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HYDROCARBON SYNTHESIS

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This invention relates to hydrocarbon syn-
thesis, and in particular concerns a process for
synthesizing hydrocarbons from hydrogen and
carbon monoxide in the presence of a catalyst.

In the commercial synthesis of hydrocarbons
by the so-called Fischer-Tropsch process, where-
by a mixture of hydrogen and carbon monoxide
is contacted with a catalyst at an elevated tem-
perature, the catalysts have usually comprised
cobalt with the addition of various activators
such as thoria and the like. Although other
metals suitable as catalysts for the synthesis are
known, e. g., iron, nickel and others, the greater
activity of cobalt catalysts has heretofore
militated against the extensive use of such other
metals. However, despite the greater activity
of cobalt catalysts, the processes based on their
use are not entirely desirable from a commercial
standpoint since the great expense involved in
the preparation of such catalysts necessitates
elaborate and costly systems for recovering spent
catalyst values after the catalyst has lost its
activity during the course of the process. Fur-
thermore, the cobalt catalysts have the disad-
vantage of producing predominately straight-
chain saturated hydrocarbons of low octane
number in the motor fuel boiling range, as well
as excessive amounts of high molecular weight
wax-like hydrocarbons which become deposited
on the catalyst during the course of the process.
The latter phenomenon reduces the activity of
the catalyst and necessitates frequent removal
of the wax-like hydrocarbons to permit of con-
tinued catalyst activity over any substantial
length of time. The necessity of removing the
wax requires the obviously disadvantageous pro-
cedure of interrupting the process at periodic
intervals.

It has long been desirable to employ a hydro-
carbon synthesis process in which a metal less
expensive than cobalt is used as the catalyst.
To this end, attempts have been made to use
finely divided iron. A process employing a
catalyst of this nature would not require elabo-
rate and costly recovery procedures for the de-
activated catalyst since, in the ordinary course,
when the iron catalyst becomes deactivated, it
is sufficiently cheap simply to be discarded.
However, the iron catalysts heretofore known
have not possessed sufficiently great activity to
warrant their commercial use for the synthesis
of hydrocarbons. Furthermore, it has been typi-
cal of such iron catalysts that a large proportion
of the carbon monoxide contained in the syn-
thesis gas is converted during the process to car-

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bon dioxide instead of to the desired valuable
hydrocarbons.

It is accordingly an object of the present in-
vention to provide a process for the synthesis of
hydrocarbons from hydrogen and carbon mon-
oxide employing an iron catalyst which com-
pares favorably in activity with cobalt catalysts.

Another object is to provide a hydrocarbon
synthesis process which employs an iron catalyst
and which does not result in the production of
excessive amounts of high molecular weight wax-
like hydrocarbons.

A further object is to provide an iron catalyzed
hydrocarbon synthesis process which produces
hydrocarbons boiling in the motor fuel range
and having a higher octane number than those
obtained from the use of cobalt catalysts.

A still further object is to provide an iron
catalyzed hydrocarbon synthesis process which
does not produce excessive amounts of carbon
dioxide.

Other objects will be apparent from the fol-
lowing detailed description of the invention, and
various advantages not specifically referred to
herein will occur to those skilled in the art upon
employment of the invention in practice.

I have now found that the above and related
objects may be realized in a process whereby a
mixture of hydrogen and carbon monoxide is
contacted at an elevated temperature with a pre-
cipitated iron catalyst which has been prepared
by adding to a water-soluble iron salt a water-
soluble alkaline compound to the point of inci-
pient precipitation and then adding gallic acid
to complete the precipitation. Such catalyst may
be of the supported or unsupported type, and
may contain activators as hereinafter more fully
explained.

In preparing the catalyst employed in the new
process, a water-soluble alkaline compound, such
as potassium carbonate, is added with stirring to
a warm aqueous solution of a water-soluble iron
salt, such as ferric nitrate, to the point of inci-
pient precipitation. At this point, an aqueous
solution of gallic acid is added with stirring and
precipitation takes place. The precipitate is then
filtered, washed with water and dried. The re-
sulting product may be used directly as the cata-
lyst in the synthesis process, in which case it will
become reduced prior to any synthesis reaction
occurring, or it may be reduced by treatment
with hydrogen in any suitable manner prior to
use in the process.

The manner in which the gallic acid acts to
complete the precipitation and the method by

which it affects the precipitate are not fully understood. While I do not desire to be limited by any theory as to the action of the gallic acid, it is my present belief that the gallic acid is either adsorbed on the precipitate or reacts therewith in some manner to produce an unusual form of catalyst. In any event, it is certain that the gallic acid produces profound changes in the nature of the catalyst as evidenced by its enhanced activity and lower carbon dioxide production in the synthesis. Furthermore, X-ray examination of iron catalysts after use in the synthesis of hydrocarbons shows that an iron catalyst prepared without gallic acid contains iron carbide and carbon and is not pyrophoric; whereas an iron catalyst prepared in accordance with my invention shows little iron carbide, no carbon, and is extremely pyrophoric.

