PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improved Process for the Catalytic Synthesis of Normally Liquid Hydrocarbons

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, 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 process of the present invention relates to the production of normally liquid hydrocarbons by reducing carbon monoxide with hydrogen in the presence of a catalyst. This process is known as the Fischer-Tropsch synthesis and has been carried out extensively, particularly where the production of motor fuels from crude oil is limited.

The conventional Fischer-Tropsch synthesis is carried out using a catalyst such as a hydrogenation metal of the Eighth Group of the Periodic System in combination with a promoter, usually a difficultly reducible metal oxide, in promotional amounts, and this mixture of metal and metal oxide is supported on a suitable carrier such as kieselguhr. The process has been carried out using various carriers such as, for example, charcoal, fuller's earth, glass wool, kaolin, pumice, silica gel, kieselguhr and a carrier known under the Registered Trade Mark " Filter-Cel ". These carriers are suitable for use in a Fischer-Tropsch synthesis where a bed type catalyst mass is employed and wherein the synthesis gas mixture of carbon monoxide and hydrogen is passed through the bed under suitable reaction conditions. These carriers are, however, with the possible exception of silica gel, not suitable for use where the Fischer synthesis is carried out using a powdered or fluid catalyst and maintaining the catalyst particles in a moving suspended state in the gas stream entering the reaction zone while maintaining the reaction conditions and effecting the reduction of carbon monoxide with hydrogen. Even with silica gel, the impregnation of the preformed dried gel with the desired metal and metal oxide does not produce a wholly satisfactory catalyst for use in the fluid catalyst operation. The chief objections of the various carriers above mentioned when employing fluid-solid catalyst operations is that the particles tend to exhibit excessive attrition and tend to break off tiny particles of active metal and metal oxide from the carrier, these materials being then removed from the system as fines. Thus it is seen that the active components of the catalyst mass are almost wholly lost because of their removal from the system as fines.

The preparation of Fischer-Tropsch catalysts in the past has involved the preparation of aqueous solutions of water-soluble metal salts, the metals being of the hydrogenating type and of the Eighth Group of the Periodic System, for example, iron cobalt or nickel, and of the promoter salts, for example, salts of magnesium, thorium, cerium, uranium, manganese and the like, or other difficultly reducible metal oxides, in each case the salts being capable of thermal decomposition to the corresponding oxides. Thus, for example, cobalt nitrate in aqueous solution is admixed with thorium nitrate in aqueous solution and to this aqueous solution of mixed salts there is added sufficient quantities of sodium or potassium carbonate to alkalize the same and precipitate the metals as their carbonates. To the slurry or precipitate in water there is added a suitable carrier such as one of the above-identified carriers and the mixture is agitated for a very short time, usually from thirty seconds to a minute and a half. The mass is then filtered and washed as quickly as possible to avoid the formation of silicates by the reaction of the alkali nitrate with the siliceous carrier. The segregated solids are then dried until the moisture content is between 6 and 10%. The carbonates deposited on these carriers and coating the same are then subjected to a calcining operation at a temperature of between about 400° F. and about 600° F. to convert the metal salts such as, for example, the metal nitrates, into the corresponding metal oxides. The

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[illegible] price 2s. 6d.

catalyst is then subjected to a stream of hydrogen to reduce the iron, cobalt or nickel oxides to the corresponding free metal and the catalyst is then ready for use as a Fischer synthesis catalyst. As before mentioned, however, this catalyst is not suitable for use in the fluid-solid technique because of the fact that the coating of active metal and metal oxide constituents tends to flake off and be removed with the fines, thus deteriorating the catalyst so far as its activity is concerned. Furthermore, the carrier itself is generally much too friable and tends to disintegrate, producing an undue amount of fines which must be removed from the system. In general, it is desired in the operation of fluid-solid catalyst technique to remove from the system all particles having a micron diameter size between 0 and 20 for the reason that the density of these particles is not sufficiently great to afford suitable fluidizing characteristics to them.

