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COMPLETE SPECIFICATION

Iron Catalyst for the Hydrogenation of Carbon Monoxide giving a High Yield of Gasoline-like Hydrocarbons

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The invention relates to a process for the synthesis of products having a high content of hydrocarbons boiling in the gasoline range by the catalytic hydrogenation of carbon monoxide.

The great flexibility of the process of the hydrogenation of carbon monoxide in the production of hydrocarbons and oxygen-containing organic compounds of various boiling ranges, is known. For chemical processing, the production of unsaturated hydrocarbons and of oxygen-containing compounds is, in general, of particular importance. By reason of their high prices, high-boiling hydrocarbons or waxes are also very desirable. On the other hand, the progressive mechanisation of daily life emphasises the need for a cheap method of producing motor fuels which means, for the Fischer-Tropsch synthesis, the production of gasoline-like hydrocarbons. Many proposals for the production of such low boiling gasoline-like hydrocarbons have been made within the scope of the Fischer-Tropsch synthesis. Mention may be made, for example, of gas recycling. The work or research in this direction has also progressed from the side of the catalyst.

According to the invention, a process for the synthesis of products having a high content of hydrocarbons boiling in the gasoline range comprises contacting a gas containing hydrogen and carbon monoxide in synthesis proportions with an iron catalyst obtained by precipitation of the iron in the form of an oxide, a hydroxide or a carbonate from a solution of an iron salt at a *p*H in the range 7—9 with subsequent reduction to convert less than 50% of the total iron into the free state, the catalyst having an internal surface area of from 110 to 180 square metres, preferably from 130 to 150 square metres, per gram of total iron in the catalyst, being free from or containing only small amounts (for example, up to 10% by weight of the total iron) of supporting material, and having an alkali-metal oxide content, calculated as K_2O, of from 0.5% to 2% and an SiO2 content of from 0.5% to 5%, both the alkali-metal content and the SiO_2 content being by weight and based on the total iron content of the catalyst; the gas being contacted with the catalyst at a temperature in the range 170°—300° C. and at a gauge pressure in the range 10—40 atmospheres and at the rate of 100—750 volumes of fresh gas per volume of catalyst per hour. The catalyst may contain one or more activators such as lime, copper, silver and metals of Groups 5 to 7 of the periodic system.

The use of a catalyst with such an internal surface area is based on the fact that the inner surface of catalysts is of decisive importance for their efficiency, particularly with respect to the chemical nature and the boiling range of the primary products. (Reference is made to the work of Tramm "Zur Technik der Kohlenoxydhydrierung", published in "Erdoel und Kohle", Vol. 5 pp. 10—17, particularly Figure 9 and the left hand column of page 14, and in "Brennstoff-Chemie", Vol. 33, pp. 21—30, particularly page 27, left hand column, Figure 9).

Where the catalyst is to be supported, kieselguhr, aluminium oxide, bauxite and the like are examples of substances suitable for the purpose. The supporting material, when it is to be used, may be introduced into the iron salt solution or into the solution of the precipitant either before or during the precipitation, but it is preferably introduced immediately after the precipitation.

The use of a catalyst obtained by the precipitation of the iron salt solution at a pH value of 7—8 has been found to be particularly advantageous. The reduction of the catalyst, prior to use, is preferably such as to convert from 20% to 30% of the iron into the free or metallic state.

The SiO_2 content of the cataystt is advantageously introduced or adjusted by a direct final impregnation of the precipitated and completely washed catalyst mass.

The alkali content of the catalyst is generally adjusted by first washing the precipitated catalyst mass intensively. Then the desired content of SiO_2 is obtained by impregnating with commercial alkali-metal silicate having a ratio by weight of $K_2O:SiO_2$ of about 1:2.5. The SiO_2 remains quantitatively in the precipitated catalyst mass and is not removed therefrom by any chemical step used during the course of the catalyst production.

The catalyst is conveniently adjusted to a $K_2O:SiO_2$ ratio by weight of from 1:1 to 1:5. This will give particularly advantageous results with respect to the life and the activity of the catalyst. To obtain a ratio of 1: more than 2.5, the catalyst mass impregnated with waterglass (alkali-metal silicate) is neutralized with dilute nitric acid whilst maintaining a pH value of 6.5—8, thereby dissolving out a more or less large proportion of the alkali-metal and shifting the ratio of $K_2O:SiO_2$ in favour of the SiO_2.

If a $K_2O:SiO_2$ ratio by weight of 1: less than 2.5 is desired, an incomplete washing of the precipitated catalyst mass is advantageously effected, that is to say, the washing of the precipitate is such as to leave from 1% to 2% by weight (based on the total iron content of the precipitate) of alkali-metal compounds in the precipitate, the alkali metal compounds being calculated as K_2O. By the subsequent direct impregnation with commercial waterglass, it is possible to obtain $K_2O:SiO_2$ ratios which are lower than 1:2.5, such, for example, as 1:1.5 or even 1:1.

