PATENT SPECIFICATION

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COMPLETE SPECIFICATION

"Process for the Catalytic Conversion of Gases containing Carbon Monoxide".

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The invention relates to a process for the conversion into hydrocarbons and/or oxygen-containing organic compounds of gases containing carbon monoxide.

Various gas mixtures are available for use in syntheses in which carbon monoxide may form one of the starting materials. The gas mixtures may be in the form of coke oven gas, blast furnace gas, producer gas, waste gases from the production of acetylene, or gases which are formed by the gasification under pressure of carbonaceous materials with the use of oxygen as the gasifying agent, or they may be derived from other sources. These gas mixtures contain varying amounts of carbon monoxide and hydrogen. Sometimes, however, only carbon monoxide and inert constituents are contained therein. Gas mixtures of this kind can be used for the hydrogenation of carbon monoxide only after conversion or oxidation of part of the carbon monoxide with water vapour or steam into carbon dioxide and hydrogen.

For such conversion or oxidation of carbon monoxide-containing gas mixtures, various catalysts which give optimum conversions at different temperatures and gas velocities, may be used. A distinction is made between normal conversion catalysts which require temperatures of approximately 400°C. for the conversion, conversion catalysts of medium activity which effect a satisfactory reaction between carbon monoxide and steam at temperatures of as low as 300°C., and highly active conversion catalysts, by means of which carbon monoxide and steam may be satisfactorily converted even at temperatures of as low as 200°C. Particularly active conversion catalysts consist, for example, of copper or copper oxide and activating metal oxides of Groups II to VII of the Periodic Classification, which have been prepared, with or without carrier materials, by sintering, fusion or pressing processes.

In addition to the carbon dioxide formed in the conversion or oxidation, the converted gas always contains larger amounts of water vapour, which has been added in excess or has not completely been consumed in the conversion. Hitherto, when such converted gases were used as synthesis gas or as part of the synthesis gas in the hydrogenation of carbon monoxide their content of carbon dioxide and water was first largely or substantially completely removed. This after treatment involved considerable expense because the gas had to be passed through heat exchangers, cooling devices and absorption devices.

It has now been found that carbon monoxide-containing gases which require such a conversion, may be used in a particularly simple manner for the catalytic hydrogenation of carbon monoxide, if the gases formed in the conversion or oxidation are charged, under substantially the same pressure and immediately following the conversion reaction, to the catalytic hydrogenation of carbon monoxide without first separating therefrom any of the conversion products.

According to the invention therefore, a process for the synthesis of hydrocarbons and/or oxygen-containing organic compounds from a carbon monoxide- containing gas, comprises catalytically oxidising part of the carbon monoxide in the gas with steam, and contacting the whole of the gas mixture so obtained with a catalyst active for the hydrogenation of carbon monoxide to hydrocarbons, the said contacting being effected under synthesis conditions of temperature and un-

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der substantially the same pressure as that employed in the prior step of oxidation.

The gas pressures used are preferably greater than 5 kilos/sq. cm.

The hydrogenation of carbon monoxide is generaly effected at temperatures in the range 170°-300°C., the particular temperature or range of temperatures employed depending on the catalyst used. By means of some iron catalysts however, the use of synthesis temperatures of approximately 300°-350°C is also possible. It is preferred to carry out the oxidation of the carbon monoxide with a catalyst which is active to effect the reaction of the carbon monoxide with the steam at a temperature in the range 200°-300°C., and to effect the hydrogenation of the carbon monoxide in the presence of one of the iron catalysts which enable the hydrogenation to be effected at a temperature in the range 300°-350°C. In this manner, the gas mixture from the step of oxidation may be passed without intermediate cooling directly into the hydrogenation zone.