It is an object of the present invention to prepare highly active Fischer synthesis catalysts having improved attrition characteristics and having the proper densities to maintain fluid catalyst conditions in the reaction zone. It is a further object of the invention to prepare Fischer synthesis catalysts which are resistant to attrition, that is, which retain their original form and are not easily broken up and which also retain within and on the carriers the active catalytic components as above stated. It is a further object of the invention to prepare a catalyst mass for use in the fluidized technique of reducing carbon monoxide with hydrogen and involving finely divided or powdered catalyst particles and to maintain the catalytic activity throughout the life of the carrier and so long as the carrier remains unchanged in physical structure. It is an object of the invention to prepare highly comminuted catalyst masses of the desired apparent densities and particle sizes suitable for use in fluid catalyst units involving the reduction of carbon monoxide and hydrogen and to minimize the production, either before or during the reaction, of fines of the order of 0 to 20 microns in diameter without sacrificing a high catalytic activity in the catalyst mass. Other objects will be apparent upon a fuller understanding of the invention to be hereinafter more fully described.

The catalysts suitable for use in this fluidized technique as applied to the Fischer synthesis reaction and which retain their highly active state while catalyzing the reduction of carbon monoxide with hydrogen under these fluidizing conditions constitute the mineral acid activated bentonitic clays as the carrier or base thereof. Highly active Fischer synthesis catalysts may be prepared using the carriers heretofore employed and as disclosed in the prior art, but their great disadvantage is that the carriers heretofore employed readily comminute by the collision of one particle with another and they do not retain tenaciously the active catalytic components impregnated in and coated on the carrier masses. On the other hand, it has been discovered that the bentonitic type of clays, upon being treated with mineral acids form highly adsorptive siliceous carriers which are not readily broken up or comminuted in fluid catalyst operations and which upon being impregnated and/or coated with the active catalytic constituents readily retain those constituents even though the resulting catalyst compositions may be employed in fluid catalyst operations employing space velocities as high as 3000 V/V/Hour.

The preferred carriers employed involve the use of mineral acid-treated "Filtrol" ("Filtrol" is a Registered Trade Mark) sold under the trade name "Super Filtrol", mineral acid-treated Filtrol which has been subsequently subjected to an independent treatment with H_2SiF_6 or HF, this latter chemical symbol being employed to denote the use of either gaseous hydrogen fluoride or aqueous hydrofluoric acid; a modified Filtrol which is prepared by treating bentonite with 75 per cent. sulfuric acid of 12% concentration for a period of six hours, followed by treatment of the material with aluminum sulfate and then ammonia to give a precipitate on the treated clay of about 5% alumina when dried and calcined; and, lastly, a mineral acid-activated bentonitic type clay such as "Super Filtrol" which has been extruded in wet condition, calcined and ground to a fine particle size followed by a reforming from the fine particles of larger sized particles with the aid of a suitable binder to give a particle size of from 20 to 60 microns in diameter. The raw bentonite may be obtained from various sources and is readily available in the United States. The Filtrol Corporation constitutes a ready source of supply. Subsequent experiments were carried out with both Cheto and Chisholm bentonites, and in general any bentonitic clay may be employed. The acid activation of the bentonite is carried out generally with sulfuric acid, although other mineral acids such as hydrochloric, or nitric, may also be employed. This treatment serves to leach out the acid-soluble impurities and gives a highly porous structure to the remaining siliceous skeleton. One form of this mineral acid-activated material is sold under the name "Super Filtrol" and in one modification of the present invention the carrier is further treated with HF or H_2SiF_6 of about 10% concentration for about 1/2 hour, after which it is separated from the treating solution and dried.

