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COMPLETE SPECIFICATION

Improvements in or relating to the Catalytic Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German Company, of Oberhausen-Holten, Germany, and LURGI GESELLSCHAFT FÜR WÄRMETECHNIK m.b.H., a German Company, of Frankfurt, a.M.-Heddernheim, Germany, 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.

The cobalt, nickel and iron catalysts conventionally used in the catalytic hydrogenation of carbon monoxide have, in practice, had a particle size of approximately 3 to 5 mm when the catalysts have been employed in fixed beds in the absence of a liquid medium. For this purpose, the particle size of the catalyst is generally determined by the mesh of the screen through which the catalyst passes. Thus if the upper limit for the particle size of the catalyst is to be 5 mm. the catalyst must completely pass through a screen having a mesh width of 5 mm. × 5mm. The lower limit of 3 mm. for the particle size of the catalyst has been used since particles smaller than 3 mm. increase the pressure drop of the gas upon its flow through the catalyst layer and also increase the danger of non-uniform gas impact.

In the past, the tubes or chambers of the reactors used in the hydrogenation of carbon monoxide have, in practice, had internal diameters or thicknesses respectively, which did not exceed 10 mm. These dimensions of the synthesis spaces controlled the upper limit of the particle size of the catalyst. Due to the fact that a sufficiently rapid removal of the heat of reaction was not possible, a larger thickness or diameter of the catalyst layers or columns has not been used. Furthermore, a catalyst having a particle size greater than 10 mm. has not been used in the industry since it was assumed that a catalyst particle of such a large size would not be sufficiently utilized and that therefore the greatest possible outer surface area of the catalyst particles was desirable, which surface area is the greater per unit volume of catalyst, the smaller the size of the individual particles. Because of this assumption it was believed that a substantial impairment of the synthesis would result if the particle size were increased.

Recently, tubes of diameters of 30 to 50 mm. have been used in the reactors for the catalytic hydrogenation of carbon monoxide. The use of these larger tubes was made possible by employing higher gas velocities which bring about stronger eddying of the gases within the tubes, which in turn considerably facilitates the removal of the heat of reaction. Furthermore, catalysts having a smaller heat of activation than those previously used in the industry were developed, which permitted higher excess temperatures in the centre of the catalyst layer, so that larger tube dimensions were possible. However, these improvements allowing the larger diameter of the tubes have had no influence on the catalyst particle sizes used up to the present time.

It is an object of the invention to provide a process for the catalytic hydrogenation of carbon monoxide in which the feed gas may have a lower H_2:CO ratio than has hitherto been used with catalysts having the smaller sizes of particle, whilst giving substantially the same conversion.

A further object of the invention is to permit the hydrogenation of carbon monoxide to be carried out with a more uniform flow of the synthesis gases. Another object of the invention is to provide a process for the catalytic hydrogenation of carbon monoxide, in which the pressure drop in the synthesis gases across the bed of catalyst is lower than the pressure drop hitherto usual in such hydrogenation.

It has now been found, according to the invention, that the catalytic hydrogenation of carbon monoxide can be successfully carried out using fixed cobalt, nickel or iron catalysts obtained by precipitation from a solution of a salt, when the particle size of the catalysts is from 10 mm. to 25 mm., preferably not more than 20 mm., and the catalysts are used in tubes the internal diameter of which is from 30 mm. to 500 mm. and is preferably not greater than 100 mm. If tubes having a relatively small inner diameter such, for example as 30 mm. to 50 mm., are used, it is advantageous to use catalysts having a particle size of about 0.3 to 0.5 times the diameter of the tube.

If catalyst chambers are used, then, in accordance with the invention, the catalyst is used in layers of a thickness of from 30 mm. to 500 mm., the thickness of the layers being determined by the distance between the plates of the catalyst chambers.

Detailed investigations with cobalt catalysts have shown that they are fully utilised in their interior so that the upper limit for the size of the catalyst particles is not determined by efficient utilisation, but by the tube diameter or the distance apart of the plates of the reactor.

