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COMPLETE SPECIFICATION

Process for the Pre-treatment of Oxidic Iron Catalysts

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FEUR BERGBAU UND CHEMIE, of Homberg, Niederrhein, Germany, a German 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 pre-treatment of oxidic iron catalysts.

It is an object of the invention to provide a process whereby the efficiency of iron catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen and/or water vapour (steam), may be increased by preliminary treatment with high percentage oxygen at elevated temperatures.

The preliminary treatment of alkalised iron catalysts with an oxidising gas, specifically air, and preferably under normal pressure at elevated temperatures, has already been proposed. Experiments are also known whereby alkali-free oxidic iron catalysts were pre-treated with oxygen at 330°C., which experiments gave a completely negative result, that is to say, no activation of the catalysts occurred.

It has now been found, according to the invention, that the efficiency of alkali-free and alkali-containing oxidic iron catalysts can be considerably increased for the synthesis of hydrocarbons from carbon monoxide and hydrogen and/or steam, by effecting the preliminary treatment at a temperature in the range 200°-500°C., with a gas the oxygen content of which is more than 50%, and preferably more than 90%, the temperature being below 300°C. when the catalyst is free from alkali and not below 300°C. when the catalyst contains alkali. The proportion of high boiling hydrocarbons in the synthesis product can be still further increased if the preliminary treatment is carried out under elevated pressure, for example, at 2-20 atmospheres gauge. The temperature of the preliminary treatment depends on and should conform to the degree of alkalisation of the catalyst. Catalysts which are not alkalised are preferably given the preliminary treatment at a temperature within the approximate range 200°-250°C., whereas alkalised catalysts require temperatures which are not below 300°C. and which increase up to approximately 500°C., according to the degree of alkalisation. Furthermore, if the catalyst contains other promoters and carrier material, the temperature of the preliminary treatment depends on and conforms to the type and amount of such promoters and the carrier materials, the greater the amount of such other promoters and/or carrier materials present in the catalyst, the higher is the temperature preferably employed in the pre-treatment. The duration of the preliminary treatment depends on the catalyst and on the temperature, and is generally of the order of from 2 to 12 hours. The most favourable conditions for the preliminary treatment are to be ascertained for each type of catalyst in the manner hereinbefore explained; such conditions are readily determined by experiment.

From the known state of the art it could not be concluded that an increase of the partial pressure of oxygen in the preliminary gas treatment would have such a strong influence on the efficiency and/or active life of the catalyst, as the iron in the catalyst is already in the trivalent state and thereby no explanation can be given for the result obtained in the process according to the invention. The preliminary treatment according to the invention is so effective that even catalysts which after preliminary treatment with air exhibit but little activity, achieve long active life and/or high efficiency after preliminary treatment with 98% oxygen.

The effectiveness of the process according to the invention is further illustrated in the following Examples which are given by way of illustration.

EXAMPLE 1

A pure iron (III) oxide (free of alkali and copper) which was produced by precipitation from an iron nitrate solution with the use of ammonia as the precipitant, was used for the production of three catalysts. The first catalyst (catalyst I) was not given a preliminary treatment, the second catalyst (catalyst II) was given a preliminary treatment by passing air over it under normal pressure for a period of 6 hours at 240°C., whilst the third catalyst (catalyst III) was given a preliminary treatment by passing 98% oxygen over it for a period of 6 hours at 240°C. and at normal pressure. Each catalyst was ground with slack wax (Gatsch) and each was tested in synthesis as a 10% suspension in the liquid phase with a carbon monoxide-rich gas (carbon monoxide/hydrogen = 3:2) under a pressure of 10 atmospheres gauge and at a temperature of 240°-300°C., under a load of 2.3 NL (normal litres) of carbon monoxide plus hydrogen/gram of iron/hour. The slack wax or Gatsch, a hydrocarbon fraction boiling in the range 320°-450°C., formed under the synthesis conditions the liquid medium in which each catalyst was suspended. The temperature during synthesis was so adjusted that the carbon monoxide conversion was always above 90%. Catalyst I (no preliminary treatment) attained a life of 587 hours, equivalent to a performance or efficiency of about 205 grams of utilisable hydrocarbons (hydrocarbons containing 3 or more carbon atoms in the molecule) per gram of iron; catalyst II (pre-treated with air) attained a life of 1368 hours equivalent to an efficiency of about 450 grams of utilisable hydrocarbons per gram of iron: and catalyst III (pre-treated according to the invention) attained a life of 2225 hours, equivalent to an efficiency of about 720 grams of utilisable hydrocarbons per gram of iron.

