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(71) Applicant
Haldor Topsoe A/S
Nymollevej 55
DK-2800 Lyngby
Denmark
(72) Inventors
Karsten Pedersen
Ib Greve Hjælm
Jorgensen
Jens Richard Rostrup-
Nielsen
(74) Agents
Elkington and Fife
High Holborn House
52/54 High Holborn
London
WC1V 6SH

(54) Process and catalyst for the preparation of a gas mixture having a high content of C_2-hydrocarbons

(57) A gas mixture rich in ethane and/or ethylene is prepared by the conversion of a synthesis gas mixture containing hydrogen and carbon oxides and optionally other gases in the presence of one or more gaseous sulphur compounds, normally in an amount of at least 10 ppm by volume and especially at least 200 ppm, calculated as H_2S, by the aid of a catalyst consisting of one or more metals of group V-B and/or VI-B of the Periodic Table of Elements, preferably molybdenum and/or vanadium, together with one or more iron group metals, both kinds in the form of free metal, oxide, or sulphide, during use mainly as sulphide, and both kinds on a porous, refractory oxidic support, conveniently aluminium oxide or titanium dioxide.

The invention also relates to the catalyst; it may be prepared by impregnation or coprecipitation techniques well-known in principle.

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SPECIFICATION

Process and catalyst for the preparation of a gas mixture having a high content of C_2-hydrocarbons

This invention relates to a process and catalyst for the preparation of a gas mixture having a high content of C_2-hydrocarbons; more particularly, it relates to a process for the preparation of a gas mixture having a high content of C_2-hydrocarbons, i.e. ethane and ethylene (ethene), by the catalytic conversion of a synthesis gas containing hydrogen and corbon oxides and possibly other gases.

Predominately synthesis gas is prepared by the gasification by steam treatment of coal or heavy petroleum fractions, in the former case by the reaction

$$(C + H_2O \longrightarrow CO + H_2$$

accompanied, however, by side reactions so that carbon dioxide and a little methane are also formed. By the gasification of petroleum fractions the amount of hydrogen in the synthesis gas becomes higher. Some coal gasification processes involve the formation of higher amounts of methane, other hydrocarbons, tar etc. During gasification oxygen is normally added in order to render the gasification self-supplying with heat.

By various reactions the synthesis gas may be converted into methane and in recent years such reactions have gained an ever-increasing importance, partly for preparing substitute natural gas (SNG) and partly as a part of special gas transport systems and in other ways as a part of the energy supply:

$$(2)\ CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

$$(3)\ 2CO + 2H_2 \rightleftharpoons CH_4 + CO_2$$

whereby carbon dioxide may however also be converted with hydrogen into methane:

$$(4)\ CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

and the socalled shift reaction causes an equilibrium between carbon monoxide and carbon dioxide:

$$(5)\ CO + H_2O \rightleftharpoons CO_2 + H_2$$

Moreover, synthesis gas may be converted by the Fischer-Tropsch synthesis (also called the FT synthesis) into methane and higher hydrocarbons, particularly paraffins and olefins, but possibly even into aromatic compounds:

$$(6)\ 2nCO + (n + 1)H_2 \longrightarrow C_nH_{2n+2} + nCO_2 \text{ (paraffin reaction)}$$

$$(7)\ 2nCO + nH_2 \longrightarrow C_nH_{2n} + nCO_2 \text{ (olefin reaction)}$$

and possibly also

$$(8)\ nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O \text{ (olefin reaction)}$$

The FT-synthesis is used for the production of motor fuel and other liquid fuels. It might be of interest for preparing C_2-hydrocarbons but is not very suitable therefor because of its low selectivity. The C_2-olefin ethylene is a very expedient starting material for many organic syntheses so that petrochemical products thereby can be formed from lignite, coal and heavy petroleum fractions.

In contradistinction to the FT synthesis the invention especially aims at an efficient conversion of synthesis gas into C_2-hydrocarbons and in this connection it is observed that it is not essential whether ethane or ethylene is directly prepared because ethane may be cracked to ethylene at a high efficiency by well-known technology.

The FT synthesis is a kind of polymerization reaction in which the yield structure follows the socalled Flory distribution (see for instance G. Henrici-Olive et al, Angew. Chemie. *15*, 136, 1976, and H Schultz et al, Fuel Proc. Technol. *1*, 31, 1977), a theoretical distribution of the various chain lengths which can be deduced mathematically from simplified kinetic assumptions. It can be shown that the Flory distribution theoretically may give a maximum yield of about 27% by weight of ethane and/or ethylene, calculated as the carbon in the hydrocarbons formed by the synthesis. In practice the yield of C_2-hydrocarbons in FT syntheses is almost always far below that expected according to the Flory distribution and only in a few cases it has been possible, under special circumstances, to obtain a C_2-hydrocarbon yield corresponding to or above that according to the Flory distribution. Moreover, it has not hitherto in FT syntheses been possible to avoid the formation of hydrocarbons having more than 4 carbon atoms.

