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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for Hydrocarbon Synthesis

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a Corporation organised under the Laws of Germany, of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to a process for the synthesis of hydrocarbons, or mixtures of hydrocarbons and oxygenated hydrocarbon derivatives.

The use of iron catalysts for the synthesis of hydrocarbon by hydrogenation of carbon monoxide is known and results in a series of products comprising, in addition to hydrocarbons, particularly oxygenated hydrocarbon derivatives such as alcohols or fatty acids. The amount of oxygenated products formed varies with the composition of the catalysts used and the conditions under which the reaction is carried out. Good results have been obtained with such iron catalysts as contain a few per cent of alkali metal oxide, especially potassium oxide, and in which the alkali metal oxide has been incorporated in the form of alkali metal silicate. When such catalysts are employed a high percentage of paraffins is formed during the reaction, the paraffin yield rising with the percentage of alkali metal in the catalyst. Water gas proved best suited as feed gas since the ratio of carbon monoxide to hydrogen in said water gas comes closest to the ratio of consumption of the catalysts, being about 1 part of carbon monoxide to 1.2 or 1.3 parts of hydrogen in the case of a catalyst having a low alkali metal content and about 1 part of CO to 1 or 0.8 or less of H, in the case of a catalyst containing a higher percentage of alkali metal. The greater consumption of hydrogen is however obtained only when the synthesis gas is recycled.

Since hitherto even iron catalysts low in alkali gave rise to the formation of considerable quantities of carbon dioxide there arose, with multi-stage operation, the disadvantage that carbon dioxide had to be removed from the synthesis gas between the individual stages so as to ensure a feed gas of suitable composition for each following stage.

The present invention aims at enabling synthesis gases with varying ratios of carbon monoxide to hydrogen to be worked up.

It has already been proposed to employ for the synthesis of hydrocarbons, catalysts which contain iron, alkali metal compounds and difficultly reducible non-volatile reactive acid anhydrides.

The process of the present invention likewise employs a catalyst containing iron, alkali metal compounds (preferably oxygen-containing potassium compounds) and difficultly reducible non-volatile reactive acid anhydrides, and is characterised by the feature that the ratio by weight of alkali metal compound (calculated in terms of alkali metal oxide) to non-volatile reactive acid anhydride in the catalyst is selected to lie between 1 : 2.5 and 1 : 7.0.

The term " reactive acid anhydrides " used herein is intended to denote a group of compounds comprising those oxides which are capable of reacting directly at elevated temperatures with alkali metal carbonates or alkali metal hydroxides to form alkali metal salts.

The reactive acid anhydrides which may be used in carrying out the invention are silicic acid or titanic acid or like oxygen containing compounds which are similarly difficultly reducible and which will not evaporate at the temperatures at which the synthesis is carried out. The acid anhydrides are applied in such a form that they can react with the alkali incorporated in the catalyst. Accordingly, silicic acid will not be employed for example in precipitated catalysts as quartz or kieselguhr, but as precipitated silicic acid or in the form of the sol. It is, however, also possible to transform the silicic acid during the preparation of the catalyst into a reactive form, for example with the aid of alkali or to

[*Price* 2s. 8d.]

Price 4s 6d.

incorporate the silicic acid partly or wholly in the form of alkali silicates in the catalyst. Similarly, also the other non-volatile reactive acid anhydrides which will be used according to this invention will be embodied in the catalyst not in the form of difficultly reactive minerals but in a finely divided reactive form, or will, alternatively be converted into such form during the preparation of the catalyst.

If catalysts are used for the herein described process which are obtained by fusion at high temperatures the acids may be employed in any form. In this case the fusion treatment converts the acid anhydrides into a reactive form even if they have been added in another form. As alkali promoters particularly oxygenated alkali metal compounds such as carbonates, nitrates, hydroxides or the like may be used. Potassium compounds are preferable. In addition, the catalysts may contain any additives common to iron catalyst compositions, e.g., copper or any other substances known to improve the efficiency of catalysts: zinc oxide, calcium oxide, aluminium oxide, thorium dioxide and other oxides of metals of the alkaline earth group. Moreover mixtures of such substances may be used. The catalyst may also be used in admixture with carrier such as kieselguhr.

In many cases it is advantageous to have two or more reactive acid anhydrides present in the catalyst, e.g., silicic acid and tungstic acid or silicic acid and titanic acid.

