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(54) Methanation process and catalyst

(57) Catalysts for the methanation of a synthesis gas containing carbon oxides, hydrogen and optionally other gases in the presence of one or more gaseous sulphur compounds, normally in an amount of at least 10 ppm preferably at least 200 ppm by volume, calculated as H_2S, comprise a vanadium and/or molybdenum component, which during the process is present as one or more sulphides, on a support comprising at least 30% by weight of an oxide of a metal of group IVB, notably titanium dioxide.

The selectivity for methane formation may be further improved by promoting the catalyst with compounds, especially sulphides of metals of groups IA, IIA and/or IIIB, particularly cerium.

SPECIFICATION

Process and catalyst for the production of a gas mixture having a high content of methane

This invention relates to a process and catalyst for the preparation of a gas mixture having a high content of methane; more particularly, it relates to a process for the preparation of a gas mixture having a high content of methane by the catalytic conversion of a synthesis gas containing hydrogen and carbon oxides and optionally other gases.

Synthesis gas is prepared predominately by gasification by steam treatment of coal or heavy petroleum fractions, in the firstmentioned case by the reaction

(1) $C + H_2O \rightarrow CO + H_2$

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 and petroleum gasification processes involve the formation of higher amounts of methane, other hydrocarbons, tar, etc. During gasification a small amount of 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) $CO + 3H_2 \rightleftarrows CH_4 + H_2O$

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

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

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

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

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

Methane may also be formed as a by-product in the Fischer-Tropsch synthesis (hereinafter also abbreviated to the FT-synthesis):

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

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

and possibly also

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

The FT-synthesis predominately produces higher hydrocarbons and is especially employed for the preparation of motor fuel and other liquid fuels. By a suitable choice of catalyst and process conditions it may give a rather high proportion of methane.

A good review of methanation processes and catalysts is given by Mills et al. in Catalysis Review 8(2), 159–210 (1873).

The best catalyst for the preparation of methane from carbon oxides and hydrogen according to reactions (2), (3), and (4) is nickel on a support which normally consists of one or more refractory oxides e.g. chromium oxide, γ-alumina, magnesium oxide, or silica, or mixtures thereof. Nickel may be present as oxide but during the methanation process in the strongly reducing environment it is predominately present as free metal. Nickel is still the most important catalyst for methane production but nickel catalysts have the drawback that they are exceedingly sensitive to sulphur poisoning. The feed gas for a nickel catalyzed methanation process must to a very high degree be freed from sulphur, specifically from gaseous sulphur compounds. In practice the sulphur content is kept below 0.1–0.01 ppm by vol., dependent on the content of H_2 in the synthesis gas and the temperature at the inlet to the catalyst bed. The sulphur coverage on the catalyst decreases with decreasing value of the ratio H_2S/H_2 and increasing temperature (see J. R. Rostrup-Nielsen, "Steam Reforming Catalysts", Teknisk Forlag, Copenhagen 1975). The methanation activity decreases strongly with increased sulphur coverage (see J. R. Rostrup-Nielsen and Karsten Pedersen, J. Catal. 59, 395 pp, 1979) for which reason it is normally desired that the sulphur coverage should be below 10%. Since the feed materials from which the feed gas is prepared, coal or heavy fuel oil which is gasified, as a rule are strongly sulphur-containing the feed gas for the methanation reaction must be subjected to a sulphur purification process. The majority of metals have been used as Fischer-Tropsch catalysts, either as such or as oxides or hydroxides or possibly in a surface-sulphided form, but all the known ones are sulphur sensitive to a higher or lesser degree. This especially holds true for the important methanation and FT catalysts which are based on iron, cobalt or ruthenium.

