PATENT SPECIFICATION

715,043

Date of Application and filing Complete Specification: Aug. 7, 1951.

No. 18639/51.

Application made in Germany on Aug. 10, 1950.

Complete Specification Published: Sept. 8, 1954.

Index at acceptance:—**Classes 1(1),** F3B1; **and 2(3),** B1G, C3A13A3(A1C: B1: J2: M).

COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German Company, and LURGIE GESELLSCHAFT FUER WAERMETECHNIK M.B.H., of Frankfurt am Main-Heddernheim, Germany, a German 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 catalytic hydrogenation of carbon monoxide wherein products having a high content of oxygen-containing organic compounds are obtained.

It is known that fixed-bed iron, cobalt, and nickel catalysts having a particle size of approximately 3 mm. to 5 mm. are used in the hydrogenation of carbon monoxide for the production of hydrocarbons; small amounts of oxygen-containing organic compounds are also generally present in the synthesis products. Hitherto, no additional effect with respect to conversion, yield or quality of the synthesis products could be obtained when using catalyst particles of a diameter of less than 3 mm.

It is also known that catalysts of a particle size of less than about 0.5 mm., preferably less than 0.2 mm., diameter, are used in the so-called "fluidized" synthesis. This size of catalyst particle is necessary in order to obtain, by means of the upwardly streaming synthesis gases, a fluid-like structure of the catalyst bed which, in this state, permits an extremely good removal of the reaction heat. If, in a fluidized process, catalyst particles of a considerably larger diameter should be used, the particles could not be maintained in the fluidized or suspended state with the gas velocities required in the hydrogenation of carbon monoxide. For trouble-free operation of such a synthesis, the maximum particle size in the use of iron catalysts is approximately 0.3 to 0.5 mm.

It has now been found that the catalytic hydrogenation of carbon monoxide for the production of gaseous, liquid and solid synthesis products with the use of pressures above 5 atmospheres, preferably above 10 atmospheres, and fixed-bed iron catalysts of the type capable of yielding at least 30 per cent., preferably more than 45 per cent., of oxygen-containing organic compounds in the synthesis products, can be carried out with particular advantage and good yield when the size range of the catalyst particles is as narrow as possible and is not greater than 1 mm., using diameters of less than 2 mm., preferably between 0.5 and 1.9 mm.

According to the invention, the catalytic hydrogenation of carbon monoxide for the production of synthesis products containing not less than 30% of oxygen-containing organic compounds is effected by contacting a mixture containing carbon monoxide and hydrogen in synthesis proportions with a fixedly provided iron catalyst of the type hereinafter defined, under synthesis conditions of temperature and at a synthesis pressure greater than 5 atmospheres, the catalyst being provided in the form of particles of a size not greater than 2 mm., the size range of the catalyst particles being not greater than 1 mm. Preferably, the size range of the catalyst particles is not greater than 0.5 mm.

Catalysts of the type referred to, namely those capable of yielding synthesis products containing not less than 30% of oxygen-containing organic compounds, are known. Such catalysts are fused, sintered or precipitated iron catalysts which, after reduction, contain more than 60% of the iron in the free state and which have an alkali content, calculated as K_2O, of at least 5 parts per 100 parts of iron. A preferred catalyst of this type is described in the co-pending Application No. 6889/51 (Serial No. 714,839). This preferred catalyst is a precipitated iron catalyst which contains free alkali which, calculated as K_2O, is present to the extent of more than 5 parts per 100 parts of iron, the free alkali being advantageously present to the extent of between 8 and 12 parts per 100 parts of iron. This preferred catalyst also contains little or no supporting material, and more than 60%, advantageously more than 80%, of the iron in the catalyst is in the metallic state.