Nearly all metals and to a considerable degree even oxides and hydroxides thereof have been proposed as catalysts for FT syntheses, frequently on support substances. There is often used one or more heavy metals with a promoter of an alkalimetal oxide. The most important of the industrially employed FT catalyst metals are iron and cobalt. It is a drawback that they are also catalysts for the conversion of carbon monoxide into free carbon and carbon dioxide by the exothermal Boudouard reaction

(9) $2CO \longrightarrow C + CO_2$.

The carbon formation causes irreversible damages of the catalyst and the reaction therefore imposes limitations of the usable process parametres. Moreover the steam formed by the synthesis under some circumstances may cause oxidation of iron catalysts, which totally or partly deactivate them (many other FT catalyst metals do tolerate oxidation without devastating deactivation). All known FT catalysts are more or less sensitive to sulphur poisoning and therefore the synthesis gas must be purified carefully of sulphur compounds before being subjected to FT synthesis. Many FT catalysts are sulphided but nevertheless are sensitive to sulphur poisoning; the sulphided catalysts only contain very small amounts of sulphur. The purification of the synthesis gas of sulphur compounds is a substantial economic charge on the FT process. In the majority of cases the sulphur content in the synthesis gas must be kept below 0.1 ppm, calculated as H_2S, whether it is to be methanated or used for FT synthesis. Dalla Betta et al (J. Catal. 37, 449, 1975) showed that 10 ppm of H_2S in the synthesis gas stream at 400°C destroyed Ru/Al_2O_3, Ni/Al_2O_3 or Raney nickel catalysts.

Shultz et al (U.S. Dept. of the Interior, Bureau of Mines report 6974, 1967) showed that ruthenium and molybdenum are promising catalysts for hydrocarbon synthesis whereas tungsten and other noble metals than ruthenium could be left out of consideration. Molybdenum, the catalytic activity of which is not on a par with that of the metals of the iron group, has since been investigated thoroughly and it is known that methanation and FT catalysts based on molybdenum are more resistent to sulphur poisoning than the metals of the iron group. Mills et al state (Catal. Rev. 8(2), 159–210, 1973) that catalysts of molybdenum oxides on Al_2O_3 or other support had a rather high activity with respect to conversion of H_2/CO and a selectivity for methane formation of 80–94% and for C_2-hydrocarbon formation of 6–16% under certain circumstances. By sulphiding to molybdenum sulphides the activity decreased, which could be compensated by pressure increase, and the yield of methane became about 94% and of C_2-hydrocarbons 5.9%. By the addition of H_2S to the synthesis feed gas the activity decreased (sulphur poisoning) and at the same time the selectivity changed with a drop of the methane yield at 64.6% and the C_2 yield at 4.1% whereas the formation of $C_3 + C_4$ hydrocarbons increased at 29.4%. The effect of H_2S on the catalyst was reversible and temporary; by its removal from the feed gas stream the activity and selectivity for C returned.

Madan and Shaw state in a review in Catal Review—Sci. Eng. 15(1), pages 69–106 (1977) that FT catalysts based on metallic, oxidic or surface sulphided molybdenum do have decreased activity in the presence of H_2S in the synthesis gas but that the effect is temporary and reversible so that the original activity of the catalyst returns when the sulphur is removed from the feed gas; in this respect molybdenum contracts strongly with nickel and ruthenium bases catalysts in which the poisoning can be considered definitive and lasting because of the strong affinity of these catalysts to sulphur and because the chemisorbed sulphur is in equilibrium with very low concentrations of H_2S. Madon and Shaw also call attention to the fact that a catalyst based on molybdenum sulphides is strongly selective for methane formation (more than 90% of the carbon converted into hydrocarbons is converted into methane), whereas the presence of larger amounts of H_2S in the feed gas causes a change so that nearly 30% is converted into C_{3-4} hydrocarbons and only about 60% into methane; the amount of C_2-hydrocarbons also here becomes very small. From South African patent specification No. 766,137 it is known that vanadium based catalysts for methane formation are rather sulphur resistant. Vanadium has a considerable selectivity for methane formation but it is stated in the said specification that by promotion of a V_2O_5 catalyst on a support of Al_2O_3 with MoO_3 a rather high yield of ethane can be obtained along with a decrease of the methane yield at concentrations of H_2S which are rather low but still much higher than those tolerated by nickel catalysts.

