	60	100	160	230	250	280	300	
a 200	–	–	3.8	3.6	3.2	3.0	3.0	–	–	–	under 0.25
250	–	–	–	–	–	–	–	7.3*	7.0*	6.9*	under 0.4
b 200	–	–	5.8	5.0	4.0	3.3	3.0	–	–	–	under 0.4
250	–	–	–	–	–	–	4.7	3.1	1.0	N/A	under 0.6
c 150	3.0	2.3	1.3	1.0	1.0	–	–	–	–	–	under 0.7
250	1.7	3.1	2.6	–	–	–	–	–	–	–	under 1.1
d 200	–	3.7 (20 h)	–	2.75	2.5	2.0	–	–	–	–	N/A

It is evident that the alumina-free catalyst c is less active initially than a, b or d and loses its activity more rapidly. Of a and b, cerium-containing catalyst a is initially less active but levels out at an activity equal to that of b. After the step increase in temperature from 200 to 250°C, a is both more active and more stable than b. Catalyst d, containing more than one rare earth oxide, is superior to c.

As in Example 1, the outlet gas contained under 0.1% ^{V}/v of water and an undetectably low content of methane. The liquid phase condensed from (a) contained less than 0.25% ^{w}/w of non-

(b)   A corresponding catalyst containing lanthanum in place of cerium was made and tested in the same way, but without the flow rate increase.

(c)   A catalyst as (a) but containing no aluminium was made

5   and tested in the same way, except that the low temperature and high temperature test runs were carried out separately and that the flow rate was not increased.

(d)   Preparation (a) was repeated using mischmetall (mainly Ce and La, minor Nd and Pr, less than 0.1% other metals) instead

10   of pure cerium, and tested in 60 CO:40 H_2 synthesis gas.

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Catalyst temp. °C	Methanol % $^V/v$ in reacted gas at various times, h										Non-MeOH organics % $^W/w$
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a 200	–	–	3.8	3.6	3.2	3.0	3.0	–	–	–	under 0.25
250	–	–	–	–	–	–	–	7.3*	7.0*	6.9*	under 0.4
b 200	–	–	5.8	5.0	4.0	3.3	3.0	–	–	–	under 0.4
250	–	–	–	–	–	–	4.7	3.1	1.0	N/A	under 0.6
c 150	3.0	2.3	1.3	1.0	1.0	–	–	–	–	–	under 0.7
250	1.7	3.1	2.6	–	–	–	–	–	–	–	under 1.1
d 200	–	3.7 (20 h)	–	2.75	2.5	2.0	–	–	–	–	N/A

It is evident that the alumina-free catalyst c is less active initially than a, b or d and loses its activity more rapidly. Of a and b, cerium-containing catalyst a is initially less active but levels out at an activity equal to that of b. After the step

30   increase in temperature from 200 to 250°C, a is both more active and more stable than b. Catalyst d, containing more than one rare earth oxide, is superior to c.

As in Example 1, the outlet gas contained under 0.1% $^V/v$ of water and an undetectably low content of methane. The liquid

35   phase condensed from (a) contained less than 0.25% $^W/w$ of non-

methanol organics, one third that from (c).

<div align="center">EXAMPLE 3</div>

The catalyst of Example 2 (a) was tested in methanol synthesis at $200^\circ C$, 50 bar abs. pressure, space velocity 20000 h^{-1} using a gas consisting of H_2 and CO in the ratio 55.45, purified as before. The percentage of methanol in the outlet gas was 3.5% initially, falling to 3% $^V/v$ after 72 hours operation.

As a control, a catalyst containing no aluminium but otherwise the same was tested in the same conditions. The methanol content of the outlet gas was 3.0% initially, falling to 1.0% after 72 hours operation.

<div align="center">EXAMPLE 4</div>

(a)   A catalyst precursor was made by melting together in a radio frequency indiction furnace 100 parts of metallic copper and 100 parts of misch-metall as used in Example 2(d). It was allowed to cool, ground to a particle size of 100-500 microns and heated in air at $300^\circ C$. The product of the heat treatment was mixed with twice its volume of 2 mm fused silica granules, charged to a tubular test reactor and heated to $150^\circ C$ in hydrogen deficient methanol synthesis gas (40 H_2, 60 CO $^V/v$) flowing at a space velocity of 22500 h^{-1} and at a pressure of 50 bar abs. After an exotherm of about $30^\circ C$, the temperature was fixed at $150^\circ C$. The outlet gas contained methanol, in a concentration stabilised at 4.0% $^V/v$ after 8 hours operation, but undetectable H_2O or CO_2. The liquid phase condensed from the gas contained less than 1.0% of organic compounds other than methanol, and only 0.4% $^W/w$ of water.

