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COMPLETE SPECIFICATION.

A Process for Producing Hydrocarbons by the Catalytic Reduction of Oxides of Carbon with Hydrogen.

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a Company organised and existing under the laws of the German State, 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:—

In a number of cases the production of hydrocarbons by the catalytic conversion of oxides of carbon with hydrogen is attended with difficulties due to the high initial activity of the catalysts employed, which necessitates the adoption of measures which greatly impede the practical carrying out of the process. Thus, at the outset, operations must be conducted at temperatures far below the normal working temperature. Even when commencing so cautiously the formation of methane cannot be entirely prevented. There is always the risk that the temperature will rise suddenly owing to excessive activity of the catalyst, with the result that the catalyst becomes dead-burned and therefore useless.

A further disadvantage of producing by synthesis hydrocarbons by the use of highly active catalysts is that the preparation and application of the catalysts—which often exhibit pyrophoric properties—necessitate certain precautionary measures, which, as will be understood, must also be used in transferring the prepared catalysts to the conversion vessels. It is generally advisable to place the plant for preparing the catalysts in the vicinity of the conversion vessels, while if the catalyst be prepared in the conversion vessel itself work must be interrupted every time the catalyst is renewed.

By means of the present invention all the inconveniences hereinbefore set forth are avoided, the high initial activity of the catalysts being reduced by treating them before, during or after their preparation, with liquid synthetic or natural hydrocarbons, or mixtures of hydrocarbons, such hydrocarbons being carried away by the flowing gases or vapours after the reaction has commenced. The liquid hydrocarbons may be replaced by solid hydrocarbons, provided these be employed in molten or dissolved condition. The products of the reaction itself are particularly suitable for this purpose. The catalysts to be employed according to the invention may be preserved by impregnating them with, or by suspension in, the liquids referred to. Thus, for example, the catalyst may be introduced into the reaction chamber as a suspension. The excess of the liquid is then removed, for example, by simply allowing it to drain off. The residual liquid in the catalytic mass is gradually carried off by the gases or vapours traversing the reaction chamber.

For impregnating or suspending the catalyst it has been found advantageous to employ a hydrocarbon mixture, consisting for example of oil and benzine, one component of which has a lower boiling point than the remainder. After treating the catalyst with the hydrocarbon mixture the benzine is vaporized by the passage of a stream of gas, and is recovered in a suitable manner; for example by means of active carbon. The effect of this measure is that the catalyst absorbs only a smaller quantity of oil. Another advantageous measure is to cool the reduced catalyst in a stream of inert gases, such as nitrogen, methane, ethane, carbon dioxide, or gases containing them —for example, the final gas from the reaction in the synthesis of benzine—and then treat it with a hydrocarbon mixture containing low-boiling components. During the cooling treatment the catalyst becomes laden with the gases mentioned and therefore cannot absorb as much of the oil mixture as it would if the still hot catalyst were impregnated with oil without being previously charged with gas. In effecting hydrocarbon syntheses, such as that of benzine, by converting oxides of carbon by the use of hydrogen, very considerable advantages result from the use of the catalysts treated in accordance with the process of the invention. Thus there is no longer any need for a lengthy preliminary treatment of the catalyst after its introduction into the

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synthesis chamber, the desired reaction being capable of being carried out at once. Owing to the catalyst being impregnated with added hydrocarbons, such as paraffin hydrocarbons, the reaction begins gently and then increases in proportion as the added hydrocarbons are carried away by the flowing gases and vapours. In this way the exceedingly great danger of initial over-heating, and possibly the dead burning of the catalyst, is removed. At the same time the yield of the desired benzines is substantially increased because the formation of methane—otherwise invariably occurring at the outset—is much reduced and the occurrence of secondary reactions is restricted. The efficiency and optimum working conditions of each charge can be exactly determined prior to its introduction into the synthesis chamber. Working can be considerably simplified by carrying out the preliminary treatment—for example, the reduction of the catalysts for a number of synthesis chambers, even when these are widely separated—in a common continuously operated simple apparatus, provided molten or dissolved hydrocarbons (such as solid paraffin) are employed, which surround the contact mass with a protective layer at ordinary temperature.

The present process in no way impairs the high activity of the catalysts. All that it accomplishes is to prevent the injurious effect of the high initial activity by the addition of hydrocarbons. After these additions have been carried away, the synthesis of the desired hydrocarbons proceeds, the activity of the catalyst being fully exercised.

