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COMPLETE SPECIFICATION

Improvements in or relating to a Catalyst for the Synthesis of Hydrocarbons

We, PHILLIPS PETROLEUM COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of Bartlesville, Oklahoma, 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 the synthesis of hydrocarbons by the catalytic reduction of carbon monoxide with hydrogen. More particularly the invention relates to novel catalysts for this reaction.

In the synthesis of hydrocarbons by the method commonly known as the Fischer-Tropsch process, carbon monoxide and hydrogen may be reacted at elevated temperatures and at atmospheric or higher pressures in the presence of a suitable catalyst, to yield hydrocarbons ranging in molecular weight and constitution all the way from methane to waxy materials, with the concomitant formation of varying amounts of oxygenated material, depending on the nature of the catalyst and the reaction conditions.

The reaction is generally carried out in a manner which will yield substantial proportions of hydrocarbons boiling in the gasoline range as well as higher boiling hydrocarbons. Catalysts used in this synthesis include cobalt, iron, nickel, or ruthenium, and these may be promoted with alkali metals, alkaline earth metals or their oxides, thoria or various other known materials. The catalyst of the prior art may be utilized on inert supports, such as kieselguhr or the like. Using cobalt-containing catalysts, temperatures in the range of about 125°—225° C. may be used with a preferred temperature being about 185°—190° C. Ordinary iron catalysts operate best in a narrow range close to 240° C. while sintered iron catalysts require temperature in the neighborhood of 320° C.

The synthesis reaction is ordinarily carried out at atmospheric or medium pressures, depending on the products desired and the catalyst used. A preferred range of pressures suitable for general use is from about 5 to about 15 atmospheres, but pressures up to 150 atmospheres or even higher may be used. Flow rates are variable depending on a number of factors such as catalyst, products desired, and the nature and extent of cooling.

Catalysts of the fused or sintered iron type are prepared by the reduction of Fe_3O_4, ferroso ferric oxide, which oxide may be obtained by the burning of iron with oxygen with the resultant formation of a molten mass of the iron oxide, followed by crushing of the mass and reduction to the metallic state. It was found, however, that the pure or unpromoted iron catalysts do not produce optimum results in reactions particularly when used in finely divided, or fluidized form. Such results are manifested by lowered efficiency and increased methane formation, as well as other effects. It was found that potassium oxide and alumina together function as effective promoters when incorporated with the metallic iron. The use of potassium oxide alone as a promoter is undesirable because if enough is added to increase the production of hydrocarbons to an economic percentage of the carbon monoxide converted, the product is too heavy. On the other hand, if less potassia is added, too much carbon monoxide is converted to methane, carbon dioxide and light gases. Alumina, of itself, as a promoter, fails to function satisfactorily as a promoter to give increased yields of hydrocarbons in the desired boiling range, and furthermore appears to hinder the reduction of iron oxide.

The use of alumina in combination with potassium oxide in the proper proportions, to doubly promote the iron catalyst provides a more efficient catalyst and improves the product. The alumina appears to modify the effects of potassium oxide and thus provides a means for narrowing the range of product distribution and at the same time obtaining product in the desired range.

It was also found that the reduction temperature is of great importance in the preparation of these catalysts. Too high a temperature produces catalysts with low activity while too low a temperature results in catalysts which are difficult to control and the time required on the reduction is too long and possibly never complete. It was further found that the optimum conditions for reduction are temperatures of 475°—550° C. for a minimum period of 42 hours, after which reduction is substantially complete. It has previously been found that, while alumina hinders the reduction of the catalyst, at these temperatures the potassia combines with the alumina and reduces this effect, so that it is possible to use up to 3—4 weight per cent alumnia provided that it is combined with potassium oxide so that the excess alumina does not exceed and is preferably below 2 weight per cent. Excess alumina is desirable because it is found that the alumina exerts a surface effect on the catalyst, increasing its rate of carbidization and increasing the surface area and its catalytic power for this synthesis. Satisfactory ranges for the potassia content are 0.05—1.0 per cent of the original Fe_3O_4 and the alumina molecularly equivalent to the potassia and in addition 1—2 weight per cent excess alumina (the total alumina not to exceed about 4 per cent.)

