# PATENT SPECIFICATION

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3784

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(Under Section 6 (1) (a) of the Patents &c. (Emergency) Act, 1939, the proviso to Section 91 (4) of the Patents and Designs Acts, 1907 to 1946, became operative on Aug. 26, 1946).

Index at acceptance: —**Classes 1(i),** F3b(1: 2a: 2x); **and 2(iii),** B1g.

COMPLETE SPECIFICATION

## Catalyst and Process for Synthesizing Organic Compounds

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 310, South Michigan Avenue, Chicago, Illinois, United States of America, 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 concerns a catalyst and process for synthesizing organic compounds such as hydrocarbons, alcohols, aldehydes, and the like by the reaction of carbon monoxide and hydrogen.

More specifically, the invention relates to improvements in the synthesis of hydrocarbons of gasoline and higher boiling range from carbon monoxide and hydrogen, said hydrocarbons having greater value as motor fuel than those produced according to conventional methods.

A process has been practiced for converting mixtures of carbon monoxide and hydrogen such as may be present in products of the water gas reaction, into gaseous and liquid hydrocarbons as well as other organic compounds. The products of this reaction consist largely of aliphatic hydrocarbons mostly paraffinic in nature, although approximately 20—30% of olefinic hydrocarbons may also be present. In addition to the gasoline, higher boiling oil and high melting waxes are formed. By suitably adjusting operating conditions other organic compounds including alcohols, aldehydes, or the like can be produced.

The catalysts used in the known process are normally selected from the metals of Group VIII of the Periodic System promoted with thoria. These catalysts, usually consisting of a composite of iron, cobalt and/or nickel and thoria, are prepared for example by precipitating the oxides of the metals on kieselguhr, followed by reducing with hydrogen.

Because of the straight-chain character of the hydrocarbon produced in the known process, the motor fuel fraction usually has poor antiknock properties, and must be treated in some manner, such as by cracking or reforming to improve the octane characteristics. The present invention offers an improvement whereby motor fuels of improved octane qualities may be produced directly from the synthesizing process by adding to the above described catalytic mass, a second catalytic mass which functions as an isomerising and cracking catalyst.

For the purpose of gasification of mineral oils by a process wherein the carbon of the liquid hydrocarbons is completely converted into gas it has been proposed heretofore to pass the vapours of the oils to be treated together with at least sufficient oxidising gas or gases to oxidise the carbon content of the hydrocarbons to carbon monoxide over a porous catalyst such as active carbon, porous earthenware, silica gel or the like containing at least one from each of the following groups of substances: (a) Cr, Mn, Ni, Co, (b) Fe, Cu, Zn, and (c) an oxide of Al, Mg, Ca, Zr or Th, the catalyst being heated to a temperature of from 600° to 1000° Centigrade and any reaction between oxidising gas and oil vapours being avoided before they come into contact with the catalyst.

The process of the present invention utilises an improved catalyst which comprises a hydrogenating component consisting essentially of thoria and at least one of the metals of group VIII of the Periodic System, in combination with an isomerising and cracking component consisting essentially of a major proportion of silica and a minor proportion of alumina and/or zirconia.

In one specific embodiment, the present invention comprises converting mixtures of carbon monoxide and hydrogen into organic compounds such as gaseous and liquid hydrocarbons containing substantial quantities of valuable motor fuel products, by contacting such mixtures with a catalytic mass comprising a hydrogenating component consisting essentially of thoria and at least one metal of Group VIII of the Periodic System, in combination with an isomerizing and cracking component essentially consisting of a calcined mixture of a major proportion of precipitated silica and a minor proportion of a precipitated compound of alumina and/or zirconia.

According to one variation of the present invention, the catalytic mass normally used in carrying out the synthesis (and which may consist of one or more reduced metals of the group of iron, cobalt and nickel deposited on kieselguhr and promoted with thoria) and herein designated as the hydrogenating component, may be mixed mechanically with the second catalytic mass herein designated as the isomerizing and cracking catalyst component. Other metals such as copper, and/or metal oxides such as the oxides of manganese and aluminium may be added in relatively minor amounts to the hydrogenating component.

Although the isomerizing and cracking catalyst component may include naturally occurring earths which have been treated with acids or other chemicals to increase their activity, it is preferred to use in the catalyst combination a special catalytic mass consisting of silica-alumina, silica-alumina-zirconia, silica-zirconia or silica-alumina-thoria. Such a mass may be prepared by precipitating silica and the component oxide or hydrogels either simultaneously or in separate steps followed by mixing and washing in such a manner that alkali metal compounds are substantially removed.

