

Hydrocarbon production

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(54) **Hydrocarbon production**

(57) Hydrocarbons are obtained by contacting a hydrogen containing moiety with a catalytically active support containing carbonaceous material deposited thereon wherein the carbonaceous material is obtainable by subjecting methane to a decomposition treatment in the presence of said support at a temperature not exceeding 600°C. Moiety source is e.g. a hydrogen stream from a refinery or can be molecular H₂. Support may be of SiO₂, Al₂O₃ or their mixture and may also contain Ru, Ir, Rh, Ni etc. as the catalyst.

PROCESS FOR THE PRODUCTION OF HYDROCARBONS
FROM METHANE

The present invention relates to a process for the production of hydrocarbons from methane and to hydrocarbons thus obtained.

It is well known that methane is both a very abundant material as well as a very stable molecule which is difficult to convert
5 into other hydrocarbonaceous materials. Whilst it is well known to react methane with air for domestic and industrial heating and also well known to react methane with steam to produce synthesis gas in the so-called steam-methane reforming process, a conversion process which catalysis has still to discover is a low temperature route to
10 convert methane into higher hydrocarbons.

Thusfar only an indirect route from natural gas to higher hydrocarbons is known whereby natural gas is firstly converted into synthesis gas at high temperature whereafter hydrocarbons are produced in a low temperature exothermic process from synthesis
15 gas. Also, the direct conversion of methane to acetylene or benzene by pyrolysis is known but such processes are only operable at very high temperatures, well above 900 °C.

Only when methane has been activated on a molybdenum-containing catalyst by photo-chemisorption, products like ethylene,
20 ethane and propane can be detected after desorption of the methane activated at low pressure and at room temperature (B.N. Shelimov and V.B. Kazansky, J. Chem. Soc., Faraday Trans. I, 83, (8), 2381 (1987)). The desorption of benzene at 147 °C under ultra-high vacuum conditions from the decomposition of preadsorbed methane on
25 a Ni (111) single crystal surface by a krypton bombardment at - 226 °C has been reported by Q.Y. Wang, A.D. Johnson, K.J. Maynard and S.T. Ceyer in J. Am. Chem. Soc., 111, 8748 - 8749 (1989).

It will be clear from the foregoing that the conversion of methane into (lower) hydrocarbons under conditions which might lend themselves attractive from an industrial point of view has not been found to date.

5 The abundance of natural gas as starting material is of course a large incentive to search for such processes but the stability of the methane molecule has been and still is a genuine obstacle which has only been attacked by using very high (pyrolysis) temperatures or very specific and industrially unattractive means like photons
10 or krypton bombardments.

Surprisingly, it has now been found that methane can be converted catalytically into (lower) hydrocarbons in the presence of hydrogen under rather mild conditions.

15 The present invention therefore relates to a process for the production of hydrocarbons by contacting a hydrogen containing moiety with a catalytically active support containing carbonaceous material deposited thereupon, wherein the carbonaceous material is obtainable by subjecting methane to a decomposition treatment in the presence of said support at a temperature not exceeding 600 °C.

20 The process according to the present invention is preferably carried out when a carbonaceous support is used which has been obtained by subjecting methane to a decomposition treatment at a temperature in the range between 200 °C and 550 °C.

25 It should be observed that it is known from various publications that carbonaceous intermediates can be deposited catalytically on supports from carbon monoxide as starting material. Reference is made in this respect to a recent article by T. Koerts and R.A. van Santen in *Catalysis Letters*, 6 (1990), pages 49 - 58.

30 It is most surprising, however, that methane being notoriously more difficult to decompose than carbon monoxide can be converted at all into carbonaceous material(s), in particular at temperatures which are rather mild compared with the pyrolysis temperatures referred to hereinabove. It is even more surprising, as will be exemplified hereinafter, that the the yield of products is rather
35 high; apparently the amounts of attractive carbonaceous material

obtainable by the decomposition of methane in accordance with the present invention are much more favourable than obtainable starting from carbon monoxide.

5 The formation of carbonaceous material on the support which is then subjected to contact with a hydrogen containing moiety to produce hydrocarbons is suitably carried out by using a support containing one or more metals or metal compounds of Group VII and/or Group VIII of the Periodic Table of the Elements. Preferably, use is made of one or more metal (compounds) of
10 ruthenium, rhodium, iridium, platinum, rhenium, cobalt or nickel. Most preferred is the use of supports containing ruthenium, cobalt or one or more ruthenium and/or cobalt compounds.

