

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 November 2006 (23.11.2006)

PCT

(10) International Publication Number
WO 2006/123158 A2

(51) International Patent Classification:

C07C 27/06 (2006.01) **C07C 31/08** (2006.01)
C07C 31/02 (2006.01) **C07C 31/10** (2006.01)
C07C 31/04 (2006.01) **C07C 31/12** (2006.01)

(21) International Application Number:

PCT/GB2006/001837

(22) International Filing Date: 18 May 2006 (18.05.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

05253137.3 20 May 2005 (20.05.2005) EP

(71) Applicant (for all designated States except US): **BP CHEMICALS LIMITED** [GB/GB]; Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7BP (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ATKINS, Martin, Philip** [GB/GB]; 29 Chaucer Road, Ashford, Middlesex TW15 2QU (GB). **BOLTON, Leslie, William** [GB/GB]; 9 Du Maurier Close, Church Crookham, Fleet, Hampshire GU52 0YA (GB). **GRACEY, Benjamin, Patrick** [GB/GB]; 5 Anson Villas, Paull, Hull, East Riding of Yorkshire HU12 8AJ (GB). **SUNLEY, John, Glenn** [GB/GB]; 7 Hall Walk, Cottingham, East Yorkshire HU16 4RL (GB).

(74) Agent: **DE KEZEL, Eric**; BP International Limited, Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE CONVERSION OF SYNTHESIS GAS TO OXYGENATES

(57) Abstract: The present invention relates to an improved process for the conversion of carbon oxide(s) and hydrogen containing feedstocks to oxygen containing hydrocarbon compounds in the presence of a particulate catalyst. In particular, the present invention relates to an improved process for the conversion of carbon oxide(s) (CO and CO₂) and hydrogen containing feedstocks, e.g. synthesis gas or syngas, to alcohols in the presence of a particulate modified molybdenum sulphide based catalyst, or a modified methanol based catalyst and/or a modified Fischer-Tropsch catalyst.



WO 2006/123158 A2

PROCESS FOR THE CONVERSION OF SYNTHESIS GAS TO OXYGENATES

This invention relates to an improved process for the conversion of carbon oxide(s) and hydrogen containing feedstocks to oxygen containing hydrocarbon compounds in the presence of a particulate catalyst.

In particular, the present invention relates to an improved process for the conversion of carbon oxide(s) (CO and CO₂) and hydrogen containing feedstocks, e.g. synthesis gas or syngas, to alcohols in the presence of a particulate modified molybdenum sulphide based catalyst, or a modified methanol based catalyst and/or a modified Fischer-Tropsch catalyst.

US 4,122,110 relates to a process for manufacturing alcohols, particularly linear saturated primary alcohols, by reacting carbon monoxide with hydrogen at a pressure between 20 and 250 bars and a temperature between 150 DEG and 400 DEG C., in the presence of a catalyst, characterized 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.

US 4,831,060 relates to the production of mixed alcohols from carbon monoxide and hydrogen gases using a catalyst, with optionally a co-catalyst, wherein the catalyst metals are molybdenum, tungsten or rhenium, and the co-catalyst metals are cobalt, nickel or iron.

The catalyst is promoted with a Fischer-Tropsch promoter like an alkali or alkaline earth series metal or a smaller amount of thorium and is further treated by sulfiding. The composition of the mixed alcohols fraction can be selected by selecting the extent of intimate contact among the catalytic components.

Journal of Catalysis 114, 90-99 (1988) discloses a mechanism of ethanol formation from synthesis gas over CuO/ZnO/Al₂O₃. The formation of ethanol from CO and H₂ over a CuO/ZnO methanol catalyst is studied in a fixed-bed microreactor by measuring the isotopic distribution of the carbon in the product ethanol when ¹³C methanol was added to the feed.

It is an object of the present invention to provide an improved process in term of selectivity and catalyst activity and operating life for the conversion of carbon oxide(s) and hydrogen containing feedstocks to oxygen containing hydrocarbon compounds in the

presence of a particulate catalyst.

