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COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT and LURGI GESELLSCHAFT FUER WAERMETECHNIK M.B.H., of Oberhausen-Holten, Germany and Frankfurt, Germany respectively, both German Companies, 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 hydrogenation of carbon monoxide.

The latest technical development of the Fischer-Tropsch synthesis with fixed-bed catalyst has shown that the following three conditions, among others, must be complied with in order to obtain operation which is satisfactory both technically and economically:—

1. Layer depths of catalyst of more than 5 metres and preferably of more than 10 metres, for example, 12 metres in order to increase the capacity of the individual reactor unit by increasing its length without increasing the cross section to a point at which hindrance to conveyance occurs).

2. Use of high absolute gas velocities (to obtain high throughputs as well as to ensure a sufficient transfer of heat to the walls of the tubes containing the catalyst).

The high absolute gas velocities are connected with or related to the layer depths. In the case of catalyst layers of about 5 metres depth, gas velocities of 60—80 cm./second, based on normal conditions are used. With catalyst beds having a layer depth of 12 metres, gas velocities of more than 1.3 metres/second, preferably of 1.6—1.8 metres/second are used. When operation is effected with recycling of the synthesis gases with the reaction gas being returned at a recycle ratio of at least 1:2.5, the corresponding velocities are about 2.4 metres/second and about 6 metres/second, respectively.

3. Recycling of the reaction gas with a recycle ratio of at least 1:2 (in order to effect as uniform a reaction as possible throughout the whole length of the bed and to obtain a rapid discharge of the reaction products and, moreover, to contribute to the high gas velocity mentioned under heading 2 above).

The three factors mentioned above result in the fact that a considerable drop of pressure which may, for example, amount to 1 to 2 atmospheres, occurs in catalyst beds of this kind. Under these conditions, the synthesis is extremely sensitive to the occurrence or presence of catalyst dust. This dust may accumulate in the catalyst bed at local spots or zones and increase the pressure drop to a degree which renders satisfactory operation of the synthesis no longer possible. Moreover, in reactors consisting of tube bundles made up of a great number of individual catalyst tubes, it may cause pressure drops which vary greatly in the tubes thereby preventing a uniform reaction throughout the tubes.

Dust is easily formed from the very sensitive Fischer-Tropsch catalysts by any movement or by any transport of the granulated catalyst. It has been proposed, therefore, to screen the catalyst mass once again or to subject it to wind-sifting immediately before it is charged into the tubular system of the reactor. Apart from the considerable technical difficulties entailed by such a measure, particularly if it involves the treatment of a reduced catalyst in the absence of air or oxygen, this measure is not decisively effective because the catalyst, which has been freed from dust upstream of the reactor, will again yield abraded particles and dust during the step of charging it into the reactor.

It has now been found, according to the invention, that high-load synthesis of the kind referred to can be operated in a satisfactory manner without hindrance by dust or formation of dust if the catalyst particles, prior to being charged into the reactor and either before or after reduction, are made abrasion-resistant by impregnating them with hydrocarbons which are solid at room or normal temperature as, for example, solid paraffins from the Fischer-Tropsch synthesis, the catalyst being

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impregnated with from 5% to 60% of the hydrocarbons such that no substantial agglomeration of the catalyst particles occurs. The preferred catalyst is an iron catalyst.

It is true that Fischer-Tropsch catalysts have already been impregnated with solid or liquid hydrocarbons. These measures were taken with the object of suppressing the initial formation of methane, and not only were no favourable observations made with regard to improvement in the passage of the gas, but, on the contrary, an aggravation of the difficulties of charging the catalyst and a non-uniform arrangement of the catalyst in the catalyst space were observed due to agglomeration of individual catalyst particles. (See Kainer, "Die Kohlenwasserstoffsynthese nach Fischer-Tropsch", 1950, page 88—89). Furthermore, catalysts which have been impregnated in this manner have not been charged to reactors with catalyst layer depths of more than 5 metres. It was not to be foreseen, therefore, that the difficulties mentioned above in the high-load synthesis with catalyst layer depths of at least 5 metres could be overcome by the process according to the invention.

The impregnation of the catalyst particles may be effected in a manner known *per se*. It is possible, for example, to apply a solution of solid hydrocarbons in lower boiling liquid hydrocarbons and to evaporate the solvent after the impregnation, or to impregnate the catalyst mass with the solid hydrocarbons in a molten state and to remove the excess of the impregnating agent whilst still hot. In any case, the impregnation must be effected in such a manner that no substantial excess of the impregnating agent remains on the surface of the individual particles so that agglomeration does not occur.

An additional and particular advantage of the process resides in the fact that a reduced catalyst mass can also be impregnated and is thereby made insensitive to the air, which fact considerably facilitates the transport and the charging of the reduced catalyst mass into a reactor.

It is important that the granular catalyst mass be completely freed from dust or undersized particles prior to the impregnation. The quantity of impregnating agent to be applied is dependent upon the porosity of the particular catalyst; very porous catalysts need more impregnating agent than very dense catalysts.

WHAT WE CLAIM IS:—

1. A process for the hydrogenation of carbon monoxide in the presence of a fixed-bed, particulate catalyst, which comprises removing dust from the catalyst particles, impregnating the catalyst particles with normally solid hydrocarbons in a liquid phase, the catalyst being impregnated with an amount of the hydrocarbons, constituting from 5% to 60% by weight of the catalyst, such that no substantial agglomeration of individual catalyst particles occurs, employing the impregnated catalyst in the hydrogenation in a layer of a depth of at least 5 metres, and using gas velocities which are sufficient to ensure adequate transfer of the heat of reaction.

2. A process according to Claim 1, in which gas velocities of more than 60 cm./second (measured under normal conditions) are used.

3. A process according to Claim 1 or Claim 2, in which the catalyst is reduced or activated after the impregnation.

4. A process for the hydrogenation of carbon monoxide with the use of a fixed-bed catalyst in a layer depth of more than 5 metres and with removal of the heat of reaction through the walls of the synthesis reactor and at a gas velocity of more than 60 cm./second measured under normal conditions, in which dust is separated from the catalyst mass, before or after reduction, the dust-free catalyst mass being then impregnated with normally solid hydrocarbons in a liquid phase, the impregnation being such that no substantial agglomeration of individual catalyst particles occurs whilst the amount of hydrocarbons on the catalyst is within the range 5—60% by weight.

5. A process according to any one of the preceding claims, in which the catalyst is an iron catalyst.

6. A process according to any one of the preceding claims, in which the normally solid hydrocarbons are hydrocarbons obtained by the Fischer-Tropsch synthesis.

7. A process according to any one of the preceding claims, in which the impregnation is effected with the normally solid hydrocarbons in solution in a liquid hydrocarbon.

8. A process according to any one of the preceding claims, in which the catalyst is employed in a layer of more than 10 metres.

9. A process according to any one of the preceding claims, in which the gas velocity is at least 1.3 metres/second (measured under normal conditions).

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