As hereinafter disclosed catalysts of the fused or sintered iron type may be materially improved in important respects by the incorporation of calcium oxide as an added promoter and/or modifier, provided this addition is carried out in certain definite and critical proportions. Catalysts promoted with K_2O and Al_2O_3 alone are highly effective. However, such catalysts frequently become "wild," resulting in excessive temperature increases and consequent formation of undesired products, etc. This "wildness" is apparently due to excess wax formation and build up on the catalyst with resultant heat transfer difficulties and uncontrollable reaction. It was further found, that calcium oxide, when added to an alumina-potassia promoted iron catalyst in certain definite proportions gave marked improvement in conversion and higher C_5+ efficiency. At the same time the catalyst could be operated for considerably longer periods before requiring reactivation or re-reduction. The calcium oxide in proper proportions therefore was found to inhibit the formation of free carbon and high molecular weight waxes.

In accordance with this invention there is provided a method for the preparation of a catalyst for the synthesis of hydrocarbons by the reduction of carbon monoxide with hydrogen, which comprises reducing the mixture of Fe_3O_4 and minor proportions of K_2O and Al_2O_3 which may be in the form of thermally decomposable salts, together with 1 to 10 per cent by weight of CaO based on the Fe_3O_4, in an atmosphere of hydrogen at a temperature of 450° and 550° C. to form metallic iron in which is incorporated minor proportions of K_2O and Al_2O_3 and 1.3 to 13 per cent. by weight of CaO based on the metallic iron.

In the preparation of the catalyst of the present invention calcium oxide is incorporated into the iron along with the other oxides in the proportion of 1 to 10 per cent by weight based on the Fe_3O_4 from which the metallic iron is obtained by reduction. Preferably the CaO is utilized in the proportion of 3—7 per cent since it appears to be most effective for the purpose in this concentration. The calcium oxide was found to be ineffective or undesirable at lower concentrations, and in the presence of K_2O and Al_2O_3 appeared to act as an inhibitor for the synthesis reaction. On the basis of metallic iron, the proportions are: K_2O, 0.07—1.4%, Al_2O_3 1.4—2.8%, excess more than the molecular equivalent of Al_2O_3 to the K_2O, and 1.3—13% CaO.

The following table contains illustrative examples of the practice of the invention:

TABLE I.

Conversion data:
Reaction Temperature - - - - - - - - - - 295° C. (563° F.)
Pressure - - - - - - - - - - - - 250 Psig
Space Velocity - - - - - - - - - - - 2400—2600
Recycle ratio - - - - - - - - - - - 6—8
Catalyst—Reduced Iron Oxide, promoted as indicated

Run No.	Catalyst	Conversion %	Recovered C_3+	% Efficiency C_5+
113—1	$\frac{1}{2}\%$ $K_2O + 1\frac{1}{2}\%$ Al_2O_3	94—95	62—65	44—48
114	$\frac{1}{2}\%$ $K_2O + 1\frac{1}{2}\%$ Al_2O_3	95—96	69—76	53—60
115	$\frac{1}{2}\%$ $K_2O + 1\frac{1}{2}\%$ $Al_2O_3 + \frac{1}{4}\%$ CaO	94—95	65—68	42—46
118	$\frac{1}{2}\%$ $K_2O + 1\frac{1}{2}\%$ $Al_2O_3 + \frac{1}{2}\%$ CaO	97—98	68—70	55—58
120—1	$\frac{1}{2}\%$ $K_2O + 1\frac{1}{2}\%$ $Al_2O_3 + 5\%$ CaO	98—99	74—77	61—65
120—2	$\frac{1}{2}\%$ $K_2O + 1\frac{1}{2}\%$ $Al_2O_3 + 5\%$ CaO	99	76—80	65—70

