PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide with Water Vapour

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of Homberg/Niederrhein, Germany, a German Joint Stock Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the synthesis of hydrocarbons with or without the synthesis of oxygen-containing organic compounds, from carbon monoxide and water vapour.

It is known to produce hydrocarbons and oxygen-containing organic compounds from a mixture of carbon monoxide and hydrogen with the use of suitable hydrogenation catalysts. Metals of the 8th group of the periodic system, particularly cobalt, iron, nickel and ruthenium, have been used as catalysts with or without a support or carrier. It is also known to incorporate promoters in such catalysts.

Furthermore, it is known to add water vapour to the carbon monoxide and hydrogen used as the feed gas in such processes, the water vapour in such circumstances being generally recognised as a diluent.

It is also known to produce methane from a mixture of carbon monoxide and water vapour in the presence of a nickel catalyst. In one such process it has been proposed to use two stages, the carbon monoxide and water vapour being reacted in the first stage to give an exit gas comprising carbon dioxide and hydrogen; water vapour is then removed from the exit gas of the first stage to provide the feed gas of the second stage, in which stage the carbon dioxide and hydrogen are reacted to give methane.

In Patent Specification No. 293,185 there is described a process for the production of hydrocarbons from carbon oxides and hydrogen in which contact masses are used which contain in addition to copper, silver, gold, zinc in the metallic state or mixtures or alloys of the same or oxides of copper, silver or gold which are reduced to metals under the conditions of working, elements of the 8th group of the periodic system or their compounds. The contact masses which are particularly described contain the metals of the 8th group or their compounds in a minor proportion only, one such contact mass consisting of 50 parts of copper oxide, 30 parts of silver oxide, 8 parts of cobalt oxide and 2 parts of chromic oxide. It is stated in this prior specification that the hydrogen needed for the reaction may also be generated in the reaction vessel itself by wholly or partially replacing the hydrogen in the initial gas mixtures by water vapour.

Patent Specification No. 300, 294 describes a process for the manufacture of synthetic organic compounds by the reduction of carbon oxides in the presence of contact masses which in addition to iron, nickel or cobalt or their compounds, contain cadmium or thallium or their compounds or mixtures of these substances. It is stated in this specification that the hydrogen needed for the reaction may be generated by the aid of the catalyst itself by wholly or partially replacing the hydrogen in the initial gases by steam.

In neither of these prior specifications is there any specific mention of the ratio in which the carbon oxides and water vapour or steam are to be used. The specific examples given in the two specifications either use water gas or a mixture of carbon monoxide and hydrogen in the ratio of 1:1.

It has now been found that in the production of hydrocarbons and/or oxygen-containing organic compounds from carbon monoxide and water vapour in the presence of a catalyst the main metal in which is a member of the eighth group of the periodic system, the activity of the catalyst drops after a short period on stream to become practically ineffective in the conversion of the carbon monoxide, if the ratio of carbon monoxide to water vapour in the feed gas is below 2. This relatively rapid fall in the activity of the catalyst and in the conversion of carbon monoxide, may be avoided by using, as feed gas, a mixture of carbon monoxide and water vapour in which the ratio $CO:H_2O$ is at least 2.

According to the invention, a process for the synthesis of hydrocarbons with or without the synthesis of oxygen-containing organic compounds comprises contacting a mixture of carbon monoxide and water vapour which contains at least two volumes of carbon monoxide per volume of water vapour, with a catalyst the main metallic constituent in which is a metal of the eighth group of the periodic system at a temperature within the range 150°—350° C. and at a pressure within the range from normal atmospheric pressure to 100 atmospheres gauge, the catalyst having been activated before use by treatment with carbon monoxide and hydrogen at a temperature within the range 150°—350° C.

The preferred temperature range for the synthesis is 180°—280° C. The activation of the catalyst may be carried out by first contacting carbon monoxide with the catalyst and thereafter contacting hydrogen with the catalyst, or it may be carried out with a mixture of carbon monoxide and hydrogen.