USA patent specification No. 4,151,190 relates to a process for optimizing the yield of saturated and unsaturated C_2–C_4 hydrocarbons. There is used a catalyst of 1–95% by weight of metal, oxide, or sulphide of Re, Ru, Pt or preferably Mo or W, 0.5–50% by weight of hydroxide, oxide or salt of an alkali or alkaline earth metal and at least 1% support, preferably carbon or alumina. The alkaline component and the support further the formation of C_2–C_4 hydrocarbons and the Examples of the specification show that up to 40.5% of the hydrocarbons formed may be C_2 hydrocarbons; this result was obtained with a catalyst of tungsten trioxide and potassium oxide and a support of carbon. The Examples of the specification also show that even small amounts of gaseous sulphur compounds in the feed gas stream alter the selectivity of the catalyst in favour of a high methane formation and usually decrease its activity strongly. By removing the sulphur from the feed gas stream the original activity and selectivity may be recovered.

Accordingly there is still a need for a process and particularly a catalyst which in Fischer-Tropsch syntheses may give a high yield of ethane and/or ethylene and at the same time has a good activity in the presence of sulphur compounds in the synthesis gas so that it becomes possible to save the costs involved in sulphur removal.

It has now surprisingly been found that a small class of catalyst metals, viz. groups V–B and VI–B in the Periodic Table of Elements, in combination with metals of the iron group and supported on certain support materials is sulphur tolerant and can give high yields of C_2-hydrocarbons.

Before describing this in detail, it should be mentioned that catalysts of a similar general type are known for various other purposes. Thus, Swedish patent specification No. 395,676 discloses a catalyst for the shift reaction (5) consisting of an alumina support impregnated with nickel and/or cobalt sulphide, aluminium sulphide and molybdenum sulphide. Swedish patent specification No. 407,680 discloses a process for the oxidation of methanol to formaldehyde using a catalyst obtained by the coprecipitation of dissolved molybdenum and iron compounds, admixing with titanium dioxide, and subsequent drying and calcination. US patent specification No. 2.830.960 discloses a catalyst containing oxides of cobalt and molybdenum on activated alumina supports and useful for hydrocatalytic desulphurisation of hydrocarbons. US patent specification No. 3,132,111 discloses a catalyst for such hydrotreating processes as hydrodesulfurization, hydrofinishing, and hydrocracking of normally liquid petroleum feedstocks; this catalyst consists of an alumina support containing a metal component of the iron transition group, metals from the fifth and sixth periods of group VIb and vanadium, for instance a $CoO.MoO_3.Al_2O_3$ catalyst. US patent specification No. 3,242,101 discloses a nickel-molybdenum-alumina hydrocarbon conversion catalyst, especially showing high activity for desulfurization, denitrogenation and hydrogenation of olefins and aromatics. Finally, US patent specification No. 4,128,505 discloses a catalyst for hydrocarbon desulfurization, denitrogenation and aromatics saturation, which catalyst consists of coprecipitated titania and zirconia, the coprecipitate having associated therewith a mixture of (1) cobalt as metal, oxide or sulphide, and (2) molybdenum as oxide or sulphide.

On this background it is surprising that the process and catalysts described more fully hereinafter are active and highly selective for converting synthesis gas into C_2-hydrocarbons.

In accordance with the present invention, there is provided a process for the preparation of a gas mixture having a high content of ethane and/or ethylene by the catalytic conversion at a pressure of 1–500 bar and a temperature of 200–600°C of a feed gas (synthesis gas) containing hydrogen and carbon oxide and optionally other gases, in which process the feed gas contains, or is caused to contain, at least 10 ppm by volume of one or more gaseous sulphur compounds (calculated at H_2S), and in which the conversion takes place in the presence of at least one metal of group V–B and/or VI–B in the Periodic Table of Elements, in the form of free metal, oxide, or sulphide, and at least one metal of the iron group in the form of free metal, oxide, or sulphide, on a porous oxidic ceramic support.

It has been found that hereby it is possible to obtain a decisive deviation from the Flory distribution and to obtain formation of ethane and/or ethylene as the predominant hydrocarbon component of the product gas with almost complete suppression of the formation of hydrocarbons containing more than 3 carbon atoms. As a rule there is formed considerable amounts of methane and small amounts of C_3-hydrocarbons, mainly propane. The propane may be cracked together with ethane to ethylene in accordance with ordinary practice in industry. The methane or part thereof may be used as an energy source for the cracking of ethane and propane when the product gas is to be used as starting material in petrochemical industries, and the remainder may, for example, be used as fuel, e.g. as substitute natural gas.

The invention also provides a catalyst for the process described. The catalyst consists of (1) at least one metal of groups V–B and/or VI–B of the Periodic Table of Elements in the form of free metal, salt, oxide, or sulphide, and (2) at least one metal of the iron group in the form of free metal, salt, oxide, or sulphide, on (3) a porous, oxidic ceramic support.