The component parts of the catalytic mass of the present invention may then be combined and formed into pellets or other shapes. Usually the catalyst is prepared in the following manner:

The hydrogenating component is prepared by precipitating the hydroxides of the metals on kieselguhr or similar suitable siliceous material. Usually the kieselguhr is suspended in an aqueous solution containing the metal salts such as mixtures of cobalt chloride, ferric chloride and a minor amount of thorium nitrate. These materials are usually made into a thick paste which is then added to a solution of an alkali metal hydroxide or carbonate in order to precipitate the metals on the kieselguhr in the form of the corresponding hydroxides or basic carbonates. The mixture of precipitate and kieselguhr is washed with water, filtered, and dried. The isomerizing-cracking component is prepared in powdered form in a separate operation. The powders of both these component masses are intimately mixed and formed into shapes such as pellets, spheres, or the like, and then calcined at a temperature above 400° C. The composite thus formed is reduced with hydrogen at a temperature above 200° C. to produce the final catalytic mass of the present invention.

According to another variation, the special silica-alumina, silica-zirconia, or silica-alumina-zirconia mass which comprises the isomerizing and cracking component of the finished catalyst is prepared in one step as indicated above, and the oxides of the materials comprising the hydrogenating component of the catalyst are precipitated thereon. In this case ammonium hydroxide is preferred as the precipitant. The mixture is filtered, washed, and dried, formed into shapes and finally calcined. The mixture is then reduced with hydrogen prior to use in the synthesizing process.

When employing earths of the chemically activated clay type as the isomerizing-cracking constituent, the two components of the catalyst may be composited in a manner similar to those employed with the precipitated mass of silica-alumina, silica-zirconia, or silica-alumina, or silica-alumina-zirconia.

As a further alternative, the components of the catalyst of the invention may be prepared as above described in separate operations and made into particles such as pellets. These pellets are then separately calcined, mixed together, and subjected to the action of hydrogen under reducing conditions prior to use in the synthesizing process.

Another alternative consists in the use of alternating layers of the individual catalytic components, said layers being disposed within the same reaction tube or chamber. For example, the isomerizing-cracking component may constitute one layer, above this may be disposed a layer of the hydrogenating component, followed by another layer of isomerizing-cracking component, and so on until the chamber is filled. Usually the metallic constituents of the catalyst are formed *in situ* by first loading the reactors with an association of isomerizing-cracking component and unreduced hydrogenating component and then reducing the oxides of the latter component to the corresponding metals. The above types of operations are not necessarily exactly equivalent. One type may be more desirable than another under a given set of circumstances.

In carrying out the process for hydrocarbon manufacture, the temperature employed is within the range of approximately 175°—300° C. The ratio of carbon monoxide to hydrogen is usually approximately 1:2, although this is not to be considered by any means an exact proportion. Water gas prepared from coal, consisting of approximately two parts carbon monoxide, four parts hydrogen, and one part carbon dioxide, has been found satisfactory. The composition of the hydrocarbon mixture resulting from this process can be varied somewhat by varying the ratio of the reactant gases; for example, olefin production is increased if the amount of hydrogen is decreased.

It is essential to the life of the catalyst and the properties of the resulting hydrocarbons that the sulfur content of the reactant gases be kept at a minimum. The sulfur may be removed from the gases by known methods, for example, by treatment with the oxides of metals such as iron, or by treatment with amines such as triethanol amine, diethanol amine, and tripropanol amine; solutions of tripotassium phosphate have also been used for this purpose. The catalyst becomes exhausted periodically, and may be reactivated by extracting with solvents to remove waxy materials deposited thereon. The catalyst may require additional reactivation at intervals, and this is done by heating in the presence of air to remove carbonaceous deposits, the catalyst being again reduced with hydrogen before use.

The synthesizing process may be operated at substantially atmospheric pressure, although higher pressures offer certain definite advantages such as that of improved heat transfer. Although the increased pressure changes the ratio of the products formed to a certain extent, pressures in the range of 5—25 atmospheres are especially useful.

If the hydrogen content is increased to too great an extent, increased methane formation results, although the degree of saturation of the hydrocarbons produced is increased. Methane formation may be reduced in cases of high hydrogen concentration by reducing the temperature of the reaction.

The following examples are given to illustrate the usefulness of the present catalyst and process, but should not be construed as limiting the invention to the exact conditions or materials used in these examples.

EXAMPLE 1.

Water gas produced by reacting steam with coke, and consisting of approximately two parts carbon monoxide, four parts hydrogen, and one part carbon dioxide, was passed over a catalyst prepared in the following manner:

Silica hydrogel was precipitated from a sodium silicate solution by addition thereto of hydrochloric acid until the reaction mixture was just acid to litmus paper. To this mixture was added aluminium chloride in an amount such that the alumina equivalent thereof was equal to 10 mol per cent of the final silica alumina component. Ammonium hydroxide was added in sufficient quantity to precipitate the oxide. The mixture was filtered, dried at 149° C., crushed to pass a "30 mesh" screen having opening of 0.59 millimeter, and washed with water to which had been added small amounts of hydrochloric acid, until the mass was substantially free of alkali metal compounds. This mass was the isomerizing and cracking component of the final catalyst.