Suitably, the formation of carbonaceous material is effected by subjecting methane to a decomposition treatment at a temperature
15 not exceeding 600 °C in the presence of a catalytically active support comprising one or more refractory oxides, crystalline (metallo) silicates or metallophosphates or combinations thereof. Suitably, use is made of a support comprising silica, alumina or silica-alumina.

20 The amount of catalytically active material on the support in order to effect formation of carbonaceous material(s) is not critical and can vary within wide ranges. Suitably, the amount of catalytically active metal(s) and/or metal compound(s) ranges from 0.1 - 30% wt, calculated on total support. Preference is given to
25 amounts in the range of from 0.5 - 15 % wt, calculated on total support.

The contacting between the hydrogen containing moiety and the catalytically active support containing carbonaceous material(s) is carried out at a temperature up to 250 °C. Preference is given to
30 carrying out the contacting between the hydrogen containing moiety and the catalytically active support containing carbonaceous material(s) at a temperature in the range between ambient temperature and 150 °C, in particular between ambient temperature and 100 °C.

Suitably, the hydrogen containing moiety to be used in the process according to the present invention comprises at least 70% by volume of molecular hydrogen. Normally, refineries produce hydrogen streams which can be suitably applied. It is of course
5 also possible to use molecular hydrogen as such. The process according to the present invention can be carried out suitably at atmospheric pressure but higher pressures, e.g. pressures up to 10 bar can also be suitably applied.

If desired, a promoter can be used in addition to the catalytically active support. Suitable promoters include one or more of
10 Group IA oxides, magnesia, zirconia and titania. Good results have been obtained using zirconia as a promoter, in particular when cobalt is used as the Group VIII metal.

The amount of promoter(s) used is not critical and ranges
15 suitably from 0.1 to 10 times the amount of the sum of the catalytically active metal(s) and compound(s) thereof as present on the support.

When contacting the carbonaceous material(s) obtained by subjecting methane to a decomposition treatment at a temperature
20 not exceeding 600 °C in the presence of a support containing one or more metal(s) and/or metal compound(s) of Group VII and/or Group VIII of the Periodic Table of the Elements with a hydrogen containing moiety such as molecular hydrogen, the products formed include methane (having been reformed by hydrogenating the active
25 carbonaceous material apparently containing a fair amount of active carbon itself), ethane, propane, butane and traces of higher hydrocarbons. Depending on the particular combination of Group VII and/or Group VIII metal (compound(s)), support and optionally promoter used, the yields of the various lower hydrocarbons will
30 vary. It has been found that the use of cobalt, ruthenium and nickel favours the formation of propane and butane whereas the use of rhodium, platinum and rhenium appears to favour the formation of ethane. The use of promoters may further enhance the selectivity towards propane and butane.

Without wishing to be bound to any particular theory it would appear that the decomposition of methane in accordance with the present invention results in the formation of a fair amount of a rather active form of carbonaceous material which lends itself to the production of lower hydrocarbons, which moreover can be produced at rather low temperatures.

It has also been found that it is possible to adsorb hydrocarbonaceous material(s) on the catalytically active support already containing carbonaceous material(s) obtained by the decomposition of methane in accordance with the present invention and to subject the catalytically active support containing both carbonaceous material(s) and adsorbed hydrocarbonaceous material(s) to contact with a hydrogen containing moiety, in particular molecular hydrogen. Apart from the production of lower hydrocarbons from carbonaceous material(s) as discussed hereinbefore it appears that also propane is formed when carbonaceous material(s) formed in accordance with the present invention and adsorbed ethylene are subjected to the treatment with hydrogen. Similarly, butane is co-produced when propylene is adsorbed in stead of ethylene. It is also possible to adsorb aromatically unsaturated materials such as benzene and toluene and to subject the support containing adsorbed aromatically unsaturated material(s) together with carbonaceous material(s) already deposited to the treatment with hydrogen.

Such reactions can already be achieved when the hydrogenation is carried at a temperature of 30 °C. Good results have been obtained in particular when cobalt or ruthenium are used as the Group VIII metals and when ethylene is the hydrocarbon which has been adsorbed on the catalytically active support already containing carbonaceous material(s). The yields, calculated on ethylene adsorbed were well above 50%.

