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(54) PROCESS FOR THE REDUCTION OF IRON CATALYSTS FOR THE HYDROGENATION OF CARBON MONOXIDE

(54) PROCEDE POUR LA REDUCTION DE CATALYSEURS DE FER POUR L'HYDROGENATION DE PROTOXYDE DE CARBONE

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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 ~~non~~ 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.

We have found that the iron catalysts, in oxidic form, can be reduced with carbon monoxide or with gases containing carbon monoxide, for example, technical or industrial mixtures of carbon monoxide and hydrogen or of carbon monoxide and an inert gas, at a space velocity greater than 300, preferably greater than 1000 litres/litre catalyst/hour, at temperatures of 180°C-600°C, preferably 200°C-400°C, the high space velocity required being obtained or adjusted by recycling the reaction gas. It was found to be advantageous to heat the catalyst and the reduction gas separately to the reaction temperature required. The reduction can be effected with gas mixtures of any carbon monoxide concentration. This has the advantage, as compared with reduction by hydrogen, that the synthetic gas provided for the synthesis or, as the case may be, the generator gas which is cheaply available, may be used for the reduction of the oxidic iron catalyst.

It has further been found that in the reduction with carbon monoxide or with gases containing carbon monoxide, it is of great advantage to pass the reducing gas over the catalyst at full space velocity from the very beginning. Catalysts of high activity and long life are obtained by such means.

According to the invention, therefore, a process for the reduction of an iron catalyst prior to its use in the hydrogenation of carbon monoxide, comprises passing carbon monoxide or gases containing carbon monoxide over the catalyst at a space velocity greater

than 300 at a temperature within the range 180°C - 600°C, the reducing gas being passed over the catalyst at full space velocity from the beginning of the process of reduction.

The space velocity during reduction is preferably 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.

The known pre-treatment of the iron catalyst with synthesis gases extends over a period of days with the use of space velocities of 60-150 volumes of gas per volume of catalyst per hour; in comparison, 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 reaction temperature is reduced by 20°C - 40°C and that the life of the catalyst is increased by several months.

By the use of recycling to obtain the high space velocity, the carbon monoxide present in the gas is better utilised. 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 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. Increase in the space velocity necessitates an increase in the temperature.

2. The reaction temperature is to be lowered with increase in 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, with advantage, be recycled or it may be passed to the synthesis process.

A particular, technical advantage lies in the fact that the carbon dioxide in the reduction gas has little or no effect on the activity of the catalyst when it is subsequently used under 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 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 catalysts according to the invention, is illustrated in the following Examples.

EXAMPLE 1.

An iron catalyst consisting of 100 parts by weight of iron, 60 parts of alkaline earth oxide, 7.5 parts of copper and 1 part of potassium carbonate was placed in an iron tube having an internal diameter of 15 m.m. and was treated by the recycle process with carbon monoxide at a temperature of 260°C-270°C. The load was 300 litres of carbon monoxide per litre of catalyst and the recycle ratio was 1:4; the space velocity therefore amounted to 1500 litres/litre of catalyst/hour. After twelve hours, the conditions were adjusted to bring the catalyst on to synthesis. Using water gas at a gauge pressure of 10 atmospheres and a temperature of 200°C-220°C, the yield was up to 180 grams of hydrocarbons having more than one carbon atom per molecule, per normal cubic metre of $CO + H_2$.

EXAMPLE 2.

A carrier-free iron catalyst containing 0.2% by weight of copper and 0.25% of potassium carbonate was treated 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 3000 litres/litre of catalyst/

hour. When the treated catalyst was used 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.

EXAMPLE 3.

A catalyst consisting of 100 parts by weight of iron, 50 parts of kieselguhr, 15 parts of magnesium, one part of copper and 2 parts of potassium carbonate, and being in a layer of a thickness of 20 cm. - 25 cm, was treated for one hour with 1000 normal litres of a hydrogen-rich synthesis gas (H_2:CO=2:1) per litre of catalyst at a temperature of 320°C - 350°C and at a recycle ratio of 1:5, that is to say, the treatment was carried out at a space velocity of 6000 litres/litre of catalyst/hour. The treated catalyst was then used in synthesis with a hydrogen-rich synthesis gas under a gauge pressure of less than 10 atmospheres and a space velocity of 600 litres/litre of catalyst/hour, the temperature being 185°C-210°C. 96%-99% of the carbon monoxide was worked up in three stages, the H_2/CO consumption ratio being 1.5 - 1.8. As there was practically no formation of methane, a yield of 160 grams to 180 grams per normal cubic metre of $CO+H_2$ was obtained.

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

1. In the method for the reduction of an iron catalyst for use in the hydrogenation of carbon monoxide, the improvement which comprises contacting a gas consisting of or containing carbon monoxide with the iron catalyst at a temperature in the range 180° - 600°C and at a space velocity greater than 300 volumes of gas per volume of catalyst per hour, the gas being passed over the catalyst at a substantially constant velocity from the beginning of the process of reduction.

2. Improvement according to claim 1, in which the space velocity is greater than 1000 volumes of gas per volume of catalyst per hour.

3. Improvement according to claim 1 or claim 2, in which the temperature is within the range 200° - 400°C.

4. Improvement according to claim 1 or claim 2, in which the reduction is carried out with the catalyst in a layer of a thickness not greater than 1 metre.

5. Improvement according to claim 1 or claim 2, in which the reduction is carried out with the catalyst in a layer of a thickness of from 10 to 50 centimetres.

6. Improvement according to claim 1 or claim 2, in which the temperature is lowered with increase in the concentration of carbon monoxide in the gas.

7. Improvement according to claim 1 or claim 2, in which the greater the space velocity used the higher the temperature at which the reduction is effected.