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(54) PROCESS FOR THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

(54) PROCEDE D'HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

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

10 It is known to reduce carbon monoxide with hydrogen to yield hydrocarbons and oxygen-containing products with the use of suitable hydrogenation catalysts. Metals of the 8th group of the periodic system, such as cobalt, iron, nickel and ruthenium, have been used as catalysts with or without a support or carrier. It is further known to incorporate promoters in these hydrogenation catalysts.

20 It has also been suggested to convert carbon monoxide with water vapour into hydrocarbons and oxygen-containing compounds with oxide catalysts which contain metals of the 8th group. In this reaction, temperatures of approximately 400°C. and pressures of several hundred atmospheres should be employed. It is considered essential for this reaction to use a sufficient quantity of water vapour in order to prevent a reduction to metal of the metal oxides used as catalyst, by the gaseous components. It appears that this reaction did not yield any practical results under the above-mentioned reaction conditions. On the contrary, the carbon monoxide introduced was substantially converted into carbon with simultaneous formation of methane. Furthermore, the oxide catalyst lost its activity in a short time.

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10 It has now been found that it is nevertheless possible to convert carbon monoxide with water vapour into hydrocarbons and oxygen-containing organic compounds. This process is effected, according to the invention, by contacting a mixture of carbon monoxide and water vapour in which the volume ratio of the carbon monoxide to the water vapour is at least 2, with a catalyst the main constituent of which is a metal of the 8th group of the periodic system, the contacting being effected at a synthesis temperature within the range 150°C. - 350°C., preferably within the range 180°C. - 280°C., and at a pressure in the range from normal atmospheric pressure to approximately 100 atmospheres gauge, the catalyst having been activated, prior to use in the synthesis, by treatment with carbon monoxide and hydrogen at a temperature within the range 150°C. - 350°C. approximately. The use of pressures substantially exceeding 100 atmospheres leads to decomposition of the carbon monoxide.

20 The known hydrogenation catalysts for the Fischer-Tropsch-synthesis, that is to say, metals of the 8th group of the periodic system, such as cobalt, iron, nickel, ruthenium, may be used as catalysts in the present invention. These catalysts may be deposited on carriers such as Kieselguhr, talc, dolomite, limestone, activated carbon, pumice stone or the like. Promoters may advantageously be added to the catalysts. Suitable promoters are, for example, the oxides, hydroxides

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and salts of alkali metals and of alkaline earth metals including magnesium, oxides difficult to reduce, such, for example, as thorium oxide or 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 are particularly suitable as promoters which are used as promoters in catalysts for the hydrogenation of carbon monoxide with hydrogen (Fischer-Tropsch synthesis).

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 in the presence of oxygen. Furthermore, commercially obtained waste products of the metals in question may be used, such for example, with iron, the so-called "Lauta" or "Lux" mass. The pre-treatment or activation of the oxide catalysts with a mixture of CO and H<sub>2</sub> can be carried out at atmospheric pressure and at elevated pressures up to approximately 100 atmospheres. The activation may also be carried out by first using carbon monoxide and then using hydrogen; this method of activation is suitably effected at atmospheric pressure or slightly 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 8th 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 the metal, such, for example, as carbide. This pre-treatment or activation of the catalysts is carried out at temperatures  
10 of 150°C. - 350°C., preferably at 230°C. - 300°C. with carbon monoxide and subsequently with hydrogen or with a CO-H<sub>2</sub> mixture.

For carrying out the process of the invention, there may be used, for example, the gases obtained in the reduction of metal oxides, such as blast furnace gas, generator gas, and the gases obtained in the oxygen gasification of coal, coke or other carbon-containing substances. The process of the invention has the particular advantage that it is  
20 not necessary, in the production of hydrocarbons, to use synthesis gases which contain elementary hydrogen, the production of which is always costly.

The proportion of water vapour used is maintained below the limit hereinbefore given. If, for example, the partial water vapour pressure of the synthesis mixture is increased to such an extent that the ratio CO : water vapour drops to below the value 2, the CO conversion decreases gradually and drops after a short reaction period  
30 to practically nil, the catalyst becoming ineffective within a few hours. In accordance with the

invention, the quantity of water vapour in the carbon monoxide-water vapour mixture is limited so that the ratio CO : water vapour, expressed in parts by volume, is not less than 2.