In particular, the present invention relates to an improved process in term of selectivity and catalyst activity and operating life for the conversion of carbon oxide(s) and hydrogen containing feedstocks, e.g. synthesis gas or syngas, to alcohols in the presence of a particulate modified molybdenum sulphide based catalyst, or a modified methanol based catalyst and/or a modified Fischer-Tropsch catalyst.

The present invention thus provides a process for the conversion of carbon oxide(s) and hydrogen containing feedstocks to oxygen containing hydrocarbon compounds in the presence of a particulate catalyst comprising the step of reacting carbon oxide(s) and hydrogen in the presence of a particulate catalyst in a conversion reactor to form oxygen containing hydrocarbon compounds characterised in that a saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or an ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms are added to the conversion reactor.

In particular, the present invention provides a process for the conversion of carbon oxide(s) and hydrogen containing feedstocks, e.g. synthesis gas or syngas, to alcohols in the presence of a particulate modified molybdenum sulphide based catalyst, or a modified methanol based catalyst and/or a modified Fischer-Tropsch catalyst comprising the step of reacting carbon monoxide and hydrogen in the presence of said catalyst in a conversion reactor to form alcohols characterised in that a saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or an ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms are added to the conversion reactor.

According to a preferred embodiment, the present invention provides a process for the conversion of hydrocarbon to alcohols comprising the steps of:

1. converting hydrocarbon to a mixture of carbon oxide(s) and hydrogen in a syngas reactor,
2. passing the mixture of carbon oxide(s) and hydrogen from the syngas reactor to a conversion reactor, and
3. reacting said mixture in said conversion reactor in the presence of a particulate modified molybdenum sulphide based catalyst, and/or a modified methanol based catalyst and/or a modified Fischer-Tropsch catalyst to form alcohols,

characterised in that a saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or an ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms are added to the conversion reactor.

5 For the purpose of the present invention and appended claims, producing oxygen containing hydrocarbon compounds from mixture of carbon oxide(s) and hydrogen (e.g. synthesis gas) means that the hydrocarbon oxygenates represent at least 10% by weight of the products obtained from the conversion reactor, preferably at least 20% by weight, more preferably at least 40% by weight.

10 According to a preferred embodiment of the present invention, the oxygen containing hydrocarbon compounds are alcohols, mainly methanol, propanol, ethanol and butanols (predominately n- butanol and isobutanol); said methanol, propanols (predominately n-propanol with low amounts of iso-propanol) ethanol and butanol preferably represent together at least 10% by weight of the products obtained from the
15 conversion reactor, more preferably at least 20% by weight, most preferably at least 40% by weight.

According to another embodiment of the present invention, water and carbon dioxide are also produced in the conversion reactor; then, water and alcohols preferably represent together at least 80% by weight of the nett products obtained from the process.

20 According to a preferred embodiment of the present invention, the saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or the ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms which are added to the conversion reactor comes from the oxygenates obtained from the conversion reactor as by-products.

25 Said saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms are thus preferably separated from the alcohols produced in the conversion reactor and sent back to the said conversion reactor.

30 According to another preferred embodiment of the present invention, the saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or the ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic

paraffinic alcohol having from 1 to 4 carbon atoms which are added to the conversion reactor are preferably selected from methyl acetate or ethyl acetate or a mixture thereof.

Quite surprisingly, the addition and/or recycle of even tiny amounts of saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or ester of a saturated
5 monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms to the conversion reactor have proven to be highly beneficial to the alcohols selectivity, especially the ethanol selectivity, while simultaneously increasing catalyst activity and improving operating life.

Beyond these unexpected advantages, other advantages have also been found when
10 applying the present process invention, amongst others:

- (i) less waste, less by-products and thus higher carbon efficiency.
- (ii) less capital, fewer separations, reduced storage tanks.
- (iii) alcohol product free from esters suitable for dehydration. Though esters can be dehydrated to carboxylic acid and olefin, the presence of carboxylic acids adds
15 complexity to the process and may cause additional corrosion duty
- (iv) no corrosion and metallurgy constraints due to the potential hydrolysis of the esters during subsequent purification and storage stages

As indicated, the particulate catalyst used in the conversion reactor is preferably a modified molybdenum sulphide based catalyst, and/or a modified methanol based catalyst
20 and/or a modified Fischer-Tropsch catalyst.

