PATENT SPECIFICATION

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COMPLETE SPECIFICATION

A Process for the Reduction of Iron Catalysts for the Hydrogenation of Carbon Monoxide

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, a German Joint Stock Company, of (22A) Homberg, Niederrhein, Germany, 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 production of iron catalysts for use in the hydrogenation of carbon monoxide. The invention relates more particularly to the step of reducing such catalysts prior to their use in the hydrogenation, whereby the catalysts are converted into an active state.

Before using the iron catalysts in the hydrogenation of carbon monoxide, it has hitherto been usual to pre-treat them with hydrogen. For such pre-treatment, the hydrogen has to be particularly pure, dry and free from carbon dioxide; the hydrogen is, therefore, comparatively expensive. The catalysts obtained upon such pre-treatment are substantially in the metallic state and they suffer from the disadvantage that they are particularly sensitive to fluctuations in the synthesis conditions, that is to say, to the conditions used in the hydrogenation of carbon monoxide. Furthermore, these catalysts tend to lead to an increase in the formation of methane and in the formation or separation of carbon.

It is also known to convert the iron catalysts into the active state by treating them with carbon monoxide, for example at a pressure below atmospheric, or by treating them with carbon monoxide/hydrogen mixtures such, for example, as the synthesis gases themselves, under the synthesis conditions. Such methods of pre-treatment, however, have disadvantages; the treatment with pure carbon monoxide at sub-atmospheric pressure is comparatively expensive and is not without danger, whilst the treatment with mixtures of carbon monoxide and hydrogen under synthesis conditions results in catalysts of low activity.

Iron catalysts, in oxidic form, have also been reduced with carbon monoxide or with gases containing carbon monoxide, for example, industrial mixtures of carbon monoxide and hydrogen or of carbon monoxide and an inert gas, at space velocities greater than 300, up to and including a space velocity of 1000. In such methods, however it has hitherto been the practice to attain the high space velocities by continually increasing the recycle ratio until the full space velocity at which it is desired to operate is attained. Thus, the full space velocity is only attained some time after the reduction of the catalyst has been commenced. At the beginning of the period of reduction, the space velocity increases slowly as the amount of recycle gas increases, and it is only after some time that the high space velocity is attained. It has been found that this period during which the space velocity is being increased to a value greater than 300, is detrimental to the progress of the reduction and is harmful to the activity of the catalyst.

According to the invention, a process for the reduction of an iron-type catalyst prior to its use in the hydrogenation of carbon monoxide, comprises passing carbon monoxide or a gas containing carbon monoxide over the catalyst at a space velocity greater than 300 at a temperature within the range 180° C.—600° C., the gas being passed over the catalyst at a substantially constant space velocity from the beginning of the process of reduction. The term "iron-type catalyst" includes any catalyst the main metal in which is iron. The iron, prior to reduction, is wholly or partly in combined form, and is generally in the form of an oxide, hydroxide or carbonate.

The space velocity during reduction is pre-

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ferably greater than 1000 volumes of gas per volume of catalyst per hour and the temperature of the reduction process is preferably within the range 200° C.—400° C. It is also advantageous to heat the gas and the catalyst separately to the reduction temperature.

In one common method of reducing iron-type catalysts, synthesis gases are used at space velocities of 60—150, the gases being passed over the catalysts for a period of days. In comparison with such a method, the process according to the invention enables the duration of the process of reduction to be shortened and yields a catalyst having an appreciably higher degree of activity. The higher activity of catalysts produced according to the invention is recognised by the fact that the synthesis temperature is reduced by 20° C.—40° C. and that the life of the catalyst is increased by several months.

If the high space velocity is not applied at once, then catalysts of lower activity are obtained. Superficially, this may even be recognised by the colour of the catalysts; catalysts of greatest activity are completely black, whilst those of lower activity are grey.

Where an iron-type catalyst has been reduced with carbon monoxide or with a hydrogen-free carbon monoxide mixture and is to be used at normal pressures, it is advantageous to treat it subsequently with hydrogen at a temperature within the range 250°C.—400° C.

The following relations exist between the temperature on the one hand, and the space velocity, the carbon monoxide content of the gas used and the reduction period on the other hand:—

1. The higher the space velocity the higher should be the temperature used.
2. The reduction temperature may be lowered by increasing the carbon monoxide content of the reducing gas.
3. The reduction period is reduced with increase in temperature.

It follows, therefore, that in order to obtain a reduction period of short duration and, with it, a high degree of activity in the catalyst, the temperature used should be as high as possible, the concentration of carbon monoxide in the reducing gas should be low and the space velocity should be high.