10 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 overheating the catalyst. This may be done in known manner.

The synthesis may be carried out in one or more stages, and also 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, such as synthesis products  
20 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 at an adequate rate of flow.

The synthesis products obtained are separated from the reaction mixture in known manner. The synthesis products consist largely of hydrocarbons having from 1 to 30 or more carbon atoms in the  
30 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.

10 Furthermore, the synthesis may be modified in such manner that hydrogen is introduced together with the CO-water vapour mixture so that the known hydrogenation of CO by means of hydrogen according to the Fischer-Tropsch synthesis takes place, simultaneously with the reduction of the carbon monoxide by means of water vapour.

The process of the invention is illustrated in the following Examples 1, 2, 3 and 6.

Example 1.

20 The catalyst used was an Fe-Cu-Kieselguhr catalyst which was alkalisied 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. For its production an aqueous solution of  $Fe(NO_3)_3$ ,  $Mg(NO_3)_2$  and  $Cu(NO_3)_2$  was precipitated at boiling temperature, 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  
30 mixture was boiled for a few minutes, filtered and the precipitate washed with a quantity of boiling

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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  $110^\circ C$ .

10 The catalyst was then activated. For this purpose, a CO-H<sub>2</sub> mixture containing 2 parts by volume of H<sub>2</sub> to 1 part by volume of CO was passed over the catalyst for 24 hours at  $270^\circ C$ ., at normal atmospheric pressure, and at a space velocity of 100, that is to say, 100 normal cubic metres of the CO-H<sub>2</sub> mixture per hour per cubic metre of catalyst space.

20 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  $235^\circ C$ ., 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 space, over the catalyst pre-treated in the above manner. 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<sub>2</sub>. The exit gas had the following average composition:-  
77.7% CO<sub>2</sub>, 1.4% unsaturated hydrocarbons, 3% CO, 14.8% H<sub>2</sub>, 2.5% saturated hydrocarbons and 0.6% N<sub>2</sub>.

30 By catalyst space is meant that part of the reaction chamber which is filled with the catalyst.



Example 2.

10 The Fe-Cu-catalyst used was free from carrier or supporting material and contained 0.1 part of copper and 0.25 part of potassium carbonate to 100 parts of iron, all parts being by weight. For its production, an aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Cu}(\text{NO}_3)_2$  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 from 70 to 90 times the amount of iron in the precipitate. The washed precipitate was then made into a paste with a little water/ well mixed with an aqueous solution of potassium carbonate (0.25 parts by weight  $\text{K}_2\text{CO}_3$  to 100 parts by weight of Fe) and dried at  $110^\circ\text{C}$ .

20 For the purpose of activating the catalyst, carbon monoxide was passed over it for 24 hours at atmospheric pressure, at a temperature of  $270^\circ\text{C}$ . and at a space velocity of 100; hydrogen was then passed over the catalyst at the same temperature, at the same pressure, and at the same space velocity and for the same period.

30 A carbon monoxide-water vapour mixture containing 1 part by volume of water vapour to 3 parts by volume of carbon monoxide was passed at a gauge pressure of 10 atmospheres and at a temperature of  $230^\circ\text{C}$ . 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.

10 Over an alkalisied Fe-Cu catalyst of the same composition as the catalyst used in Example 2, and which was produced and activated 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, thus had the value 2.4. A carbon monoxide conversion of 98.5% was obtained with a yield of 162 grams hydrocarbons and oxygen-containing organic compounds, and very small quantities of methane per normal cubic  
20 metre of carbon monoxide.

The harmful effects of using too large a quantity of water vapour is shown in the following Example given by way of comparison:-

Example 4.

When, under otherwise the same conditions as those used in Example 3, a synthesis mixture which contained 2 volumes of water vapour to 3 volumes of carbon monoxide ( $\text{CO}:\text{H}_2\text{O} = 1.5$ ) there was first  
30 obtained a carbon monoxide conversion of 95% with a yield of 75 grams of synthesis products per normal cubic metre of carbon monoxide. After 24 hours,

however, 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. This is shown in the following Example given by way of comparison:-

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Example 5.

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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 part by volume of water vapour to two parts by volume of carbon monoxide. As is shown in the sample analysis of the exit gases given below, 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 had become completely ineffective, due to a heavy deposit of carbon.