Preferably, the catalyst used in the present invention contains at least molybdenum and/or copper; it is preferably promoted by the addition of an alkali metal salt. Molybdenum sulphide based catalysts are preferred; a salt of potassium, especially potassium carbonate, is the preferred promoter.

25 Most preferably, the catalyst used is a molybdenum sulphide based catalysts containing cobalt, the molybdenum to cobalt molar ratio being preferably comprised between 1.5 and 2.5, more preferably 2; the said molybdenum sulphide based catalysts containing cobalt is most preferably promoted with potassium carbonate.

According to an embodiment of the present invention, the catalyst used in the
30 conversion reactor does not produce any acid and/or ester compound. Thus, according to another embodiment of the present invention, the acid and/or ester compound added to the conversion reactor does not come from the recycling of a compound produced in the said

conversion reactor.

The hydrocarbon feedstock used for syngas generation is preferably a carbonaceous material, for example biomass, plastic, naphtha, refinery bottoms, smelter off gas, municipal waste, coal and/or natural gas, coal and natural gas being the preferred ones, most preferably natural gas.

Processes for producing mixtures of carbon oxide(s) and hydrogen (synthesis gas) are well known. Each has its advantages and disadvantages and the choice of using a particular reforming process is dictated by economic and available feed stream considerations, as well as by the desired mole ratio of $H_2:CO$ in the feedstock resulting from the reforming reaction. The synthesis gas may be prepared using any of the processes known in the art including partial oxidation of hydrocarbons, steam reforming, gas heated reforming, microchannel reforming (as described in, for example, US 6,284,217 which is herein incorporated by reference), plasma reforming, autothermal reforming and any combination thereof. A discussion of these synthesis gas production technologies is provided in "Hydrocarbon Processing" V78, N.4, 87-90, 92-93 (April 1999) and "Petroleum Techniques", N. 415, 86-93 (July-August 1998). It is also envisaged that the synthesis gas may be obtained by catalytic partial oxidation of hydrocarbons in a microstructured reactor as exemplified in "IMRET 3: Proceedings of the Third International Conference on Microreaction Technology", Editor W Ehrfeld, Springer Verlag, 1999, pages 187-196. Alternatively, the synthesis gas may be obtained by short contact time catalytic partial oxidation of hydrocarbonaceous feedstocks as described in EP 0303438. Preferably, the synthesis gas is obtained via a "Compact Reformer" process as described in "Hydrocarbon Engineering", 2000, 5, (5), 67-69; "Hydrocarbon Processing", 79/9, 34 (September 2000); "Today's Refinery", 15/8, 9 (August 2000); WO 99/02254; and WO 200023689.

Any hydrocarbon-containing feed stream that can be converted into a feedstock comprising carbon monoxide and hydrogen, most preferably a synthesis gas (or "syngas"), is useful in the processes of the invention. The ratio of hydrogen to carbon monoxide in the reaction zone is preferably in the range of 20:1 to 0.1:1 by volume, more preferably in the range of 5:1 to 0.2:1, most preferably in the range of 1.5:1 to 0.5:1, e.g. 1:1. The alcohol synthesis catalysts can also catalyse the water gas shift reaction. A consequence of this is that hydrogen and carbon dioxide are interconvertable with carbon monoxide and water. For high partial pressures of carbon dioxide (at or above the water gas shift

equilibrium), carbon dioxide can act as a carbon monoxide source and a hydrogen sink and this can effect the apparent preferred syngas ratio. Useful feed streams include natural gas (mainly methane, but natural gas composition can vary depending on location and source), naphtha, refinery off-gas, LPG, gas oil, vacuum residuals, shale oils, asphalts, various
5 types of fuel oils, coal based /lignin deposits and hydrocarbon containing process recycle streams. According to a preferred embodiment of the present invention, methane is used as the hydrocarbon-containing feed stream to be converted into carbon oxides(s) and H₂.

