



Canadian Patents Database

12/20/2001 - 16:17:58

(11) CA 554382

(12) Patent:

(54) CATALYTIC HYDROGENATION OF CARBON MONOXIDE

(54) HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

(72) Inventor (Country): **WALTER BROTZ (Not Available)**
HERBERT SPENGLER (Not Available)

(73) Assignee (Country): **RUHRCHEMIE AKTIENGESELLSCHAFT**
LURGI GESELLSCHAFT FUR WARMETECHNIK N.B.H.

(71) Applicant (Country):

(74) Agent:

(45) Filing Date: **Mar. 11, 1958**

(22) International Class:

(43) Publication Date:

(52) International Class: **260/753.1**

(51) International Class: **N/A**

(30) Priority: **No**

(30) Priority: **None**

(30) Priority: **N/A**

(30) Priority: **Unknown**

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

View or Download Images :

- Cover Page Image
- Abstract Image
- Claims Image
- Disclosures Image

This invention relates to improvements in catalytic hydrogenation of carbon monoxide.

The cobalt, nickel and iron catalysts conventionally used in catalytic carbon monoxide hydrogenation have a particle size of approximately 3 to 5 mm. The particle size of the catalyst is generally determined by the screen size through which the catalyst passes. Thus if the upper limit for the particle size of the catalyst is determined to be 5 mm, the catalyst must completely pass through a screen having a mesh width of 5 x 5 mm. 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 contact layer and also increases the danger of non-uniform gas impact.

In the past synthesis tubes or synthesis chambers used in carbon monoxide hydrogenation had dimensions or layer thicknesses which did not exceed 10 mm. These dimensions of the synthesis spaces were controlling in determining 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 of the catalyst layer was not used. An increase of the particle size of the catalyst to above 10 mm. was not undertaken in the industry for it was assumed that the contact particle of such a large size would not be sufficiently utilized and that therefore the greatest possible outer surface of the contact particles was desirable, the smaller the size of the individual particles, the greater the surface area per unit volume. Because of this assumption it was believed that a substantial impairment of the synthesis would result if the particle size were increased.

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

One object of this invention is the catalytic hydrogenation of carbon monoxide using a lower ratio of $H_2:CO$ than was heretofore used.

20 A further object of this invention is carbon monoxide hydrogenation with a more uniform flow of the synthesis gases. A still further object of this invention is to decrease the pressure drop over the reaction path of the synthesis gases during catalytic carbon monoxide hydrogenation.

These and still further objects will become apparent from the following description;

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, the particle size of which is more than 10 to 25 mm. and preferably 11 to 20 mm. These catalysts are preferably used in synthesis tubes, the diameter of which is 20 to 500 mm. and preferably 30 to 100 mm.

If tubes having a relatively small inner diameter as, for example, 30 to 50 mm., are used, it is advisable to use catalysts having a particle size of about 0,3 to 0,5 times the diameter of the synthesis tube.

If contact chambers are used then in accordance with the invention, the distance is computed as the distance between the plates of the contact chambers. Therefore catalyst grain sizes of preferably 11 to 25 mm. are used in such tubes and chambers.

10

Detailed investigations with cobalt catalysts have shown that they are completely used up in their inside so that the upper limit for the size of the contact particles is not determined by efficient utilization but by the tube diameter or the distance apart of the plates of the synthesis furnaces.

20

Experiments have shown that the transport velocity of the hydrogen in the inside of the particles is substantially greater than that of carbon monoxide. Due to this the larger the contact particles are, the larger will be the H_2 : CO ratio inside the particles than in the gas space between the particles. Thus by using larger contact particles and a synthesis gas which is poorer in hydrogen, the same effect is obtained as is obtained by the use of smaller contact particles and a gas richer in hydrogen. This is true without any noticeably reduced conversion taking place in the catalyst furnace. Thus by following the method according to the invention catalytic carbon monoxide hydrogenation is possible using synthesis gases having an H_2 : CO ratio which is 10^{Ed} - 25%^{Ed} lower than was heretofore possible in the industry when using contact particles of smaller diameter.

10 It is known that in carbon monoxide hydrogenation using, for example, iron contact agents, a smaller ratio of H_2 : CO exists at the gas inlet than at the gas outlet. Furthermore, it is known that the course of the synthesis is considerably influenced by this ratio. As stated above, by the use of larger contact particles, the H_2 : CO ratio within the particles is increased. Thus, if it is desired to have the contact agent at the beginning of the contact layer operate as if it were tendered a gas having a higher H_2 : CO ratio, despite the smaller ratio of H_2 : CO actually present, larger contact particles may 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 contact particle size is decreased along the reaction path, the agent at the beginning of the path will operate as if it were contacted with a gas having a higher H_2 : CO ratio.

20 Aside from the advantage which can be obtained by the diffusing effect, the use of larger contact particles for catalytic carbon monoxide hydrogenation has still further advantages. It has been found that when using these larger contact particles according to the invention a considerably more uniform gas flow through the contact is obtained than was hitherto-fore obtained with the use of contact particles having a smaller particle size. In addition to this the pressure drop over the reaction path decreases in a desirable manner with this increasing of the catalyst particle size according to the invention. Due to this the gas charge can be increased or the mechanical strain on the contact particles with the same gas charge can

reduced. Thus, the wear on the particles is reduced.
Finally, in certain cases and particularly for the production
of low-boiling hydrocarbons or oxygen-containing hydrocarbons,
the greater increase of the temperature on the inside of the
5 large contact particles as compared with the temperature
increase prevailing in connection with the use of smaller
particles, may be of advantage.

The method, in accordance with the invention, appears
to be practicable for all types of catalysts, such as melting
10 catalysts, sintered catalysts, and precipitation catalysts.
The method has been tried especially for precipitation cata-
lysts and showed particularly favourable results for this
type of catalyst.

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

1. In the method for the hydrogenation of carbon monoxide using fixed cobalt, nickel or iron catalysts the improvement which comprises passing synthesis gas along a path of gas flow, intimately contacting said synthesis gas along said path of gas flow with such catalyst having a particle size of 11 to 25 mm, and recovering synthesis products.
2. Improvement according to claim 1 in which such catalysts have a particle size of 11 to 20 mm.
3. Improvement according to claim 1 in which such catalysts have been precipitated from their metal salt solutions.
4. Improvement according to claim 1 in which particles size of such catalysts decreases in the direction of gas flow.

Alex. E. MacRae, ~~Inc.~~,
P. O. Box 1077,
Ottawa, Ontario, Canada,
Patent Agents for Applicants.