Karla Wencke showed (Freiburger Forschungsh., A151, 11–29 (1960)) that molybdenum as free metal or oxide catalyzed the methanation of a synthesis gas with CO and H_2, that it was advantageous to operate in fluid bed and that the activity of the Mo-based catalysts for methane production decreased when small amounts of sulphur compounds were present in the synthesis gas. Madan and Shaw state in a reviewing paper in Catal. Review-Sci Eng. 15 (1), pages 69–106 (1977) that FT-catalysts based on metallic, oxidic or surface-sulphided molybdenum do get reduced activity by the presence of H_2S in the synthesis gas but that the effect is temporary and reversible so that the initial activity of the catalyst returns when sulphur is removed from the feed gas stream; in this respect molybdenum is in strong contrast to, for example, nickel and ruthenium based catalysts in which the poisoning can be considered definitive and lasting because of strong affinity of these catalysts to sulphur and because the chemisorbed sulphur is in equilibrium with very low concentrations of H_2S. Madan and Shaw also call attention to the fact that a catalyst based on molybdenum sulphide is strongly selective for methane formation (more than 90% of the carbon converted into hydrocarbons are converted into methane) but that the presence of larger amounts of H_2S in the feed gas causes a shift so that almost 30% are converted into C_{3-4} hydrocarbons and only about 60% into methane.

From South African patent specification No. 766,137 it is known that i.a., thoria, zirconia, hafnia and titania are FT-catalysts and comparatively sulphur-resistant. However, their catalytic activity is low and moreover they are selective to a considerable degree for forming aromatic and other higher hydrocarbons. The specification first and foremost is concerned with the use of vanadium based catalysts for making methane and various forms of vanadium have been tested. It was found that a pre-sulphided catalyst of V_2O_5 on a zeolite support had higher activity and selectivity for the formation of methane with the presence of up to 2% by vol. of H_2S in the feed gas than without that presence. Similar results were obtained with pure vanadium oxide (without support) and a similar yet improved activity was obtained with a high concentration of vanadium oxide on a support of alumina.

However, the activity of vanadium catalysts for methanation is not very high and in order to obtain a reasonable satisfactory activity a high concentration of vanadium on the catalyst is necessary, be it as oxide or sulphide. Correspondingly, known molybdenum catalysts are not satisfactory for methane production, partly because the activity is not satisfactory, partly because the activity usually decreases by the presence of sulphur, and particularly because known molybdenum catalysts favour higher hydrocarbons, notably C_{3-4} hydrocarbons, at the expense of methane.

Vanadium and molybdenum based catalysts are known for various other purposes. Thus, US patent specification No. 2,605,238 discloses a catalyst composition for use in vapor phase processes for the partial oxidation of organic compounds, e.g. for the manufacture of maleic anhydride from butylene; this catalyst consists essentially of molybdenum trioxide and amorphous titanium dioxide. US patent specification No. 3,464,930 disclosed a catalyst for the gas phase oxidation of armotic or unsaturated aliphatic hydrocabons into carboxylic acid; it consists of an inert non-porous carrier coated with a mixture of vanadium pentoxide and titanium dioxide. US patent specification No. 3,565,829 discloses a supported catalyst for oxidation reactions, e.g. the oxidation reactions, e.g. the oxidation of o-xylene into phthalic anhydride, which comprises a non-porous support material and thereon a thin layer of an active composition consisting of a mixture of vanadium pentoxide, titanium dioxide and at least one oxide of aluminium, lithium and/or zirconium. German published patent application No. 24 36 009 discloses a supported catalyst for the oxidation of o-xylene or naphthalene into phthalic anhydride, comprising an inert, non-porous support with a thin coating of vanadium pentoxide, titanium dioxide and rubidium and/or cesium.

None of these processes and catalysts are usable for methane production and hence there still exists a need for providing a synthesis gas conversion which utilizes a catalyst which is fully sulphur-resistant, which is highly selective for producing methane and which has a high activity.

