PATENT SPECIFICATION

728,074

Date of Application and filing Complete Specification: July 21, 1952.

No. 18433/52.

Application made in Germany on July 21, 1951.

Complete Specification Published: April 13, 1955.

Index at acceptance:—**Classes 1(1),** F3B1; **and 2(3),** B1G, C2A(1:11:14), C2R15, C3A (10E3:13A3A1C), C3A13A3B(1:2:3), C3A13A3(J2:M).

COMPLETE SPECIFICATION

Improvements in the Catalytic Hydrogenation of Carbon Monoxide

We, Ruhrchemie A.G., of Oberhausen Holten, and Lurgi Gesellschaft Fuer Waermetechnik m.b.H., of Frankfurt a.M.-Heddernheim, German Companies, 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 improvements in the catalytic hydrogenation of carbon monoxide. More particularly, the invention relates to a process for the catalytic hydrogenation of carbon monoxide with the production of primary synthesis products which have a relatively high content of oxygen-containing organic compounds, particularly alcohols, in addition to a high content of nitrogen-containing organic compounds and olefins.

In the co-pending Application No. 6932/50 (Serial No. 672,405) there is described and claimed a process for the catalytic hydrogenation of carbon monoxide in which ammonia and/or a derivative, such as methylamine, is added to the hydrogen-containing synthesis gas. This process has been effected at both atmospheric and elevated pressures and a certain quantity of nitrogen-containing compounds consisting chiefly of primary amines, is present in the synthesis products. Alcohols and other oxygen-containing organic compounds, however, are only formed in very small amounts.

It is an object of the invention to provide a process for the catalytic hydrogenation of carbon monoxide in which the primary synthesis products contain nitrogen-containing organic compounds in addition to a relatively high content of oxygen-containing organic compounds particularly alcohols.

According to the invention, a process for the synthesis of a mixture containing hydrocarbons, oxygen-containing organic compounds and nitrogen - containing organic compounds comprises contacting a mixture of hydrogen and carbon monoxide in synthesis proportions with a precipitated iron catalyst under synthesis conditions of temperature and pressure in the presence of a small quantity of an alkaline, nitrogen-containing compound which is gaseous under the synthesis conditions, the catalyst having little or no supporting material incorporated therein and containing an alkali-metal compound which, calculated as K_2O, is present to the extent of from 1% to 15% by weight of the total amount of iron in the catalyst, with at least 60% of the iron in the catalyst being in the metallic state.

The hydrogenation is preferably effected at gauge pressures in the range 1-100 atmospheres, and advantageously at gauge pressures of from 10 to 30 atmospheres with synthesis gases which contain from 0.5 to 6 volumes of hydrogen for each volume of carbon monoxide. The quantity of the alkaline-reacting, nitrogen-containing compounds which are gaseous under the synthesis conditions and which are added to the synthesis gas, preferably constitutes from 0.5% to 2% by volume of the synthesis gas. The preferred alkaline, nitrogen - containing compounds are ammonia and derivatives thereof, such for example as methylamine. The synthesis is effected at temperatures of 170° to 300°C. and preferably at temperatures of 190° to 260°C.

The catalysts used in the process of the invention are precipitated iron catalysts which are free from or contain only relatively small quantites of supporting materials. Kieselguhr and activated bleaching earth have been found to be particularly useful as such supporting materials. Not more than 25% by weight, and preferably

[*Price* 3/-]

Price 25p

less than 10% by weight of supporting material is present based on the total amount of iron in the catalyst. Prior to use in the synthesis, the catalyst is reduced to convert at least 60% and preferably more than 80% of the total iron content into the metallic state. Reduction is effected with reduction gases such as, for example, carbon monoxide and/or hydrogen. The catalyst may be promoted with one or more of the metals of the class consisting of copper, silver, and metals of the second to seventh groups of the periodic system. Of these metals, the metals of Group II of the periodic classification, and also the metals titanium, vanadium, cerium, thorium and manganese have been successfully used.