Two methods are generally employed in the preparation of the catalysts when utilizing the mineral acid-activated bentonitic type clays as carriers. In the first method, water-soluble salts of iron, cobalt and nickel, such as the nitrates, oxalates and the like are admixed with aqueous solutions of water-soluble salts of metals such as thorium, magnesium, uranium, manganese, and aluminum, e.g. the nitrates, acetates, or oxalates of these metals, and the resultant aqueous mixture is taken up in the suspended particles of the acid-activated bentonitic type clay which is added to this solution. The clay is then freed of water, calcined at a temperature between about 400° F. and about 600° F. for between about 4 and about 16 hours, care being taken that the temperature does not exceed 600° F. since this destroys to some extent the subsequent activity of the catalyst for catalyzing the Fischer synthesis reaction. This calcining treatment converts the metal salts to the corresponding oxides. The mass is then heated at a temperature ranging between about 600° F. and about 900° F. for a period between about 2 and about 6 hours while molecular hydrogen at a linear velocity of between about 1000 and about 1500 meters per hour and at a space velocity between about 3000 and about 8000 V/V/Hour is passed thereover to reduce the Eighth Group metal oxides to the corresponding free metal. Generally speaking, the amount of water-soluble metal salts of the Eighth Group of the Periodic System and the metal salts whose oxides are difficultly reducible are proportioned so that the final composition contains between about 25% and about 40% of the free Eighth Group metal and the promoter, that is, the metal oxide of the difficultly reducible metal, is present in between about 3% and about 10%. A typical composition comprises 32% cobalt and 5% thoria or magnesia, or 25% cobalt and 4% thoria or magnesia. Prior to the reduction of the metal oxides to give the final catalyst, the same may be comminuted and pilled to give particle sizes having apparent densities between about 10 and about 35 pounds per cubic foot when used in the reaction chamber in the fluidized operating procedure.

The second method of preparing the catalyst involves not only the impregnation method above described but also a combination of impregnation and precipitation. The respective water-soluble metal salts are impregnated into the suspension of the particular mineral acid-activated bentonitic type clay employed and of the type heretofore described. The solution is then made alkaline through the addition of an alkaline-reacting carbonate such as ammonium, potassium or sodium carbonate which precipitates the water-soluble metal salts in the form of the metal carbonates, although at times a portion of the nitrates, particularly those deeply imbedded within the pores of the clay, may remain unchanged and unconverted. The combined carbonates and nitrates, if any, are then retained on and in the clay carrier which is drained of excess solution and calcined at temperatures above defined. This material may then be pilled either before or after the heat treatment of the carbonates and the same reduced as before described. Generally, the catalysts which have been heated to a temperature at which the carbonates are decomposed to oxides before pilling give pellets which are mechanically stronger than those in which the carbonates were decomposed by heat treatment after the pilling operation. It is believed that the evolution of the carbon dioxide from the pellets gave a much weaker mechanical structure, but this is purely theoretical and if care is taken either alternative may be employed in the heat decomposition of the metal carbonates.

The Fischer synthesis is carried out when employing a hydrogen to carbon monoxide ratio of between about 0.5:1 and about 5:1, preferably between about 1:1 and about 2.5:1; with nickel and cobalt catalysts the temperature is maintained between about 325° F. and about 550° F., preferably between about 375° F. and about 475° F. If an iron catalyst is employed, the temperature ranges between about 375° F. and about 700° F., preferably between about 475° F. and about 625° F. Atmospheric pressure may be employed, but pressures up to as high as 50 atmospheres may be employed. Particularly the higher pressures, that is, those above atmospheric, are employed where iron catalysts constitute the activating agent for effecting the reaction of carbon monoxide with hydrogen. In carrying out the fluid catalyst technique, the reactor employed may be denoted as a hindered settler in which the incoming reactant gases are passed upflow through the reactor at such a space velocity as to cause the finely divided catalyst particles to be maintained in a continuous state of motion and turbulence but to be relatively stationary so far as their removal from the reaction chamber is concerned. In other words, the catalyst particles remain suspended within the reaction zone and the linear velocity of the operation, if conducted downflow (i.e., the catalyst being withdrawn by gravity from the bottom of the reaction zone, while the reactant gases flow upwardly through it), is between about 0.3 and about 1.5 feet per second, while upflow is between about 1 and about 5 feet per second. The space velocity of the feed gas is generally between 100 and 3000 V/V/Hour, preferably between 300 and 1000. The catalyst particle size depends to some extent upon the other reaction conditions but generally it varies between 20 and 150 microns, with care being taken in preparing the catalyst to avoid in so far as possible the production of catalyst particles below 20 microns in diameter since in general the reaction conditions above specified cannot be maintained and still retain the bulk of the catalyst within the reaction zone if particle sizes much below 20 microns are present in any substantial quantities. These particle sizes are usually denoted as "fines" and are withdrawn from the system by means of a cyclone separator, Cottrell precipitator or other suitable gas-solids separating means.

