(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 100 607**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 83303895.3

(22) Date of filing: 04.07.83

(51) Int. Cl.³: C 07 C 29/15
C 07 C 31/04, B 01 J 23/89

(30) Priority: 09.07.82 GB 8220083

(43) Date of publication of application:
15.02.84 Bulletin 84/7

(84) Designated Contracting States:
BE DE FR GB IT NL

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(54) Catalyst compostion and its use in a process for the production of alcohols from synthesis gas.

(57) A catalyst composition suitable for use in the production of alcohols from synthesis gas comprises as essential elements:

(a) cobalt
(b) one or more of copper, silver, gallium, zirconium, zinc and thorium
(c) one or more of palladium, platinum and nickel, and
(d) one or more alkali metals,

in the atomic ratio of component (a): component (b): component (c) of 100:1 to 400:1 to 500, the alkali metal or metals forming up to 5% by weight of the composition. A suitable catalyst composition has the empirical formula:

$$^{(a)}100\ ^{(b)}1 \text{ to } 400\ ^{(c)}1 \text{ to } 500\ ^{(d)}x^{Oy}$$

wherein (a), (b), (c) and (d) are as above, the value of x is such that (d) forms up to 5% by weight of the composition and y is a number such that the valence requirements of the other elements for oxygen is satisfied.

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CATALYST COMPOSITION AND ITS USE IN A PROCESS FOR THE PRODUCTION OF ALCOHOLS FROM SYNTHESIS GAS

The present invention relates to a catalyst composition suitable for use in a process for the production of alcohols, in particular saturated straight-chain primary alcohols, from synthesis gas and to its use in such a process.

Two main types of process have been proposed for preparing alcohols from gaseous mixtures comprising carbon monoxide and hydrogen (synthesis gas). One of these is the modified Fischer Tropsch process which involves alkali metal-containing iron catalysts. Generally, this process suffers from poor selectivity and low productivity. The other process is the isobutyl synthesis as used in Europe between 1935 and 1945. This process is analogous to the methanol synthesis process and utilises a similar catalyst, ie zinc chromite, modified by addition of an alkali metal salt, at high temperatures (380 to 450°C) and high pressures (300 to 400 bars). Typically the main products from this reaction comprise methanol (50%), ethanol (20-40%), n-propanol and higher alcohols which are predominantly non-linear primary and secondary alcohols. For both these processes it has been proposed in the prior art to incorporate in the catalyst a wide variety of metals.

USP 4122110 claims a process for manufacturing linear saturated primary alcohols, by reacting carbon monoxide with hydrogen at a pressure between 20 and 250 bars and a temperature between 150 and 400°C, in the presence of a catalyst, characterised in that the catalyst contains at least 4 essential elements:-

(a) copper,

(b) cobalt,

(c) at least one element M selected from chromium, iron, vanadium and manganese, and

(d) at least one alkali metal A, in the following atomic proportions: $Cu_xCo_yM_zA_v$ where x is from 0.1 to 1, y from 0.1 to 1, z from 0.2 to 1 and v from 0.001 to 0.25 times the sum (x + y + z).

By comparison with the aforesaid prior art processes it is claimed in USP 4122110 that the selectivity to alcohols is high (it may be higher than 95%, particularly when using the preferred method for manufacturing the catalyst); practically no hydrocarbons, particularly methane are formed; the selectivity to linear saturated primary alcohols of C_2 or more is often higher than 70% by weight; the productivity is great, higher than 100 kg of C_2^+ alcohols per cubic metre of catalyst per hour; and the operating conditions are milder.

According to the present invention there is provided a catalyst composition suitable for use in a process for the production of alcohols from synthesis gas which composition comprises as essential elements:-

(a) cobalt,

(b) one or more of copper, silver, gallium, zirconium, zinc and thorium,

(c) one or more of palladium, platinum and nickel, and

(d) one or more alkali metals,

in the atomic ratio of component (a): component (b): component (c) of 100:1 to 400:1 to 500, the alkali metal or metals forming up to 5% by weight of the composition.

Whilst the precise form of the elements during use in a process for the production of alcohols from synthesis gas is not entirely known, they are thought to be in the form of their oxides, though it is possible that certain of the elements may be present in elemental form. It is known, however, that active catalytic compositions comprise the elements in the form of their oxides or in the form of salts which are decomposable by heat to oxides, such as carbonates, sulphates, nitrates or carboxylates.