In addition to being carried out in the synthesis reactor, the reduction of the catalyst may, according to the invention, be effected in particularly thin layers of catalyst having a thickness of less than 1 metre, preferably of a thickness of 10 cm.—50 cm., in which case the reducing gas must first be heated to the required temperature. Space velocities of 60—150 litres/litre catalyst/hour, such as are generally used in the synthesis, are unsuccessful because the catalyst is overheated as a result of the complete conversion of the gas with insufficient removal of the heat. However, if according to the invention high space velocities are used, only a small portion of the carbon monoxide in the reduction gas put through at the time is converted, even at high temperatures, and damage by overheating will not occur. The exit gas may be passed to the synthesis process.

A particular, technical advantage lies in the fact that the presence of carbon dioxide in the reduction gas has little or no effect on the activity of the catalyst when the catalyst is subsequently used in a synthesis carried out at elevated pressure. In this case, therefore, it is not necessary that the gas used for the reduction should be scrubbed for the removal of carbon dioxide.

Iron-type catalysts reduced according to the process of the invention, are distinguished by their high activity which enables the synthesis temperatures to be reduced by 20° C.—40° C. The life of the catalysts is also increased from a period of 3—5 months which has hitherto been normal, to 6—12 months. A notable feature of the use of iron catalysts reduced according to the invention, is the low formation of methane. It is thus possible to increase the conversion of carbon monoxide to 95% and over and to use the catalyst for all methods of carrying out the synthesis. Furthermore, catalysts reduced according to the invention have a greater tendency to effect the CO-reduction with the formation of water than have catalysts pre-treated according to the processes hitherto known. As a catalyst reduced according to the process of the invention forms scarcely any methane, permits a carbon monoxide conversion of 95% and over and acts strongly with the formation of water, a yield of from 180 grams to over 190 grams of hydrocarbons having more than one carbon atom per molecule, can be obtained per normal cubic metre of $CO + H_2$.

The reduction of iron-type catalysts according to the invention, is illustrated in the following Example.

A carrier-free iron-type catalyst containing 0.2% by weight of copper (the iron and the copper being in the form of carbonates after precipitation as such from a mixed solution of their nitrates) and 0.25% of potassium carbonate was reduced for six hours in a synthesis reactor with water-gas of the following composition by volume:—6% CO_2, 38% CO, 47% H_2 and 9% N_2 at a temperature of 290° C.—310° C. The space velocity was 3000volumes/volume of catalyst/hour, this space velocity being used from the very beginning of the process of reduction. When the reduced catalyst was used in synthesis with water gas under a gauge pressure of less than 10 atmospheres and at a temperature of 190° C.—215° C., a yield of up to 180 grams per normal cubic metre of $CO + H_2$ was obtained.

What we claim is:—

1. A process for the reduction of an iron

type catalyst prior to its use in the hydrogenation of carbon monoxide, which comprises passing carbon monoxide, or a gas containing carbon monoxide, over the catalyst at a space velocity greater than 300 and at a temperature within the range 180° C.—600° C., the gas being passed over the catalyst at a substantially constant velocity from the beginning of the process of reduction.

2. A process according to claim 1, in which the reduction temperature is lowered with increase in concentration of carbon monoxide in the reducing gas.

3. A process according to claim 1 or claim 2, in which the temperature is increased with increase in the space velocity.

4. A process according to claim 3, in which the period of reduction is made shorter as the temperature and the space velocity are increased.

5. A process according to any one of the preceding claims, in which carbon dioxide is not removed from the gas used for reduction if the catalyst is subsequently used in a hydrocarbon synthesis carried out at elevated pressure.

6. A process according to any one of the preceding claims, in which the reduction is carried out with the iron catalyst in a layer of a thickness not greater than 1 metre.

7. A process according to claim 6, in which the layer of iron catalyst is of a thickness of 10cm—50cm.

8. A process according to any one of the preceding claims, in which the temperature lies within the range 200° C.—400° C.

9. A process according to any one of the preceding claims, in which the space velocity is greater than 1000 volumes/volume of catalyst/hour.

10. A process according to any one of the preceding claims, in which the duration of the period of reduction is at least one hour.

11. A process according to any one of the preceding claims, in which the reduction is effected with a gas free from hydrogen, the catalyst being subsequently treated with hydrogen at a temperature within the range 250°—400° C.

12. A process for the reduction of an iron catalyst prior to its use in the hydrogenation of carbon monoxide, substantially as hereinbefore described.

13. A process for the reduction of an iron catalyst prior to its use in the hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to the Example.

14. An iron catalyst whenever produced according to the process of any preceding claim.

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