The known hydrogenation catalysts for the Fischer-Tropsch synthesis, that is to say, the metals of the eighth group of the periodic system, such as cobalt, iron, nickel and ruthenium, may be used as catalysts. These catalysts may be deposited on carriers such as kieselguhr, talc, dolomite, limestone, activated carbon, pumice or the like. Promoters may advantageously be added to the catalysts. Suitable promoters are, for example, the oxides, hydroxides and salts of alkali-metals and alkaline earth metals including magnesium; oxides difficult to reduce, such, for example, as thorium oxide and cerium oxide; aluminium oxide and chromium sesquioxide; and compounds of manganese, vanadium, boron, copper, nickel, silver and gold. It has been found that those compounds which are used for the activation of catalysts in the hydrogenation of carbon monoxide according to the Fischer-Tropsch synthesis, are particularly suitable for use as promoters in the process according to the invention.

The catalysts may be produced by precipitation from metal salt solutions with alkali compounds; by decomposition of easily decomposable metal compounds, such for example as the nitrates; by decomposition of metal carbonyls, or by fusing the metals with the addition of oxygen. Furthermore, commercially obtained waste products of the metals in question may be used, such for example, with iron the so-called "Lanta" or "Lux" mass. The pre-treatment of the oxide catalysts with a mixture of CO and H_2 can be carried out at atmospheric pressure and at elevated pressures up to approximately 100 atmospheres. The pre-treatment with carbon monoxide and subsequently with hydrogen is suitably effected at atmospheric pressure or at elevated pressures up to approximately 20 atmospheres. In this case, the use of pressures higher than 20 atmospheres is detrimental, as the carbon monoxide tends to decompose with the formation of carbon.

In the present process it is essential to transform the metal of the eighth group in the catalyst, prior to the synthesis and for the purpose of activating the catalyst, either into the metallic condition or into such condition where carbon enters into a definite or indefinite compound with these metals, such, for example, as carbide. This pre-treatment of the catalysts is carried out at temperatures of 150° C.—350° C. preferably at a temperature within the range 230° C.—300° C. with carbon monoxide and subsequently with hydrogen or with a $CO—H_2$ mixture.

It is advantageous to free the synthesis gases prior to the reaction from catalyst poisons such as sulphur, phosphorus and the like. It is further essential to provide for a substantially uniform and rapid removal of the reaction heat in order to avoid an overheating of the catalyst. This may be done in known manner.

The synthesis may be carried out in one or more stages, and with recycling of the synthesis gases, the carbon monoxide/water vapour ratio being advantageously adapted to the actual synthesis conditions after each stage. The synthesis may be carried out with a fixed bed catalyst, or with the catalyst suspended in a suitable liquid medium, for example, synthesis products of suitable boiling range for example, 150° C.—350° C. It is further possible to use the catalyst in a finely divided condition and to maintain it suspended in the reaction chamber by passing the synthesis gas upwardly through the reaction chamber.

The synthesis products may be separated in known manner. The synthesis products consist largely of hydrocarbons having 1—30 or more carbon atoms in the molecule. Furthermore, oxygen-containing organic compounds, such as alcohols, aldehydes, ketones, acids and esters, may be contained in the synthesis product.

The carbon dioxide present in the exit gas may be separated in known manner, reduced to carbon monoxide and returned to the synthesis, so that practically the total amount of carbon used in the synthesis may be obtained in the form of hydrocarbons or oxygen-containing organic compounds.

The process of the invention is illustrated in the following examples:—

EXAMPLE 1.