It is advantageous to prepare the catalyst by precipitation from an aqueous solution under alkaline conditions, preferably at a pH in the range 8 to 10. The solution used may, for example, be a solution of iron nitrate or iron sulphate, whilst the precipitant may be a solution of an alkali metal oxide or carbonate. The content of the alkali-metal compound in the catalyst should constitute between 1% and 15%, preferably between 5% and 10%, when calculated as K_2O and based on the total iron content of the catalyst. The final alkali-metal compound content may be obtained by washing the precipitated catalyst mass completely free from alkali-metal compounds and thereafter impregnating the catalyst with an alkali-metal compound or by partially washing the precipitated mass to reduce the alkali-metal compound content of the mass to the amount desired. The two methods may also be used in combination.

If an increased yield of esters rather than of alcohols is desired, the catalyst should be impregnated either partially or exclusively with salts of non-volatile acids, such as, for example, alkali-metal phosphates, borates, and tungstates. Also in this case, the alkali-metal compound is added in quantities of between 1% and 15%, calculated as K_2O. If the oxygen-containing organic compounds are to consist largely of alcohols, the alkali metal compound introduced into the catalyst is preferably a salt of a volatile acid, a salt of an acid which decomposes during the reduction or a hydroxide.

It has been found that the life and activity of the iron catalyst used in the process according to the invention may be increased if it is dried prior to reduction at a temperature of 80° to 150°C., preferably at 100° to 120°C. to a residual water content of 4% to 7% by weight of H_2O.

Catalysts reduced from suitable oxygen-containing compounds with reducing gases at linear gas velocities of at least 30 to 50 cm. per second, preferably 100 to 200 cm. per second, measured in the cold state (0°C.; 760 mm. Hg), and temperatures of approximately 200° to 400°C. have been found to be particularly active. For this reduction, the use of reduction gases rich in carbon monoxide has been found particularly advantageous under certain circumstances. The reduction may even be effected with pure carbon monoxide. In general, a reducing gas containing carbon monoxide and hydrogen in ratios by volume from 1:1 to 1:2 is satisfactory. The use of carbon monoxide or gases containing carbon monoxide during the reduction is of particular advantage in cases where a high reduction value (that is, a high proportion of the iron is in the metallic state) along with lowest possible reduction temperatures is desirable.

If the catalyst has a copper content of more than 15% and preferably between 15% and 50%, a particularly high formation of oxygen-containing organic products will be effected, and the synthesis may be carried out at relatively low temperatures.

This result is also obtained by using catalysts having a grain size which is below 2 mm. in diameter and preferably between 0.5 and 1.5 mm. in diameter and as uniform as possible. With respect to the uniformity of grain size, a tolerance of approximately 0.3 mm. is permissible. With the use of these catalysts, it has been found particularly advantageous under certain circumstances to effect the synthesis by passing the synthesis gases upwardly through the catalyst layer. This expedient has been found to be advantageous where high gas loads or space velocities of, for example, more than 300 volumes of gas per volume of catalyst per hour are used in the synthesis, since a lowering of the pressure loss is possible in this way.

In the past it has only very rarely been possible to precipitate catalysts from sulphate solutions. However, the catalyst used in the process according to the invention may be precipitated from sulphate solutions with approximately 10% to 50% and preferably 25% to 30% of the iron present being converted into the trivalent form. The washing of the precipitated mass obtained should be carried out with aqueous solutions of compounds which permit the alkali-metal sulphate, which is adsorbed by the iron hydroxide in the precipitate, to be substantially completely removed by ion-exchange. The preferred compounds to be used for this purpose are readily soluble ammonium compounds and compounds derived from ammonia. The washing, predrying and drying is suitably effected with the abundant supply of air in order to obtain oxidation of the bivalent iron still present to convert it into the trivalent form. In any case, more than 70% and preferably more than 80% of the total iron in the catalyst should be present in the trivalent form before the reduction. It is of advantage to increase the concentration of the ion exchange compounds in the wash water during the course of washing the precipitated mass in order to obtain a maximum washing with small quantities of water. In general, the wash waters advantageously contain from 0.2% to 20%, preferably from 0.2% to 2%, of the ion exchange compound.

