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(54) PROCESS FOR THE REACTIVATION OF CATALYSTS

(54) PROCEDE POUR LA REACTIVATION DE CATALYSEURS

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ABSTRACT

CLAIMS

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

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The invention relates to the reactivation of catalysts which are suspended and maintained in suspension in a medium which is liquid under the reaction conditions, and particularly to catalysts for the hydrogenation of the 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 effectiveness or activity being additional to the normal, gradual reduction in activity which is in most cases substantially equalized by raising the temperature slightly or by any other suitable means. It is known to regenerate dry catalysts used in gas reaction processes by means of hydrogenation, oxidation, and extraction. However, the effect of these known regenerating means is in most cases unsatisfactory when applied to catalysts suspended in a liquid medium. More effective are those means by which the chemical and physical structure of the catalyst are at intervals completely changed. Regenerating processes of this latter kind sometimes resemble the processes for the preparation of catalyst, 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 that the activity of

5 catalysts which are suspended in a medium which is liquid under the operating conditions, and the conversion performance of which tends to decrease during operation may be maintained in continuous operation at an approximately constant level of effectiveness by reducing the catalyst content of the suspensions as the operating time increases. The effect obtained according to the invention is completely new and unexpected in so far as according to the prior state of technical experience it was 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 the reaction products, and the trend has therefore been to avoid as much as possible a reduction of the content of active basic catalyst metal in the reaction zone. It is conceivable that continuous changes in the catalyst during the period on stream disadvantageously effect the distribution of gas in the suspension, and that this disadvantage is removed by diluting the catalyst suspension.

15 Considerable changes may occur in those catalyst suspensions in which, in view of the nature of the reaction, a separation of elementary carbon cannot be avoided. As this elementary carbon occurs in an extremely finely-divided form and occupies a relatively large volume, it may impair the quasi-liquid character of the suspension to a greater degree than a comparable percentage by weight content of the catalyst itself. The volume of the catalyst

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itself may also increase during the period on stream, even when no or relatively little separation of elementary carbon occurs.

5 In those types of processes in which a separation of elementary carbon may occur, the carbon will adhere so firmly to the catalyst that it would be disadvantageous from a technical point of view to separate them completely from each other by mechanical means. According to the process of the invention, in these cases the reduction of the catalyst content is automatically combined with a reduction of the carbon content in the suspension, that is to say, in order to prevent the particularly deleterious elementary carbon from increasing in the suspension beyond a maximum limit which may readily be determined in each case by observing the activity of the catalyst, or to reduce the content of elementary carbon below this limit, it is sufficient to reduce the catalyst content of the suspension during the period on stream.

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30 However, if it is desired to leave all of the catalyst in the reaction zone throughout the period on stream, without interrupting the synthesis or reaction for a short interval from removal of the catalyst, the diluting of the suspension according to the invention is effected by at first charging only part of a fresh suspension of conventional catalyst concentration to the reaction chamber, and increasing the volume of the suspension during the period on stream by introducing additional liquid medium or by allowing

reaction products which are liquid under the operating conditions to accumulate in the reaction chamber. In this modification, the space-time yield of reaction products, based on the volume of suspension at the end of the period on stream, may be maintained constant over the entire period of operation.

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

The catalyst removed from the reaction zone is still sufficiently active, for example to continue to be used in a different reaction 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 space velocity or gas throughput is not impaired by dilution of the catalyst suspension as effected according to the invention, because the relative space velocity based on the catalyst metal, may be increased approximately in accordance with the degree of dilution, whilst maintaining a constant and high degree of conversion of the gas.

Moreover, according to the process of the

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invention the diluting of the catalyst suspension effects in the hydrogenation of carbon monoxide an improvement in the composition of the product, in that the formation of methane and ethane, which is known to increase gradually as the operating time increases, is kept at a constantly low level. 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 period on stream is determined by the initial concentration and by the manner of operation. Catalysts which contain supporting materials are diluted to a lesser degree than are unsupported catalysts. Concentrated suspensions should be diluted more rapidly and more strongly than suspensions which are lower ⁱⁿ concentration from the start. The diluting may range between a catalyst content of 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 measures such as hydrogenation, oxidation, or extraction.