Specific catalysts were prepared as follows:

EXAMPLE 1.

A sulfuric acid-treated bentonite was further treated with HF as before described. The carrier was then finely ground to a particle size averaging approximately 50 microns in diameter and this material was added to an aqueous solution containing cobalt nitrate and thorium nitrate, the cobalt nitrate containing as an impurity a very small amount of nickel nitrate. The amounts of the respective nitrates employed were such that the final catalyst preparation contained 32% cobalt, 5% thoria and 0.37% nickel. The HF-treated sulfuric acid-activated bentonite, prior to the removal from the aqueous nitrate solution, was further treated by adding to the suspension in solution sufficient sodium carbonate to convert the major portion of the nitrates present into the corresponding carbonates. The material was then drained of liquid and calcined at a temperature of about 500° F. for a period of about 8 hours. The mass was then pilled into 1/8" diameter pills for further treatment. These pills were then charged to a reduction furnace and contacted with a stream of nitrogen while the temperature was raised to between about 650° F. and about 900° F. When this temperature was reached, hydrogen replaced the nitrogen stream and was passed through the catalyst at a space velocity of about 5000 V/V/Hour for about 4 hours while maintaining the temperature as above specified. The pills produced had a density of about 0.95.

EXAMPLE 2.

Another catalyst mass was prepared using as the carrier a modified Filtrol or bentonitic clay, this being a bentonite which had been previously treated and activated with sulfuric acid as before described in the amount of 75 weight per cent. and of 12% concentration for a period of 6 hours. This acid-activated material was then impregnated with aluminium sulfate and then made alkaline with ammonia to precipitate upon final heating about 5% of alumina in the clay. This base was then added to a mixed solution of thorium nitrate and cobalt nitrate, and here again the cobalt nitrate contained a small amount of nickel nitrate. The amounts of the solutions and the amount of the final composition on the carrier were the same as described in Example 1. The precipitation with sodium carbonate and the subsequent oxidation-reduction were as described in Example 1. The catalyst pills produced had a density of about 1.10.

EXAMPLE 3.

The catalyst produced according to Example 1 was charged in the amount of 100 cc. to a reaction vessel to which was fed a mixture of carbon monoxide and hydrogen in the ratio of 1:2 at a rate of about 100 V/V/Hour while maintaining an average temperature of about 390° F. over a period of 185 hours. The maximum yield of normally liquid hydrocarbons was about 142 cc. of liquid hydrocarbon per cubic meter of gas fed under standard temperature and pressure conditions, with an average yield being about 132 cc. per cubic meter.

EXAMPLE 4.

The catalyst produced in Example 3 was charged to a reaction zone in the amount of about 100 cc. and under the same temperature conditions and using the same feed stock as described in Example 3. A reduction of carbon monoxide with hydrogen was carried out with the following results: The maximum yield of normally liquid hydrocarbons was about 144 cc. per cubic meter of feed gas, with an average being 132 cc. per cubic meter. The total length of time of the test was 185 hours.