It is the object of the invention to meet this need. In accordance with the present invention, there is provided a process for the preparation of a gas mixture having a high content of methane by the catalytic conversion at a pressure of 1–150 bar and a temperature of 250–850°C of a synthesis gas (feed gas) containing hydrogen and carbon oxides and optionally other gases, wherein the feed gas contains at least 10 ppm (calculated as H_2S) of one or more sulphur compounds and the conversion takes place in the presence of a catalyst containing vanadium and/or molybdenum in the form of free metal, salt, oxide, or sulphide, on a porous, oxidic, support consisting of or containing at least 30% by weight of one or more oxides of one or more metals belonging to group IV on the Periodic Table of Elements. It has been found that thereby it is possible to obtain a product gas having a high proportion of methane and a special advantage is that a high proportion of the higher hydrocarbons resulting in the product gas is C_2-hydrocarbons.

The invention also relates to the catalyst for use in the process. In accordance with the invention this catalyst comprises vanadium and/or molybdenum in the form of free metal, salt, oxide, or sulphide on a porous oxidic support at least 30% by weight of which is one ore more oxides of metals belonging to group IV–B in the Periodic Table. Advantageously the catalyst is promoted with one or more salts, hydroxides, oxides or sulphides of one or more metals belonging to groups I–A, II–A and/or III–B in the Periodic Table. Preferably the catalyst is vandium sulphide promoted with cerium sulphide on a support substantially only consisting of porous titanium dioxide.

It has been found that the catalysts described possess high activity and high selectivity for methane formation. They do not only catalyze reactions (2)–(4) and/or (6)–(8) but also the shift reaction (5). By the conversion a high proportion of methane result in the product gas but part of the carbon monoxide converted is converted into higher hydrocarbons. It is surprising and a special advantage of the present process that the proportion converted into higher hydrocarbons is preferentially converted into C_2-hydrocarbons (ethane and ethylene). The reason why this circumstance is surprising is as follows:

The Fischer-Tropsch 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 on simplified kinetic assumptions. It can be shown that the Flory distribution theoretically can give a maximum yield of about 27% by weight of ethane and/or ethylene, calculated on the amount of carbon in the synthesis gas converted into hydrocarbons. In practice the yield of C_2-hydrocarbons in FT syntheses is almost always considerably below that theoretically 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. But using the abovementioned catalysts the ethane and ethylene content can constitute almost the entire non-methane amount of hydrocarbons in the product gas and it can often be above the theoretical maximum amount of C_2 according to the Flory distribution.

As mentioned the methane first and foremost is to be used as fuel, e.g. SNG, or as part of energy transport systems, and small amounts of higher hydrocarbons are permissible or even desirable since small amounts hereof are often present in natural gas; they increase the calorific value of the gas. Larger amounts of higher hydrocarbon particularly C_2-hydrocarbons in the product gas as a rule will not be desired. If such larger amunts are formed by the present process, however, they may be separated off and constitute or be converted into a valuable raw material for organic syntheses in the petrochemical industry. Ethylene is much used as such and ethane and C_3-hydrocarbons an easily by known technique be cracked to ethylene in high yield.

As feed gas there can be employed synthesis gas having varying contents of hydrogen and carbon oxides, mainly in the form of carbon monoxide, and optionally also containing other gases such as steam, methane and small amounts of other hydrocarbons; contents of nitrogen and the inert gases, for example from combustion air, will not do any harm. The volume ratio of hydrogen to carbon moonoxide will typically be from about 0.4:1 to about 3:1, preferably close to equal part of hydrogen and carbon monoxide as is obtained according to equation (1) shown hereinbefore. It is a special advantage of the process that it can be carried out at such low amounts of hydrogen since thereby one saves the work and expenditure involved in enriching the synthesis gas with hydrogen. In known methanations it is usually necessary to maintain a higher volume ration (mole ratio) H_2/CO than 1 in order to avoid the formation of free carbon on the catalyst according to the exothermal Boudouard reaction

(9) $2CO \rightarrow C + CO_2$

The carbon formation causes irreversible damages on the catalyst and the reaction therefore imposes limitations of the usable process parameters. It has been found that the sulphur addition 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 Rostrup-Nielsen and Karsten Pedersen, loc.cit.).

