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(54) CATALYTIC CARBON MONOXIDE HYDROGENATION

(54) HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

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This invention relates to improvements in catalytic carbon monoxide hydrogenation.

The catalytic hydrogenation of carbon monoxide to obtain valuable synthesis products is well known. Various gas mixtures may be used as the synthesis gas for the hydrogenation. Gas mixtures which are known and have been used include coke oven gas, blast furnace gas, producer gas, waste gases from the production of acetylene, gases formed by the pressure gasification of carbonaceous materials with the use of oxygen as the gasifying agent, and gases derived from other sources.

The gas mixtures which are used as the synthesis gas for the hydrogenation must contain carbon monoxide and hydrogen. The proportions of carbon monoxide and hydrogen may vary within certain limits, but a minimum proportional amount of hydrogen must always be present. The various proportions of carbon monoxide and hydrogen and the limits of these proportions are, of course, well known and described in the art.

Very often gases are available which do not contain the required amounts of hydrogen or which only contain carbon monoxide in addition to inert constituents. It is, of course, not possible to use gases of this type as the synthesis gas for catalytic carbon monoxide hydrogenation until the required amount of hydrogen is present. The required hydrogen content to render these gases useful as synthesis gases for hydrogenation is generally effected by converting a portion of the carbon monoxide admixed with water vapor into carbon dioxide and hydrogen.

This conversion of the carbon monoxide containing gas mixtures is effected in the presence of a catalyst. Various catalysts are well-known in the art which are suited to give

optimum conversions at different temperatures and gas velocities. These catalysts are generally divided into three broad classes. The normal conversion catalysts which require temperatures of approximately 400°C. for the conversion; 5 medium activity conversion catalysts which effect a satisfactory reaction between the carbon monoxide and water vapor at temperatures as low as 300°C.; and highly active conversion catalysts which effect a satisfactory conversion between the carbon monoxide and water vapor at temperatures as low as 10 200°C.

The exact compositions and methods for preparing the catalysts of these three general types are well-known and described in the art. In accordance with the above explanation, therefore, a skilled artisan will know exactly 15 what catalysts are referred to when referring to normal conversion catalysts; medium activity conversion catalysts and highly active conversion catalysts. Thus, for example, particularly effective highly active conversion catalysts consist of copper or copper oxide and activating metal oxides 20 of the second or seventh group of the Periodic System which have been prepared with or without carrier materials by a sintering, fusing or pressing process.

The conversion of the carbon monoxide and the water vapor into hydrogen as has been mentioned also results in the 25 production of carbon dioxide. In addition to this carbon dioxide, the converted gases always contain relatively large amounts of water vapor which has been added in excess or which has not been completely consumed in the conversion. It was always believed that these substances would be very injurious to the 30 hydrogenation process and prior to the instant invention, these converted gases which were to be used for the catalytic hydrogenation

of carbon monoxide were treated for the removal of carbon dioxide and water. This treatment for carbon dioxide and water removal was relatively complicated and expensive. Considerable operating expenses were involved due to the fact that the gas had to pass heat exchangers, cooling devices and absorption devices.

One object of this invention is to effect catalytic carbon dioxide hydrogenation with synthesis gases obtained by the catalytic conversion of carbon monoxide containing gas mixtures without the disadvantageous carbon dioxide and water purifying steps. This and still further objects will become apparent from the following description:

It has now been very surprisingly and unexpectedly found that carbon monoxide containing gases which have been catalytically converted in the presence of water vapor and the gases containing carbon monoxide, hydrogen, carbon dioxide and water vapor may be used directly, i.e. without any carbon dioxide or water removal in the catalytic carbon monoxide hydrogenation synthesis process as the synthesis gas.

In accordance with the invention, the carbon monoxide containing gases which require a conversion so that the required amount of hydrogen will be present are subjected to the catalytic conversion in the presence of water vapor in the conventional manner and are thereafter directly charged at nearly the same pressure as synthesis gas for the catalytic hydrogenation of carbon monoxide. By directly charged, it is meant that the gases from the catalytic conversion are passed to the catalytic carbon monoxide hydrogenation without separation therefrom of any of the conversion products. The gas pressures used for the hydrogenation are preferably above 5 kilograms of square centimeters.

The catalytic hydrogenation of carbon monoxide is generally effected at temperatures between 170° and 300°C. depending on the catalyst used. With the use of special iron catalysts, as is known in the art, synthesis temperatures of approximately 300° to 350°C. are also possible. Under these conditions and with the use of suitable conversion catalysts, the converted gases may be passed directly without any cooling from the conversion zone directly into the hydrogenation zone. It is preferable in most cases to use highly active conversion catalysts which cause a satisfactory reaction between the carbon monoxide and water vapor at temperatures as low as 200° to 300°C. since with the use of these highly active conversion catalysts, the gases passing out of the conversion zone will have a temperature closest to the temperature at which the catalytic carbon monoxide hydrogenation is effected.