As feed gas it is possible to use synthesis gas as described and having varying proportions of hydrogen and carbon oxides and which optionally also contain other gases such as steam, carbon dioxide, methane and small amounts of other hydrocarbons; a content of nitrogen and the inert gases, e.g. for combustion air, will do no harm. The volume ratio hydrogen to carbon monoxide will typically be from about 0.4:1 to about 3:1, preferably close to equal parts of hydrogen and carbon monoxide as is obtained according to the above equation (1). It is a special advantage of the process that it can be carried out at such low relative amounts of hydrogen because thereby firstly labour and costs involved in enriching the synthesis gas with hydrogen are saved, and secondly inherently is closer to a stoichiometric ratio corresponding to longer carbon chains than C_1. In known methanations and FT-syntheses it is usually necessary to have a higher volume ratio (mole ratio) H_2/CO than 1 in order to avoid formation of free carbon on the catalyst according to the Boudouard reaction (9) and consequent destruction of the catalyst. Formation of carbon causes irreversible damages of the catalyst and the Boudouard reaction therefore imposes limitations on the usable process parametres. It has been found that the addition of sulphur stated suppresses the carbon formation and also the formation of graphite (socalled "gum-forming' reaction) which often precedes the carbon formation and consists in a polymerization to form long carbon chains having a low content of hydrogen; see J.R. Rostrup-Nielsen and Karsten Pedersen, J. Catal. 59, 375, 1979.

It is important that sulphur is present in the feed gas in the form of one or more gaseous sulphur compounds because the sulphur establishes the catalytically active sulphide phase of the catalyst metals. The amount of sulphur is not very critical since the amount of sulphur needed to preserve the sulphide phases is very low compared to the amount of gas to become reacted. The minimum amount of sulphur, calculated as H_2S, is about 10 ppm, calculated on the volume of the feed gas. In most cases the practical minimum amount will be 200 ppm by volume and very frequently the content will be of the order of magnitude 1000 to 1000–3000 ppm by volume, calculated as H_2S. The amount will rarely be above 2% by volume of sulphur, calculated as H_2S. This in practice means that it is not at all necessary to remove sulphur from the synthesis gas or from the raw materials such as coal or heavy oil gasified to synthesis gas. The amount of sulphur, however, is not very critical and neither is the kind of the gaseous sulphur compound. As examples may be mentioned hydrogen sulphide, sulphur dioxide, carbonyl sulphide, carbon disulphide, mercaptans, thioethers, disulphides and thiophene. It is not known why the presence of sulphur in such high amounts gives another result than the presence of sulphur in known FT syntheses but it must be assumed that in the process according to the invention a fundamentally different reaction mechanism is involved than the polymerization causing the Flory distribution in the FT synthesis and the deficit in ethane compared to that distribution. There may however be reasons to assume that sulphur-containing carbon compounds, particularly carbon disulphide and carbonyl sulphide occur as intermediates.

The process may be operated over a wide pressure range and the working pressure chosen therefore to a high degree may be determined by such factors as the actual pressure of the available synthesis gas and the pressure desired for the product gas. As will be seen from Example 3 hereinafter, increased pressure will favour the formation of ethane and propane and suppress the formation of olefins and higher hydrocarbons, whereas a low pressure will favour formation of methane. Increased pressure also increases the activity and thus allows a high space velocity (SV, i.e. the velocity of the flow measured as volumes of gas per amount of catalyst per unit time). By balancing the various considerations the process usually will be operated at 1–500 bar, particularly 15–150 bar and preferably 20–100 bar, e.g. about 80 bar which is a frequently occuring coal gasification pressure.

The temperature at the reaction may vary within wide limits and will normally be within the range 200–600°C. A high temperature within the range stated will favour the formation of methane, a lower temperature the formation of ethane and/or ethylene as will be seen from Example 2 hereinafter. It is therefore preferred to keep the temperature as low as consistent with a reasonable rate of reaction, and most often there will be used a temperature in the range 270–400°C, preferably 300–350°C.

The catalyst in the process according to the invention firstly contains at least one metal of group V–B (vanadium, niobium and tantalum) and/or VI–B (chromium, molybdenum and tungsten) in the Periodic Table. It is surprising that molybdenum and vanadium are valuable for forming of C_2-hydrocarbons since as shown hereinbefore they are mainly methane catalysts. The reason probably is that groups V–B and/or groups VI–B metals are accompanied by a catalyst metal of the iron group (iron, cobalt, nickel), since the C_2-formation is hereby favoured at the cost of methane.