Composition of the exit gases:-

Hours of operation	CO <sub>2</sub>	unsaturated hydrocarbons	O <sub>2</sub>	CO	H <sub>2</sub>	saturated hydrocarbons	N <sub>2</sub>
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

The harmful effects of excessive reaction temperatures is shown by the following:-

In the reaction of carbon monoxide with water vapour in the volume ratio 2:1, at temperatures of about  $400^{\circ}\text{C}$ ., and at normal pressure, or at gauge pressures up to 10 atmospheres, and using the catalysts described in Examples 1 or 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 catalysts became inactive after a short time owing to a heavy deposit of carbon.

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If, while maintaining the high reaction temperature of  $400^{\circ}\text{C}$ ., 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.

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Having regard to the foregoing disclosure, the patent of which this specification forms part confers, subject to the conditions prescribed in the Patent Act, 1935, the exclusive right, privilege, and liberty of making, constructing, using and vending to others to be used, the invention as defined in claims submitted by the patentee as follows:-

1. A process for the catalytic hydrogenation of carbon monoxide, which comprises contacting a mixture of carbon monoxide and water vapour in which the volume ratio CO/water vapour is at least 2 : 1 with a catalyst the main constituent of which is a metal of the 8th group of the periodic system, at a synthesis temperature within the range  $150^{\circ}$  -  $350^{\circ}\text{C}$ . and at a synthesis pressure in the range normal atmospheric pressure to approximately 100 atmospheres gauge, the catalyst having been activated prior to use by treatment with carbon monoxide and hydrogen at a temperature within the range  $150^{\circ}$  -  $350^{\circ}\text{C}$ . approximately, and recovering hydrocarbons and/or oxygen-containing organic compounds from the synthesis products.

2. A process according to claim 1, 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) thorium oxide and cerium oxide;
- (c) aluminium oxide and chromium oxide  $\text{Cr}_2\text{O}_3$ ;

(d) oxygen-containing compounds of manganese, vanadium, boron, copper, nickel, silver and gold.

3. A process according to claim 2, in which a carrier is incorporated in the catalyst.

4. A process according to claim 1, 2 or 3, in which the synthesis temperature is within the range  $180^{\circ}$  -  $280^{\circ}\text{C}$ .

5. A process according to claim 1, 2 or 3, in which the catalyst is activated at a temperature within the range  $230^{\circ}$  -  $300^{\circ}\text{C}$  by treatment with carbon monoxide and thereafter with hydrogen.

6. A process according to claim 1, 2 or 3, in which the catalyst is activated at a temperature within the range  $230^{\circ}$  -  $300^{\circ}\text{C}$ . by treatment with a mixture containing carbon monoxide and hydrogen.

7. A process according to claim 1, 2 or 3, in which the synthesis is effected in two or more stages, the volume ratio CO/water vapour being adjusted between each stage to bring the ratio to a value of at least 2.

8. A process according to claim 1, 2 or 3, in which the exit gases are recycled.

9. A process according to claim 1, 2 or 3, in which the synthesis is carried out with the catalyst suspended in a suitable liquid medium.

10. A process according to claim 1, 2 or 3, in which the synthesis is carried out with a finely divided catalyst suspended in the synthesis gas.

11. A process according to claim 1, 2 or 3,

in which the carbon dioxide formed during 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 claim 1, 2 or 3, in which the main constituent of the catalyst is iron in elementary or combined form.

13. A process according to claim 1, 2 or 3, in which hydrogen is added to the mixture of carbon monoxide and water vapour whereby synthesis products are produced by the reaction of carbon monoxide and hydrogen simultaneously with those produced by the reaction of carbon monoxide and water vapour.

14. A process according to claim 1, 2 or 3, in which the pressure is maintained in the higher part of the range in order to increase the yield of oxygen-containing organic compounds.

15. A process according to claim 1, 2 or 3, in which the volume ratio CO/water vapour is not greater than 3 : 1.

16. A process according to claim 1, 2 or 3, in which the duration of the period of activation of the catalyst has been such as to convert the metal of the 8th group substantially completely into the elementary state.

17. A process according to claim 1, 2 or 3, in which the duration of the period of activation of the catalyst has been such as to convert the metal of the 8th group substantially completely into a compound with carbon.