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COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German Joint-Stock 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 catalytic hydrogenation of carbon monoxide, at normal or superatmospheric pressure, may be carried out for the preferred production of hydrocarbons of high molecular weight as well as for the production of hydrocarbons of low molecular weight in both cases the formation of methane is suppressed as far as possible.

In general, and particularly with iron catalysts, the formation of high molecular weight hydrocarbons and solid paraffins is desired, since these synthetic products are very useful, and may be used to yield lower hydrocarbons by molecular fission. The formation of hydrocarbons of high molecular weight depends, to a considerable extent, upon the content of alkali-metal compounds in the catalysts since a high alkali content favours the development of such synthetic products and simultaneously and to a large extent, suppresses the methane formation.

By the use of catalysts of low alkali content, the formation of hydrocarbons of low molecular weight may, for example, with suitable synthesis conditions, be appreciably increased. Synthetic products boiling within the benzine range are particularly desirable if the primary products of the hydrogenation of carbon monoxide are to be treated for the production of fuels of high octane number as, for example, by catalytic after-treatment, if need be with the admixture of polymer benzine obtained by the polymerisation of gaseous synthetic products. If, with the usual catalysts, there is an increase in synthetic products boiling in the benzine range, there will nevertheless still be formed 15%—20% of products of high molecular weight. Furthermore, the relatively high methane formation is in this case also very disadvantageous. This circumstance has led to the endeavour in almost all cases to ensure the highest possible yield of synthesis products of high molecular weight, since it is only in this way that a small quantity of methane is formed.

It has been found, according to the invention, that surprising effects are obtained, preferably with iron catalysts, both in synthesis at normal pressure and also in synthesis at superatmospheric pressure, with gas pressures of approximately 10—30 kg per sq. cm., and also at higher synthesis pressures, if small amounts, preferably 0.5—5% by volume, of compounds having an alkaline reaction are added to the synthesis gas, the compounds being gaseous under the conditions of synthesis, and being ammonia and/or its derivatives such as methylamine. As synthesis gas water gas may, for example, be used, that is to say, gas mixtures containing 1—1.4 volumes of hydrogen per volume of carbon monoxide. The process may, however, also be carried out with synthesis gases of different composition containing, for example, 0.5—2 volumes of hydrogen per volume of carbon monoxide.

Gaseous ammonia is the compound which is preferably added to the synthesis gas, particularly because, even in relatively small quantities of, for example, 1%, it has a considerable influence on the composition of the resultant synthetic products, both at normal pressure and also at superatmospheric pressure. Ammonia has the further advantage that it is relatively cheap. It is particularly fortunate that catalysts which have a high alkali content are suitable for the treatment at normal pressure of synthesis gases which have been mixed with ammonia and/or its derivatives, such as methylamine, which are gaseous under the synthesis conditions, in accordance with the present invention. Such catalysts, which, in synthesis at normal pressure favoured the formation of paraffin wax and extensively suppressed the methane formation, yield hardly any of such hydrocarbons when ammonia and/or its derivatives are added to the synthesis gas in accordance with the invention. In spite of this, however, no increased methane formation occurs. Particularly favourable results are obtained when iron catalysts are used which have been reduced at gas velocities of at least 1.5 metres per second.

The feed can be increased considerably above the normal extent, particularly when operating at increased pressure. The catalysts may be contacted hourly with 200—1000 litres of synthesis gas per litre without there being any need to fear overloading. The synthesis may be carried out particularly advantageously if the gases are recycled.

In carrying out the process according to the invention, operation is preferably effected with catalyst temperatures which rise slowly in the direction of the gas flow. In this way, on the one hand an overloading of the catalyst at the point of entry of the gas is avoided, and, on the other hand, a uniform utilisation of the whole catalyst mass is obtained.

The olefine content of the liquid hydrocarbons obtained from the synthesis gases containing NH_3 is relatively high, particularly in the higher boiling ranges. The normally gaseous synthetic products also contain a large proportion of olefines, so that by polymerisation of the olefines and by mixing the polymerisate with the primary hydrocarbons, high grade fuels may be obtained in a relatively simple manner.

It is particularly surprising that, in the method of operation according to the invention, a more or less extensive production of organic compounds containing nitrogen is also possible. The amount of these nitrogen compounds, consisting in the main of primary amines, is dependent on the synthesis conditions and on the composition of the catalysts (the catalysts being of the category of catalysts known for the catalytic hydrogenation of carbon monoxide.

Together with the amino-compounds, other compounds containing nitrogen are also formed, for example, ammonium carbonate, ammonium carbamate, urea, and the like. Their production and utilization is, in connection with hydrocarbon synthesis, sometimes of considerable economic importance.

The invention is illustrated, but in no way limited, by the following examples.

EXAMPLE 1.