Using this method of operation instead of catalytic granules of a greater size, the synthesis temperature may be decreased to an appreciable degree, resulting in a very favourable effect on the activity and the life of the catalyst as well as a decrease in the formation of methane. The size range of the catalyst particles, which is not greater than 1 mm., should be as narrow as possible. The effects obtained in the synthesis prove to be the more favourable the greater the uniformity that exists in the particle size of the catalyst used. It would appear that it is just the narrow range of particle size which brings about the advantageous effects in the process according to the invention. It is also a feature of this effect that the formation of oxygen-containing organic compounds, particularly of alcohols, is considerably increased as compared with catalysts having a diameter above 2 mm. Super-atmospheric pressure, generally between 10 and 70 atmospheres, is normally used when employing the catalyst particle size according to the invention. However, higher synthesis pressures may also be used.

The gas load of the catalyst, or the space velocity, may be varied from 10 litres to more than 1000 litres per litre of catalyst per hour. It is advantageous to recycle the synthesis gases, part of the residual or exit gases being returned to the synthesis reactor. In this manner, a more uniform removal of heat may be obtained as compared with single passage of the gas.

In many cases it is of advantage to pass the synthesis gases upwardly through the synthesis reactor, particularly when working with a catalyst having a size of approximately 0.5 to 1 mm. diameter. Obstructions of the catalyst tubes may occasionally occur with the particle size of catalyst according to the invention when passing the gases in the usual downward direction. By passing the gas stream upwardly, a method which is not in general usual with fixed-bed catalysts, these difficulties can be be avoided without changing the synthesis properties of the catalyst.

The preparation of catalyst particles having a diameter not greater than 2 mm. may be effected in any suitable way. In the preparation of precipitation catalysts, the moist catalyst mass is moulded to the desired particle size by means which are known *per se*, for example, by means of a sieving screen. Also catalysts which are prepared by decomposition of metal compounds, for example, of nitrates, may be moulded in this way. Where fused or sintered catalysts are used, these are mechanically crushed to the corresponding particle size and then screened.

The reduction of the catalysts of the invention is advantageously carried out at high gas velocities of, for example, 60 to 100 cm. per second, measured linearly and cold, and at temperatures between 200° C. and 350° C.

The invention is illustrated by the following examples:—

EXAMPLE 1.

A catalyst consisting of 100 parts by weight of iron (Fe), 5 parts by weight of copper (Cu), 10 parts by weight of calcium oxide (CaO) and 10 parts by weight of kieselguhr and containing 8.5 parts by weight of sodium carbonate (calculated as K_2O), was moulded to give particles of 1.9 mm., 3.1, and 5 mm. diameter respectively by means of a thread or filament extrusion press. The catalyst particles were then reduced at a temperature of 300° C. with hydrogen so that 80 per cent of the iron was in the metallic state.

The reduced catalysts, separated according to the individual particle sizes, were placed in three separate synthesis tubes. These synthesis tubes were of the double-tube type, the annular space between the pair of tubes being of a width of 10 mm. The length of the double-tubes was 4.5 metres. The catalysts in the three tubes were then used in synthesis, 150 volumes of water-gas per volume of catalyst being charged per hour with the recycling of 2.5 volumes of residual or exit gas per volume of fresh water gas. The synthesis pressure was 10 kilograms per square centimetre.

After operating times of 300 and 600 hours, the yield of oxygen-containing organic compounds, the conversion and the synthesis temperature attained the values shown in the following table:

After an operating time of 300 hours:

Catalyst particle size	Synthesis temperature	$CO+H_2$ conversion	Oxygen-containing organic compounds	Methane formation
1.9 mm.	195° C.	53%	53%	3%
3.1 mm.	195° C.	44%	49%	6%
5.0 mm.	195° C.	40%	48%	11%

After an operating time of 600 hours:

Catalyst particle size	Synthesis temperature	$CO+H_2$ conversion	Oxygen-containing organic compounds	Methane formation
1.9 mm.	210° C.	53%	50%	10%
3.1 mm.	215° C.	48%	46%	11%
5.0 mm.	225° C.	50%	44%	14%

In the course of the continuous operation it became apparent that the life of the catalysts of the invention exceeded that of the catalysts moulded to a particle size of 3 to 5 mm., by several months.