The catalyst used was an Fe-Cu-Kieselguhr catalyst which was alkalised with potassium carbonate, and which contained 100 parts of iron, 10 parts of magnesium, 10 parts of copper, 60 parts of Kieselguhr and 2 parts K_2CO_3, all parts being by weight. The catalyst was precipitated at boiling temperature from an aqueous solution of $Fe(NO_3)_3$, $Mg(NO_3)_2$ and $Cu(NO_3)_2$ after the addition of the 60 parts of Kieselguhr, the stoichiometric quantity of sodium carbonate in aqueous solution being used for the precipitation. The precipitated mixture was boiled for a few minutes, filtered and the precipitate washed with a quantity of boiling water amounting to 70 to 90 times the quantity of the iron. The washed precipitate was then made into a paste with a little water, blended well with an aqueous solution of potassium carbonate (2 parts by weight of K_2CO_3 to 100 parts by weight Fe) and dried at 110° C.

The catalyst was then activated. For this purpose, a CO—H_2 mixture containing 2 volumes of H_2 per volume of CO was passed over the catalyst for 24 hours at a temperature of 270° C., at atmospheric pressure, and at a space velocity of 100, that is to say 100 normal cubic metres of the CO—H_2 mixtures per hour per cubic metre of catalyst.

A carbon monoxide-water vapour mixture, which contained 1 volume of water vapour to 2 volumes of CO, was passed at atmospheric pressure, at a temperature of 235° C., and at a space velocity of 20, that is to say 20 cubic metres of CO-water vapour mixture per hour per cubic metre catalyst, over the catalyst pre-treated as above. 145 grams of hydrocarbons were formed per cubic metre of carbon monoxide, which is 94% of the theoretical yield. The proportion of methane amounted to 8%. The carbon monoxide used in the synthesis contained 98.5% CO and 1.5% N_2. The exit gas had the following average composition:—77.7% CO_2, 1.4% unsaturated hydrocarbons, 3% CO, 14.8% H_2, 2.5% saturated hydrocarbons and 0.6% N_2.

EXAMPLE 2.

The Fe-Cu-catalyst used was free from carrier substances and contained 0.1 part of copper and 0.25 parts of potassium carbonate to 100 parts of iron, all parts being by weight. For its production, an aqueous solution of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ containing 5% by weight of Fe was precipitated at boiling temperature with the stoichiometric quantity of sodium carbonate in aqueous solution. The precipitated mixture was boiled quickly for a few minutes, filtered and the precipitate washed with boiling water in an amount equal to 70—90 times the amount of iron in the precipitate. The washed precipitate was subsequently made into a paste with a little water, well mixed with an aqueous solution of potassium carbonate (0.25 parts by weight K_2CO_3 to 100 parts by weight of Fe) and dried at 110° C.

For the purpose of activating the catalyst, carbon monoxide was passed over it for 24 hours at atmospheric pressure, at a temperature of 270° C. and at a space velocity of 100; hydrogen was then passed over the catalyst at the same temperature, at the same pressure, at the same space velocity and for the same period.

A carbon monoxide-water vapour mixture containing 1 volume of water vapour to 3 volumes of carbon monoxide was passed at a gauge pressure of 10 atmospheres and at a temperature of 230° C. over the catalyst which had been pre-treated as above. Between the 100th and 150th hour on stream, the carbon monoxide conversion amounted to 97.6%, a yield of 201 grams hydrocarbons and oxygen-containing organic compounds together with minute quantities of methane being obtained per normal cubic metre of carbon monoxide.

EXAMPLE 3.

Over an alkalised Fe-Cu catalyst of the same composition as the catalyst used in Example 2, and which was produced and actuated in the same manner as that catalyst, a carbon monoxide-water vapour mixture containing 1.25 volumes of water vapour to 3 volumes of carbon monoxide was passed under a gauge pressure of 10 atmospheres and at a temperature of 230° C. The ratio carbon monoxide water vapour was thus 2.4. A carbon monoxide conversion of 98.5% was obtained with a yield of 162 grams of hydrocarbons and oxygen-containing organic compounds, and minute quantities of methane per normal cubic metre of carbon monoxide.

