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(54) CATALYTIC CARBON MONOXIDE HYDROGENATION

(54) HYDROGENATION D'OXYDE DE CARBONE CATALYTIQUE

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This invention relates to improvements in the catalytic carbon monoxide hydrogenation resulting in products with a high content of oxygen-containing compounds.

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

It is also known that catalyst particle sizes of less than about 0.5 mm, preferably less than 0.2 mm. diameter, are used in the so-called "fluidized" synthesis. This magnitude of catalyst particles is necessary in order to obtain, with the interaction of the upwardly streaming synthesis gases, a liquid 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 would be used, they could not be maintained in the fluidized state at the gas velocities required for the carbon monoxide hydrogenation. The maximum particle size for the use of iron catalysts is approximately 0.3 to 0.5 mm. for the undisturbed performance of this synthesis.

It has now been found that the catalytic carbon monoxide hydrogenation for the production of gaseous, liquid and solid synthesis products using pressures above 5 atm., preferably above 10 atm., and fixed bed iron catalysts of the type yielding at least 30 per cent, preferably more than 45 per cent, of oxygen-containing compounds in the synthesis

products can be carried out with particular advantage and good yield when the range of grain sizes of these catalysts is as narrow as possible, using diameters of less than 2 mm., preferably between 0.5 and 1.9 mm.

Using this method of operation instead of catalyst granules of a greater size, the synthesis temperature may considerably be decreased resulting in a very favorable effect on the activity and life as well as on the methane formation. Special care is to be taken that when using grain sizes of less than 2 mm. diameter the range of particle sizes is maintained as narrow as possible. The effects obtained in the synthesis proved to be the more favorable the more uniformity exists in the particle size of the catalysts used. It is just the maintenance of relatively small tolerances in the use of small granules which brings about the effect in accordance with the invention. It is also a feature of this effect that the formation of oxygen-containing compounds, preferably of alcohols, is considerably increased as compared with catalysts having a diameter above 2 mm. Superatmospheric pressures, preferably between 10 and 70 atm., are generally used when employing the catalyst particle size according to the invention. However, also higher synthesis pressures may be used.

The gas load of the catalyst may be varied from hourly 10 litres up to more than 1000 litres per litre of catalyst. It is expedient to recycle the synthesis gases, part of the residual gas being returned into the synthesis reactor. In this manner a considerably more uniform heat removal may be obtained as compared with a straight passage of the gas.

In many cases it is of advantage to pass the synthesis gases upwardly through the synthesis reactor, preferably

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. These difficulties can be avoided without changing the synthesis properties of the catalyst by conducting the gas stream upwardly as being not usual in general with fixed bed catalysts.

The preparation of catalyst grains with a diameter of less than 0.2 mm. may be effected in any way. In the preparation of precipitation catalysts the moist catalyst mass is shaped out to the particle size desired by means of devices known per se, for example by means of a sieving screen. Also catalysts which are prepared by decomposition of metal compounds, e.g. of nitrates, may be shaped out in this way. Melting and sinter catalysts are mechanically crushed to the corresponding grain size and then screened.

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

EXAMPLE 1

A catalyst consisting of 100 parts by weight of iron (Fe), 5 parts by weight of copper (Cu), 10 parts by weight calcium oxide (CaO) and 10 parts by weight of kieselguhr and containing 8.5 per cent of K_2O in the form of sodium carbonate, calculated on and referred to the present iron, was molded to granules of 1.9 mm, 3.1 mm, and 5 mm diameter, respectively, by means of a filament molding press. Then the catalyst granules were reduced at 300° C with hydrogen so far that they contained 80 per cent of their iron content in the form of metallic iron.

The reduced catalysts, separated according to the individual particle sizes, were filled into three different synthesis tubes. These synthesis tubes consisted of a double tube, the annular space between both tubes having a width of 10 mm. The length of the double tubes was 4.5 m. In all of the three tubes the synthesis was performed in such a manner that 150 parts by volume of water gas per part by volume of catalyst were charged per hour and moreover 2.5 parts by volume of residual gas per part by volume of fresh gas were admixed. The synthesis pressure was 10 kilograms per square centimeter.

After 300 and 600 hours, respectively, the yield of oxygen-containing compounds, the conversion and the synthesis temperature reached 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 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 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 molded to 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 grain 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 the catalyst contained 80% of its iron content in the form of metallic iron. A comparison was made between these four catalysts at a gas load of hourly 1000 parts by volume of gas per part by volume of catalyst and at a synthesis pressure of 200 kilograms per square centimeter 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	52%	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 reached at all with the catalyst grains of a size of more than 2 mm in spite of a further temperature increase by approximately 30° C., a good CO conversion over an extended period of time could be obtained with the 1 - 2 mm particles, but first of all with the 0.5 - 1 mm particles, at temperatures of approximately 10 - 15° C. in excess of the above mentioned.

Working up of the formed synthesis products showed that the yield of oxygen-containing compounds obtained with the 0.5 - 1 mm particles was about 20 per cent higher than that obtained with the 2-3 and 3-4 mm particles.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the conversion of carbon monoxide and hydrogen into gaseous and liquid synthesis products containing at least 30 per cent of oxygen-containing compounds at synthesis pressures above 5 atmospheres with fixed bed iron catalysts, which comprises the use of catalyst particle sizes of less than 2 mm and maintaining the range of particle sizes as narrow as possible.

2. A process according to claim 1 in which synthesis products with a content of more than 45 per cent of oxygen-containing compounds are produced.

3. A process according to claim 1 in which synthesis pressures above 10 atmospheres are used.

4. A process according to claim 1 in which catalysts of a particle size between 0.5 and 1.9 millimeters are used.

5. A process according to claim 1 in which catalyst loads of 10 to 1000 litres of gas per litre of catalyst per hour are used.

6. A process according to claim 1 in which catalyst loads of more than 1000 litres of gas per litre of catalyst per hour are used.

7. A process according to claim 1 in which the synthesis gases are passed in upward direction through the catalyst bed.

8. A process according to claim 1 in which the catalysts are reduced at high gas velocities of 60 to 100 centimeters per second, measured linear and cold, and at temperatures in the range of 200 - 350° C.

9. A process for the conversion of carbon monoxide and hydrogen into gaseous and liquid synthesis products containing more than 45 per cent of oxygen-containing compounds at synthesis pressures above 10 atmospheres by means of fixed bed iron catalysts, which comprises passing synthesis gases in amounts of 10 to 1000 litres of gas per litre of catalyst per hour in upward flow direction through said catalysts which have been reduced at temperatures between 200 and 350° C. and high gas velocities of 60 to 100 centimeters per second, measured linear and cold, the particle size of catalyst being between 0.5 and 1.9 mm diameter.