The hydrogenating component of the catalytic mass was prepared in the following manner:

Kieselguhr was suspended in an aqueous solution of cobalt chloride, ferric chloride, and a minor amount of thorium nitrate, so that a thick paste was formed. The corresponding hydroxides were precipitated by adding this paste with stirring to a solution of potassium hydroxide. The product was then washed until essentially free of chloride ions, and dried. The isomerizing-cracking component was mixed with this mass and the mixture was compressed into pellets which were subjected to the action of hydrogen at a temperature of 250° C.

The water gas was contacted with the catalyst at 190° C. and substantially atmospheric pressure. The liquid hydrocarbons were recovered and a portion of the unreacted hydrogen and carbon monoxide was returned to contact with the catalytic mass. The hydrocarbons boiling within the motor fuel range were separated. The yield amounted to 145 g. per cubic meter of reactant gases. This compared with 130 g. produced by the regular catalyst. The octane number of the motor fuel fraction produced according to the present process was 65, while that produced in the usual manner was 20.

EXAMPLE 2.

The catalyst used in this example was prepared in a similar manner to that described above, except that the isomerizing and cracking component contained added thereto precipitated zirconia in an amount equal to four mol per cent of the final silica-alumina zirconia mass. The powdered catalyst components were mixed together to form the catalytic composite of the invention, dried and formed into pellets, and used in the proces substantially as described in Example 1. In this case, 142 g. of hydrocarbons were formed per cubic meter of reactant gas. The octane number of the gasoline fraction was 62.

In the above examples, the yield of liquid hydrocarbons was increased when using the present catalyst over that obtained by the usual catalytic masses. Moreover, the amount of hydrocarbon boiling in the gasoline range was increased by approximately 15%. The most useful result is the greatly superior antiknock quality of the gasoline produced by this process.

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 catalyst for synthesizing organic compounds which comprises a hydrogenating compounds consiting essentially of thoria and at least one of the metals of Group VIII of the Periodic System, in combination with an isomerizing and cracking component consisting essentially of a major proportion of silica and a minor proportion of alumina and/or zirconia.

2. Catalyst as claimed in claim 1 wherein the isomerizing and cracking component consists essentially of a major proportion of silica and a minor proportion of alumina.

3. Catalyst as claimed in claim 1 wherein the isomerizing and cracking component consists essentially of a major proportion of silica and a minor proportion of zirconia.

4. Catalyst as claimed in claim 1 wherein the isomerizing and cracking component consists essentially of a major proportion of silica and minor proportions of alumina and zirconia.

5. Catalyst as claimed in any of the claims 1 to 4, which comprises a hydrogenating component consisting essentially of thoria and at least one reduced metal selected from the metals of Group VIII of the Periodic System, in combination with an isomerizing and cracking component consisting essentially of a mixture of a major proportion of precipitated silica and a minor proportion of precipitated alumina and/or precipitated zirconia.

6. Catalyst as claimed in claim 5, wherein the isomerizing and cracking component consists of a calcined mixture of silica hydrogel and at least one of the hydrogels of the group consisting of alumina hydrogel and zirconia hydrogel, said mixture being substantially free of alkali metal impurities.

7. Catalyst as claimed in any of the claims 1 to 6 consisting of a mechanical mixture of particles of separately produced hydrogenating component and isomerizing and cracking component.

8. Catalyst as claimed in any of the claims 1 to 6, consisting of particles of the isomerizing and cracking component on which the hydrogenating component has been deposited by way of precipitation.

9. Catalyst as claimed in any of the claims 1 to 6 in the manufacture of which the hydrogenating component has been deposited on a siliceous carrier and thereafter mixed intimately with the isomerizing and cracking component and the resultant mixture has been transformed into compressed, shaped particles.

10. Catalyst as claimed in any of the claims 1 to 9 in the manufacture of which a combination of the isomerizing and cracking component with the oxide form of the hydrogenating component has been reduced by treatment with hydrogen prior to use in the synthesizing of organic compounds.

11. The improved catalyst for synthesizing organic compounds produced in a manner substantially as described.

12. Process for synthesizing hydrocarbons by reaction of carbon monoxide with hydrogen in the presence of a hydrogenating catalyst consisting essentially of thoria and at least one of the metals of Group VIII of the Periodic System, characterized thereby that the antiknock value of the hydrocarbons produced by the synthesis is increased by associating with said catalyst an isomerizing and cracking catalyst consisting essentially of a major proportion of silica and a minor proportion of alumina and/or zirconia.

13. Process as claimed in claim 12, wherein the hydrocarbon synthesis is effected in the presence of the catalyst defined in any of the claims 2 to 11.

14. The process for synthesizing organic compounds from carbon monoxide and hydrogen in the presence of catalysts substantially as described.

Dated this 26th day of August, 1946.

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## ERRATUM

SPECIFICATION No. 626,071.

Page 4, line 26, *for* " compound consiting " *read* " component consisting "

THE PATENT OFFICE,
*22nd November*, 1949.

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[*Price*

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