The above data show that the C_5+ efficiency of $K_2O + Al_2O_3$ promoted catalysts is slightly decreased by the use of CaO as a promoter in small proportions. On the other hand, 5% CaO effects a material increase both in conversion, and C_3+ and C_5+ efficiency. The beneficial effect of the calcium oxide becomes apparent at concentrations of about 1 per cent based on Fe_3O_4. There appears to be no advantage in using more than about 10 per cent, and catalysts containing more than 10 per cent calcium oxide, based on Fe_3O_4, have the disadvantage of comparatively low resistance to attrition during use.

The catalyst may be prepared in the following manner:

Iron in the form of short lengths of wire or strips, is tied into small bundles and weighed. It is then placed in a steel crucible of suitable dimensions and the crucible with its contents is brought to a dull red heat by means of a gas burner. The gas flame is then removed and oxygen streams from two nozzles are placed on the heated iron, causing it to oxidize and melt. The oxygen streams are ejected with a velocity sufficient to agitate the molten mass. The iron is completely molten in ten to fifteen minutes. After the oxidation has continued for three to five minutes beyond this point, the promoter is added in small amounts in granular form so that it is thoroughly fused and mixed with the molten material. Thorough agitation is accomplished by means of the oxygen jets. The addition of the promoters requires about two minutes. The oxidation is continued until it is complete, as evidenced by the formation of a crust on the surface, followed by the cooling and hardening of the entire mass. The total oxidation requires about 25 minutes.

After the oxidation is complete, the mass is allowed to cool to room temperature and is then broken out of the crucible and ground to the desired size, usually 65 to 140 mesh on the Tyler scale. It is then ready for the reduction step which will be described subsequently.

The Fe_3O_4 may be prepared in other ways, as by oxy-hydrogen fusion of Fe_2O_3 according to the following reaction:

$$3\ Fe_2O_3 \rightarrow 2\ Fe_3O_4 + \frac{1}{2}O_2$$

The promoters are added to the iron oxide before fusing and the product is ground to the desired mesh size. Fe_3O_4 from other sources may also be used as a starting material in the fusion.

The reduction step is carried out by introducing the finely divided oxide into a vertical cylindrical reactor. The material is maintained in a fluidized condition by introducing hydrogen into the reducing zone at a velocity of about 0.3 feet per second (standard conditions) and the reduction temperature is maintained at a point between 450°—550° C. for a minimum period of about 42 hours and until reduction is complete. The optimum temperature for the reduction of the catalyst is about 500° C. When reduced at lower temperatures the catalyst appears to be "wild" during the initial stages of the synthesis reaction and temperatures are almost impossible to control. When reduced at higher temperatures, among other effects, the activity of the catalyst falls off. In general good results are obtained in the temperature range specified. During the reduction, space velocities of about 1500—2500 are preferably utilized.

The promoters may be added in the form of the oxides themselves, or in the form of compounds thermally decomposable to form the oxides such as the nitrates, carbonates, hydroxides, etc. For example, potassium oxide may be incorporated as the nitrate or hydroxide, while the alumina may be incorporated as the oxide, aluminate, aluminium nitrate, etc. Calcium oxide may be incorporated as the carbonate or the oxide itself.