(b)   Preparation (a) was repeated with the difference that the ground alloy was oxidised in 100% carbon monoxide instead of air and then handled in oxygen free atmospheres. When contacted with the synthesis gas an exotherm of about $60^\circ C$ was observed. The synthesis activity of the catalyst was equal to that of (a), and the product purity was similar.

<div align="center">EXAMPLE 5</div>

A mixture of small particles of cerium metal (50.3 parts),

copper metal (48.2 parts) and manganese metal (1.5 parts), all by
weight, was melted for 20 min in vacuo (10^{-6} Torr) in a radio
frequency induction furnace, then allowed to cool. The resulting
alloy ingot was transferred to a glove box and ground under nitro-
5 gen to the size range 600 to 850 microns, then mixed with twice its
volume of 2 mm silica granules and charged to a laboratory extern-
ally heatable isothermal methanol synthesis reactor. The charge
was heated to 60 - 65°C in a mixture of % $^V/v$ composition H_2 65 +
H_2 35 passed over it at 50 bar abs. pressure, 20000 h^{-1} volume
10 space velocity calculated on the density of the alloy as charged.
In the synthesis gas the precursor underwent no observable exother-
mic reaction, but after 15 h methanol was detected in the outlet
gas, and the rate of production of methanol rose to over 1% and
remained there for several days until the run was voluntarily
15 stopped, as shown in Table 2.

Table 2

Hours on line	0	15	21	52	72	96	118	142
Methanol % $^V/v$	0	0.67	1.23	1.46	1.25	1.92	1.23	1.34
Space velocity x 10^{-3}	20	17	10.5	10.5	2.5	4	5	4.5
Inlet temp.	65	68	68	69	70	71	82	97

25 The decreasing space velocity as the test proceeded is attributed
to disintegration of the catalyst, causing obstruction of gas flow.
        It is evident that the catalyst has remarkable methanol
synthesis activity at temperatures well below those previously con-
sidered necessary for methanol synthesis. The decline in activity
30 is believed to have been at least in part due to carbon dioxide,
the concentration of which was initially too small to detect in
the inlet gas but rose to 0.02 after about 68 hours on line.

EXAMPLE 6

        A mixture of small particles of cerium metal (50 parts),
35 copper metal (45 parts) and palladium metal (5 parts), all by

weight was melted for 20 min *in vacuo* (10^{-6} Torr) on a cooled copper hearth by means of an electron beam, then allowed to cool. The resulting alloy ingot, a catalyst precursor, was transferred to a glove box and ground under nitrogen to the size range 600

5   to 850 microns, then charged to a laboratory externally heatable isothermal methanol synthesis reactor. The charge was heated to 150°C in a mixture of % $^V/v$ composition H_2 72 + CO 28 passed over it at 50 bar abs. pressure, 40000 h^{-1} volume space velocity. An exothermic reaction, resulting in a temperature rise to 400°C, was

10 observed: it is believed that a lower temperature would have sufficed to form the catalyst. Then, at the same gas flow rate the temperature was raised to 250°C and the outlet gas analysed chromatographically. The content of methanol vapour was 2% $^V/v$. The temperature was raised to 275°C, giving 2.6% $^V/v$ of methanol,

15 then to 300°C, giving 2.9% $^V/v$ of methanol. These percentages of methanol vapour correspond respectively to 35.7, 46.4 and 51.8 grammols of methanol per litre of catalyst per hour. Such space time yields are approximately the same as obtained using a conventional copper-zinc-alumina methanol synthesis catalyst but with

20 CO_2-containing synthesis gas so that the crude methanol product contained water. Using the catalyst according to the invention the outlet gas contained only 0.1% $^V/v$ of water and an undetectably low content of methane. In the liquid phase condensed from it there was, besides methanol, under 1.0% $^W/w$ of organic compounds.