The metals in the fresh catalyst are present in the form of free metal, salt, oxide or sulphide. It is not very important which one of these since it must be assumed that salt and oxide because of the presence of the hydrogen in the synthesis gas are duced to free metal and that free metal is sulphided under the influence of the sulphur to sulphide, e.g. mono-, di- or polysulphides and/or oxysulphides, whereby the metals in operation of the process are always present on the catalyst as sulphide. The amount of catalyst metals on the catalyst and the ratio of the two metals or classes or metals (metal of group V–B or VI–B on one hand and of the iron group on the other hand) does not seem very critical. Conveniently the content of metal(s) of group V–B and/or VI–B will be 1–40%, calculated as oxide on the total weight of support plus metal (oxide); and 0.5–10% of metal of the iron group, which will normally constitute a smaller amount than the metals first mentioned, calculated in the same manner. A particularly high sensitivity for C_2-hydrocarbons combined with a high activity is possessed by molybdenum and vanadium, each combined with iron or cobalt.

Optionally an alkali metal or alkaline earth metal compound may be present on the catalyst as promoter but preferably the catalyst does not contain such promoter because it will tend to favour methane in the product gas.

The support material may be chosen amongst a number of support materials which *per se* are common support materials for catalysts.

As examples of suitable support materials may be mentioned titanium dioxide and other oxides of metals of group IV–B in the Periodic Table of Elements, alumina, magnesium aluminium spinel, zirconia, silica, chromium oxide, zinc oxide, burnt clay and H-mordenite.

It has been found that a good activity and selectivity for ethane/ethylene is obtained with TiO_2 and Al_2O_3 for which reason these two and mixtures thereof are preferred according to the invention, and especially the former which gives the highest activity.

The best results with respect to a high selectivity for C_2 and a high activity are obtained if the catalyst is molybdenum sulphide and cobalt sulphide supported on a carrier of porous titanium dioxide.

The reaction is conducted substantially in a manner which is well-known *per se* in Fischer-Tropsch and methanation reactions. Thus the catalyst is placed as a fixed bed or fluid in a reactor into which the synthesis gas is passed via suitable lines, optionally in a preheated condition. The reaction is exothermal and it is therefore necessary to limit the increase of temperature in the reactor, which can be done in various manners. The reactor may be an adiabatic reactor where part of the product gas is recycled and mixed with the feed gas, which is thereby diluted with ensuing limitation of the increase in temperature. Advantageously the reactor may be a cooled reactor wherein the catalyst is placed in tubes surrounded by a cooling medium such as boiling water, boiling Dowtherm® (high-boiling heat transfer media) or flowing gas, or vice versa. Possibly an adiabatic and a cooled reactor may be combined according to similar principles as those described in British patent application No. 79.42734. Irrespectively of which of the principles mentioned there is utilized, the reaction may be operated with or without recycling of part of the product gas; by recycling the temperature increase is reduced. It is preferable to conduct the reaction in a fluidized catalyst bed with cooling.

The main purpose of the product gas is the utilization of the ethane and ethylene formed as a petrochemical raw material. Like propane present they may be sold as such or be subjected to steam cracking especially into ethylene. Part of the methane may be used as fuel for this, or it may be used as substitute natural gas or in another manner as fuel. When the synthesis is conducted with a H_2/CO ratio close to 1 : 1, a considerable part of the product gas, about half thereof, be present as CO_2. This carbon dioxide must be removed if the hydrocarbons are to be separated; it should also be removed from the product gas if it is to be passed a feed gas stream to a steam cracking plant which is used according to wellknown principles for producing ethylene and small amounts of propylene. Carbon dioxide separated off may, if desired, be used as oxidation agent in cases where the synthesis gas has been prepared from natural gas or liquid hydrocarbons. Methane and carbon dioxide separated from the product gas from the process according to the invention may optionally together be passed into a steam reformer and together with more added methane and possibly addition of steam there be converted into synthesis gas for use as feed gas in the process.

If the ratio H_2/CO of the synthesis gas is below 1, as is the case with gases formed by the gasification of coal, the amount of hydrogen necessary for the methanation may be brought about by adding steam to the synthesis gas. Concurrently with the hydrocarbon/methane reaction the catalyst will then cause the formation of the necessary hydrogen via the shift reaction (5).

The catalyst can be prepared in manners well-known *per se*. The support may for instance be formed by precipitation from a suitable solution of a salt of a suitable metal, e.g. titanium or aluminium, drying and optionally calcination, yet with care so that sintring is not caused to such high degree that the pore volume becomes too small. Specific surface areas of the order of magnitude of 10 m^2/g and above are desirable, especially of 20–200, for instance 30–100 m^2/g.

Before drying and calcination the support material is shaped into suitable bodies, for examples pellets, tablets or rings. The shaped bodies thereafter are impregnated with a solution, preferably aqueous solution of suitable compounds of the group V–B and/or VI–B metal and of the iron group metal, either successively or simultaneously, whereby the catalyst metals are deposited on the support as salts. Drying and calcination to convert the metals into oxides thereafter takes place. The bodies thus formed are ready for use, optionally after crushing of large bodies into irregular fragments.

