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COMPLETE SPECIFICATION

Hydrocarbon Synthesis

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, 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:—

The present invention relates to improvements in the synthesis of hydrocarbons and oxygenated organic compounds from carbon monoxide and hydrogen in the presence of a powdered iron catalyst which is maintained in the form of a fluidized bed in a reaction zone. In particular the invention relates to preconditioning the catalyst prior to actual use in the synthesis reaction, the purpose of the preconditioning of the catalyst being to render it highly active and selective for the formation of desirable compounds, and at the same time, resistant to fragmentation or physical disintegration during the synthesis reaction.

Prior to this invention, it was known that iron, particularly iron promoted with minor amounts of certain alkali metal compounds such as potassium fluoride, potassium carbonate, potassium or sodium acetate and numerous others, provided an active catalyst in the synthesis of hydrocarbons and oxidized hydrocarbons from a synthesis feed gas containing carbon monoxide and hydrogen. It has also been disclosed in the literature that this type of operation may be carried out employing the so-called fluidized catalyst technique, a procedure in which powdered catalyst is suspended in the gasiform reactants in a reaction zone to form a dense, turbulent, ebullient suspension of catalyst in said gasiform material.

However, researches have demonstrated that when the hydrocarbon synthesis operation is conducted in the presence of an iron catalyst, the catalyst becomes contaminated with carbonaceous deposits as synthesis proceeds and the time comes when the catalyst tends to undergo fragmentation or physical disintegration to the extent that an inordinately large proportion of fines (0—20 micron size material) is formed. When the fluidized mass or bed of catalyst contains a large quantity of fines it becomes difficult, if not impossible, to maintain the powdered catalyst in a well fluidized state. An attribute of the ordinary fluidized catalyst operation is that a separation is effected in the reactor of the main bulk of the catalyst from the gasiform reactants. When, however, the catalyst contains an excessive quantity of fines, such separation is not possible or is difficult. Then, obviously, it is desirable to prevent fragmentation of the catalyst since the fines thus produced tend to pass out of the reactor with the gaseous products rather than to remain in the said reactor. Furthermore, the presence of fines in excessive quantities in the fluidized bed of catalyst impairs the uniformity of mixing of the catalyst which is a characteristic advantage of a well fluidized bed. As a result of this impaired or poor mixing of the catalyst, it is difficult, if not impossible, to maintain a substantially uniform temperature throughout the bed of catalyst and there is a tendency to develop localized "hot spots" in the bed and the fluidization is otherwise unsatisfactory.

It is the main purpose of the present invention to pretreat a powdered, iron catalyst to obtain an improved catalyst which is highly active and selective for the formation of desirable products and at the same time resistant to serious disintegration by fragmentation of the powdered iron catalyst to sizes which can not be satisfactorily maintained in the fluidized state.

It is also the object of this invention

[*Price* 2/-]

to "condition" or pretreat a powdered iron catalyst adapted for use in the fluidized catalyst hydrocarbon synthesis reaction, which catalyst contains a substantial quantity of a promoter and which pretreatment effects the conversion of a substantial portion of the iron to iron carbide (probably Fe_2C) whereby the catalyst is rendered highly active and selective but at the same time is resistant to fragmentation or physical disintegration when used in the fluidized catalyst hydrocarbon synthesis operation.

Other and further objects of the invention will appear in the following more detailed description.

To the accomplishment of the foregoing and relating ends the powdered iron catalyst, preferably having a particle size from 0 to about 200 microns, is subjected to a pre-treatment at substantially atmospheric pressure with a gas containing hydrogen and carbon monoxide, the ratio of the hydrogen and carbon monoxide being from 2 to 35 or 40 mols of hydrogen per mol of carbon monoxide. It is preferred that this ratio be greater than 8 mols of hydrogen per mol of carbon monoxide. The treatment is carried out in the temperature range of from 500° F. to 800° F. The preferred temperature range is from 550° F. to 700° F. The duration of the treatment may be less than 100 hours and may be as low as from 1 to 25 hours. It is preferable to pretreat or "carbide" the catalyst while the same is in reduced form, that is to say, it should not contain more than 10% of oxygen by weight.

The pretreating of the catalyst is accomplished while the catalyst is in the form of a dense, fluidized mass in the treating vessel. The synthesis is carried out in the presence of the powdered iron catalyst in the form of a dense, turbulent, fluidized mass of the powdered catalyst in the gasiform material in the reaction zone.

