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COMPLETE SPECIFICATION

Process for the treatment of Catalysts.

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of Homberg, Niederrhein, Germany, a Germany Company, 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 treatment, particularly for the reactivation and for extending the active life, of catalysts which are suspended in a medium which is liquid under the reaction conditions, and which are used in the hydrogenation of oxides of carbon.

Catalysts suspended in liquid media occasionally tend to lose their effectiveness suddenly and to a substantial degree after a period on stream, such sudden loss of activity or effectiveness being in addition to the normal, gradual loss of activity which may, in most cases, be substantially nullified by a slight increase in the synthesis temperature or by other suitable means. It is known to regenerate dry catalysts used in the hydrogenation of carbon monoxide by hydrogenation, oxidation, and/or extraction. However, the effect of these known regenerating steps is in most cases unsatisfactory when applied to catalysts suspended in a liquid medium. More effective are those steps by which the chemical and physical structure of the catalyste is at intervals completely changed. Regenerating processes of this kind sometimes resemble the processes used for the preparation of catalysts, both with respect to the chemical and physical phenomena as well as with respect to the cost involved, particularly in those cases in which the raw materials from which the catalysts are produced are cheap as compared with the cost of production, as is, for example, the case with iron catalysts.

It has now been found, according to the invention, that a catalyst used in suspension in a liquid medium in the synthesis of hydrocarbons and/or oxygen-containing organic-compounds by the hydrogenation of an oxide of carbon, particularly carbon monoxide, may be reactivated or have its active life extended, by a process which comprises lowering the content of catalyst in the suspension during the course of the synthesis. By means of the process according to the invention, the degree of conversion of the gaseous reactants, which tends to decrease during the course of the synthesis, may be maintained at a substantially constant level over an extended period of time.

The effect obtained by the process of the invention is unexpected, as it has hitherto been accepted in the art that a reduction in the quantity of an apparently exhausted catalyst would result in a further reduction in the yield of synthesis products, and the trend has therefore been to avoid as much as possible a reduction of the content of the catalyst metal in the reaction or synthesis zone. It is conceivable that continuous changes in the catalyst during the period on stream disadvantageously affect the distribution of the synthesis gas in the suspension, and that this disadvantage is removed or substantially reduced by diluting the catalyst suspension.

Considerable changes may occur in the catalyst suspension due to the separation of elementary carbon during the course of the synthesis. As this elementary carbon occurs in an extremely finely divided form and occupies a relatively large volume, it may, by functioning as a thickener, impair the quasi-liquid character of the suspension to a greater degree than would a comparable percentage by weight content of the catalyst itself. The volume of the catalyst may also increase during the course of the synthesis even when no or relatively little separation of elementary carbon occurs.

The carbon which separates during the synthesis adheres so firmly to the catalyst

that it would be disadvantageous from a technical point of view to separate the carbon completely from the catalyst by mechanical means. In the process of the invention, the lowering of the catalyst content of the suspension automatically effects a lowering of the carbon content in the suspension. Thus, in order to prevent the particularly deleterious effect which arises from the separation of elementary carbon from increasing beyond a maximum limit, which limit may readily be determined in each case by observing the activity of the catalyst, or to lower the content of elementary carbon in the suspension to a value below this limit, it is sufficient to lower the catalyst content of the suspension during the course of the synthesis. The elementary carbon in the suspension is preferably maintained at a value not in excess of 6% by weight of the suspension.

However, if it is desired to leave all of the catalyst in the synthesis zone throughout the run without interrupting the synthesis for one or more short intervals for removal of the catalyst, the dilution of the suspension according to the invention is effected by introducing an additional quantity of the liquid medium into the synthesis zone during the run, or by allowing synthesis products which are liquid under the synthesis conditions to accumulate in the synthesis zone. The quantity of fresh catalyst suspension of known concentration introduced into the synthesis zone at the beginning of the run will be less than normal to allow for this increase in the volume of the suspension. In this modification, the space-time yield of synthesis products (weight or organic compounds produced per unit volume of catalyst suspension per unit time), based on the volume of suspension at the end of the run, may be maintained substantially constant over the entire period of operation by increasing the space velocity (volume of synthesis gas per volume of catalyst per unit of time) as the catalyst content in the suspension is increasingly reduced.