The catalyst may also be prepared by the co-precipitation technique in which salts of the group V–B and/or VI–B metal and the iron group metal as well as salts of a suitable material for the carrier, e.g. magnesium salts, aluminium salts such as aluminium nitrate, silicates, or particularly titanium salts or titanium dioxide are precipitated as hydroxides of, for instance, alkali or alkaline earth metal hydroxide or basic ammonium compounds. The precipitated material is filtered, washed and dried. A subsequent calcination sets the hydroxides into oxide form. The material is shaped into suitable bodies, e.g. granulate, tablets, or rings. An after-calcination may optionally be carried out in order to increase the strength of the catalyst.

Whether the catalyst has been prepared by impregnation or coprecipitation it is ready for use but since the catalyst metals are present as oxide, they may if desired be presulphided to convert the oxides into sulphides (mono-, di-, poly-, and/oxysulphides) but this conversion may also be omitted since it automatically will take place when the catalyst is used according to its purpose in hydrocarbon syntheses in the presence of gaseous sulphur compounds.

In the following the process of the invention will be illustrated by some Examples.

Example 1

Various catalysts were prepared in the following manner:

A ceramic support (Al_2O_3 or TiO_2) was impregnated with the desired metal salts in ammoniacal solution while adding about 2% by volume of alkanol amine to avoid precipitation of metal hydroxides. After air drying overnight there was calcined by heating in air at 550°C for 4 hours whereby salt residues were removed. Hereafter the metals were present on the catalyst as oxides. The catalysts were activated by sulphiding by heating under nitrogen at atmospheric pressure at 300°C and replacing of the nitrogen stream with a stream of 2% hydrogen sulphide in hydrogen. Sulphiding can also take place during the beginning of the conversion reaction or, for instance, with carbon disulphide in hydrogen. The composition of the unused catalysts is seen in Table I hereinafter, the support constituting the entire weight beyond catalyst metal and sulphur.

The testing of the catalysts was carried out with a synthesis gas consisting of 48% by volume H_2, 48% CO, 1% H_2S and 3% Ar, the lastmentioned of which serves as an internal standard, e.g. for determining the gas concentration during synthesis. The temperature of the synthesis gas stream was 300°C, the pressure 30 bar. During the synthesis first and foremost reactions (5), (6), and (7) take place and of those the two lastmentioned are supposed to be irreversible at temperatures below 500°C and to take place via CS_2 and/or COS. Reaction (5) is reversible and faster than the hydrocarbon reactions.

The results appear from Table I. The standard activity is the amount of carbon monoxide that has reacted to form hydrocarbons, expressed as N1 C_1/kg catalyst/hour, the amount of higher hydrocarbons having been calculated as the equivalent amount of methane and added to the amount of methane. The total conversion is the total amount of carbon monoxide which has been converted partly into hydrocarbons, partly into carbon dioxide, expressed in % of the initial amount of CO in the feed gas. The standard activity has moreover been calculated on the basis of the content of catalyst metal so that catalysts having different metal content can be compared directly. The Table also shows the space velocity (SV) in N1 synthesis gas per hour per kg catalyst; the total conversion of CO and the distribution of the hydrocarbons formed in the synthesis, whereby C_n- means paraffins and $C_n=$ olefins; na means not analyzed. The amount of the individual hydrocarbons has been stated in % by weight, calculated on the distribution of the carbon therein; accordingly, the figures show the amount of carbon converted into the hydrocarbon in question, expressed as proportion of the carbon of CO of the feed gas converted into hydrocarbons.

In the Table experiments Nos. 1–9 are in accordance with the invention, the remainder are not. The Table shows that the catalysts which are most selective for ethane are Mo/Co, Mo/Fe, Cr/Co, W/Co and V/Co and the most active amongst these those which contain Mo or V. As support TiO_2 clearly gives higher activity than Al_2O_3 whereas they are equal with respect to selectivity.

As a matter of form it is mentioned that catalysts Nos. 8, 14, and 17 gave a small deposition of carbon (0.2–0.4%) on the catalysts, yet so faint as to be insignificant.