The iron catalyst may be prepared from iron compounds from a number of sources and should be ground to proper particle size. For instance, it may be a sintered pyrites ash catalyst, that is to say, the material remaining after the sulfur has been more or less completely removed from pyrites ore. This ash may be subjected to further sintering either in the presence of oxygen or air or in hydrogen either with or without other materials added. The source of the iron may also be magnetite or other naturally occurring iron ores or various pigment iron oxides. Any of the above may be used with or without the addition of other materials.

Heretofore it has been known to sinter iron to form a hydrocarbon synthesis catalyst in a so-called sintering machine, wherein the iron is in the form of a more or less loosely contacted mass wetted with about 5 to 25% water and where it is subjected during a short period of time to the influence of an oxygen containing gas. The sintering operation is usually conducted at temperatures of from about 2000° F. to about 2500° F. The sintering operation when performed in the presence of oxygen or air results in the removal of extraneous and undesired substances such as sulfur, carbon and the like. Following such sintering operations, the catalyst is ground to a powder and reduced. In the case where hydrogen is employed as the sintering atmosphere, the catalyst of desirable particle size may or may not be reduced prior to the sintering operation which may be carried out in a conventional fluidized catalyst treating vessel at temperatures of from about 1200° F. to 1800° F.

In the accompanying drawing there is shown diagrammatically a form of equipment in which a preferred modification of the invention may be carried into effect.

Referring in detail to the drawing, (1) represents a hydrocarbon synthesis reactor containing a bed of powdered fluidized catalyst (C). The gasiform reactants, that is, the synthesis gas containing carbon monoxide and hydrogen, enter the present system through line (2) and are thereafter discharged into the reactor below a foraminous member (C_1), such as a grid or screen. The superficial velocity of the gasiform material charged into reactor (1) is controlled within the limits of from about ½ to 1½ feet per second and this velocity in conjunction with properly sized catalyst forms the dense, turbulent suspension or fluidized bed previously mentioned. By superficial velocity reference is made to the velocity that would be obtained if there were no catalyst present in the reactor. Depending upon the amount or actual weight of catalyst in the reactor and the superficial velocity of the gasiform material, the dense, turbulent suspension has an upper level at (L_1). Between (L_1) and the top of the reactor is a disengaging space (S_1), in which the concentration of catalyst decreases upwardly and as the gasiform products issue from the reactor (1) through line (5) they should contain very little if any entrained catalyst. However, in order to effect the substantially complete separation of catalyst from the gasiform material before it issues from the reactor, it is preferable to dispose one or more solids separating devices (4) through which the gas about to issue from the reactor is forced for the purpose of separating the catalyst remaining therein, which separated catalyst is then returned by dip pipes (*d*) (one shown) to the dense phase.

Under conditions which will be described in greater detail hereinafter, the reactants contact the catalyst for a sufficient period of time to effect the desired conversion and, as indicated, the raw product is withdrawn through line (5). It is then discharged into a cooler (6) where it is cooled sufficiently to condense normally liquid hydrocarbons, oxygenated hydrocarbons, and water, or to a temperature of about 100° F. The cooled product then passes from the cooler (6) through line (7) and is discharged into a separation drum (8). From the bottom of separation drum (8) the condensate is withdrawn through a line (9) and delivered to a product recovery system (10). In the interest of simplicity it will not be necessary to illustrate in the drawing, or describe in words, the method of recovering in purified form, the various desired products of this process for the gasoline, kerosene, gas oil, and various oxygenated compounds may be recovered according to conventional methods.

Referring again to the separation zone (8), the gasiform material may be withdrawn therefrom through line (11) and recycled to line (2) for it will usually contain unconverted hydrogen and carbon monoxide. If desired, however, the gasiform material in line (11) may be subjected to the influence of a material such as ethanolamine for the purpose of removing therefrom carbon dioxide in equipment not shown. On the other hand at least a portion of the gasiform material in line (11) may be rejected from the present system through line (12). This material in lines (11) and (12) may, and often does, contain olefinic hydrocarbons, such as for example propylene or the butylene isomers, which may be subjected to polymerization according to known methods to form hydrocarbons boiling within the gasoline boiling range or the olefins may be otherwise processed to form valuable products such as isopropyl alcohol, secondary butyl alcohol and butadiene.