Moreover it has been found that the performance of these catalysts depends on the pressure under which the synthesis is carried out; the hydrogen consumption increases with increasing pressure. For example, a feed gas of given composition, i.e., with a carbon monoxide to hydrogen ratio of 1 : 1.2, may be reacted over a catalyst of the composition :—

total Fe	100
Cu	25
ZnO	18
K_2O	11
SiO_2	45

at 10 atmospheres gauge pressure and while recycling the tail gas. The carbon monoxide to hydrogen consumption may then be 1 CO : 1.4 H_2. Increasing the pressure to 20 atm. raises the ratio in which the two gases are worked up to about 1 CO and 1.7 H_2. On the other hand, increasing the alkali metal oxide content of above catalyst so that the K_2O : SiO_2 ratio lies between 14 and 17 K_2O : 45 SiO_2 will again lower the ratio in which CO and H_2 are worked up to 1 : 1.3 or 1.4, given the same composition of feed gas and the same pressure. The higher K_2O content moreover results in a higher yield of paraffins.

If instead of water gas there is used a gas of a CO to H_2 ratio of 1 : 1.8 or 2.0 such as is commonly fed to cobalt catalysts, the ratio of consumption rises towards higher consumption of hydrogen and practically no carbon dioxide will be formed. This is true particularly when setting the K_2O to SiO_2 ratio to 1 : 6 or 1 : 7. The invention thus also affords the possibility of processing over iron catalysts such fresh feed gases as are used with the cobalt-catalysed synthesis. In addition, with multi-stage operation, the removal of carbon dioxide from the feed gases for the subsequent stages may be dispensed with.

A further advantage offered by the present invention is that it facilitates the operation of synthesis plants which combine stages where the reactors are filled with cobalt catalysts with those where the reactors are filled with iron catalyst, since the formation of carbon dioxide on the iron catalysts can be kept so low that it need no longer be taken into account.

These numerous possibilities of varying the operating conditions provided by the invention render it adaptable to conditions obtaining in various types of plant.

It has moreover been found that the advantages of the hereindescribed process depend to a certain degree on the ratio of e.g., K_2O to SiO_2 rather than on the actual alkali oxide and acid (e.g., potassium oxide and silicic acid) content of the catalyst. Hence, already 6 parts of K_2O and 25–30 parts of SiO_2 suffice, when added to 100 parts of iron which is present as metal and in the form of chemical compounds (total iron), to maintain ratios of consumption of CO to H_2 from 1 : 1.2 to 1.7 and higher, depending on the pressure and the temperature under which the synthesis is carried out.

It is a remarkable fact that also the paraffin yield does not decrease substantially with these relatively low alkali contents.

The ratio of consumption is influenced not only by the ratio of alkali oxide to non-volatile reactive acid anhydride, the CO–H_2-ratio of the feed gas and the pressure but also is determined by the way and the degree of reduction to which the catalyst is subjected previous to use in the synthesis. The catalyst has been found to form the more CO_2, the greater its content of free iron. If for example a catalyst of a composition hereinbefore set forth is reduced with hydrogen to such an extent that about 16% of the total iron is present as free metal, water gas in a recycle operation will be worked up at a ratio of 1 CO : 1.4 to 1.5 H_2. Reduction, previous to use in the reactor, to 27% of free iron causes the ratio of consumption to drop to 1 CO : 1.1 to 1.2 H_2.

In carrying out the invention there exists a further possibility of influencing the course of the synthesis in addition to those hereinbefore set forth, such as pressure, ratio of alkali oxide to acid non-volatile components and the like, namely the degree of reduction of the catalyst. In general it may be said, that the preferred high molecular synthesis products, mainly of paraffinic character, are obtained, if the iron is reduced to the metal before the synthesis, to the extent of 10 to 50%. Lower boiling products will generally be obtained if the reduction is carried out to give higher percentages of metallic iron, for example, of 55 to 60% and up to, for example, 99%. This applies especially to catalysts which have been produced by precipitation.

The catalysts used in carrying out the invention may be prepared in the conventional manner. It has already been stated that the hereindescribed process may be carried out with such catalysts as are obtained by precipitation from solutions as well as with those which are obtained by fusing together the components. These may be applied in the form of metals or oxides or metals and oxides. In place of the metal oxides also other oxygenated compounds such as carbonates, nitrates, oxalates, tartrates and the like may be used.

The hereindescribed process may be adjusted to either high yields of paraffin or high yields of gasoline and Diesel oils. Substantial amounts of paraffin will be formed when the synthesis is carried out at low temperatures, e.g., 190–250° C., while at higher temperatures the synthesis tends toward a higher yield of gasoline and Diesel oil. In the latter case higher feed gas charges and higher conversions of carbon monoxide plus hydrogen should be applied. Moreover high contents of free metallic iron in the catalyst, e.g., 50 to 99% of the total iron, lead to higher yields of gasoline and Diesel oil. Thus it is also possible to use such iron catalysts as contain practically all the iron in the form of the metal and also such as contain the bulk of the iron in an oxidic form.

