We, RHEINPREUSSEN AKTIENGESELLSCHAFT FÜR BERGBAU UND CHEMIE, of Homburg, 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:—

10 The invention relates to a process for the pre-treatment of oxidative 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.

20 The preliminary treatment of alkali-free oxidative 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 oxidative 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.

30 It has now been found, according to the invention, that the efficiency of alkali-free and alkali-containing oxidative 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 alkaliisation of the catalyst. Catalysts which are not alkaliised are preferably given the preliminary treatment at a temperature within the approximate range 200°-250°C, whereas alkaliised catalysts require temperatures which are not below 300°C and which increase up to approximately 500°C, according to the degree of alkaliisation. 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 pro-65 moters 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 temper-70 ature, 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 hereinafter explained; such conditions are readily determined by experiment.

80 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 90
air exhibit but little activity, achieve long
active life and/or high efficiency after
preliminary treatment with 98% oxygen.
The effectiveness of the process accord-
ing 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
20 catalyst (catalyst III) was given a pre-
liminary 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
25 each was tested in synthesis as a 10% suspension in the liquid phase with a
carbon monoxide-rich gas (carbon mon-
oxide/hydrogen = 3:2) under a pressure of
10 atmospheres gauge and at a tem-
perature 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,
35 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 treat-
ment) attained a life of 587 hours, equiva-
 lent to a performance or efficiency of about
295 grams of utilisable hydrocarbons
(hydrocarbons containing 3 or more
45 carbon atoms in the molecule) per gram of
iron; catalyst II (pre-treated with air)
attracted 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
50 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
65 normal pressure for 6 hours at 400°C,
whilst the third part (catalyst III) was
6 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 atmos-
pheres gauge at 275°-280°C, and subse-
sequently placed on stream in synthesis with
a carbon dioxide-containing generator gas
(97%-98% 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
55 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 of about 90
about 180 grams of utilisable hydrocarbons
per gram of iron, catalyst II an efficiency
of about 300 grams of utilisable hydro-
carbons per gram of iron, and catalyst
35 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
35 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 115 oxide iron catalyst for use in the synthesis
of hydrocarbons from carbon monoxide
and hydrogen and/or steam, which com-
prises contacting the catalyst with an
oxidising gas containing more than 50% of 
120 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
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 20 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 25 of Examples 1 to 3.

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