Feedstocks comprising carbon monoxide and hydrogen, e.g., synthesis gas may undergo purification prior to being fed to any reaction zones. Synthesis gas purification
10 may be carried out by processes known in the art. See, for example, Weissermel, K. and Arpe H.-J., Industrial Organic Chemistry, Second, Revised and Extended Edition, 1993, pp. 19-21.

The particular reaction conditions for the conversion reactor embodiments described below are not narrowly critical and can be any effective reaction conditions
15 sufficient to produce mainly oxygen containing hydrocarbon compounds. The exact reaction conditions will be governed by the best compromise between achieving high catalyst selectivity, activity, lifetime and ease of operability, as well as the intrinsic reactivity of the starting materials in question and the stability of the starting materials and the desired reaction product to the reaction conditions.

In one embodiment of this invention, feedstock comprising the desired molar ratio of H₂:CO is fed to a conversion reactor at a controlled rate and the reaction is carried out in a reaction zone under controlled conditions of temperature and pressure in the presence of a catalyst to convert the feedstock into oxygenates. The temperature in the reaction zone is selected from the range of from about 150°C to about 400°C, preferably a
20 temperature in the range of from about 200°C to about 350°C and most preferably from 250-330°C. The gas hourly space velocity (GHSV) of the feedstock (liters of feedstock/hr/liter of catalyst) passing through the reaction zone can vary significantly, depending upon a variety of factors such as, for example, reaction conditions, composition of the feedstock and quantity and type of catalyst being used. The GHSV can be
25 maintained at any rate in the range of from about 1 to about 30,000 hr⁻¹ or more, preferably will be maintained at a rate of at least about 500 hr⁻¹, and more preferably will be maintained at a rate of at least 1,000 hr⁻¹. The pressure in the conversion reaction zone
30

may be selected from the range of from about 5 to 200 bar, preferably a pressure in the range of from about 50 to 150 bar and most preferably at 80-120 bar. The hydrogen and carbon monoxide partial pressures should be sufficient to enable the production of oxygenates. Hydrogen and carbon monoxide may be fed separately to the conversion reactor or, preferably in combination, e.g., as synthesis gas.

For purposes of this invention, GHSV is gas hourly space velocity which is the rate of gas flow over the catalyst. It is determined by dividing the volume of gas (at 25°C. and 1 atmosphere) which passes over the catalyst in one hour by the volume of the catalyst. LHSV is liquid hourly space velocity which is the rate that the liquid organic substrate is fed to the conversion reactor. It is determined by dividing the liquid volume pumped in one hour by the volume of catalyst.

The conversion to oxygenates reaction can be carried out by passing the mixture of hydrogen and carbon monoxide over the conversion catalyst as a vapor phase reaction or as a liquid phase reaction, e.g., slurry reaction or trickle bed fluidized bed reactor.

The reaction may be carried out in any appropriate reactor, e.g. a tubular reactor using a fixed bed of the catalyst. The reactants may be fed to the catalyst by feeding down or up, or a combination of both, to a fixed bed located in a tubular reactor. It may be desirable to use a reactor design that operates by plug flow and causes minimal turbulence in the reactor zone. The reaction may be effected in a dynamic bed of the catalyst. In such a reaction, the bed of catalyst is moving such as in the case of a fluid bed of the catalyst. The alcohol conversion reactor may preferably be chosen amongst tubular, multitubular, slurry, moving bed, fluidised bed, radial bed, multibed or reactive distillation reactor. It is preferably a multibed or multitubular vapour phase reactor.

Example

Catalyst Preparation

A cobalt/molybdenum sulphide catalyst was prepared by co-precipitation.

1. Preparation of Solution A

30g of ammonium molybdate tetrahydrate was dissolved in 212cm³ of 22wt% ammonium sulfide aqueous solution and stirred for 1 hour at 60°C.

2. Preparation of Solution B

21g of Cobalt Acetate was dissolved in 400cm³ of deionised water.

3. Preparation of cobalt/molybdenum sulphide precipitate C

Solutions A and B were transferred into two separate dropping funnels. The 2 solutions were simultaneously added dropwise to a stirred solution of 30wt% aqueous acetic acid (200cm³) over a 1 hour period, the temperature was kept constant at 50°C. The precipitate C in acetic acid was allowed to stir for a further 1 hour before filtering under vacuum. The filtrate was dried at room temperature for 18 hours and was subsequently calcined in a furnace at 500°C under an atmosphere of nitrogen for 1 hour.