Tabel I

Exp. No.	Type	Catalyst composition, % by weight	Support	Standard activity $NlC_1/h/kg$		SV Nl/h/kg	Total conv. of CO, %	Distribution of carbon converted into hydrocarbons, % by weight							
				Cat.	metal			C_1	C_2^-	$C_2^=$	C_3^-	$C_3^=$	C_4^-	$C_4^=$	C_5^-
1	Mo/Co	12.4 Mo 1.1 Co 5.9 S	Al_2O_3	62.4	460	1650	15.0	37	44		16	3			
2	Mo/Co	13.9 Mo 2.3 Co 6.9 S	Al_2O_3	99.2	610	1650	23.8	27	48		19		5		1
3	Mo/Co	6.6 Mo 4.7 Co 5.3 S	Al_2O_3	32.2	133	1200	11.2	16	47		28		7		2
4	Mo/Co	6.8 Mo 1.2 Co 4.2 S	TiO_2	53.0	662	1700	13.4	32	48	1	15	1	3		
5	Mo/Fe	11.5 Mo 2.8 Fe 5.9 S	Al_2O_3	54.5	380	1600	15.3	23	54		19		3		1
6	Cr/Co	8.7 Cr 2.9 Co 2.0 S	Al_2O_3	7.9	68	7400	0.8	40	47	6	5	2			
7	W/Co	28.0 W 2.2 Co 2.9 S	Al_2O_3	3.5	55	970	6.1	26	52	1	18	1			
8	V/Co	5.9 V 3.5 Co 5.9 S	Al_2O_3	39.0	410	1900	9.3	23	48	1	21	1	5		1
9	V/Fe		Al_2O_3	39.0		1400	9.5	61	33	1	4		1		
10	Mo	12.5 Mo 4.1 S	Al_2O_3	149	845	3200	17.8	47	39		12		2		
11	Mo	6.7 Mo 2.8 S	TiO_2	112	1670	3300	18.6	46	40	1	11	1	1		
12	Cr		Al_2O_3	3.6		3700	1.5	83	15	1	1				
13	W	25.5 W 1.5 S	Al_2O_3	7.7	30	2300	2.7	85	1	8		1	6		
14	V	6.7 V 1.3 S	Al_2O_3	37.6	560	1900	11.3	76	21	1	2		1		
15	Fe	3.4 Fe 1.7 S	Al_2O_3	14.4	480	3400	2.4	48	39		7		7		
16	Co	3.0 Co 1.0 S	Al_2O_3	7.2	240	3700	0.8	12	25	13	17	25	4	3	1
17	Ni	5.8 Ni 2.2 S	Al_2O_3	3.7	64	1300	2.0	24	18	2	24	7	26		

Example 2

The experiments of Example 1 were repeated with some selected catalysts in order to illustrate the influence of the temperature. The reaction conditions were as in Example 1, with the only exception that the temperature was varied. Table II shows that increased temperature favours the formation of methane at the cost of notably C_2, and increases the activity.

Table II

Catalyst No.	Temp., °C	Activity Nl/h/kg metal	Carbon distribution (% by weight) of hydrocarbons								
			C_1	C_2-	C_2=	C_3-	C_3=	C_4-	C_4=	C_5-	C
2	300	610	27	48		19		5		1	
	489	4300	87	12		1					
5	295	380	23	54		19		3		1	
	378	1470	37	47		14		2			
	494	2590	85	14		1					
8	300	410	23	48	1	21	1	5		1	
	403	3560	64	31	1	4					
	501	7780	86	14		1					

Example 3

Increased pressure increases the selectivity for ethane and propane at the cost if methane, pentane and higher hydrocarbons as well as olefins. This is seen from Tables III and IV below, where the experiments were carried out almost as in Example 1, only with the exception that the pressures were varied. Table III shows the results with a catalyst where the ratio Mo to Co was 3.6 and the feed gas consisted of 49% H_2, 49% CO and 2% H_2S. The experiments in Table IV were carried out with the same feed gas as in Example 1 and with a catalyst containing 10.6% Mo, 2.0% Co and 0,08% K.

Table III

Pressure, bar	Act. Nl/h/kg metal	Conv. %	C_1 %	C_2- %	C_2= %	C_3- %	C_3= %	C_4- %	C_4= %	C_5- %
30	8320	9.3	55	39	1	5	na	na	na	na
2	400	2.4	82	8	10	na	na	na	na	na

Table IV

Pressure, bar	Act. Nl/h/kg metal	Conv. %	C_1 %	C_2- %	C_2= %	C_3- %	C_3= %	C_4- %	C_4= %	C_5- %
31.2	350	31.3	29	49	-	18	4	4	-	1
11.0	190	1.2	33	42	3	13	4	4	-	1
4.0	88	0.7	41	28	10	9	5	5	-	2
2.1	47	0.7	45	25	11	7	4	5	-	4

Example 4

In experiments over a long period with a Mo/Co-catalyst (16% Mo, 3.2% Co) it was found that it maintained the activity reasonably well. The hydrocarbon distribution at integral conversion up to about 97% does not show a great difference from the distribution obtained at differential conditions, which partly is connected with the fact that a certain concentrating of the gas takes place during the synthesis. The results of these experiments are shown in Table V below. The feed gas consisted of 48% H_2, 48% CO, 1% H_2S, 3% Ar (all % by vol.). The temperature was 300°C, the pressure varied as shown in the Table. The integral conditions have been underlined in the first column of the Table.