The catalyst charges used for the oxidation and for the hydrogenation steps may be disposed within the synthesis apparatus in any suitable way, provided that the conversion or oxidation catalyst is placed before the hydrogenation catalyst in the direction of gas flow. In a reactor through which the gas mixture is passed downwardly, the lower layer will consist of a hydrogenation catalyst, such as a cobalt catalyst or an iron catalyst whilst a catalyst layer which is suitable for the conversion or oxidation will be provided in the upper part of the reactor. If the gases are pased in an upward direction through the reactor, then a catalyst layer suitable for the oxidation step will be provided in the lower part of the reactor and a catalyst layer suitable for the hydrogenation step will be provided in the upper part of the reactor. The process according to the invention may also be carried out with catalyst charges through which the gas mixture is passed horizontally, which method of operation has the advantage that the two catalyst masses cannot mix with each other by dropping down through a sieve or perforated plate, the openings or perforations in which are provided to permit the passage of gas. The oxidation and the hydrogenation steps may also be carried out by the "fluidized" process. In this case, the oxidation step is effected with a fluidized bed of a suitable conversion catalyst, after which the products of the oxidation step are passed through a fluidized bed of a conventional "fluidized" catalyst suitable for the hydrogenation of carbon monoxide in another reactor or in another section of the same reactor.

The catalyst zones required for carrying out the process according to the invention need not be arranged one above the other. It is also possible to operate with aggregates lying separately side by side if care is taken that no substantial degree of cooling occurs in the transition from one aggregate to the other.

In other respects, the oxidation step and the hydrogenation step may be carried out by any method conventionally used for gas reactions of this kind. The catalyst may be disposed in tubes of small or large diameter or in pockets. Water or aqueous salt solutions are preferred as cooling media. However, it is also possible to operate with steam or other gaseous or liquid cooling agents.

Both the section for the conversion or oxidation and that for the hydrogenation of carbon monoxide must be provided with a cooling system for the removal of the heat of reaction. These cooling systems may be connected in series and the same cooling medium may flow through them. However, it is also possible to provide the conversion or oxidation zone with independent cooling systems. This has the advantage that the temperature in each of the two catalyst zones may be varied independently.

The section for the hydrogenation of carbon monoxide may be operated with recycling of the gas in the usual manner. If necessary or desired, several synthesis stages may be used, in which case suitable synthesis products in the gaseous or liquid form may be separated from the gas mixture between the individual synthesis stages.

The gaseous and liquid synthesis products leaving the zone in which the hydrogenation of carbon monoxide occurs, may be worked up in known manner and separated into desired individual fractions.

What we claim is:—

1. A process for the synthesis of hydrocarbons and/or oxygen-containing organic compounds from a carbon monoxide-containing gas, which comprises catalytically oxidising part of the carbon monoxide in the gas with steam, and contacting the whole of the gas mixture so obtained with a catalyst active for the hydrogenation of carbon monoxide to hydrocarbons, the said contacting being effected under synthesis conditions of temperature and under substantially the same pressure as that employed in the prior step of oxidation.

2. A process according to Claim 1, in which the pressure is greater than 5 kilograms per square centimeter.

3. A process according to Claim 1 or Claim 2, in which the step of oxidising part of the carbon monoxide is carried out in the presence of a catalyst which enables the oxidation to be effected at a temperature within the range 200°-300°C, and the hydrogenation step is effected in the presence of an iron catalyst at a temperature within the range 300°-350°C.

4. A process according to any one of the preceding claims, in which the catalyst used

in the oxidation step is provided adjacent to the catalyst used in the hydrogenation step.

5. A process according to Claim 4, in which the catalysts are provided one above the other in the same reactor.

6. A process according to Claim 4, in which the catalysts are provided side by side in the same reactor.

7. A process according to any one of Claims 1 to 5, in which the oxidation step and/or the hydrogenation step are carried out with a catalyst in the fluidized state.

8. A process according to any one of the preceding claims, in which the zones in which the oxidation step and the hydrogenation step are effected, are provided with independent cooling means.

9. A process for the synthesis of hydrocarbons and/or oxygen-containing organic compounds, substantially as hereinbefore described.

10. Hydrocarbons and oxygen-containing organic compounds, whenever obtained by the process of any preceding claim.

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