As stated, the main purpose of the invention is to improve the operation of the hydrocarbon synthesis process by treating the catalyst so as to render it highly active and selective and at the same time its tendency to form large quantities of "carbon" during the hydrocarbon synthesis, which carbon will tend to cause physical breakdown or physical disintegration of the catalyst, is repressed. Toward this end, therefore, catalyst is withdrawn from reactor (1) through a drawoff pipe (13) controlled by a valve (14) and directed into a line (15) in which flows a stream containing hydrogen and carbon monoxide in the ratio of from 2 to 35 to 40 mols of hydrogen per mol of carbon monoxide. It should be stated at this point that the drawoff line (13) carries a series of gas taps (t_1) through which flow currents of gas such as, for example, a gas containing hydrogen and carbon monoxide. This gas is injected for the purpose of increasing the fluidity of the catalyst flowing downwardly in said standpipe (13). The withdrawn catalyst is carried in suspension through line (15) to a pretreating vessel (16) after first passing through a foraminous member (G), forming within the treating vessel (16) a dense, turbulent, fluidized mass of catalyst, in gas similar to that previously described in reactor (1).

As in the case of reactor (1) the amount of iron catalyst present in the conditioning vessel (16) in conjunction with the superficial gas velocities maintained therein, which are of the same order as those in reactor (1), causes the formation of a dense, turbulent, fluidized mass of catalyst in gasiform material extending from the grid (G) to the upper dense range level (L). Also as in the case of reactor (1), above (L) and extending to the top of the reactor, there is a dilute phase suspension of catalyst in gasiform material. This space between (L) and the top of the reactor has been designated as (S) signifying a catalyst disengaging space in which catalyst therein tends to settle by gravity toward the dense phase. However, as in the case of reactor (1), it is usually desirable to dispose one or more centrifugal separators or the like (17) (one shown) in the upper portion of the treating vessel (16) through which the gasiform material is forced for the purpose of separating entrained catalyst which is then returned to the dense phase through dip pipes. The gasiform material emerges from the treating vessel (16) through line (18) and may be recycled to the process, at least in part, through line (19). It may be desirable to cool the gas in line (19) to separate water therefrom. It may also be desirable to adjust the gas composition, in equipment not shown, before the actual recycling.

In the conditions which will be more fully set forth hereinafter the iron catalyst in treating vessel (16) is "carbided," that is, a portion of the iron is converted to iron carbide (nominally Fe_2C). The thus carbided catalyst may then be returned to reactor (1) through drawoff pipe (20) at a rate controlled by valve (21). The catalyst is maintained in the fluidized state by the fluidizing gases which enter through taps (*t*).

The carbiding of the catalyst may be performed continuously; that is to say, the catalyst may be withdrawn continuously from reactor (1), carbided in (16), and continuously returned to reactor (1) at a rate the same as or commensurate with its rate of withdrawal. On the other hand, the catalyst may be withdrawn from reactor (1) for the purpose of carbiding the catalyst intermittently. Since the carbiding vessel is operated at a pressure higher than that of the synthesis vessel, the transfer of catalyst is effected by the use of one or more lock hoppers or similar equipment (not shown in diagram).

In order to explain the invention more fully, there are set forth below specific examples as illustrating the invention and the conditions under which it may be carried out.

EXAMPLE I.

In the first example two tests were made, one with a reduced but not precarbided catalyst (Catalyst I) and a second with a reduced and precarbided catalyst (Catalyst II). The catalyst in this case was sintered pyrites ash catalyst containing 1½ wt. per cent. potassium carbonate (promoter). The precarbiding treatment was carried out at atmospheric pressure at a temperature of 600° F. for 7 hours using a synthesis gas containing 2 mols of hydrogen per mol of carbon monoxide. The resulting catalyst had 49% of its iron content present as iron carbide calculated as Fe_2C. There was also 3.5 weight per cent. excess carbon present, based on the iron. It will be noted in studying the data summarized in the following tabulation that the precarbided catalyst was much more active and gave a higher degree of selectivity than the catalyst which was not precarbided.

Precarbided Synthesis Catalyst
Pyrites Ash + 1.5% K_2CO_3 – Resintered with Coke

Catalyst No. Catalyst Treatment	I Reduced	II Reduced and Precarbided
CO Conv., % Output	89	97
C_4+, cc./m^3(H_2+CO) Cons.*	177	197

(*) Yield is on basis of cubic meters of hydrogen plus carbon monoxide consumed.

EXAMPLE II.

A test was also made to determine the effect of precarbiding an iron synthetic ammonia catalyst which was subsequently employed in the hydrocarbon synthesis process. The synthetic ammonia catalyst is, as is known, a fused magnetite and the sample used contained 1.2 wt. % of K_2O, based on the composite. The catalyst was precarbided at atmospheric pressure for ten hours at a temperature of 625° F. using as a treating gas a hydrogen and carbon monoxide containing gas in which the molecular ratio of hydrogen to carbon monoxide was about 8/1. At the conclusion of the carbiding treatment 37 wt. % of the iron was present as iron carbide calculated as Fe_2C.