25 The catalyst was discharged and found to contain metallic palladium and copper finely dispersed on cerium oxide.

The methanol space time yield is almost 9 times as great as that reported by Baglin et al (US 4181630) using an alloy-derived catalyst containing cerium oxide (52.44% Ce as metal) and copper

30 (47.56%). It is also more than double the best reported in European patent application 31244.

In a comparison run using conventional copper-zinc-alumina methanol synthesis catalyst in the same conditions (temperature 250°C) as for the above catalyst according to the invention, the space time

35 yield of methanol was only 8.0 grammols per litre of catalyst per hour.

EXAMPLE 7

Effect of various treatments of catalyst precursor

Three samples of copper-cerium alloy made as described in Example 1 and ground to the size range 600 to 650 microns were treated as follows:

5 A.   exposed to pure dry air at room temperature for 17 days in a closed vessel;

B.   exposed to nitrogen at room temperature for 17 days;

C.   in the same period of 17 days subjected 12 times to a hydrogen cycle consisting of exposure to hydrogen

10   initially at 50 bar abs. pressure until absorption of hydrogen ceased, then re-pressurising to 50 bar abs, all at room temperature.

A sample of C was analysed immediately after the last release of hydrogen pressure and found to have the atomic composition Cu_2Ce H_{14}.

15   The synthesis activity of each sample was tested by charging 2 ml of each to a laboratory reactor, heating it to 65 - 75°C and passing over it at 50 bar abs. pressure mixture of 33% $^V/v$ CO and 67% $^V/v$ H_2 purified as described in Example 1 at flow rates in the range 25 - 50 1 h^{-1}. The volume percentage of methanol in

20 the outlet gas was measured and converted to a relative activity parameter RA by the equation:

$$RA = \% \text{ methanol} \times \frac{\text{flow rate 1 } h^{-1}}{40} \times \frac{6}{\text{weight of catalyst}}$$

The relative activities at run times up to 40 h were as shown in

25 Table 3.

Table 3

Time h	10	20	30	40
Catalyst A	0.8	0.35	0.25	0.2
B	0.4	0.5	0.55	0.6
C	0.6	0.7	0.8	0.85

It is evident that the air treatment produces a catalyst

35 of high initial activity which is, however, not maintained. On

the other hand, the hydrogen pre-treatment produces a catalyst
of lower intial activity which, however, increases with time
and levels out at a value well above that to which the air-
treated catalyst declines. The nitrogen treated catalyst is
5 intermediate in activity and stability.

                         EXAMPLE 8

Synthesis in presence of liquid (design)

          A sample of ground catalyst precursor prepared as in
Example 4 is suspended in 10 times its weight of octane and
10 charged to a nitrogen-filled vertical reactor having a bottom
run-off for catalyst suspension, a catalyst suspension feed
point near its upper end, an inlet sparger for synthesis gas and
an upper outlet for reacted synthesis gas. The catalyst suspen-
sion circuit includes an agitated vessel, a slurry pump and a
15 heat exchanger, in that order, between the run-off and the feed
point. The synthesis gas outlet includes a droplet separator, a
feed/effluent heat exchanger, cooler and liquid methanol separator
and includes means to recycle unreacted synthesis gas.

          The gas circuit is closed, purged with nitrogen, then
20 filled with methanol synthesis gas (33% ^{V}/v CO, 67% ^{V}/v H_2) at a
pressure of 50 bar abs., which is set in circulation. The catalyst
suspension is set in circulation and slowly heated to $150^{o}C$. After
a few hours at this temperature the catalyst becomes active and
methanol is observed to be collecting in the separator. From this
25 time onwards the catalyst suspension heat exchanger is adjusted
so as to cool the suspension instead of heating it, so as to com-
pensate for the exothermic heat of the synthesis reaction.

          As a result of the density of the catalyst, very little
of it is carried overhead into the droplet separator. From time
30 to time catalyst is allowed to settle in the agitated vessel and
is drawn off therefrom and replaced by fresh catalyst.

Raw methanol purity

          Table 4 sets out the condensate compositions for a variety
of catalysts, synthesis temperatures and space velocities, all runs
35 using synthesis gas containing 33% CO and 67% H_2. It is evident that

the non-methanol organics level, although variable, remains low.