The invention will be illustrated by the following Examples:—

EXAMPLE I

Preparation of a precipitated catalyst containing silicic acid.

12 kgs. of calcined soda are dissolved in water to yield a 100 litre solution and the solution is brought to the boil. To this solution is slowly added, while vigorously stirring, a solution of the nitrates of iron, copper and zinc in the ratio by weight of the metals of 100 : 25 : 14. In this solution, the concentration of the iron is to amount to 3.31 kgs. of metal to 100 litres of solution. The solution is kept boiling till the liberated carbon dioxide is removed, and is then filtered. Precipitation is carried out at a final pH of 6.8 to 7.0. In order to remove the sodium nitrate formed during the precipitation the filter cake is thoroughly washed with hot water. The wash water is finally drawn off. The filter cake is then impregnated with potassium nitrate solution and silicic acid and is kneaded. Potassium carbonate solution may be used alternatively. The concentration of the potassium nitrate solution is so calculated that the desired ratio of K_2O to SiO_2 is obtained. The silicic acid may be applied either in the form of sol or of precipitated silicic acid. The catalyst mass is reduced in the conventional manner with hydrogen at about 320° C. for a period of 40 to 50 minutes. After this preliminary reduction the catalyst has a content of free iron of about 20% of the total iron.

Composition of the catalyst:

100 parts by weight	Fe
25 ,, ,, ...	Cu
18 ,, ,, ...	ZnO
11 ,, ,, ...	K_2O
45 ,, ,, ...	SiO_2

The synthesis was carried out at

10 atm. gauge; a gas recycle of 1 : 2.57; a temperature of 230° C. and a load of 3.72 cb. ft. water gas (60° F., 30" dry) per hour and per litre of catalyst.

	Feed gas %	Tail gas %	
CO_2	4.9	21.6	
C_nH_m	—	0.4	
O_2	0.1	0.1	
CO	41.0	35.1	
H_2	48.8	30.1	
CH_4	0.3	2.4	
N_2	4.9	10.3	
Average number of C-atoms in hydrocarbons	1.0	1.2	
$CO+H_2$-conversion ..	—	—	65.4%
Ratio of consumption	—	$1\,CO : 1.42\,H_2$	
Paraffin content (b.p. higher than 320° C.) in % by weight of the liquid products	—	66.0	

EXAMPLE II

The synthesis was carried out under the same conditions as those set forth in Example I but at 20 atm. and 220° C.

	Feed gas %	Tail gas %
CO_2	5.2	18.9
C_nH_m	—	0.5
O_2	0.1	0.1

	Feed gas %	Tail gas %
CO	41.2	43.4
H_2	49.8	27.4
CH_4	0.3	2.3
N_2	3.2	7.4
Average number of C-atoms in hydrocarbons	1.0	1.21
CO+H_2-conversion	—	— 66.3%
Ratio of consumption	—	1 CO : 1.69 H_2
Paraffin contents	—	70.9%

EXAMPLE III

The composition of the catalyst employed was 100 parts by weight of total Fe ; 25 Cu ; 18 ZnO ; 8.5 K_2O ; and 40 SiO_2.

Conditions of the synthesis were : 10 atm. pressure gauge ; temperature of 225° C. ; gas recycle of 1 : 2.9 ; load 3.908 cb. ft. water gas (60° F., 30″ dry) per hour and per litre of catalyst.

Preliminary reduction : 26.8% free Fe.

	Feed gas %	Tail gas %
CO_2	7.2	31.0
C_nH_m	—	0.8
O_2	0.1	0.1
CO	37.4	19.1
H_2	47.2	28.5
CH_4	0.1	5.1
N_2	8.0	15.4
Average number of C-atoms in hydrocarbons	1.0	1.07
CO+H_2-conversion	—	— 70.8%
Ratio of consumption	—	1 CO : 1.18 H_2
Paraffin content	—	58.0%

EXAMPLE IV

The method of operation was the same as that set forth in the preceding Example ; the gas recycle, however, was 1 : 2.4 (i.e., 1 volume of fresh feed gas to 2.4 volumes of recycled gas).

Preliminary reduction of the catalyst resulted in a content of 15.6% free Fe of the catalyst.

	Feed gas %	Tail gas %
CO_2	6.5	26.3
C_nH_m	—	0.7
O_2	—	0.1
CO	37.0	27.6
H_2	50.9	29.4
CH_4	0.2	3.9
N_2	5.4	12.0
Average number of C-atoms in hydrocarbons	1.0	1.09
CO+H_2-conversion	—	— 70.7%
Ratio of consumption	—	1 CO : 1.52 H_2
Paraffin contents	—	61.5%

EXAMPLE V

The synthesis was aimed at the preferential formation of light hydrocarbons. The catalyst composition was similar to that set forth in Example I except that there were only 7.5 parts of K_2O to 100 parts of iron. Reduction was carried to 55% free iron referred to total iron. The operating pressure was 20 atm., gas recycle was 1 : 2.93 at 295° C. ; the load was 14.52 cb. ft. of water gas (60° F. and 30″ dry) per hour and per litre of catalyst.