Water gas, free of carbon dioxide and containing 1% of gaseous ammonia was passed over an iron catalyst consisting of 100 parts iron, 5 parts copper and small quantities of alkali-metal silicate. The synthesis was carried out at normal atmospheric pressure at a temperature of 220° C. with a gas feed of 100 litres of synthesis gas per litre of catalyst per hour. A CO conversion of 85%—95% was obtained, which corresponded to a $(CO+H_2)$ conversion of 66%—68%. The methane formation was between 8% and 10%. The consumption ratio amounted to approximately 0.7 volumes of hydrogen per volume of carbon monoxide.

Because of the very slight formation of hydrocarbons of high molecular weight, it was possible to operate the synthesis for long periods of time and with constant conversion without deterioration of the catalyst

The processing of the synthesis products obtained showed that of the total yield only 5% to 6% boiled above 320° C. The high olefine content in all the fractions was remarkable. In the C_8 fraction, for example, an olefine content of 70% was found, whilst in the crude paraffin wax (320° C.—460° C.) approximately 59% of olefines was present. In the benzine boiling range (40° C.—220° C.) the synthetic products contained 5% of oxygen-containing compounds, chiefly alcohols, and 9% of compounds containing nitrogen, preponderately primary amines. In the Diesel oil range (220° C.—320° C.) there were present 4% of products containing oxygen, chiefly alcohols, and a further 6% of compounds containing nitrogen, mainly primary amines.

EXAMPLE 2.

From a boiling solution of suitable nitrates a catalyst was precipitated with a hot soda solution. The catalyst contained 5 parts copper (Cu) per 100 parts iron (Fe). The precipitated mass was impregnated with potassium phosphate (KH_2PO_4) in such manner that the final catalyst contained, per 100 parts of iron, 3 parts of K_2O in the form of KH_2PO_4. After drying, the catalyst was reduced with hydrogen at a speed of flow of 1.5 metres per second. For the synthesis, water gas was used mixed with 1.5% by volume of NH_3. The synthesis temperature was 213° C. The synthesis pressure was 20 kgs. per sq. cm. and 100 litres of synthesis gas per litre of catalyst were passed through per hour.

The liquid synthetic products obtained contained 35% of compounds boiling above 320° C. 57% of the C_{11} hydrocarbon fraction consisted of olefines whilst olefines were present to the extent of approximately 15% in the C_{18} hydrocarbon fraction.

EXAMPLE 3.

By precipitation with a boiling soda solution there was produced, in the usual manner, a catalyst which consisted of 100 parts Fe, 5 parts Cu, 10 parts CaO and 10 parts kieselguhr. After washing the precipitated catalyst mass, the catalyst was impregnated with caustic soda solution in such manner that the final catalyst, in respect of its iron content, and reckoned as K_2O, had an alkali content of 8% K_2O. For the synthesis a water gas was used which contained 3% NH_3, whilst the catalyst was contacted, per litre of volume, with 100 litres of synthesis gas per hour. The synthesis pressure was 10 kg per sq. cm. and the synthesis temperature to 193° C.

The synthetic products obtained consisted of approximately 15% of compounds boiling above 320° C. In the total liquid products obtained there were present 18% of organic compounds containing nitrogen, which products consisted predominantly of primary amines.

What we claim is:—

1. A process for the catalytic hydrogenation of carbon monoxide, preferably with the use of iron catalysts at atmospheric or higher gas pressure, in which there are added to the synthesis gas small quantites, preferably 0.5—5% by volume, of compounds having an alkaline reaction and gaseous under the conditions of synthesis, these compounds being ammonia and/or its derivatives, such as methylamine.

2. A process according to claim 1, in which iron catalysts are used having a high alkali content.

3. A process according to claim 1 or claim 2, in which synthesis gases are used which contain 0.5—2 volumes of hydrogen per volume of carbon monoxide.

4. A process according to any one of the preceding claims, in which the synthesis gas is passed over the catalyst at a rate of 200—1000 volumes of gas per volume of catalyst per hour.

5. A process according to any one of the preceding claims, in which synthesis tail gas is recycled.

6. A process according to any one of the preceding claims, in which the operation is carried out with catalyst temperatures which increase in the direction of flow of the synthesis gas.

7. A process according to any one of the preceding claims, in which an iron catalyst is used, the iron catalyst, prior to being placed on-stream in the synthesis, having been reduced with gas velocities of at least 1.5 metres per second.

8. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to any one of Examples 1 to 3.

9. A process for the catalytic hydrogention of carbon monoxide, substantially as hereinbefore described.

10. Hydrocarbons, oxygen-containing organic compounds and nitrogen-containing organic compounds, whenever produced by the process claimed in any one of the preceding claims.

Dated this 20th day of March, 1950.

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