It is important that sulphur is present in the synthesis gas (feed gas) in the form of one or ore gaseous sulphur compounds because the sulphur establishes the catalytically active sulphide phase of the catalyst metal. The amount of sulphur is not very critical since the amount of sulphur needed to preserve the active sulphide phases is very low compared to the amount of gas to be reacted. The minimum amount of sulphur is about 10 ppm, calculated as H_2S on the volume of the feed gas. In most cases the practical minimum amount will be 200 ppm by vol. and very frequently the content will be 1000 ppm by vol. or more e.g. 1000–3000 ppm by volume, still calculated as H_2S. Increased amounts of sulphur can be considered advantageous for the activity and there is no critical upper limit for the content of gaseous sulphur compounds; in practice, however, it will rarely exceed about 2% by volume, calculated as hydrogen sulphide. 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.

The methanation of the synthesis gas may take place at low pressure, such as atmospheric pressure, but will in practice always be carried out at elevated pressure. The working pressure is not critical and will mainly be determined by practical considerations such as the pressure at which the gasification is carried out and hence the synthesis gas formed, which will frequently be of the order of magnitude 5–150 bar, as well as the pressure at which it is desired to use the methane formed. Under otherwise equal conditions an increase in pressure promotes the formation of C_2- and higher hydrocarbons, decrease in pressure the formation of methane. It will normally be expedient to operate the reaction at a pressure of 15–150 bar, especially 20–100 bar, although both lower and higher pressure may come into question.

The temperature is significant for the process. It cannot be carried out at a reasonable rate of reaction at temperatures below 250°C but in practice considerably higher temperatures will be preferred. Methane formation by reactions (2)–(4) as well as the formation of higher hydrocarbons by reactions (6)–(8) are exothermal and it will frequently cause greater difficulties to keep temperature down than up. High temperature favours the formation of methane, lower temperature the formation of higher hydrocarbons. With regard partly to this, partly to the stability of catalysts and reactors at higher temperatures it is normally preferred according to the invention to carry out the methanation at a temperature of 250–850°C, preferably 300–700°C, for example 350–600°C.

The metal, vanadium and/or molybdenum, is present in the freshly prepared catalyst in the form of free metal, salt, oxide or sulphide. It is not very important which of these since it must be assumed that salt and oxide are reduced to free metal under the presence of the hydrogen in the synthesis gas, and the free metal is sulphided under the influence of the sulphur compound in the synthesis gas to some sulphidic compound, mono-, di- or polysulphide so that the metal during the process itself always is present as sulphide.

The amount of catalyst metal is not critical but usually is in the range 1–50% by weight, calculated as metal oxide on the weight of the entire catalyst, calculated as metal(s) or metal compound(s) and support. In practice the amount of catalyst metal most often will be of the order of magnitude 3–40%, preferably 5–30%, calculated in the same manner. If the catalyst is promoted as discussed later in this specification, the amount of vanadium and/or molybdenum, calculated in the manner stated, is below the highest of the above values.

The vanadium and/or molybdenum compound and the optional promoter are deposited, preferably by impregnation, on a porous support which as mentioned is constituted by or to a considerable degree consists of one or more oxides of one or more metal belong to group IVB, i.e. titanium, zirconium, or hafnium. It has been found that such oxides increase the activity of the catalyst significantly without substantially reducing its selectivity for methane formation. It is preferred that the support exclusively consists of one or more oxides as stated but it is indeed sufficient that a substantial part is such materials, whereby it is meant that at least 30% of the carrier is one or more such oxides. The remainder of the support may consist of traditional support materials for methanation catalysts such as alumina, silica, magnesia, magnesium aluminium spinel. As a support especially titanium dioxide, TiO_2, is preferred, either alone or together with other oxides since firstly it is readily available and secondly gives the catalyst a high activity.

It is known to promote FT and methanation catalysts with compounds of alkali or alkaline earth metals whereby one especially suppresses graphite and carbon formation reactions as mentioned hereinbefore. It has been found that it may be particularly advantageous to promote the catalyst employed in the present process with one or more compounds, particularly salts, oxides, hydroxides or sulphides, of one or more metals of groups IA (the alkali metals), IIA (the alkaline earth metals) or IIIB (Sc, Y, the actinides and the lanthanides). It has been found that such a promoter increases the selectivity for methane formation. If such a promoter is present, it should preferably constitute a lesser proportion of the entire catalyst weight than the vanadium or molybdenum component.