The harmful effects of using too large a quantity of water vapour is shown in the following run. A gas mixture consisting of water vapour and carbon monoxide in the mol ratio of 2:3 was used in synthesis under the precise conditions given in Example 3. A carbon monoxide conversion of 95% with a yield of 75 grams of synthetic products per normal cubic metre of carbon monoxide was at first obtained. After 24 hours, the carbon monoxide conversion dropped to approximately 20%, and after a few more hours the catalyst became completely inactive.

Just as too large a quantity of water vapour is harmful to the hydrogenation of carbon monoxide with water vapour, it is also harmful to use pressures which are considerably higher than 100 atmospheres. Thus the catalyst described in Example 1 was found to have only a short active life when used in synthesis at a pressure of 140 atmospheres, a temperature of 235° C. and a space velocity of 50 with a carbon monoxide-water vapour mixture containing 1 volume of water vapour to two volumes of carbon monoxide.

in the following examples:—

EXAMPLE 1.

The catalyst used was an Fe-Cu-Kieselguhr catalyst which was alkalised with potassium carbonate, and which contained 100 parts of iron, 10 parts of magnesium, 10 parts of copper, 60 parts of Kieselguhr and 2 parts K_2CO_3, all parts being by weight. The catalyst was precipitated at boiling temperature from an aqueous solution of $Fe(NO_3)_3$, $Mg(NO_3)_2$ and $Cu(NO_3)_2$ after the addition of the 60 parts of Kieselguhr, the stoichiometric quantity of sodium carbonate in aqueous solution being used for the precipitation. The precipitated mixture was boiled for a few minutes, filtered and the precipitate washed with a quantity of boiling water amounting to 70 to 90 times the quantity of the iron. The washed precipitate was then made into a paste with a little water, blended well with an aqueous solution of potassium carbonate (2 parts by weight of K_2CO_3 to 100 parts by weight Fe) and dried at 110° C.

The catalyst was then activated. For this purpose, a CO—H_2 mixture containing 2 volumes of H_2 per volume of CO was passed over the catalyst for 24 hours at a temperature of 270° C., at atmospheric pressure, and at a space velocity of 100, that is to say 100 normal cubic metres of the CO—H_2 mixtures per hour per cubic metre of catalyst.

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EXAMPLE 3.

Over an alkalised Fe-Cu catalyst of the same composition as the catalyst used in Example 2, and which was produced and actuated in the same manner as that catalyst, a carbon monoxide-water vapour mixture containing 1.25 volumes of water vapour to 3 volumes of carbon monoxide was passed under a gauge pressure of 10 atmospheres and at a temperature of 230° C. The ratio carbon monoxide water vapour was thus 2.4. A carbon monoxide conversion of 98.5% was obtained with a yield of 162 grams of hydrocarbons and oxygen-containing organic compounds, and minute quantities of methane per normal cubic metre of carbon monoxide.

The harmful effects of using too large a quantity of water vapour is shown in the following run. A gas mixture consisting of water vapour and carbon monoxide in the mol ratio of 2:3 was used in synthesis under the precise conditions given in Example 3. A carbon monoxide conversion of 95% with a yield of 75 grams of synthetic products per normal cubic metre of carbon monoxide was at first obtained. After 24 hours, the carbon monoxide conversion dropped to approximately 20%, and after a few more hours the catalyst became completely inactive.

Just as too large a quantity of water vapour is harmful to the hydrogenation of carbon monoxide with water vapour, it is also harmful to use pressures which are considerably higher than 100 atmospheres. Thus the catalyst described in Example 1 was found to have only a short active life when used in synthesis at a pressure of 140 atmospheres, a temperature of 235° C. and a space velocity of 50 with a carbon monoxide-water vapour mixture containing 1 volume of water vapour to two volumes of carbon monoxide.

As is shown in the sample analysis of the exit gases, the carbon monoxide conversion attained a maximum after fifteen hours of operation. After this period, the conversion dropped very quickly. After 36 hours, the catalyst has become completely ineffective, due to a heavy deposit of carbon.