Any water-soluble iron salt may be used as a starting material in the preparation of the catalyst. Either ferric or ferrous salts may be used. In general, the ferric salts are preferred because they are cheaper and more stable than the ferrous salts. Ferric nitrate is preferred among the ferric salts because the nitrate ion is more readily washed out of the precipitated iron compound and is decomposed at the temperatures of either the reduction or synthesis. Traces of sulfate and chloride ion on the finished catalyst tend to act as poisons, and therefore the use of iron sulfates and chlorides as starting materials in the preparation of the catalyst is not preferred because sulfate and chloride ions are difficult to remove completely.

Any water-soluble alkaline compound, that is, a compound which will yield hydroxyl ions in aqueous solution, may be used to bring the iron salt to the point of incipient precipitation. For example, the alkali metal hydroxides, such as sodium and potassium hydroxides, the alkali metal carbonates, such as sodium and potassium carbonates, ammonium hydroxide and the water-soluble amines, such as triethanolamine, are suitable.

As previously stated, the water-soluble alkaline compound is added to the water-soluble iron salt in an amount sufficient to produce incipient but not complete precipitation. The exact amount of water-soluble alkaline compound to add to produce incipient precipitation may vary depending on whether a ferrous or ferric salt is used as the starting material. Regardless of the type of iron salt used, however, the water-soluble alkaline compound should not be added in any substantial excess of the amount theoretically necessary to precipitate iron hydroxide. For example, when the iron salt is a ferric salt, the alkaline compound is added in such an amount that the pH of the resulting solution lies in the range 2.1 to 2.3. When the iron salt is a ferrous salt, the alkaline compound is added in such an amount that the pH of the resulting solution lies in the range 5.3 to 5.5.

The amount of gallic acid added when the mixture of water-soluble iron salt and water-soluble alkaline compound is at the point of incipient precipitation is such that the iron compound is completely precipitated from the mixture. In general, at least 0.08 mol of gallic acid per mol of iron salt used as starting material is required. Although large amounts of gallic acid may be used, no advantage is ordinarily obtained thereby, and I prefer not to use more than 0.15 mol of gallic acid per mol of iron salt. When further amounts of alkaline compound are added

after precipitation of the iron compound to precipitate activator compounds, as hereinafter disclosed, the larger amounts of gallic acid are preferably used to offset any possible consumption of gallic acid by the alkaline compound.

As previously mentioned, various promoters or activators may be added to the iron catalyst and, in addition, various supporting materials for the finished catalyst, such as kieselguhr, silica gel and the like, may be used. The activators and the supporting materials are conveniently added to the water-soluble iron salt prior to addition of the water-soluble alkaline compound. In such case, the activator is also added in the form of a water-soluble salt. When it is desired to incorporate an activator which is to be precipitated by the water-soluble alkaline compound, it is preferred to complete the precipitation of the iron compound first in the manner described above, that is, by the addition of a water-soluble alkaline compound to the point of incipient precipitation followed by the addition of gallic acid to complete the precipitation of the iron compound, and then to add additional water-soluble alkaline compound to precipitate the activator. In such case, greater amounts of gallic acid, as set forth hereinabove, are preferably used to precipitate the iron compound, in order to offset any leaching effect on the gallic acid occasioned by the addition of further amounts of water-soluble alkaline compound after the gallic acid has been added.

Among the activators which may be used are manganous oxide, copper, magnesium oxide and calcium oxide. The activators are generally used in a minor amount, and the proportion of activator to iron metal in the reduced catalyst may vary from about 1 per cent to 25 per cent. The amount of activator used in any specific instance will vary depending on the specific activator chosen. Also more than one activator may be employed.

The following examples will illustrate the preparation of the catalysts employed in the process of the invention. Unless otherwise stated, all parts are by weight.

Example 1.—To 607 parts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in 3000 parts of water and heated between about 70° and 90° C., there was added, with stirring, a solution of 290 parts of potassium carbonate dissolved in 450 parts of water. At this point of incipient precipitation, 15 parts of gallic acid dissolved in 1000 parts of hot water were added and precipitation took place. The precipitate was filtered, washed with water until the washing showed negligible nitrate content, and was oven-dried at 110° C. As previously stated, carriers or supporting materials for the finished catalyst, such as kieselguhr, may be added to the solution prior to precipitation. Other water-soluble alkaline compounds, such as ammonium hydroxide, may be used in lieu of the potassium carbonate.

Example 2.—To a hot solution, between about 70° and 90° C., of 607 parts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 28 parts of $\text{Mn}(\text{NO}_3)_2$ dissolved in 3000 parts of water, there was added, with stirring, a solution of 290 parts of potassium carbonate in 450 parts of water. At this point of incipient precipitation, 30 parts of gallic acid dissolved in 1000 parts of hot water was added and precipitation of the iron compound took place. At this point, the pH of the mixture is on the acid side and the manganous compound does not precipitate. In order to precipitate the manganous compound which becomes the activator an additional 50 parts of potassium

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carbonate dissolved in 500 parts of water was added. The precipitate was filtered and washed with hot water until it showed negligible nitrate content. The catalyst was then dried at 110° C. The larger amount of gallic acid shown in this example is used, in accordance with the previous disclosure, to offset the leaching effect of the additional water-soluble alkaline compound used to precipitate the activator.