The catalyst was prepared by grinding 6.6g of the calcined precipitated cobalt/molybdenum sulphide with 2g Bentonite clay and 1g K₂CO₃.

Catalyst Testing

- 10 The catalyst (9.6g) was loaded into a tubular reactor (15mm internal diameter) and a carborundum pre-heat mixing zone (20cm³) loaded upstream of the catalyst and brought to 200degC in 100 BarG nitrogen. The catalyst is then brought to a reaction temperature of 310°C (~1degC/min) in 1:1 CO:H₂ gas at 100barg pressure at a flow rate giving a gas hourly space velocity (GHSV, defined as volume flow of reactant gas at STP per volume of catalyst per hour) of ~1300h⁻¹ (The actual flow rates are 108.9mlmin⁻¹ CO and 108.7mlmin⁻¹ H₂). The reaction products were analysed by an on-line Gas Chromatogram (CP9001 – 80-100 Mesh Carbosieve SII and 0.25 micron Innowax columns). The reaction was allowed to run for 125 hours on stream after which point a 5mol% flow of methanol was fed to the reactor, after 240 hours on stream an additional 2mol% flow of methyl acetate was added to the reactor.

The results of the experiment (Table 1) demonstrate that on addition of methyl acetate to the reactor feed a significant improvement in EtOH productivity relative to propanol and methane productivities is achieved.

Table 1

Feed	Time on Stream (hours)	Average Ratio g/hr EtOH / g/hr ProOH	Average Ratio g/hr EtOH / g/hr CH ₄
CO/H ₂	125 - 190	1.42	1.95
CO/H ₂ + 5mol % MeOH	191 - 239	1.70	1.03
CO/H ₂ + 5% MeOH + 2% MeOAc	240 - 330	2.64	1.65

Claims:

1. Process for the conversion of carbon oxide(s) and hydrogen containing feedstocks to oxygen containing hydrocarbon compounds in the presence of a particulate catalyst comprising the step of reacting carbon oxide(s) and hydrogen in the presence of a
5 particulate catalyst in a conversion reactor to form oxygen containing hydrocarbon compounds characterised in that a saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or an ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms are added to the conversion reactor.
- 10 2. Process according to claim 1 wherein the carbon oxide(s) and hydrogen containing feedstocks are synthesis gas or syngas, the oxygen containing hydrocarbon compounds are alcohols, the particulate catalyst is a particulate modified molybdenum sulphide based catalyst, or a modified methanol based catalyst and/or a modified Fischer-Tropsch catalyst.
3. Process for the conversion of hydrocarbon to alcohols comprising the steps of
15 a. converting hydrocarbon to a mixture of carbon oxide(s) and hydrogen in a syngas reactor,
b. passing the mixture of carbon oxide(s) and hydrogen from the syngas reactor to a conversion reactor, and
c. reacting said mixture in said conversion reactor in the presence of a
20 particulate modified molybdenum sulphide based catalyst, and/or a modified methanol based catalyst and/or a modified Fischer-Tropsch catalyst to form alcohols,
characterised in that a saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or an ester of a saturated monocarboxylic acid having
25 from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms are added to the conversion reactor.
4. Process according to any of the preceding claims wherein the saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or the ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic
30 paraffinic alcohol having from 1 to 4 carbon atoms which are added to the conversion reactor are selected from methyl acetate or ethyl acetate or a mixture thereof.
5. Process according to any of the preceding claims wherein the saturated

monocarboxylic acid having from 1 to 3 carbon atoms and/or the ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms which are added to the conversion reactor comes from the oxygenates obtained from the conversion reactor as by-products.

- 5 6. Process according to claim 5 wherein said saturated monocarboxylic acid having from 1 to 3 carbon atoms and/or ester of a saturated monocarboxylic acid having from 1 to 3 carbon atoms with a monohydric aliphatic paraffinic alcohol having from 1 to 4 carbon atoms are separated from the alcohols.

10

15

20

25

30