The content of free iron which is desired, is obtained by suitable reduction conditions. The catalysts, according to the invention, are reduced with gases containing hydrogen and/or carbon monoxide at temperatures within the range 175°—320° C. and preferably at temperatures between 200° C. and 250° C. The use of high gas velocities of, for example, 1—2 metres per second and preferably of 1.2—1.5 metres per second (measured at 0° C. and 760 mm. Hg) has been found to be advantageous in the reduction of the catalyst.

The formation of an inner surface of the dimensions hereinbefore given is of decisive importance for the activity and the selectivity of the catalyst in the formation of low boiling gasoline-like hydrocarbons. An inner or internal surface of the given dimensions is a function of the alkali and SiO_2 contents of the catalyst as well as of the amount of free iron present in the catalyst; it is, moreover, determined by the pH value at which the precipitation is carried out.

The determination of the inner surface area is effected by the preparation of an adsorption isotherm and its evaluation by the method of Brunauer, Emmet and Teller (the so-called BET-method). The apparatus required consists substantially of a graduated burrette in which the volume of the gas to be adsorbed (such as nitrogen or argon) is measured, a manometer for the determination of the gas pressure, and a small flask in which the adsorbing substance or adsorbent to be tested is placed.

The invention is illustrated by the following example.

EXAMPLE.

A solution containing 50 grams of iron, 2.5 grams of copper and 5 grams of CaO in the form of nitrates was precipitated in the hot state by adding to it a boiling solution of sodium carbonate in such a manner that the pH value of the mixed solutions after precipitation was 8. The precipitated catalyst mass was then washed to a residual alkali content of 0.3% calculated as K_2O and based on the total amount of iron in the precipitate, and was thereafter impregnated with a 20% solution of potassium waterglass (potassium silicate) having a $K_2O:SiO_2$ ratio of 1:2.6 by weight so that the impregnated catalyst had a total K_2O content of 1.2% and an SiO_2 content of 2.3%, both based on the total amount of iron.

The impregnated catalyst mass was dried at a temperature of 105° C. to a water content of 5%, crushed and sieved to a grain size of 2—4 mm. This catalyst was reduced for 60 minutes at a temperature of 225° C. using a gas mixture consisting of 75% H_2 and 25% N_2. After the reduction, 30% of the iron in the catalyst was in the free or metallic state. This reduced catalyst mass was then charged into a reactor formed of two concentric tubes of a length of 4.5 metres, the catalyst being placed in the annular space between the two tubes. A synthesis run was then carried out with water gas at a synthesis pressure of 25 atmospheres, a temperature of 230° C., a gas load of 500 volumes of water gas per volume of catalyst per hour, and a recycle ratio of 1:3, whilst the temperature of the synthesis was maintained by passing a cooling medium through the inner tube of the reactor. A $CO + H_2$ conversion of 69% was obtained, the methane formation being 7%.

The liquid products were subjected to fractional distillation; 59% of the liquid products had a boiling range of 30°—180° C., 23% had a boiling range of 180°—320° C. whilst the remaining 18% boiled above 320° C.

It will be noted that the alkali-metal oxide content of the catalyst is always expressed and calculated at K_2O. Thus where the alkali-metal oxide content of the catalyst is wholly or partly an oxide of an alkali-metal other than potassium, for example, sodium monoxide, the sodium monoxide will be determined as such and will then be expressed as the equivalent in K_2O.

The term "total iron" used with reference to the catalyst, includes both the iron in the free or metallic state as well as the iron which is in the form of oxides or other compounds.

What we claim is:—

1. A process for the synthesis of products having a high content of hydrocarbons boiling in the gasoline range, which comprises contacting a gas containing hydrogen and carbon monoxide in synthesis proportions with an iron catalyst obtained by precipitation of the iron in the form of an oxide, a hydroxide or a carbonate from a solution of an iron salt at a *p*H of from 7 to 9 and subsequent reduction to convert less than 50% of the total iron into the free state, the catalyst having an internal surface area of from 110 to 180 square metres per gram of total iron, being free from or containing only small amounts of supporting material, and having an alkali-metal oxide content (calculated as K_2O) of from 0.5% to 2% and an SiO_2 content of from 0.5% to 5%, both contents being by weight and based on the total iron content of the catalyst, the contacting of the gas with the catalyst being effected at a temperature in the range 170°—300° C. and at a pressure in the range 10—40 atmospheres gauge and at the rate of from 100 to 750 volumes of fresh gas per volume of catalyst per hour.

2. A process according to claim 1, in which the catalyst used is one in which the iron was precipitated at a *p*H in the range 7—8.

3. A process according to claim 1 or claim 2, in which the catalyst used is one the SiO_2 content of which has been introduced or adjusted by impregnation of the completely washed precipitate with an alkali-metal silicate.

4. A process according to any one of the preceding claims, in which the catalyst used contains from 20% to 30% of its total iron in the free state.

5. A process according to any one of the preceding claims, in which the catalyst used has an internal surface area of from 130 to 150 square metres per gram of total iron.

6. A process according to any one of the preceding claims, in which the catalyst contains an activator selected from the group consisting of lime, copper, silver and metals of the 5th to 7th groups of the periodic system.

7. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described.

8. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to the Example.

9. Hydrocarbons whenever produced by the process of any preceding claim.

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