The catalyst is prepared by a technique known *per se*. The support may for instance be formed by precipitation from a suitable solution of a salt or other compound of the group IVB metal, drying and optionally calcination, yet with care so that sintring is not caused to such high degree that the pore volume and thereby the specific inner surface area becomes too small. Specific surface areas of the order of magnitude of 10 m^2/g and above are desirable, especially of 20–300, for instance 100–200 m^2/g.

Before drying and calcination the support material is shaped into suitable bodies, for examples pellets, tablets or rings. The bodies formed thereafter are impregnated with a solution, preferably aqueous solution of a suitable compound of vanadium and/or molybdenum, whereby the catalyst metal is deposited on the support. Drying and calcination to convert the catalyst metal into oxide thereafter takes place. The bodies thus formed are already for use; large bodies may, however, if desired prior to or after the impregnation be crushed to irregular fragments.

The finished catalyst, in which the catalyst metal is present as oxide, may, if desired, be pre-sulphided to convert the oxides into sulphides (mono-, di-, poly-, and/or 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 synthesis in the presence of gaseous sulphur compounds. The pre-sulphiding can, for instance, be carried out with hydrogen sulphide or carbon disulphide in hydrogen.

The catalyst may also be prepared by a co-precipitation technique in which metal salts of vanadium and/or molybdenum together with salts of oxides of the group IVB metal, notably titanium salts or titanium dioxide are precipitated as hydroxides by the addition of, for instance, alkali metal hydroxide 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, which is thereupon optionally sulphided as described above.

According to the invention the catalyst particularly advantageously contains vanadium in the form of free metal, salt, oxide or preferably sulphide on a support substantially consisting of porous titanium dioxide. By "substantially" in this connection is meant that small amounts of impurities may be present, originating from the titanium raw material or the salts or other compounds from which the support material has been precipitated during the preparation.

Very advantageously according to the invention the catalyst consists of one ore more sulphides of vanadium and one or more sulphides of cerium on a catalyst substantially consisting of porous titanium dioxide.

The methanation reaction is conducted substantially in manners which are well-known *per se* in Fischer-Tropsch and methanation reactions. Thus the catalyst is placed preferably as a fixed bed 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 temperature increase 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 temperature increase. 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 adiabatisk 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 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 also possible to conduct the reaction in a fluidized catalyst bed with cooling.

The main purpose of the product gas is utilization of the methane formed a fuel, notably SNG. Small amounts of higher hydrocarbons, especially ethylene as well as particularly ethane and propane after steam cracking into ethylene may be used as a petrochemical raw material. When the synthesis is carried out with a H_2/CO ratio close to 1:1 a substantial part of the product gas, about half, will be present as CO_2. This carbon dioxide must be removed if the hydrocarbons are to be separated, and when the main part is to be used as fuel. The separation of carbon dioxide takes place by well-known methods and does not form any part of the invention. Separated carbon dioxide may if desired be used as oxidation agent in cases where the synthesis gas has been prepared from natural gas or liquid hydrocarbons.

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

In the following the process of the invention will be illustrated by an Example.

Example

Catalysts according to the invention and comparison catalysts were prepared in the following manner:

Ceramic supports of TiO_2 and for comparison of Al_2O_3 in the form of irregular small particles of the size (determined by sieve) 0.5–1 mm and a specific surface area of about 200 m^2/g were impregnated with either ammonium vanadate or ammonium molybdate in ammonical 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% by volume of hydrogen sulphide in hydrogen. The content of V or Mo on 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 pressure of the synthesis gas stream was 30 bar and space velocities of 2000–3000 Nl/h/kg were used.

Two series of experiments were carried out under the conditions described. The first series was carried out at a temperature of 300°C and served at determining the standard activities. The second series of experiments was carried out at 450°C and served at determining the distribution of hydrocarbons.