The catalysts fillings used for the conversion and for the hydrogenation of the carbon monoxide may be arranged within a single synthesis apparatus in any manner provided that the conversion catalyst is positioned before the hydrogenation catalyst in the direction of gas flow. Thus, when using a reactor in which the gas mixture is passed in a downward direction, the lower catalyst layer must consist of a hydrogenation catalyst such as a cobalt or iron catalyst, while a conversion catalyst layer must be positioned in the upper part of the reactor. If the gases flow through the catalyst furnace in upward direction, then a conversion catalyst layer must be positioned in the lower portion of the furnace and a hydrogenation catalyst layer must be positioned in the upper portion of the reactor. It is also possible to effect the process in accordance with the invention in reactors through

which the gas mixture passes horizontally. This latter arrangement has the advantage that the two catalyst masses cannot mix with each other by one dropping down from a sieve plate or the like on which it is held and through which the gas passes as when using vertical reactors.

The catalyst for the conversion and/or the hydrogenation besides being in the form of a fixed bed may be moving or suspended catalysts such as are used in the "fluidized" process. In these cases, the gases may be converted with the use of a fluidized bed of a suitable conversion catalyst. Thereafter, it may be passed to a different apparatus and passed through a fluidized bed of a conventional fluidized hydrogenation catalyst. By so connecting in series to such fluidized catalyst processes, the results of the invention are obtained, i.e. the separation of water and carbon dioxide from the converted gas as no longer necessary.

It is, of course, not absolutely necessary that the catalysts zones for effecting the process be arranged in superposition. It is also possible to operate with aggregates lying side by side, but care should be taken that no substantial cooling occurs in the transition from one to the other.

Both the catalytic hydrogenation process and the catalytic conversion process are in all other respects identical in reaction, condition, procedure, etc. The catalysts may be positioned in tubes of small or large diameter or in pockets. Water for aqueous salt solutions are preferably used as the cooling medium. It is, however, possible to work with water vapor or other gaseous or liquid cooling agents or to effect the cooling in any other conventional manner.

As both the catalytic conversion and the catalytic carbon monoxide hydrogenation are substantially exothermic

reactions, it is generally necessary to provide a cooling system with a removal of the reaction heat in each of the conversion and hydrogenation. In accordance with the invention, the cooling systems for the conversion and hydrogenation may be connected in series and the same cooling media may flow therethrough. It is, however, also possible in accordance with the invention to provide a separate cooling system for each of the conversion and hydrogenation zones. The latter arrangement has the advantage that both catalyst zones may be individually controlled with respect to the operating temperature. The operating temperature in the conversion zone should be nearly as high as that in the hydrogenation zone, i.e. the temperature difference should not be so large that an intermediary separation of water will occur.

As has been mentioned, the catalytic carbon monoxide hydrogenation process in accordance with the invention is effected in any of the ~~conventional~~ or known manners. Thus hydrogenation may be operated with gas recycling to the conventional extent. If necessary or desired, different synthesis stages may be used, in which case, suitable synthesis products in gaseous or liquid form may be separated from the gas mixture between the individual stages.

The gaseous or liquid synthesis products leaving the zone in which the hydrogenation occurs are worked up in the known and conventional manner and separated into the desired fractions.

In the claims, when there is mentioned "hydrogen lean carbon monoxide containing gas" there is specifically meant thereby a carbon monoxide containing gas which contained no hydrogen or which does not contain the required amount

of hydrogen for carbon monoxide hydrogenation. The amount of hydrogen which must be present in the gas for the hydrogenation is of course, well known in the art.

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

1. Process for catalytic reaction of carbon monoxide containing gases by conversion and subsequent carbon monoxide hydrogenation which includes the steps of contacting such a gas in the presence of water vapor with a highly active conversion catalyst at a temperature of approximately 200-300°C., passing the gases from said catalytic conversion directly to the catalytic carbon monoxide hydrogenation without separation therefrom of any of the conversion products, and utilizing an iron catalyst as the hydrogenation catalyst with a synthesis temperature of approximately 300-350°C.
2. Process according to claim 1, in which a gas pressure of more than 5 kilo/sq.cm. is used.
3. Process according to claim 1 in which said conversion catalyst and said carbon monoxide hydrogenation catalyst are substantially adjacently positioned in a common reactor.
4. Process according to claim 1, which includes separately cooling the zone containing said conversion catalyst and the zone containing said hydrogenation catalyst.
5. Process according to claim 1, in which at least one of said conversion catalyst and said carbon monoxide hydrogenation catalyst is in fluidized form.

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