Table V

Time, hours	Pressure bar	Activity, NlC_1/h/kg metal	Total conv. of CO %	Hydrocarbon distribution (weight-% C)								SV Nl/h/ kg cat.
				C_1-	C_2-	C_2=	C_3-	C_3=	C_4-	C_4=	C_5-	
1	30.9	340	12.6	28	48		19			4	na	2300
5.5	30.7	–	50.4	28	47		16			9	na	130
<u>30</u>	30.2	–	73.0	31	47		15			7		130
30.5	29.9	250	9.4	26	47		17			10		2300
<u>73</u>	30.5	–	62	29	47		16			8		160
74	30.5	250	9.6	25	47		17			11		2200
<u>117</u>	29.5	–	84.7	36	46		13			5		70
150	34.6	230	9.4	26	51		19			4	1	2100
151	64.0	330	14.4	24	51		20			5	1	2000
<u>170</u>	64.0	–	96	32	49		16			3		125
<u>194</u>	64.7	–	97	32	47		17			3	1	60
195	64.2	375	11.8	26	50		19			4	1	2400
196	33.0	200	6.6	27	50		19			4	1	2300

Example V

In a similar manner as in Example 4 a V/CO catalyst (5.9% V, 3.5 % Co) was tested at integral conditions. The duration of the experiment was almost 100 hours and the catalyst showed stable activity In contradistinction to the experiment with the Mo/Co catalyst the proportion of hydrocarbons higher than methane increased from about 80 to about 89% at the integral conversion; the increase mainly was in the C_3-fraction.

The results are shown in Table VI which has been set up in analogy with Table V, and the experiments were carried out with the same feed gas. The pressure was almost unvaried.

Table VI

Time, hours	Pressure bar	Activity, NlC_1/h/kg metal	Total conv. of CO %	Hydrocarbon distribution (weight-% CO)								SV Nl/h/ kg cat.
				C_1-	C_2-	C_2=	C_3-	C_3=	C_4-	C_4=	C_5-	
1.5	37.2	550	10	19	45	1	24	1	8		2	2100
7	37.2	–	27	19	47		25		7		1	550
<u>69</u>	37.5	–	49	12	44		32		10		3	90
74	37.2	690	6.5	17	48	2	23	2	6		2	4100
<u>96</u>	38.0	–	51	11	44		32		11		3	80
97	37.0	500	3.6	21	47	2	19	3	4		1	5100

CLAIMS

1. A process for the preparation of a gas mixture having a high content of ethane and/or ethylene by the catalytic conversion at a pressure of 1–500 bar and a temperature of 200–600°C of a feed gas containing hydrogen and carbon oxides and optionally other gases, wherein the feed gas contains at least 10 ppm of one or more gaseous sulphur compounds, calculated as H_2S, and the conversion takes place in the presence of a catalyst containing at least one metal of group V–B and/or VI–B in the periodic Table of Elements in the form of free metal, oxide, or sulphide, and at least one metal of the iron group in the form of free metal, oxide, or sulphide, on a porous oxidic support.

2. A process as claimed in claim 1, wherein the amount of gaseous sulphur compounds in

the feed gas is 200 to 2000 ppm by vol., calculated as H_2S.

3. A process as claimed in claim 1 or claim 2, wherein the convention takes place at 270–400°C and a pressure of 15–150 bar.

4. A process as claimed in claim 3, wherein the conversion takes place at 300–350°C and a pressure of 15–150 bar.

5. A process as claimed in anyone of the preceding claims, wherein the group V–B or VI–B metal is molybdenum or vanadium and the iron group metal is cobalt or iron.

6. A process as claimed in anyone of the preceding claims, wherein the catalyst support is porous titanium dioxide or porous alumina.

7. A process as claimed in anyone of the preceding claims, wherein the catalyst is molybdenum sulphide and cobalt sulphide on a support of porous titanium dioxide.

8. A catalyst for use in the catalytic conversion of synthesis gases containing hydrogen, carbon oxides, a small amount of at least one gaseous sulphur compound and optionally other gases, which consists of at least one metal of groups V–B and VI–B of the Periodic Table of Elements in the form of free metal, salt, oxide, or sulphide, and at least one metal of the iron group in the form of free metal, salt, oxide, or sulphide, on a porous oxidic support.

9. A catalyst as claimed in claim 8, wherein the group V–B or VI–B metal is molybdenum or vanadium and the iron group metal cobalt or iron.

10. A catalyst as claimed in claim 8 or claim 9, wherein the support is porous titanium dioxide or porous alumina.

11. A catalyst according to anyone of claims 8–10, which consists of molybdenum sulphide and cobalt sulphide on a support of porous titanium dioxide.

12. A process substantially as herein described with particular reference to Experiments Nos. 1–9 in Example 1 and in Examples 2–5.

13. A catalyst substantially as herein described with particular reference to Experiments Nos. 1–9 in Example 1 and in Examples 2–5.

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