Table 4

Catalyst	Cu:Ce 50:50	Cu:Ce 17:83	Cu:Ce 33:67	Cu:Ce:Pd 49:50:1	Cu:Ce:Mn (Ex 5)	Cu:Ce:Al 45:45:10
Temp. $^{\circ}$C	70	70	100	70	70	125
$\neq$ SV h^{-1}	40	40	40	40	20	20
*HCO_2CH_3	345	290	170	300	410	2000
$AcOCH_3$	925	70	115	140	650	160
EtOH	1100	600	505	440	1300	640
iso-PrOH	<5	10	<5	15	<5	<5
n-PrOH	5	<5	<5	5	10	15
sec-BuOH	80	<5	<5	<5	<5	<5
iso BuOH	<5	<5	<5	<5	<5	<5
n BuOH	<5	<5	<5	<5	<5	<5
+water	1.4	<1.0	<1.0	1.0	1.0	2.0

* Organics in ppm ^{W}/w

+ Water in % ^{W}/w

$\neq$ x 10^{-3}

1.   A process of methanol synthesis by reacting carbon monoxide with hydrogen over a catalyst comprising at least one active metal and/or oxide and a difficultly reducible oxidic support material made by oxidation of at least one element, characterised by a catalyst temperature under $240^{\circ}C$.

2.   A process of methanol synthesis by reacting carbon monoxide with hydrogen over a catalyst comprising at least one active metal and/or oxide and a difficultly reducible oxidic support material made by oxidation of at least one element, characterised in that the composition of the gas mixture passed over the catalyst corresponds to

$$R = \frac{H_2 - CO_2}{CO + CO_2} = 0.5 \text{ to } 2.0$$

3.   A process of methanol synthesis by reacting carbon monoxide with hydrogen over a catalyst comprising at least one active metal and/or oxide and a difficutly reducible oxidic support material made by oxidation of at least one element, characterised in that the catalyst is contained in a body of liquid substantially inert in the conditions of synthesis.

4.   A process according to anyone of the preceding claims in which the temperature is in the range $140 - 180^{\circ}C$.

5.   A process according to any one of claims 1 to 3 in which the temperature is in the range $50 - 120^{\circ}C$.

6.   A process according to any one of the preceding claims in which the element from which the support material is derived is a metal having a standard electrode potential at least 1.8 volts negative with respect to the standard hydrogen electrode.

7.   A process according to claim 6 in which the catalyst is derived from a composition comprising an activatable metal, at least one rare earth metal and aluminium and/or manganese.

8.   A process according to any one of the preceding claims in which the gas passed over the catalyst contains carbon dioxide and steam to the extent of less than 0.1 bar in total.

9.   A process according to any one of the preceding claims in which the oxidation is carried out by means of the methanol

synthesis gas.

10.   A process according to any one of claims 1 to 8 in which the oxidation is carried out by means of a reactive medium of oxidising power less than half that of air at a temperature not over 200°C.

11.   A process according to any one of the preceding claims in which the catalyst comprises the oxidation product of a metal capable of forming an unstable hydride and has been made from an alloy of such a metal with a metal active or activatable for methanol synthesis by hydriding followed by oxidation.

12.   A process according to any one of the preceding claims in which the gas contacting the catalyst contains less than 1 part . in 10^6 by weight of volatile metal compounds, less than 1 part in 10^6 by volume as equivalent HCl of halogen and less than 100 parts in 10^9 by volume as equivalent H_2S of sulphur compounds.

13.   An alloy convertible to a methanol synthesis catalyst by oxidation and comprising copper, at least one metal having an electrode potential above 1.8 volt negative to the standard hydrogen electrode and at least one metal having such a potential in the range 0.8 to 1.8.

14.   A hydrided alloy convertible to a methanol synthesis catalyst by oxidation and having the composition
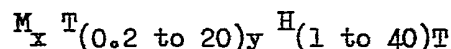
$$M_x \; T_{(0.2 \text{ to } 20)y} \; H_{(1 \text{ to } 40)T}$$

where M is copper and/or at least one platinum group metal

          T is selected from rare earth metals, yttrium, titanium, zirconium, hafnium and thorium

          x = y = 1 when M is copper, y = 20x when M is a platinum group metal.

15.   An alloy comprising a platinum group metal having methanol synthesis activity, optionally copper, and at least one rare earth metal, and a methanol synthesis catalyst derived therefrom by oxidation.