It would appear that under such circumstances the net effect of the process according to the present invention amounts to the production in a two stage process of the next homologue of a lower hydrocarbon by adding methane (via its indirect carbonaceous

material decomposition product) to it : propane being produced from methane (or carbonaceous material and hydrogen) and ethylene.

5 The temperature at which the adsorption of (aromatically) unsaturated material(s) is readily carried out is normally below 150 °C, preferably at a temperature below 50 °C. Lower olefins, in particular ethylene and/or propylene can be suitably adsorbed to serve as additional starting materials in the contacting of the carbonaceous material(s) with hydrogen.

10 The contact between the catalytically active, carbonaceous material(s) bearing, lower hydrocarbon adsorbed support material(s) and the hydrogen containing moiety is suitably carried out at a temperature below 200 °C, in particular below 150 °C.

15 The hydrocarbons produced by the present process can suitably be used in many applications, e.g. as chemical feedstocks, optionally after further separation and/or purification treatments.

The present invention will now be elucidated with the following Examples.

Example 1

a) Preparation of the catalyst.

20 A cobalt on silica catalyst was prepared by incipient wetness impregnation of silica (Grace 322, surface area 240 m²/g) with an aqueous solution of Co(II) (NO₃)₂, followed by drying at 110 °C. Before using the catalyst in the decomposition of methane it was subjected to a treatment in hydrogen at a temperature between 313
25 °C and 560 °C. The ready catalyst contained 10 % by weight of cobalt, calculated on carrier. The metal average particle diameter as measured with TEM (Transition Electron Microscope) amounted to 8.5 nm.

b) The decomposition of methane.

30 The decomposition of methane was carried out using 300 mg of the catalyst as prepared under a) in a plug flow reactor using a flow of helium containing 0.5% vol of methane. The decomposition experiment was carried out at a temperature of 461 °C using a three
35 minutes pulsed flow. After the methane decomposition the catalyst was cooled within 100 seconds to below 150 °C to avoid ageing of the surface carbonaceous species.

c) The hydrogenation of the carbonaceous deposits.

The hydrogenation experiment was carried out at a temperature of 95 °C using 22.4 ml/min of molecular hydrogen at 1 atmosphere (calculated under conditions of standard temperature and pressure).

5 The selectivity towards hydrocarbons was measured by means of GLC (gas-liquid chromatography) and amounted to CH₄ : 79.6%, C₂H₆ : 11.3%, C₃H₈ : 6.1 % and C₄H₁₀ : 2.9%.

Example 2

10 The experiment as described in Example 1 was repeated using a ruthenium salt as source for the Group VIII metal giving a ready catalyst containing 5% wt of Ru, calculated on carrier. The average metal particle diameter amounted to 5.5 nm. The results of the GLC analysis amounted to : CH₄ : 80.5 %, C₂H₆ : 15.8%, C₃H₈ : 2.7% and C₄H₁₀ : 1.0 %.

15 Example 3

The experiment as described in Example 1 was repeated using a nickel salt as source for the Group VIII metal giving a ready catalyst containing 10% wt of Ni, calculated on carrier. The average metal particle diameter amounted to 9.2 nm. The results of the GLC analysis amounted to : CH₄ : 89.3%, C₂H₆ : 7.3%, C₃H₈ 1.9% and C₄H₁₀ : 1.4%.

Example 4

25 The experiment as described in Example 1 was repeated using a rhodium salt as source for the Group VIII metal giving a ready catalyst containing 3% wt of Rh, calculated on carrier. The average metal particle diameter amounted to 2.2 nm. The results of the GLC analysis amounted to : CH₄ : 95.8%, C₂H₆ : 4.1% and C₃H₈ : 0.1%.

Example 5

30 The experiment as described in Example 1 was repeated using a cobalt on silica catalyst which also contained zirconia in the carrier (16% wt of zirconia, calculated on silica), the amount of cobalt being 5% wt as in Example 1. The total selectivity towards ethane and higher hydrocarbons amounted to 22.9%.

Example 6

5 The experiment as described in Example 2 was repeated but
using different hydrogenation temperatures in part c) of the
Example. It was found that at the highest hydrogenation
temperatures used (at about 150 °C) the selectivity towards the
production of ethane and higher hydrocarbons decreases as does the
amount of the highest homologues found. At rather low hydrogenation
temperatures, e.g. at ambient temperature the formation of ethane
is preponderant and only a small amount of propane is produced at
10 well. The optimum hydrogenation temperatures for the Ru/SiO₂
catalyst used are in the range between 65 °C and 95 °C, both with
respect to yield and selectivity.