In the table below the results obtained during synthesis with the catalyst precarbided in the manner described above (Catalyst IV) as compared to the results obtained with the same catalyst that had not been precarbided (Catalyst III), are set forth. The synthesis tests were made under essentially identical operating conditions.

Catalyst No. Catalyst Treatment	III Reduced	IV Reduced and Precarbided
CO Conv. % Output	96.6	99.3
H_2+CO Conv. % Output	88.3	95.2
C_3+, cc/m^3 H_2+CO Cons.	226	227
C_4+, cc/m^3 H_2+CO Cons.	168	169

The improved results obtained with the precarbided catalyst, particularly the greatly increased conversions of synthesis gas, are of utmost economic importance in commercial operation.

To recapitulate briefly, it is known that pretreating hydrocarbon synthesis catalysts with carbon monoxide-containing gases imparts certain beneficial properties to these materials. In order to overcome some of the undesirable limitations of the previous methods of treating, an improved and novel process for conditioning these catalysts before use in the hydrocarbon synthesis reaction is set forth herein.

The present improvement consists in pretreating the fluidized powdered iron catalyst with gases containing hydrogen and carbon monoxide in a ratio of between 2 and 40 mols., preferably between 2 and 35 mols., of hydrogen per mol of carbon monoxide in a carbiding zone at substantially atmospheric pressure and at elevated temperatures for a sufficient period of time to effect substantial formation of iron carbide. Suitable temperatures range from 500—800° F. The treatment may be accomplished in about one to 100 hours, usually in less than 25 hours depending upon the conditions employed. The above conditions are applicable to iron hydrocarbon synthesis catalysts in general either with or without a supporting or spacing material.

It is highly desirable that as small an amount of free carbon (carbon not combined with iron) as possible be laid down on the catalyst during the precarbiding. It has been found that a treating gas containing about 2 mols of hydrogen per mol of carbon monoxide is quite effective in converting the iron to iron carbide, but this gas also forms considerable amounts of free carbon. On the other hand, a treating gas containing 8 or more mols of hydrogen per mol of carbon monoxide is equally effective in converting iron to iron carbide but forms less than one half as much free carbon as is formed when using a $2/1\ H_2/CO$ containing gas at the same conditions. Therefore, it is preferred to use a gas containing at least 8 or more mols of hydrogen per mol of carbon monoxide for the carbiding treatment. The treating gas should not contain gases which are deleterious to the catalyst such as, for example, sulfur-containing gases. However, the presence of inert gases, even to the extent that they predominate in a mixture, is not objectionable.

In plant scale operation the process of this invention may be carried out in two or more fluidized catalyst vessels. One of these vessels may be suitably employed for treating the catalyst under the above specified conditions while one or more of the remaining vessels is employed for carrying out the synthesis reaction proper. Used catalyst may be withdrawn continuously or intermittently from the vessel in which the hydrocarbon synthesis reaction is proceeding and may then be treated as described above before being returned again to the synthesis stage.

The benefits of the above process are to be found in the production of a fluidizable catalyst that is more highly resistant to carbon formation and particle disintegration while maintaining improved activity and selectivity to normally liquid hydrocarbons.

The pretreated catalyst is successfully employed in the hydrocarbon synthesis reaction as carried out under the usual conditions of operation, namely, at a temperature of from 550 to 775° F.; at a total pressure in the reaction zone of from about 250—600 p.s.i.g. or higher; at feed rates of 10 to 40 volumes of fresh feed per pound of iron in the reactor per hour; with iron base catalysts which may be derived from numerous sources such as are obtained by the roasting and subsequent reduction of pyrites, by the reduction of fused magnetite, or by the reduction of various pigment iron oxides and other similar oxides from known sources.

The specification of British Patent No. 518,614 discloses and claims a process for hydrocarbon synthesis wherein an iron catalyst is conditioned by a pre-treatment with gases containing carbon monoxide under normal pressure or some other pressure that is lower than that used in the subsequent synthesis stage.

However, no disclosure is there made as to the desirability of using the ratios of hydrogen and carbon monoxide specified herein or of conducting the pretreating and synthesis reactions under fluidised conditions.