However, according to the invention it is also possible to maintain the volume of the suspension constant from the beginning of the synthesis, by removing part of the catalyst suspension from the synthesis zone during the period of operation and replacing it by a corresponding volume of liquid medium, either by introducing the liquid medium, or by allowing a part of the synthesis products which are suitable for the purpose, to accumulate in the synthesis zone.

The catalyst removed from the synthesis zone is still sufficiently active, for example to continue to be used in a different synthesis zone.

By means of the process according to the invention, the yield obtained from the catalyst over the whole period of its operation is appreciably greater than what has hitherto been possible. The gas throughout need not be impaired by dilution of the catalyst suspension according to the invention, because the space velocity (volume of synthesis gas per volume of catalyst per unit of time) may be increased substantially in accordance with the degree of dilution, whilst maintaining a substantially constant and high degree of conversion of the synthesis gas.

Moreover, the process of the invention results in an improvement in the composition of the synthesis product, in that the formation of methane and ethane, which is known to increase gradually as the operating time increases, is kept at a low level throughout. When, at longer intervals, the diluting of the catalyst suspension is carried out suddenly and to an increased degree, the formation of $C_1 - C_2$ hydrocarbons is likewise suddenly reduced as compared with the conditions prevailing prior to the diluting operation.

The extent to which the catalyst concentration changes during the synthesis period is determined by the initial concentration and by the manner of operation. Catalysts which contain supporting material are diluted to a lesser degree than are unsupported catalysts. Concentrated suspensions should be diluted more rapidly and more strongly than suspension which are of lower concentration from the start. The diluting may be to a catalyst content of between approximately 70% and 5% based on the initial catalyst content.

The diluting measures taken according to the invention may also be combined with known regenerating steps, such as hydrogenation, oxidation, or extraction.

A decrease of the carbon content of catalyst suspension withdrawn from the synthesis zone, may be effected by centrifuging, the specific gravity of the articles richer in carbon being lower than those which are poorer in carbon. The speed of rotation of the centrefuge and the duration of the centrifuging are so provided that the catalyst particles poorer in carbon separate out whilst the other catalyst particles remain in suspension. The catalyst in the suspension withdrawn from the reactor may thus, to a certain extent, be separated into portions richer in carbon and portions poorer in carbon, and the latter portions, after again being suspended in the liquid medium, may be returned to the synthesis zone.

Alternatively, the separation of the catalyst into two portions one of which is richer in carbon than the other, may be effected by settling. The suspension withdrawn from the synthesis zone is advantageously allowed to settle in a heated container; the catalyst particles poorer in carbon will separate out first. The supernatant liquid phase containing the catalyst particles richer in carbon is

decanted, and the sludge-like residue containing the catalyst particles poorer in carbon is then stirred with a liquid medium, for example, hydrocarbons boiling in the range 250°—500°C., if necessary with heating, and the suspension so formed is returned to the synthesis zone.

For the same purpose, it is possible to utilize the very good separating effect of a magnetic field where the catalyst metal is iron, cobalt or nickel.

The invention is illustrated in the following example.

EXAMPLE

6000 kilograms of a suspension of an unsupported iron catalyst containing 750 kilograms Fe, the suspending medium being a hydrocarbon fraction having an initial boiling point above 300°C. under normal pressure and being a product of a Fischer-Tropsch synthesis, were used in synthesis over a period of several hundred hours with a synthesis gas containing carbon monoxide and hydrogen. The synthesis was effected at a pressure of approximately 10 atmospheres gauge and at temperatures in the range 255°—270°C. in a pressure-resistant synthesis reactor provided with internal cooling means, the gas load being 1.5 normal cubic metres of $CO + H_2$ per kilogram Fe per hour. During the initial part of the run, the $CO + H_2$ conversion was approximately 88%, the conversion remaining at this level for approximately 400 hours. After this time, the $CO + H_2$ conversion dropped within a few days to approximately 40%. The conversion could not then be effectively increased by raising the synthesis temperature or by changing the gas load.