The synthesis should be effected in a manner which assures careful treatment of the catalyst. Whilst the synthesis may be effected in once-through operation, it is preferred to recycle the synthesis gas, using 1 to 10 volumes, preferably 3 to 5 volumes, of recycled gas for each volume of fresh synthesis gas.

The gas load should generally be about 10-1,000 volumes of fresh gas per volume of catalyst per hour, preferably 100-500 volumes.

The use of temperature gradient, i.e., an increasing catalyst temperature in the direction of gas flow, is of advantage in special cases. This is true, for example, if in a synthesis carried out with once-through operation or with only little gas recycling, as, for example, 1 volume of fresh gas + 0.5 volumes of recycle gas, the concentration between the inlet and the outlet of the reactor becomes considerably lower so that an increased temperature at the reactor outlet as compared with that at the reactor inlet is favourable for increasing the rate of conversion at the reactor outlet.

The process according to the invention may be carried out with the catalyst provided as a fixed bed or with the catalyst suspended in a liquid medium, or it may be carried out as a fluidised process. When working with the fluidised bed process, the synthesis is effected in a gaseous phase with a bed of finely divided catalyst, the particles of which are maintained in a lively whirling motion.

The synthesis products obtained in accordance with the invention, generally contain more than 20% of oxygen-containing organic compounds and more than 10% of amines, together with a high content of olefins.

The invention is illustrated by the following examples:—

EXAMPLE 1

A catalyst was precipitated from a boiling solution containing 40 grams of iron and 12 grams of copper per litre in the form of their nitrates, by pouring the solution into a boiling solution of sodium carbonate containing 101 grams of sodium carbonate per litre. The pH was 9.2. The filtered catalyst mass was freed from excess alkali by repeated washing with distilled water and was then impregnated with potassium carbonate to the extent of 8 parts by weight of potassium carbonate calculated as K_2O per 100 parts by weight of iron. The grain size of the dried and moulded mass was between 1 and 3 mm.

The reduction of the catalyst mass was carried out at a temperature of 320°C. with the use of a gas mixture consisting of 75% of hydrogen and 25% of nitrogen at a linear gas velocity of 1.4 metres per second. The reduction time was 120 minutes, at the end of which time 65% of the iron was in elementary form.

When water gas containing 2% of NH_3 was passed over this catalyst at a gauge pressure of 30 atmospheres, and a gas load of 100 litres of gas per litre of catalyst per hour, a conversion rate of 56% of $(CO + H_2)$ was obtained at a temperature of 183°C.

The synthesis product obtained contained 35% of oxygen-containing organic compounds consisting chiefly of primary aliphatic alcohols, in addition to 17% of nitrogen-containing compounds consisting chiefly of primary aliphatic amines. The remainder of the synthesis product consisted of hydrocarbons. 60% of the hydrocarbons boiling in the gasoline range were olefins, as were 50% of the hydrocarbons boiling in the diesel oil range.

When the same catalyst was charged with twice the gas quantity, a $CO + H_2$ conversion of 50% was obtained at a temperature of 196°C.

When the gas load was increased to three times its original value, that is, to 300 v./v./hr., a $(CO + H_2)$ conversion of 55% was obtained at a temperature of 210°C.

The yield of nitrogen-containing and oxygen-containing products was slightly reduced under these conditions.

EXAMPLE 2

An aqueous solution of iron nitrate and copper nitrate of the concentration mentioned in Example 1 was poured into a boiling solution of sodium carbonate containing 100 grams of Na_2CO_3 per litre. After filtration, the precipitated catalyst slurry was partially washed with hot distilled water so that 8 parts of alkali, calculated as K_2O, per 100 parts of iron remained in the catalyst. The mass was moulded, dried at a temperature of 105°C. and sieved to a grain size of between 1.5 and 3 mm.

The reduction was carried out for 90

minutes at a temperature of 310°C. with hydrogen at a linear gas velocity of 1.5 metres per second, measured in the cold state. 70% of the iron in the catalyst was then in the metallic state.

Water gas containing 2% of NH_3 was passed over the catalyst at a gauge pressure of 30 atmospheres, a temperature of 190°C. and a gas load of 100 litres of gas per litre of catalyst per hour. The $(CO + H_2)$ conversion was 60%.