A decrease of the carbon content, which carbon functions as a suspension thickener, may be effected by centrifuging suspension withdrawn from the reaction zone, whereby the catalyst may be separated to a certain extent into portions richer

in carbon and portions poorer in carbon which latter portions, after again being suspended in the liquid medium, are returned to the reaction zone. Analogously, it is possible to utilize the very good separating effect of a magnetic field.

According to the invention, the elementary carbon formed during the reaction should preferably be maintained at or reduced to approximately below 6% by weight based on the weight of the suspension.

EXAMPLE.

6000 kilograms of a suspension of an unsupported iron catalyst containing 750 kilograms Fe in synthesis hydrocarbons which under normal pressure had an initial boiling point above 300°C, were used in synthesis for several hundred hours with a synthesis gas containing carbon monoxide and hydrogen. The synthesis was effected at medium pressure and at temperatures in the range 255°C - 270°C. in a pressure-resistant synthesis reactor provided with internal cooling means, the load being 1.5 normal cubic metres of CO + H₂ per kilogram Fe per hour. During the initial part of the run, the CO + H₂ conversion was approximately 88% the conversion remaining at this level for approximately 400 hours. After this time, the CO + H₂ conversion dropped within a few days to approximately 40%. The conversion could not thereafter 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 hydrocarbons as that used to form the original suspension, the CO + H₂ conversion increased to 90%, the conditions being otherwise the same. The 370 kilograms (approximately) Fe still present in the reactor were then loaded with almost three normal cubic metres of CO + H₂ per kilogram Fe per hour. After a further operating period of 600 hours, the catalyst suspension was removed from the synthesis reactor and was replaced by the catalyst suspension first removed, the latter having first been diluted with a liquid medium to an Fe content of approximately 6% by weight. Synthesis was then resumed under otherwise the same conditions for approximately 600 hours. During the total time of operation, approximately 88% of 2300 normal cubic metres of CO + H₂ were converted over a period of 1600 hours of operation per kilogram of the catalyst which had apparently become inactive within 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.

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

1. A process for maintaining the level of activity of a catalyst employed in suspension in a liquid medium in a gaseous reaction, in which one of the reactants contains carbon, which comprises decreasing the concentration of the catalyst in the suspension during operation to maintain the content of elementary carbon in the suspension at a level such that the activity of the catalyst is substantially maintained.

2. A process for extending the active life of a catalyst used in suspension in a liquid medium in the hydrogenation of carbon monoxide, which comprises lowering the concentration of the catalyst in the suspension during the course of the hydrogenation whereby the content of elementary carbon present in the suspension is maintained at or reduced to below an amount which deactivates the catalyst.

3. A process for extending the active life of a catalyst employed in suspension in a liquid medium in the synthesis of hydrocarbons by the hydrogenation of carbon monoxide, which comprises maintaining the content of elementary carbon in the suspension below 6% by weight by lowering the concentration of the catalyst in the suspension during the course of the synthesis.

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

the volume of the suspension.

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

6. A process according to any one of claims 1 to 3, in which the catalyst concentration is lowered by withdrawing part of the suspension from the reaction zone and replacing it by a liquid medium.

7. A process according to any one of claims 1 to 3, in which the catalyst concentration is lowered by withdrawing part of the suspension from the reaction zone, the withdrawn suspension being centrifuged to separate the catalyst into a portion poorer in carbon and a portion richer in carbon, the catalyst poorer in carbon being suspended in a liquid medium and the suspension so formed being passed to the reaction zone.

✓8. A process according to any one of claims 1 to 3, in which the catalyst concentration is lowered by withdrawing part of the suspension from the reaction zone, the withdrawn suspension being settled and decanted to separate the catalyst therein into a portion richer in carbon and a portion poorer in carbon, the portion poorer in carbon being suspended in the liquid medium and fed into the reaction zone.

✓9. A process according to any one of claims

1-3, in which the catalyst comprises a ferromagnetic metal and the catalyst concentration is lowered by withdrawing part of the suspension from the reaction zone, the catalyst in the withdrawn suspension being separated into a portion richer in carbon and a portion poorer in carbon, the portion poorer in carbon being suspended in the liquid medium and fed into the reaction zone.

10. A process according to any one of claims 1 to 3, in which the space velocity is increased as the concentration of the catalyst in the suspension is lowered, to maintain the space-time yield of reaction products approximately constant.