When approximately half of the suspension was withdrawn from the reaction space and replaced by an equal volume of the same hydrocarbon fraction as that used to form the original suspension, the $CO + H_2$ conversion increased to 90%, the synthesis conditions being otherwise the same. The 370 kilograms (approximately) Fe still present in the reactor were thus loaded with almost three normal cubic metres of $CO + H_2$ per kilogram Fe per hour. After a further operating period of 600 hours, the remainder of the catalyst suspension was removed from the synthesis reactor and was replaced by the catalyst suspension first removed, the latter having been diluted with a liquid medium (hydrocarbons boiling in the range 250°—500°C.) to an Fe content of approximately 6% by weight. Synthesis was then resumed for a period of approximately 600 hours under otherwise the same conditions. During the total time of operation, approximately 88% of 2300 normal cubic metres of $CO + H_2$ were converted over a period of 1600 hours of operation per kilogram of the catalyst which had apparently become inactive within the first 400 hours, approximately 380 kilograms of hydrocarbons having 3 or more carbon atoms in the molecule, and oxygen-containing organic compounds, being formed in addition to approximately 28 kilograms of methane, ethane, and ethylene.

What we claim is:—

1. A process for the reactivation of a catalyst used in suspension in a liquid medium in the synthesis of hydrocarbons and/or oxygen-containing organic compounds by the hydrogenation of an oxide of carbon, which comprises lowering the concentration of the catalyst in the suspension during the course of the synthesis.

2. A process for extending the active life of a catalyst used in suspension in a liquid medium in the synthesis of hydrocarbons and/or oxygen-containing organic compounds by the hydrogenation of carbon monoxide, which comprises lowering the concentration of the catalyst in the suspension during the synthesis so as to maintain the content of elementary carbon in the suspension below an amount sufficient to deactivate the catalyst.

3. A process for extending the active life of a catalyst used in suspension in a liquid medium in the synthesis of hydrocarbons and/or oxygen-containing organic compounds by the hydrogenation of carbon monoxide, which comprises maintaining the content of elementary carbon in the suspension at a value not in excess of 6% by weight, by lowering the concentration of the catalyst in the suspension during the synthesis.

4. A process according to any one of Claims 1 to 3, in which the concentration of the catalyst is lowered by the addition of the liquid medium to increase the volume of the suspension.

5. A process according to any one of Claims 1 to 3, in which the concentration of the catalyst is lowered by permitting synthesis products which are liquid under the synthesis conditions to remain in the synthesis zone to increase the volume of the suspension.

6. A process according to Claim 4 or Claim 5, in which the space velocity is increased as the catalyst content of the suspension is increasingly reduced, to maintain the space-time yield of synthesis products approximately constant.

7. A process according to any one of Claims 1 to 3, in which the concentration of the catalyst is lowered by withdrawing part of the suspension from the synthesis zone and the introduction of a liquid medium.

8. A process according to Claim 7, in which the catalyst withdrawn from the synthesis zone is separated into a portion poorer

in carbon and a portion richer in carbon, the catalyst poorer in carbon being suspended in a liquid medium and again used in synthesis.

9. A process according to Claim 8, in which the separation of the catalyst into portions richer and poorer in carbon, is effected by centrifuging.

10. A process according to Claim 8, in which the separation of the catalyst into portions richer and poorer in carbon, is effected by settling.

11. A process according to Claim 8, in which the separation of the catalyst into portions richer and poorer in carbon, is effected by magnetic means when the catalyst contains iron, cobalt or nickel.

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

13. A process according to any one of the preceding claims, in which the catalyst is unsupported.

14. A process for the reactivation of catalysts substantially as hereinbefore described with respect to the Example.

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