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 the catalytic synthesis of hydrocarbons and oxygenated organic compounds from carbon monoxide and hydrogen comprising pretreating a powdered iron catalyst in the form of a fluidised bed with a gaseous mixture containing hydrogen and carbon monoxide in a ratio of between 2 and 40 mols., preferably between 2 and 35 mols., of hydrogen per mol. of carbon monoxide, in a

carbiding zone at temperatures between 500 and 800° F. and at substantially atmospheric pressure, and contacting the carbided iron catalyst so formed as a fluidised mass in a synthesis zone with a mixture of gases containing carbon monoxide and hydrogen under synthesizing conditions of temperature, pressure and feed rate as hereinbefore defined.

2. A process as claimed in claim 1 wherein the powdered iron catalyst is reduced prior to its pretreatment in the carbiding zone.

3. A process as claimed in either of the preceding claims wherein the carbiding treatment is conducted for a time between 1 and 100 hours, preferably 1 to 25 hours.

4. A process as claimed in any of the preceding claims wherein the temperature in the carbiding zone is between 550 and 700° F.

5. A process as claimed in any of the preceding claims wherein there is present in the carbiding zone more than 8 mols. of hydrogen per mol. of carbon monoxide.

6. A process for the pretreatment of powdered iron catalysts for subsequent use in the catalytic synthesis of hydrocarbon and oxygenated organic compounds from carbon monoxide and hydrogen wherein the said powdered iron catalyst is treated in a fluidised bed with a gaseous mixture of hydrogen and carbon monoxide in a ratio of over 8 mols of hydrogen per mol. of carbon monoxide in a carbiding zone at temperatures between 500 and 800° F. and at substantially atmospheric pressure.

Dated this 14th day of December, 1948.

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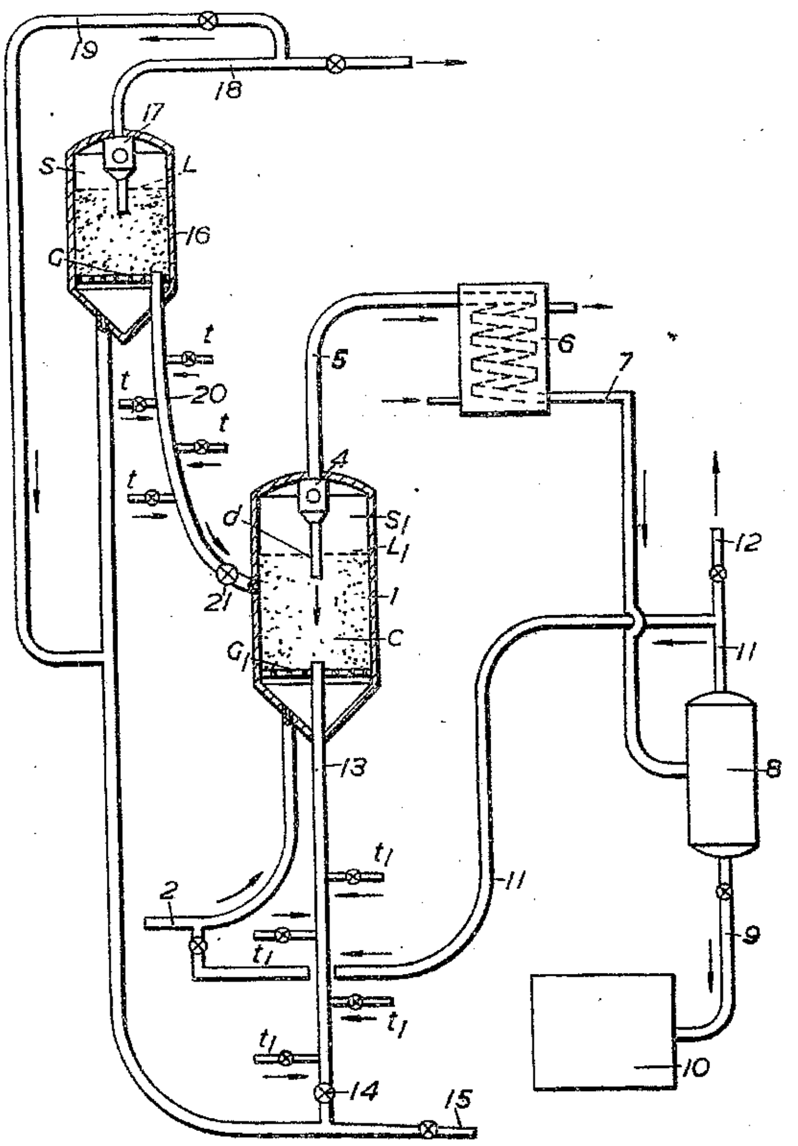
657,528 COMPLETE SPECIFICATION

1 SHEET

This Drawing is a reproduction of the Original on a reduced scale



H.M.S.O. (M.F.P.)