The synthesis product contained 39% of oxygen-containing organic compounds, chiefly primary aliphatic alcohols, in addition to 15% of nitrogen-containing compounds consisting chiefly of primary amines.

EXAMPLE 3

A catalyst was prepared in the manner described in Example 1. The ratio of iron to copper was 100 to 10. After reduction 80% of the iron in the catalyst was in the metallic state. The impregnation was effected with the use of primary potassium phosphate in such a manner that 8 parts of potassium phosphate, calculated as K_2O, per 100 parts of Fe were present in the catalyst. Under the reduction and synthesis conditions of Example 1, a $(CO + H_2)$ conversion of 58% was obtained at a gas load of 100 litres of gas per litre of catalyst per hour. The proportion of nitrogen-containing compounds, mainly primary aliphatic amines, was 12% in addition to 30% of oxygen-containing organic compounds consisting chiefly of aliphatic alcohols.

EXAMPLE 4

A solution consisting of iron sulphate and copper sulphate and containing 5 parts of copper for every 100 parts of iron and having a concentration of 40 parts of iron for every 1,000 parts of water was heated to boiling point and precipitated in the hot state by pouring it into a solution of sodium carbonate containing 90 grams of Na_2CO_3 per litre, the temperature of the sodium carbonate solution before the addition of the sulphate solution being 80°C. During the precipitation, a stream of air was blown through the precipitation apparatus. The quantity of air so used was 600 litres for every 25 grams of iron, the blowing time being 3.5 minutes. Immediately thereafter, the precipitate was freed from the mother liquor by subjecting it to suction filtration. The precipitate was then washed twice, each time with a quantity of boiling distilled water corresponding to twelve times the quantity of iron present. Finally, the catalyst mass was washed three times by suspending it in an ammonium carbonate solution containing from 5 to 10 grams of ammonium carbonate dissolved in 1,500 cc. of solution. 1,500 cc. of the washing solution for every 25 grams of iron were used in each of the three washings. After the last washing, the sulphur content of the catalyst mass was only 0.02%. 28% of the total Fe was now present as Fe (III), the balance being Fe (II). The catalyst mass was then impregnated in a potassium carbonate solution in such a manner that 8 parts of alkali, calculated as K_2O, for every 100 parts or iron were contained in the mass.

The catalyst mass was dried for 24 hours at a temperature of 110°C. with circulating air and crushed to a grain size of 2-4 mm. The content of Fe (III) was now 88%. Thereafter, the catalyst was reduced for 1 hour at a temperature of 300°C. using a gas mixture consisting of 75% of hydrogen and 25% of nitrogen at a linear gas velocity of 1.4 metres per second, measured in the cold state. 68% of the iron in the catalyst was then in elementary form.

A gas consisting of 35 parts of CO, 55 parts of H_2, 2% of ammonia, the remainder being carbon dioxide, nitrogen and methane, was passed over this catalyst at a gas load of 100 litres of gas per litre of catalyst per hour, a synthesis pressure of 30 atmospheres gauge and a synthesis temperature of 192°C. A $(CO + H_2)$ conversion of 65% was obtained. The resulting product was worked up and found to contain 33% of oxygen-containing organic compounds consisting chiefly of primary aliphatic compounds, in addition to 18% of nitrogen-containing compounds consisting chiefly of primary amines.

What we claim is:—

1. A process for the synthesis of a mixture containing hydrocarbons, oxygen-containing organic compounds and nitrogen-containing organic compounds, which comprises contacting a mixture of hydrogen and carbon monoxide in synthesis proportions with a precipitated iron catalyst under synthesis conditions of temperature and pressure in the presence of a small quantity of an alkaline, nitrogen-containing compound which is gaseous under the synthesis conditions, the catalyst having a little or no supporting material incorporated therein and containing an alkali-metal compound which, calculated as K_2O, is present to the extent of from 1% to 15% by weight of the total amount of iron in the catalyst, with at least 60% of the iron in the catalyst being in the metallic state.