As previously stated, the catalysts employed in accordance with my invention may be reduced with hydrogen prior to use in synthesis, or they may be reduced directly in the synthesis operation. Reduction of the catalyst prior to the synthesis may be accomplished in any known manner, as for example, by passing hydrogen over the catalyst at 500° C.

As previously stated the process of the invention consists essentially in contacting a mixture of hydrogen and carbon monoxide with the hereinbefore described catalyst at an elevated reaction temperature. The process may be carried out in any suitable manner employing any of the known engineering techniques. Thus, the mixture of hydrogen and carbon monoxide may be passed over thin layers of the catalyst in a reactor, and the products of the synthesis recovered from the exit gases. If desired, the "fluidized" catalyst technique may be used, wherein the catalyst, in finely divided form, is suspended in a stream of the synthesis gas mixture and passed into a reactor. The catalyst may also be suspended in an inert liquid reaction medium into which the synthesis gas mixture is passed.

The reaction conditions for the synthesis may vary widely. In general, the temperature ranges from about 200° to 350° C.; the pressure may vary from 1 atmosphere to about 10 atmospheres; the space velocity (volumes of synthesis gas per volume of catalyst per hour) may range from about 100 to 400; and the mol ratio of hydrogen to carbon monoxide in the synthesis gas mixture may vary from about 2:1 to 1:1. If desired, unreacted synthesis gas mixture may be recycled to the reactor. The catalysts may be used in finely divided form or they may be agglomerated or pelleted, if desired.

The following examples will illustrate the process of the invention, but are not to be construed as limiting the same.

Example 3.—A synthesis gas mixture of hydrogen and carbon monoxide in a mol ratio of 1.9:1 was passed into a reactor over a reduced catalyst prepared by the method of Example 1 at a temperature of about 340° C. and at a space velocity of about 156. Under these conditions, 96 per cent of the carbon monoxide in the synthesis gas was converted. A yield of C₂ and higher hydrocarbons was obtained amounting to 131 grams per cubic meter of the synthesis gas. This compares favorably with previous cobalt catalysts which have yielded approximately 130 grams of similar hydrocarbons per cubic meter of synthesis gas.

Example 4.—In order to determine the relative activity of catalysts prepared with and without the use of gallic acid, the following syntheses were performed using in both cases Fe-MnO catalysts, one of which was prepared in accordance with Example 2 and the other of which was similarly

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prepared except that no gallic acid was used. The synthesis was conducted at a temperature of 260° C. using a mol ratio of hydrogen to carbon monoxide of about 1.8:1 and a space velocity of about 160. The space-time-yield, that is, the volume of carbon monoxide reacted per volume of catalyst per hour, was 19 for the gallic acid catalyst and only 10.5 for the catalyst prepared without gallic acid.

As shown by Example 4 above, the process of the invention secures a space-time-yield almost twice as great as that attained in a process which employs an iron catalyst prepared in the usual manner. The new process has the further advantage of yielding largely liquid products of high octane number. In this respect it is markedly superior to the known processes which employ cobalt catalysts since the latter produce large amounts of wax-like hydrocarbons. Such products are not only injurious to the synthesis in that they reduce the activity of the catalyst, but are not as valuable as the liquid products of the synthesis. The new process is similarly advantageous in that it does not produce excessive amounts of carbon dioxide.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the materials or procedure employed, provided the step or steps stated by any of the appended claims, or the equivalent of such step or steps, be employed. This application is a division of my copending application, Serial No. 731,403, filed February 27, 1947.

I, therefore, particularly point out and distinctly claim as my invention:

1. A process for the synthesis of hydrocarbons from hydrogen and carbon monoxide which comprises passing a mixture of hydrogen and carbon monoxide over a catalyst prepared by adding a water-soluble alkaline compound to an aqueous solution of a water-soluble iron salt to the point of incipient precipitation, then adding gallic acid to the resulting mixture to complete the precipitation, and recovering the resultant precipitate.

2. A process for the synthesis of hydrocarbons from hydrogen and carbon monoxide which comprises passing a mixture of hydrogen and carbon monoxide over a catalyst prepared by adding a water-soluble alkaline compound to an aqueous solution of a water-soluble ferric salt, the amount of water-soluble alkaline compound being such that the pH of the resulting solution lies in the range 2.1 to 2.3, then adding gallic acid to the resultant mixture in such amount that the mol ratio of gallic acid to ferric salt is not less than 0.08:1 thereby obtaining a precipitate, and recovering the resultant precipitate.

3. The process of claim 2, wherein the catalyst is reduced prior to passing the mixture of hydrogen and carbon monoxide thereover.

4. The process of claim 2, wherein the mol ratio of hydrogen to carbon monoxide in the mixture is from about 2:1 to about 1:1.

5. The process of claim 4, wherein the reaction temperature is from about 200° C. to about 350° C.

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No references cited.