The present process offers particular advantages in that case where the reduction temperature of the catalyst is substantially higher than the subsequent working temperature during synthesis, for example, as in the case with nickel catalysts for the synthesis of benzine. Hitherto, in effecting the synthesis of benzine with nickel catalysts, special difficulties were encountered because, during the preparation of the catalyst, the synthesis chamber had to be heated to a temperature considerably above the working temperature, a measure which in many cases was difficult if not impossible to carry out in practice. On the other hand special precautions are needed in transferring to the synthesis chamber a catalyst much effected by the atmosphere and which has been prepared in a furnace provided for the purpose. These difficulties are overcome in effecting the synthesis of benzine with nickel catalysts by the present process.

EXAMPLE 1.

Equal parts of kieselguhr and cobalt carbonate, with small quantities of activating additions, are treated with such an amount of a benzine solution of paraffin (melting point 40° C.) that, after the evaporation of the benzine, 5% of paraffin—calculated with respect to the mass of the catalyst—remains in the catalyst. This catalytic mass is moulded into cakes, measuring 4 mm. in diameter and 4 mm. in height, in an eccentric press. The addition of the paraffin much facilitates the pressing operation; the charging of the moulds is more uniform, the material does not adhere to the metal walls and, for a given density, the cakes are firmer and retain their shape better than in the absence of paraffin.

The cakes are placed in a synthesis chamber, where they are reduced with hydrogen at about 200° C. in the usual manner. Such of the surplus paraffin as is not retained on the surface of the catalyst drips from the catalyst which is lying on perforated plates. The mixture of carbon monoxide and hydrogen intended for conversion is then introduced into the synthesis chamber. The reaction between the carbon monoxide and hydrogen begins slowly, even when the normal working temperature is immediately employed. After the reaction has begun, the gases and vapours passing continuously carry away portions of the added substances. After the complete removal of these substances the reaction proceeds with maximum intensity. The activity of the catalyst has not suffered from the temporary presence of the additions; the only result is that the injurious effect of the high initial activity is avoided, so that overheating accompanied by excessive formation of methane is prevented. With the catalyst hereinbefore described, working with the synthesis gas can be commenced without troublesome and time-wasting precautions, and with maximum efficiency.

Instead of preparing cakes in the manner hereinbefore described by the use of a solution of paraffin in benzine, grains, for example, may be employed, which are formed out of the catalytic materials by treating them with a small quantity of paraffin oil in a rotating drum. For this purpose the initial material is first compressed and then (after being crushed, if necessary) forced through a sieve, the mesh of which corresponds to the size of grain required. The resulting mixture of grains and powder is treated for some time in a slowly rotating drum which is only partially filled. The powder disappears by the injection of finely distributed paraffin oil, so that finally the drum contains nothing but small grains of uniform size. The addition of the oil binds the particles together. Thus this method of treatment both impregnates the mass with hydrocarbons and also granulates it without loss in the form of powder.

EXAMPLE 2.

Finely divided nickel carbonate is precipitated on kieselguhr from a solution of nickel nitrate and a small amount of aluminium nitrate, by the use of a slight excess of soda. The precipitate contains kieselguhr and nickel in the proportion of 2:1; it is washed with water, dried and then granulated by crushing, the grains being reduced with hydrogen in a rotating drum at 450° C. The reduced mass is introduced into melted paraffin, air or gases containing oxygen being excluded; when the mass is impregnated the surplus paraffin is removed. The granular mass hardens on cooling, retains its shape and is quite unaffected by air; it can be stored without special precautions, transported as desired, and charged into the synthesis chambers as required.

When the synthesis chambers have received the charge, conversion is carried out at a temperature of 200° C., in the manner hereinbefore described.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for producing hydrocarbons by the catalytic conversion of oxides of carbon and hydrogen at a high temperature, and under pressure if desired, characterised by the use of catalysts which are charged before, during or after their preparation, with natural or synthetic hydrocarbons or hydocarbon mixtures—but preferably with products of a previous conversion—in a liquid, molten or dissolved condition, the additions being carried away by the flowing gases or vapours after the reaction has commenced.

2. A process according to claim 1, characterised by the use of a catalyst provided with a protective layer and prepared by treating it with molten hydrocarbons or hydrocarbon mixtures (such as paraffin), which are solid at ordinary temperature.

3. A process according to claim 1, characterised in that to the catalyst are added liquid substances in such quantities as to enable the catalytic mass to be conveyed and introduced into the reaction chamber as a suspension.

4. A process according to claims 1 to 3, characterised in that the surplus of the liquid, molten or dissolved addition is removed by draining or the like.

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EDWARD EVANS & CO.,
40—43, Chancery Lane, London, W.C.2,
Agents for the Applicants.

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