A suitable composition has the empirical formula:

$(a)_{100}\ (b)_{1 + 400}\ (c)_{1 \text{ to } 500}\ (d)_x O_y$

wherein (a) is cobalt,

(b) is one or more of copper, silver, gallium, zirconium, zinc and thorium,

(c) is one or more of palladium, platinum and nickel, and

(d) is one or more alkali metals

and wherein the value of x is such that (d) forms up to 5% by weight of the composition and y is a number such that the valence requirements of the other elements for oxygen is satisfied.

A particularly suitable composition comprises $Co.Cu.Pd_{0 \cdot 05}K_xO_y$.

The composition may be prepared by a variety of different methods. Thus it may be prepared by simply admixing the individual oxides, or by precipitating the oxides either individually or collectively, or by impregnating an oxide with a solution or solutions of other oxides. Alternatively, instead of the oxides, heat decomposable salts may be used in any of the aforesaid methods for preparing the composition and the composition heated thereafter at a temperature above their decomposition temperatures.

Shaping may be affected by any conventional technique, for example by tabletting or extrusion, or by pill-forming, optionally incorporating also binders such as alumina, magnesia and aluminous refractory cements. The preferred aluminous cements contain from 40 to 85% b.w. Al_2O_3 and 15 to 30% b.w. CaO with optionally small amounts of other components.

In another aspect, the invention provides a process for the production of alcohols which process comprises reacting carbon monoxide with hydrogen at elevated temperature and pressure in the presence as catalyst of a composition as described hereinbefore.

Before use as a catalyst it is particularly preferred to heat the composition in a reducing atmosphere, eg in a stream of a reducing gas. Typically, this may be effected by heating at a temperature of about 350°C in a stream of hydrogen for a period of 18 hours. Following reduction, and until its use as a catalyst in the process of the invention, the composition must be stored in a substantially oxygen-free atmosphere.

Mixtures of the gases carbon monoxide and hydrogen are abundantly available in the form of synthesis gas. Methods for preparing synthesis gas are well known in the art and usually involve the partial oxidation of a carbonaceous substance, eg coal. Alternatively, synthesis gas may be prepared, for example, by the catalytic steam reforming of methane. Although it is preferred to use substantially pure synthesis gas, the presence of such impurities as carbon dioxide and nitrogen can be tolerated. On the other hand, impurities which have a deleterious effect on the reaction should be avoided. The molar ratio of carbon monoxide to hydrogen may suitably be in the range 5:1 to 1:5. In general, a high proportion of hydrogen favours the formation of hydrocarbons whilst a low proportion of hydrogen favours the formation of oxygenated hydrocarbons. Methods for adjusting the molar ratio of hydrogen to carbon monoxide by the so-called shift reaction are well known in the art.

The elevated temperature may suitably be in the range from 200 to 450°C and the elevated pressure may suitably be in the range from 25 to 300 bars.

Although the process may be carried out batchwise, it is preferably operated in a continuous manner. Suitably, the contact time, defined as:-

$$\frac{\text{Volume of catalyst in millilitres}}{\text{Total volume of gas (in millilitres/second at NTP)}}$$

may be in the range from 1 to 30 seconds.

The catalyst may be employed in the form of a fixed or a fluidised bed.

The liquid product principally comprises saturated straight-chain primary alcohols such as methanol, ethanol, propanol and butanol.

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

Example

Preparation of Cu Co $Pd_{0.05}$ Kx Oy Catalyst

$Cu(NO_3)_2 3H_2O$(48.3g) and $Co(NO_3)_2\ 6H_2O$(58.2g) were dissolved in deionised water (200 ml). To this was added a solution of palladium

acetate (1.48g) dissolved in conc nitric acid (10 ml). This mixture was then added to a solution of potassium carbonate (68.1g) in deionised water (300 ml) maintained at 60°C. The pH was adjusted to about 7.0 by the addition of potassium carbonate, and the resulting precipitate filtered, washed with deionised water (3 x 500 ml) and dried. The resulting dark solid was heated in air at 400°C for 4 hours, cooled and made into pellets. The pellets were broken down and were sieved to give 16 to 20 mesh granules. The catalyst was reduced at 350°C under a slow flow of hydrogen for 18 hours before use.

Use of catalyst in a process for the production of alcohols from synthesis gas

A mixture of carbon monoxide and hydrogen was contacted with the Cu Co $Pd_{0\cdot05}$ Kx Oy catalyst prepared in the manner hereinbefore described. The reaction conditions were as follows:-

Run pressure	= 50 bar
Run temperature	= 348°C
Catalyst	= 15 ml
Feed $CO:H_2$ molar ratio	= 1:1
Contact time	= 2.21 sec

Under these operating conditions the carbon monoxide conversion was 19.4% and a liquid organic product was obtained with the following composition (% w/w):-

Methanol	- 30
Ethanol	- 49
n-Propanol	- 14
Butanol	- 7

The main byproducts were methane and carbon dioxide.