	Feed gas %	Tail gas %
CO_2	6.3	47.1
C_nH_m	—	0.3
O_2	—	0.1
CO	39.1	9.9
H_2	48.4	16.7
CH_4	—	9.2
N_2	6.0	16.7
Average number of C-atoms in hydrocarbons	1.0	1.17
CO+H_2-conversion	—	— 89.1%
Ratio of consumption	—	1 CO : 1.19 H_2
Paraffin contents	—	9.5%

EXAMPLE VI

Precipitation of catalyst from the solution of the nitrates of iron, copper and zinc with soda was carried out under the same conditions and under application of the same ratios of quantities as previously set forth concerning the preparation of precipitated catalysts containing silicic acid. The titanic acid used was prepared by boiling a solution of titanium nitrate for a comparatively long period. The precipitated titanic acid was filtered off, was formed into a paste with water, and was kneaded intensively with a concentrated solution of 730 grammes potassium nitrate to 1,980 grammes of precipitated titanium dioxide. Shaping and drying of the catalyst was carried out in a similar manner to that described for the catalyst set forth in Example I. Reduction took place at a temperature of 350° C. The synthesis employing the catalyst containing the titanic acid took place at a temperature of 240° C. and 20 atm. pressure gauge, at a load of 3.722 cb. ft. of water gas (60° F., 30″ dry) per hour and per litre of catalyst. Co+H_2—conversion was 61.3%, the paraffin yield 56%. The ratio of consumption was 1 CO to 1.23 H_2.

EXAMPLE VII

A thorough mixture of 3,300 grammes of Ferrum reductum, 1,480 grammes of very finely ground quartz, 730 grammes of potassium nitrate, 600 grammes of zinc oxide, and 550 grammes of copper oxide was melted by means of an oxy-hydrogen blow pipe, a portion of the mixture at a time. The melt was allowed to cool down and the mass was then disintegrated and granulated and subsequently reduced in a stream of hydrogen at a temperature of 450° C. The catalyst was thereby brought to a content of 60% free iron referred to total iron. The synthesis reaction was carried out at 20 atm. gauge and 231° C. Water gas was used the load being 3.833 cb. ft. of water gas (60° F., 30" dry) per hour and per litre of catalyst. The recycle ratio was 1 : 2.9. At a conversion of 62% the paraffin yield was 57% of the liquid products. Carbon monoxide and hydrogen had been consumed at a ratio of 1 : 1.14.

What we claim is:—

1. Process for the synthesis of hydrocarbons or mixtures of hydrocarbons and oxygenated hydrocarbon derivatives by the catalytic hydrogenation of carbon monoxide with the aid of catalysts which contain iron, alkali metal compounds (preferably oxygen-containing potassium compounds) and difficultly reducible non-volatile reactive acid anhydrides as hereinbefore defined, characterised in that the ratio by weight of alkali metal compound (calculated in terms of alkali metal oxide) to non-volatile reactive acid anhydride in the catalyst is selected to lie between 1 : 2.5 and 1 : 7.0.

2. A process as claimed in Claim 1, which comprises varying the consumption of hydrogen in relation to that of carbon monoxide, under given operating conditions, by varying the pressure under which the synthesis is carried out.

3. A process as claimed in Claim 1 or 2, which comprises varying the consumption of hydrogen in relation to that of carbon monoxide, under the given operating conditions, by modifying the ratio of alkali metal oxide to non-volatile reactive acid anhydride in the catalyst.

4. A process as claimed in any of Claims 1 to 3, which comprises increasing the consumption of hydrogen in relation to that of carbon monoxide by using a synthesis gas of increased hydrogen content.

5. A process as claimed in any of Claims 1 to 4, which comprises adjusting the conditions under which the synthesis takes place to give a high consumption of hydrogen in relation to that of carbon monoxide, whilst not removing the carbon dioxide from the synthesis gas between the stages of a two-stage or multi-stage operation.

6. Process as claimed in any of Claims 1 to 5, in which, for the purpose of producing low boiling products, catalysts are employed which contain iron preponderantly in metallic form up to contents of 99%.

7. A process as claimed in any of Claims 1 to 5, which comprises the employment of catalysts the iron content of which has been reduced to between 10 and 50% of metallic iron advantageously by treatment in a current of dry hydrogen.

8. Process for the synthesis of hydrocarbons substantially as described with reference to the foregoing Examples.

Dated this 22nd day of June, 1949.

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