The synthesis reaction is preferably carried out in a vertical cylindrical reactor. The catalyst, in finely divided form, preferably 65—140 mesh, is introduced into the reactor and a mixture of H_2 and CO in the proportions of about 2 to 1, respectively, is flowed through the reactor at a linear velocity sufficient to efficiently fluidize the catalyst. A minimum linear velocity of about 0.6 feet per second is required. The catalyst is retained within the reactor and is not carried over into the product outlet, most of the catalyst settling by gravity and then being re-fluidized. Small proportions of catalyst which might carry over are prevented from doing so by providing a screen or other separating means ahead of the outlet. The result is what is known as a fluidized fixed bed with a portion of the catalyst preferably remaining in a more or less settled condition at the bottom of the chamber with the major portion existing in the chamber in a fluidized condition. The reaction is preferably carried out at a temperature of about 270°—320° C. and with a space velocity of about 1500—3500 (vol/vol. cat/hr). The pressure is preferably about 150—250 pounds per sq. in. gauge. The products of reaction are recovered for separation of C_3+ hydrocarbons and other desired materials, from which a gasoline boiling range material is separated as the chief product. A gaseous fraction, containing mostly unreacted CO and H_2, is recycled to the reactor in a ratio of 3:1 to about 7.5:1 based on the fresh synthesis gas feed. Recycling of tail gas has a twofold function. First, it reduces the carbon monoxide concentration at the inlet so that an inordinate amount of reaction will not take place in the inlet zone of the reactor thus causing erratic temperatures. Second, it aids in maintaining the catalyst in a fluidized state.

The catalyst activity decreases slightly over successive periods of 24 to 48 hours. In order to maintain a high level of activity it has been found that short periodic flushings with hydrogen at reaction temperature and pressure are sufficient to restore the catalytic activity.

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 method for the preparation of a catalyst for the synthesis of hydrocarbons by the reduction of carbon monoxide with hydrogen, which comprises reducing the mixture of Fe_3O_4 and minor proportions of K_2O and Al_2O_3 which may be in the form of thermally decomposable salts, together with 1 to 10 per cent by weight of CaO based on the Fe_3O_4, in an atmosphere of hydrogen at a temperature of 450° and 550° C. to form metallic iron in which is incorporated minor proportions of K_2O and Al_2O_3 and 1.3 to 13 per cent by weight of CaO based on the metallic iron.

2. A method according to claim 1, in which the K_2O and Al_2O_3 are incorporated in molten Fe_3O_4, the resultant mixture is cooled, and the cooled mixture is ground to a finely divided form.

3. A method according to claim 1 or 2 in which the said mixture contains 0.05 to 1.0 per cent by weight of K_2O based on the Fe_3O_4 and Al_2O_3 in a molecular equivalent proportion to K_2O plus an excess of 1 to 2 per cent by weight based on the Fe_3O_4.

4. A method according to any of the preceding claims in which the reduction is effected at a temperature of 500° C.

5. A method according to any of the preceding claims in which the mixture of Fe_3O_4, K_2O, Al_2O_3 and CaO is prepared by incorporating in molten Fe_3O_4; 0.05 to 1.0 per cent of K_2O based on Fe_3O_4, Al_2O_3 in a molecular equivalent proportion to the K_2O plus an excess of 1 to 2 per cent by weight based on the Fe_3O_4, and CaO in the proportion of 1 to 10 per cent by weight of the Fe_3O_4, cooling the resultant mixture and grinding the cooled mixture to a finely divided form.

6. A method according to claim 4 in which the cooled mixture is ground to a fineness of 65 to 140 mesh (Tyler Scale).

7. A catalyst for the synthesis of hydrocarbons by the reduction of carbon monoxide with hydrogen, when prepared by the method of any of the preceding claims.

8. A catalyst according to claim 7 containing 0.07 to 1.4 per cent. by weight of K_2O based on the metallic iron and Al_2O_3 in a molecular equivalent proportion to K_2O plus an excess of 1.4 to 2.8 per cent by weight based on the metallic iron.

9. A catalyst according to claim 7 containing substantially 0.5 per cent K_2O and substantially 5 per cent CaO.

10. A catalyst whenever prepared by the process substantially as hereinbefore described.

11. Hydrocarbons whenever prepared

by a synthesis which comprises contacting a synthesis gas mixture comprising carbon monoxide and hydrogen with a catalyst according to any one of the preceding claims.

12. A process for the synthesis of hydrocarbons which comprises contacting a synthesis gas mixture comprising carbon monoxide and hydrogen with a catalyst according to any one of claims 1 to 10.

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