Composition of the exit gases:—

Hours of operation	CO_2	unsaturated hydrocarbons	O_2	CO	H_2	saturated hydrocarbons	N_2
8	31.0	1.1	0.0	62.6	0.9	2.0	2.4
15	65.5	1.3	0.0	22.0	5.0	3.0	2.2
24	39.9	1.1	0.0	50.2	7.1	0.2	1.5
36	8.2	0.2	0.0	85.4	4.2	0.0	2.0

Excessive reaction temperatures are also harmful. Thus with carbon monoxide with water vapour in the volume ratio 2:1, at a temperature of about 400° C., and at normal pressure, or at gauge pressures up to 10 atmospheres, and with the use of the catalyst described in Example 1 or Example 2, the synthesis of liquid hydrocarbons was found to be practically impossible. Apart from a large formation of methane at the beginning of a run, the catalyst became inactive after a short time, owing to a heavy deposit of carbon.

If, while maintaining the high reaction temperature of 400° C., the pressure is at the same time greatly increased, the harmful effects of high temperature and high pressure increase to such an extent that within a short time the catalyst is completely loaded with elementary carbon and thus becomes ineffective.

What we claim is:—

1. A process for the synthesis of hydrocarbons with or without the synthesis of oxygen-containing organic compounds, which comprises contacting a mixture of carbon monoxide and water vapour which contains at least two volumes of carbon monoxide per volume of water vapour, with a catalyst, the main metallic constituent of which is a metal of the eighth group of the periodic system, at a temperature within the range 150°—350° C. and at a pressure within the range from normal atmospheric pressure to 100 atmospheres gauge, the catalyst having been activated prior to use by treatment with carbon monoxide and hydrogen at a temperature within the range 150°—350° C.

2. A process according to claim 1, in which the mixture of carbon monoxide and water vapour is contacted with the catalyst at a temperature within the range 180°—280° C.

3. A process according to claim 1 or claim 2, in which the catalyst is activated at a temperature within the range 230°—300° C. by treatment with carbon monoxide and thereafter with hydrogen.

4. A process according to claim 1 or claim 2, in which the catalyst is activated at a temperature within the range 230°—300° C. by treatment with a mixture containing carbon monoxide and hydrogen.

5. A process according to any one of the preceding claims, in which the catalyst contains one or more promoters selected from the following groups:—

(a) oxides, hydroxides and salts of alkali-metals and of alkaline-earth metals including magnesium;

(b) oxides which are difficult to reduce, such as thorium oxide and cerium oxide;

(c) aluminium oxide and chromium sesquioxide;

(d) compounds of manganese, vanadium and boron; and

(e) compounds of copper, nickel, silver and gold.

6. A process according to any one of the preceding claims, in which a carrier such, for example, as kieselguhr, talc, dolomite, limestone, activated carbon or pumice, is incorporated in the catalyst.

7. A process according to any one of the preceding claims, in which the synthesis is carried out in two or more stages with adjustment of the carbon monoxide/water vapour ratio in the feed gas to the second and each succeeding stage.

8. A process according to any one of claims 1 to 6, in which the exit gases are recycled to the synthesis.

9. A process according to any one of the preceding claims, in which the synthesis is carried out with the catalyst suspended in a suitable liquid medium.

10. A process according to any one of claims 1 to 8, in which the synthesis is carried out with a finely divided catalyst suspended in the synthesis gas.

11. A process according to any one of the preceding claims, in which the carbon dioxide formed in the synthesis is separated from the products and is reduced to carbon monoxide, the carbon monoxide so obtained being fed to the synthesis.

12. A process according to any one of the preceding claims, in which the main constituent of the catalyst is iron in elementary or combined form.

13. A process for the reaction of carbon

monoxide and water vapour, substantially as hereinbefore described.

14. A process for the production of hydrocarbons, substantially as hereinbefore described in any one of Examples 1 to 3.

15. Hydrocarbons with or without oxygen-containing organic compounds whenever prepared by the process claimed in any one of the preceding claims.

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