Example 2

Preparation of Cu Co $Pd_{0\cdot05}$ K_x Oy wherein x is approximately 1.5% wt/wt and y is a number such that the valence requirements of the other elements for oxygen is satisfied

$Cu(NO_3)_2\cdot3H_2O$(48.3g) and $Co(NO_3)_2\cdot6H_2O$(58.2g) were dissolved in separate beakers of water and then combined to give one solution. To this was added a solution of palladium chloride (1.54g) dissolved in conc. nitric acid (10ml). The solutin was heated to about 90°C and a

warm solution of potassium carbonate (68.1g) added slowly with stirring until pH9.0 was obtained. The pH was adjusted to pH7.0 by the careful addition of 20% nitric acid. The mixture was cooled and the precipitate filtered off. The precipitate was washed by slurrying several times with deionised water and oven dried at about 120°C overnight. The powder was heated at 275°C for 4 hours and finally at about 400°C for 16 hours to decompose any remaining nitrates or carbonates. The hard cake was broken up and sieved to 8-16 BSS granules. The catalyst was reduced by contact at 200°C with nitrogen initially and gradually changing over a period of 7 hours to hydrogen (100%), followed by hydrogen (100%) at 200°C for 16 hours

Use of catalyst in a process for the production of alcohols from synthesis gas

A mixture of carbon monoxide and hydrogen was contacted with the catalyst prepared in the aforesaid manner. The reaction conditions were as follows:

Run pressure	=	50 bars
Run temperature	=	335°C
Catalyst	=	15ml
Feed $CO:H_2$ molar ratio	=	1:1
G.H.S.V.	=	$8373h^{-1}$

Under these operating conditions the carbon monoxide conversion was 21.5% and a liquid organic product was obtained with the following composition (%w/w):-

Methanol	25.1
Ethanol	35.1
Propanol	20.2
Butanol	19.6

Claims:

1. A catalyst composition suitable for use in a process for the production of alcohols from synthesis gas which composition comprises as essential elements:

(a) cobalt,

(b) one or more of copper, silver, gallium, zirconium, zinc and thorium,

(c) one or more of palladium, platinum and nickel, and

(d) one or more alkali metals,

in the atomic ratio of component (a):component (b):component (c) of 100:1 to 400:1 to 500, the alkali metal or metals forming up to 5% by weight of the composition.

2. A catalyst composition according to claim 1 wherein the essential elements are present in the form of their oxides or in the form of salts which are decomposable by heat to oxides.

3. A catalyst composition according to either claim 1 or claim 2 having the empirical formula:

$$(a)_{100}\ (b)_{1\text{ to }400}\ (c)_{1\text{ to }500}\ (d)_x O_y$$

wherein (a) is cobalt

(b) is one or more of copper, silver, gallium, zirconium, zinc and thorium,

(c) is one or more of palladium, platinum and nickel, and

(d) is one or more alkali metals

and wherein the value of x is such that (d) forms up to 5% by weight of the composition and y is a number such that the valence requirements of the other elements for oxygen is satisfied.

4. A catalyst composition according to claim 3 comprising $Co.Cu.Pd_{0\cdot05}K_xO_y$.

5. A process for the production of alcohols which process comprises reacting carbon monoxide with hydrogen at elevated temperature and pressure in the presence as catalyst of the catalyst composition as claimed in claims 1 to 4.

6. A process according to claim 5 wherein the catalyst before use in the reaction of carbon monoxide with hydrogen is heated in a reducing atmosphere.

7. A process according to either claim 5 or claim 6 wherein the elevated temperature is in the range 200 to 450°C and the elevated pressure is in the range from 25 to 300 bars.

8. A process according to any one of claims 5 to 7 wherein the contact time is in the range from 1 to 30 seconds.

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EUROPEAN SEARCH REPORT

0100607
Application number

EP 83 30 3895

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	DE-A-2 748 097 (INSTITUT FRANCAIS DU PETROL) & US-A-4 122 110 (Cat. A,D)	1	C 07 C 29/15 C 07 C 31/04 B 01 J 23/89
A	EP-A-0 044 740 (BRITISH PETROLEUM) * Claims 1, 10 *	1	
A	EP-A-0 005 492 (STANDARD OIL) * Claim 1 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

B 01 J 23/89
C 07 C 29/15
C 07 C 31/04

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	19-10-1983	KNAACK M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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EPO Form 1503. 03.82