Experiments have shown that the transport velocity of the hydrogen in the interior of the particles is substantially greater than that of carbon monoxide. Due to this the larger the catalyst particles are, the greater will be the H_2:CO ratio in the interior of the particles as compared with the ratio in the gas space between the particles. Thus by using larger catalyst particles and a feed gas which is poorer in hydrogen, the same effect is obtained as is obtained by the use of smaller catalyst particles and a gas richer in hydrogen, and without any appreciable reduction in conversion occurring in the reactor. Thus, in the process according to the invention it is possible to use feed gases having an H_2:CO ratio which is 10—25% lower than was heretofore used in the industry when using catalyst particles of smaller diameter.

It is known that in carbon monoxide hydrogenation using, for example, iron catalysts, the H_2:CO ratio in the exit gas is greater than the H_2:CO ratio in the feed gas. Furthermore, it is known that the course of the synthesis is considerably influenced by this ratio. As hereinbefore stated, by the used of larger catalyst particles, the H_2:CO ratio within the particles is increased. Thus if it is desired to have the catalyst function at the beginning of the catalyst layer or column as if the gas fed into it had a higher H_2:CO ratio then, despite the smaller ratio of H_2:CO actually present, larger catalyst particles should be used at the beginning of the reaction path than are used at the end. Since the ratio of H_2:CO naturally increases along the reaction path, if the catalyst particle size is decreased along the reaction path, the catalyst at the beginning of the path will operate as if it were contacted with a gas having a higher H_2:CO ratio.

Apart from the advantage which can be obtained by the diffusion effect, the use of larger catalyst particles for the catalytic hydrogenation of carbon monoxide has still further advantages. It has been found that when using these larger catalyst particles according to the invention, a more uniform gas flow through the catalyst is obtained than is obtained with the use of catalyst particles of a smaller size. Furthermore, the pressure drop over the reaction path decreases in a desirable manner with this increase of the catalyst particle size according to the invention. For this reason, the gas throughput can be increased or, with the same gas throughput, the mechanical strain on the catalyst particles can be reduced with a consequent reduction in the wear or disintegration of the particles. Finally, in certain cases, particularly for the production of low-boiling hydrocarbons or oxygen-containing organic compounds, the higher temperature in the interior of the large catalyst particles as compared with the temperature prevailing with the use of smaller particles under the same synthesis conditions, may be of advantage.

The catalysts are obtained by the precipitation of the solution of the nitrate of the metal with an alkaline material, for example, a solution of sodium carbonate. The solution of the catalyst metal may also contain nitrates of activator metals such as copper or other metal known to be effective as an activator, and a supporting material, such as kieselguhr, may be added. The precipitate is washed after which an alkali-metal compound may be incorporated in the precipitate. The moist mass is then moulded in a thread press, the moulded rods so obtained being then dried in known manner and sieved to size, after breaking of the dried rods if necessary.

What we claim is:—

1. A process for the hydrogenation of carbon monoxide in the presence of a fixed cobalt, nickel or iron catalyst, in which the catalyst, obtained by precipitation from a solution of a salt, has a particle size of from 10 mm. to 25 mm. and is used within tubes having an internal diameter of from 30 mm. to 500 mm. or is used in layers of a thickness of from 30 mm. to 500 mm.

2. A process according to claim 1, in which the catalyst has a particle size of not

more than 20 mm.

3. A process according to claim 1 or claim 2, in which the internal diameter of the tubes or the thickness of the layers is not greater than 100 mm.

4. A process according to any one of the preceding claims, in which the internal diameter of the tubes or the thickness of the layers is not greater than 50 mm. and the catalyst has a particle size of from 0.3 to 0.5 of the internal diameter of the tubes or of the thickness of the layers.

5. A process according to any one of the preceding claims, in which the H_2:CO ratio in the feed gas is 10—25% lower than has hitherto been normally used with smaller catalyst particles in a fixed bed to give substantially the same conversion.

6. A process according to any one of the preceding claims, in which the particle size of the catalyst decreases in the direction of gas flow.

7. A process for the hydrogenation of carbon monoxide carried out in the presence of a fixed bed of a cobalt, nickel or iron catalyst substantially as hereinbefore described.

8. Hydrocarbons and oxygen-containing organic compounds, whenever obtained by the process claimed in any preceding claim.

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