EXAMPLE 2

An iron catalyst containing 0.2 parts Cu and 0.6 parts potassium carbonate per 100 parts iron and which was produced by precipitation with ammonia from an iron nitrate solution, was divided into three parts to give three catalysts. The first part (catalyst I) was given no preliminary treatment, the second part (catalyst II) was treated with air under normal pressure for 6 hours at 400°C., whilst the third part (catalyst III) was treated with 98% oxygen under normal pressure for 6 hours at 400°C., and each was used as a 10% suspension in a liquid medium (slack wax or Gatsch boiling in the range 320°-450°C.), for the synthesis of hydrocarbons from carbon monoxide and steam. The three catalysts were first activated for 20 hours with carbon dioxide-free generator gas (approximately 0.9 NL (normal litres) generator gas/gram iron/hour) under a pressure of 1.8 atmospheres gauge at 275°-280°C., and subsequently placed on stream in synthesis with a carbon dioxide-containing generator gas (37%-39% carbon monoxide; 1%-2% hydrogen) and steam under a pressure of 20 atmospheres gauge at a temperature of 250°-290°C. The synthesis gas contained 3 volumes of carbon monoxide per volume of steam, the load being 2.7 NL generator gas/gram of iron/hour. The temperature was so adjusted that the carbon monoxide-conversion was always over 90%. Catalyst I achieved an efficiency or yield of about 180 grams of utilisable hydrocarbons per gram of iron, catalyst II an efficiency of about 300 grams of utilisable hydrocarbons per gram of iron, and catalyst III an efficiency of about 450 grams of utilisable hydrocarbons per gram of iron. The methane formation of catalyst III was about 40% less than that of the two other catalysts.

EXAMPLE 3

With catalyst III of Example 2, methane comprised about 7%-8% of the hydrocarbons formed and about 18% of the hydrocarbons had boiling points above 320°C. When, however, the same catalyst was pre-treated under a gauge pressure of 8 atmospheres under otherwise the same conditions, the methane content of the hydrocarbons formed from carbon monoxide and steam dropped to 3%-4% and the proportion of the hydrocarbons having boiling points above 320°C., increased to 30%-35%.

What we claim is:—

1. A process for the pre-treatment of an oxidic iron catalyst for use in the synthesis of hydrocarbons from carbon monoxide and hydrogen and/or steam, which comprises contacting the catalyst with an oxidising gas containing more than 50% of oxygen at a temperature in the range 200°-500°C., the temperature being below 300°C. when the catalyst is free from alkali and not below 300°C. when the catalyst contains alkali.

2. A process according to Claim 1, in which the gas contains more than 90% of oxygen.

3. A process according to Claim 1 or Claim 2, in which the pre-treatment is

effected under elevated pressure.

4. A process according to Claim 3, in which the pre-treatment is effected at a gauge pressure in the range 2-20 atmospheres.

5. A process according to any one of the preceding claims, in which the pre-treatment is effected at a temperature in the range 200°-250°C. when the catalyst is free from alkali.

6. A process according to any one of Claims 1 to 4, in which the catalyst contains alkali and the temperature of the pre-treatment is the higher the greater the content of alkali in the catalyst.

7. A process according to any one of the preceding claims, in which the duration of the pre-treatment is from 2 to 12 hours.

8. A process for the pre-treatment of an iron catalyst for use in the synthesis of hydrocarbons, substantially as hereinbefore described.

9. A process for the pre-treatment of an iron catalyst, substantially as described with reference to catalyst III in any one of Examples 1 to 3.

EDWARD EVANS & CO.,
14-18, High Holborn, London, W.C. 1,
Agents for the Applicants.

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