A comparison of the results obtained in

Examples 3 and 4, using the catalysts prepared as described in Examples 1 and 2, with the results obtained where the catalyst was prepared on a bentonitic clay base by the straight conventional carbonate precipitation method previously described would indicate the superiority of the novel catalyst. Thus, for example, by the conventional carbonate precipitation method the catalyst, reaction conditions being in all other respects comparable to the data presented in Example 3, produced a yield of only 107 cc. per cubic meter with an average yield of 96 cc. per cubic meter as compared with an average yield of 132 cc. per cubic meter in Example 3. A catalyst prepared by the method of and identical with that used in Example 4 but differing in its preparation only in that the conventional carbonate precipitation method previously described was employed, produced only 112 cc. per cubic meter as against 141 reported in Example 4. The average yield in the case of the carbonate precipitation method alone was 97 cc. per cubic meter as compared with 132 cc. per cubic meter in Example 4.

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 production of normally liquid hydrocarbons which comprises reacting carbon monoxide with hydrogen in the presence of a hydrogenation catalyst and under hydrogenation conditions of temperature and pressure, the catalyst being prepared by impregnating a mineral acid-activated bentonitic type clay in aqueous suspension with a major portion of a water-soluble salt of an Eighth Group hydrogenation metal and a minor portion of a water soluble salt of a metal which forms a difficultly reducible oxide, both said salts being thermally decomposable to the corresponding oxides, draining and drying the impregnated clay, heating the impregnated clay only sufficiently to convert the salts to the metal oxides, and reducing the Eighth Group metal oxide to the free metal.

2. A process according to Claim 1, wherein a water soluble alkaline reacting carbonate is added to the clay suspension after impregnation with the metal salts, thus partially converting the said salts to metal carbonates.

3. A process according to Claim 1 or Claim 2, wherein the Eighth Group metal is iron, cobalt or nickel, and the other metal is thorium, magnesium, uranium, manganese or aluminium.

4. A process according to Claim 3, wherein the acid radicle of the salts is acetate, oxalate or nitrate.

5. A process according to any of the preceding Claims, wherein the dried impregnated clay is heated to a temperature between 400° F. and 600° F. to convert the salts to oxides and then heated at a temperature between 600° F. and 900° F. in a stream of hydrogen to reduce the Eighth Group metal oxide.

6. A process according to any of the preceding Claims, wherein the amounts of metal salts present are so adjusted that the catalyst contains from 25 to 40% of the Eighth Group metal, and from 3 to 10% of the difficultly reducible metal oxide.

7. A process according to any of the preceding Claims, wherein the bentonitic type clay is activated with hydrochloric, nitric or preferably sulfuric acid.

8. A process according to Claim 7, wherein the acid-activated clay is subsequently treated with H_2SiF_6 or HF before the suspension in water.

9. A process according to Claim 7, wherein the acid-activated clay is impregnated with a minor portion of a water soluble aluminium salt, treated with ammonia whereby aluminium hydroxide is precipitated, and dried and calcined before the suspension in water.

10. A process according to Claim 7, wherein the acid-activated clay is extruded wet, ground to a fine particle size and reformed with the aid of a binder to larger particles of frim 20 to 60 microns diameter.

11. A process according to any of the preceding Claims, wherein the catalyst is employed in finely divided condition, fluidised by the reactants.

12. A process according to any of the preceding Claims, wherein the reaction temperature is from 325—550° F. when using a nickel or cobalt catalyst, or from 375—700° F. when using an iron catalyst and the reaction pressure is from 1 to 50 atmospheres.

13. A process according to Claim 11, wherein the particle size of the catalyst is from 20 to 150 microns.

14. A process according to any of the preceding Claims, wherein the salts are cobalt nitrate and thorium nitrate.

15. A process according to Claim 14, wherein the catalyst contains 32% cobalt and 5% thoria or 25% cobalt and 4% thoria.

Dated this 20th day of June, 1945.

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