2. A process for the synthesis of a mixture containing hydrocarbons, oxygen-containing organic compounds and amines, which comprises contacting a synthesis gas

containing hydrogen and carbon monoxide in the proportion of 0.5-6 volumes of hydrogen per volume of carbon monoxide together with 0.5-2% by volume of an alkaline, nitrogen-containing compound gaseous under the synthesis conditions, with a precipitated iron catalyst at a temperature within the range 170°-300°C. and at a gauge pressure within the range of 1-100 atmospheres, the catalyst being one which is free from or contains not more than 25% of supporting material, which contains one or more alkali-metal compounds which, calculated as K_2O, together constitute from 1% to 15% by weight of the total amount of iron in the catalyst, and in which at least 60% of the iron is in the metallic state.

3. A process according to Claim 1 or Claim 2, in which the catalyst is promoted with one or more metals from the class consisting of copper, silver and metals of the second to the seventh groups of the periodic system.

4. A process according to Claim 3, in which the catalyst is promoted with one or more of the following metals: titanium, vanadium, cerium, thorium, manganese and metals of the second group of the periodic system.

5. A process according to any one of the preceding claims, in which the catalyst is precipitated under alkaline conditions, preferably at a pH in the range 8-10.

6. A process according to any of the preceding claims, in which the synthesis is effected at a pressure within the range 10-30 atmospheres.

7. A process according to any one of the preceding claims, in which the synthesis is effected at a temperature within the range 190°-260°C.

8. A process according to any one of the preceding claims, in which the alkali-metal compound, calculated as K_2O, in the catalyst constitutes from 5% to 10% by weight of the total amount of iron in the catalyst.

9. A process according to any one of the preceding claims, in which part or all of the alkali-metal compound in the catalyst is introduced in the form of a salt of a non-volatile acid.

10. A process according to Claim 9, in which part or all of the alkali-metal in the catalyst is introduced in the form of a phosphate, borate or tungstate.

11. A process according to any one of the preceding claims, in which the catalyst is dried, prior to use, at a temperature within the range 80°-150°C., preferably within the range 100°-120°C., to a residual water content of 4-7% by weight.

12. A process according to Claim 11, in which the catalyst is dried at a temperature of about 110°C.

13. A process according to any one of the preceding claims, in which the catalyst contains at least 15% of copper.

14. A process according to Claim 13, in which the copper content is not greater than 50%.

15. A process according to any one of the preceding claims, in which the particle size of the catalyst is less than 2 mm. in diameter.

16. A process according to any one of the preceding claims, in which the alkaline, nitrogen-containing compound is ammonia or a derivative of ammonia such as methylamine.

17. A process according to any one of the preceding claims, in which the catalyst is precipitated from a sulphate solution, 10%-50%, preferably 25%-35%, of the iron being converted into the trivalent form during precipitation, the washing of the precipitate being effected with a solution of an ion-exchange compound, preferably an ammonium compound or other compound derived from ammonia, and further oxidation of the iron being effected so that more than 70%, preferably more than 80%, of the iron is in the trivalent form prior to reduction.

18. A process according to Claim 17, in which the concentration of the compound used in the wash water is increased during the course of the washing operation.

19. A process according to Claim 17 or Claim 18, in which the wash water contains 0.2-20%, preferably 0.2-2%, of the compound or compounds.

20. A process according to any one of the preceding claims, in which the space velocity of the synthesis gas is within the range 10-1,000 v./v./hr.

21. A process according to any one of the preceding claims, in which the temperature of the catalyst increases in the direction of flow of the synthesis gas.

22. A process for the synthesis of hydrocarbons, oxygen-containing organic compounds and nitrogen-containing organic compounds, substantially as hereinbefore described in any one of Examples 1 to 4.

23. A process for the catalytic hydrogenation of carbon monoxide in the presence of an alkaline reacting, nitrogen-containing compound which is gaseous under the reaction conditions, substantially as hereinbefore described.

24. Hydrocarbons, oxygen-containing organic compounds and nitrogen-containing organic compounds whenever produced by the process of any preceding claim.

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14-18, High Holborn, London, W.C.1.
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Printed for Her Majesty's Stationery Office by Wickes & Andrews, Ltd., E.C.4. 684/2.—1955.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.