EXAMPLE 2.

A catalyst consisting of 100 parts by weight of iron (Fe), 5 parts by weight of copper (Cu), 10 parts by weight of kieselguhr, and 5 parts by weight of K_2O (added in the form of K_2CO_3) was prepared in four different particle sizes of 0.5—1 mm., 1—2 mm., 2—3 mm., and 3—4 mm. The reduction of the catalyst was carried out at about 300° C. with hydrogen at high gas velocities (1.5 m/sec.) until 80% of the iron content of the catalyst was in the form of metallic iron. A comparison was made between these four catalysts at a gas load of 1000 volumes of gas per volume of catalyst per hour and at a synthesis pressure of 20 kilograms per square centimetre without recycling part of the residual gas into the synthesis reactor.

After an operating time of 200 hours the following results were obtained at 218° C.:

Particle size	$CO+H_2$ conversion	CO conversion
0.5—1 mm.	50%	69%
1.0—2 mm.	41%	52%
2.0—3 mm.	31%	41%
3.0—4 mm.	31%	41%

Whereas a satisfactory conversion could not be attained with the catalysts having particle sizes of more than 2 mm. in spite of a further temperature increase of approximately 30° C., a good CO conversion over an extended period of time could be obtained with the 1—2 mm. particles, and particularly with the 0.5—1 mm. particles, at temperatures of approximately 10°—15° C. above 218° C.

Upon working up the synthesis products formed, the yield of oxygen-containing organic compounds obtained with the 0.5—1 mm. particles was found to be about 20% higher than that obtained with the 2—3 mm. and 3—4 mm. particles.

What we claim is:—

1. A process for the catalytic hydrogenation of carbon monoxide for the production of synthesis products containing not less than 30% of oxygen-containing organic compounds, which comprises contacting a gas mixture containing carbon monoxide and hydrogen in synthesis proportions with a fixedly provided iron catalyst of the type hereinbefore defined, under synthesis conditions of temperature and at a synthesis pressure greater than 5 atmospheres, the catalyst being provided in the form of particles having a size not greater than 2 mm., the size range of the particles being not greater than 1 mm.

2. A process according to claim 1, in which the size range of the catalyst particles is not greater than 0.5 mm.

3. A process according to claim 1 or claim 2, in which the size of the catalyst particles lies within the range 0.5 to 1.9 mm.

4. A process according to any one of the preceding claims, in which the synthesis pressure lies within the range 10—70 atmospheres.

5. A process according to any one of the preceding claims, in which the catalyst is a precipitated catalyst.

6. A process according to any one of the preceding claims, in which the space velocity lies within the range 10—1000

volumes of gas per volume of catalyst per hour.

7. A process according to any one of the preceding claims, in which the gas mixture containing carbon monoxide and hydrogen is water-gas.

8. A process according to any one of the preceding claims, in which the carbon monoxide and hydrogen are passed upwardly through the catalyst.

9. A process according to any one of the preceding claims, in which in the reduction of the catalyst prior to its use in the synthesis, the reducing gases are passed over or through the catalyst at high velocity, for example at 60—100 centimetres per second (measured linearly and in the cold), at a temperature within the range 200°—350° C.

10. A process for the hydrogenation of carbon monoxide in the presence of an iron catalyst, substantially as hereinbefore described.

11. A process for the hydrogenation of carbon monoxide in the presence of an iron catalyst, substantially as hereinbefore described with reference to Example 1 or Example 2 with the use of catalyst particles of a size not greater than 2 mm.

12. Oxygen-containing organic compounds, particularly alcohols, and hydrocarbons whenever produced according to the process of any preceding claim.

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**Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1954.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.**

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ERRATUM

SPECIFICATION No. 715,043

Page 3, line 46, *for* "50%" *read* "52%"
THE PATENT OFFICE,
8th October, 1954.

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