The results appear from the Table below. 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 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 distribution of the hydrocarbons formed in the synthesis, whereby C_1- means methane, C_2- ethane, and C_3- propane. 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 experiments also other hydrocarbons were formed, specially ethylene, but in very small amounts.

In the Table experiments Nos. 1, 3 and 4 are in accordance with the invention, Nos. 2 and 5 comparison experiments with a support of alumina. The Table shows that replacement of the alumina support with a titanium dioxide support roughly speaking does not influence the selectivity for methane formation but increases the activity, relative to the amount of V or Mo. For a catalyst containing vanadium the activity was increased 3, 5 times and with molybdenum the increase was 5 times. The Table also shows that almost the entire amount of hydrocarbons beyond methane occurs as ethane, especially when using the vanadium catalysts, and that the hydrocarbon distribution thus is radically different from the Flory distribution and especially from the distribution normally obtainable in FT syntheses.

In the experiments small amounts of C were formed on the catalysts but the amount was so small (about 0.2%) that it did not have any significance.

During the synthesis and foremost reactions (2), (3), (4), and (5) take place and furthermore (6) and (7), which 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.

TABLE

Catalyst No.	% V or Mo	Support	Standard activity N1C$_1$/h/kg		Distribution of carbon converted into hydrocarbons, % by weight + +		
			cat.	metal	C$_1$ –	C$_2$ –	C$_3$ –
1	6,2 V	TiO_2	183	2950	94	6	<1
2	6,7 V	Al_2O_3	58	850	96	4	<1
3	7,9 Mo	TiO_2	320	4100	88	11	1
4	6,3 Mo	TiO_2/Al_2O_3 +)	182	2890	90	10	<1
5	12,5 Mo	Al_2O_3	149	815	93	7	<1

+) The ratio TiO_2 to Al_2O_3 in this suport is 1:1 by weight
+ +) Rounded to whole numbers

CLAIMS

1. A process for the preparation of a gas mixture having a high content of methane by the catalytic conversion at a pressure of 1–150 bar and a temperature of 250–850°C of a synthesis gas mixture 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 vanadium and/or molybdenum in the form of free metal, salt, oxide, or sulphide, on a porous oxidic support consisting of or containing at least 30% by weight of one or more oxides of one or ore metals belonging to group IVB in the Periodic Table of Elements.

2. A process as claimed in Claim 1, wherein the amount of gaeous 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 conversion takes place at a temperature of 300–700°C and a pressure of 15–150 bar.

4. A process as claimed in claim 3, wherein the conversion takes place at a temperature of 350–600°C and a pressure of 20–100 bar.

5. A process as claimed in anyone of the preceding claims, wherein the catalyst substantially consists of vanadium or molybdenum in the form of salt, oxide, free metal or sulphide deposited on a support substantially consisting of porous titanium dioxide.

6. A process as claimed in anyone of the preceding claims, wherein the catalyst is promoted with a salt, hydroxide, oxide, or sulphide of one or more metals belonging to grup I–A, II–A, and/or III–B of the Periodic table of Elements.

7. A catalyst for use in the catalytic conversion synthesis gases containing hydrogen, carbon oxides, a small amount of at least one gaseous sulphur compound and optionally other gases, which comprises vanadium and/or molybdenum in the form of free metal, salt, oxide, or sulphide on a porous oxidic support at least 30% by weight of which is one or more oxides of metals belonging to group IVB in the Periodic Table.

8. A catalyst as claimed in claim 7, which comprises vanadium and/or molybdenum in the form of free metal, salt, oxide or sulphide on a support substantially consisting of porous titanium dioxide.

9. A catalyst as claimed in claim 7 and claim 8, which is promoted with a salt, hydroxide, oxide, or sulphide of one or more metals belonging to groups I–A, II–A, and/or III–B in the Periodic Table of Elements.

10. A process substantially as herein described with specific reference to Experiments 1, 3 and 4 in the Example.

11. A catalyst subststantially as herein described with specific reference to experiments 1, 3 or 4 in the Example.

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