Example 7

15 The experiment as described in Example 1 was repeated but
allowing for co-adsorption of ethylene onto the cooled catalyst
obtained after the decomposition of methane as described in Example
1a). The yield on ethylene basis, having carried out the
hydrogenation as described in Example 1c) at a temperature of 30 °C
amounted to 70%.

C L A I M S

1. Process for the production of hydrocarbons by contacting a hydrogen containing moiety with a catalytically active support containing a carbonaceous material deposited thereon wherein the carbonaceous material is obtainable by subjecting methane to a decomposition treatment in the presence of said support at a temperature not exceeding 600 °C.
2. Process according to claim 1, wherein the decomposition treatment is carried at a temperature in the range between 200 °C and 550 °C.
3. Process according to claim 1 or 2, wherein use is made of a support containing one or more metal(s) or metal compound(s) of Group VII and/or Group VIII of the Periodic Table of the Elements.
4. Process according to claim 3, wherein use is made of one or more metals or metal compounds of ruthenium, iridium, rhenium, nickel, cobalt or platinum.
5. Process according to claim 4, wherein use is made of one or more metal (compound(s)) of ruthenium or cobalt.
6. Process according to one or more of claims 1-5, wherein use is made of a support containing one or more refractory oxides, crystalline (metallo)silicates, metallophosphates or combinations thereof.
7. Process according to claim 6, wherein use is made of silica, alumina or silica-alumina.
8. Process according to one or more of claims 1-7, wherein use is made of from 0.1-30% wt of catalytically active material, calculated on total support.
9. Process according to claim 8, wherein use is made of from 0.5-15 % wt of a Group VII and /or Group VIII metal (compound).
10. Process according to one or more of claims 1-9, wherein use is made of a promoter in addition to the catalytically active support.
11. Process according to claim 10, wherein use is made of a Group IA oxide, magnesia, zirconia or titania as promoter.

12. Process according to claim 10 or 11, wherein use is made of an amount of promoter ranging from 0.1-10 times the amount of catalytically active material present on the support.
- 5 13. Process according to one or more of claims 1-12, wherein the contacting between the hydrogen containing moiety and the catalytically active, carbonaceous material containing support is carried out at a temperature of up to 250 °C.
- 10 14. Process according to claim 13, wherein the contacting is carried out at a temperature in the range between ambient temperature and 150 °C, in particular between ambient temperature and 100 °C.
- 15 15. Process according to one or more of claims 1-14, wherein the contacting is carried out with hydrogen containing at least 70% vol of molecular hydrogen.
- 16 16. Process according to one or more of claims 13-15, wherein the contacting is carried out at a hydrogen pressure of up to 10 bar.
- 17 17. Process according to one or more of claims 1-16, wherein use is made of a hydrocarbonaceous material which is adsorbed on the catalytically active support prior to its contacting with a
- 20 18. Process according to claim 17, wherein the adsorption of hydrocarbonaceous material is carried out after formation of the carbonaceous deposit.
- 25 19. Process according to claim 18, wherein the adsorption is carried out at a temperature below 150 °C, in particular at a temperature below 50 °C.
- 30 20. Process according to one or more of claims 17-19, wherein use is made lower alkenes to be adsorbed on the catalytically active support.
- 35 21. Process according to claim 20, wherein ethylene and/or propylene are adsorbed on the catalytically active support.
22. Process according to one or more of claims 17-21, wherein the contact between the hydrogen containing moiety and the catalytically active support containing carbonaceous deposit is carried out at a temperature below 200 °C, in particular below 150 °C.

23. Process according to one or more of the preceding claims, substantially as described hereinbefore with reference to Examples 1-7.

5 24. Hydrocarbons whenever produced by a process as claimed in one or more of the preceding claims.

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

-12 Application number
 9106062.4

<p>Relevant Technical fields</p> <p>(i) UK Cl (Edition K) G5E (ECA, ECB, ECC, ECF)</p> <p>(ii) Int Cl (Edition 5) C07C</p> <p>Databases (see over)</p> <p>(i) UK Patent Office</p> <p>(ii) ONLINE DATABASES: WPI AND CLAIMS</p>	<p>Search Examiner</p> <p>M R WENDT</p> <hr/> <p>Date of Search</p> <p>11 MARCH 1990</p>
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Documents considered relevant following a search in respect of claims 1-24

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	



Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

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