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COMPLETE SPECIFICATION

Improvements in or relating to Catalytic Conversion of Carbon Monoxide with Hydrogen

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at 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:—

This invention relates to the catalytic conversion of CO with H_2 and improved catalysts therefor. More specifically the invention is concerned with improved iron catalysts for the catalytic synthesis of normally liquid hydrocarbons and oxygenated compounds from CO and H_2.

Iron type catalysts are normally employed in the hydrocarbon synthesis at relatively high temperatures of about 450°—800° F. and relatively high pressures of about 3—100 atm. abs. or higher, to obtain predominantly unsaturated and oxygenated products from which motor fuels with high octane ratings may be recovered.

The extreme temperature sensitivity and relatively rapid catalyst deactivation in the hydrocarbon synthesis have led in recent years to various attempts and proposals to employ the so-called fluid catalyst technique wherein the synthesis gas is contacted with a dense turbulent bed of finely divided catalyst fluidized by the gaseous reactants and products which permits continuous catalyst replacement and greatly improved temperature control. However, the adaptation of the hydrocarbon synthesis to the fluid catalyst technique has encountered serious difficulties, particularly when iron catalysts are used.

Application of the fluid catalyst technique requires ease of fluidization and attrition resistance in additon to the conventional characteristics determining catalyst utility, such as total desired yield and active catalyst life.

The activity and utility of iron catalysts decline steadily in the course of the strongly exothermic reaction, chiefly due to the deposition of fixed carbon or coke-like material formed by the dissociation and cracking of CO and unstable hydrocarbons which take place at the relatively high temperature and pressures associated with the use of iron-base catalysts.

If allowed to accumulate excessively, these carbon or coke deposits adversely affect particularly those characteristics of the catalyst which determine its utility as a fluidizable solid in processes employing the fluid solids technique. More particularly, carbon or coke deposits have been found to cause rapid disintegration of the catalyst particles leading to a substantial and undesirable expansion of the fluidized bed and ultimately to the requirement of complete catalyst replacement because of fluidization difficulties. Catalyst broken down in this manner must be restored to a fluidizable particle size or is lost for further use.

Iron catalysts are usually prepared by a substantially complete reduction of various natural or synthetic iron oxides, their catalytic activity being enhanced by the addition of such promoters as various compounds of alkali metals or the oxides of chromium, zinc, magnesium, manganese, the rare earth metals, and others, in small amounts of about 0.5—10%. Hydrogen or mixtures of hydrogen and carbon monoxide, such as fresh synthesis gas, are normally used as the reducing agent at temperatures of about 600°—1600° F. All these catalysts are either subject to excessive carbonization and disintegration in fluid operation or their activity and/or selectivity to useful products are too low for satisfactory operation.

The present invention substantially

[*Price* 2/-]

Price 4s 6d

reduces these difficulties and affords various additional advantages as will be fully understood from the detailed description given below.

It is therefore the principal object of the present invention to provide an improved process for the catalytic conversion of CO with H_2.

Another object of the invention is to provide improved iron catalysts for the catalytic conversion of CO with H_2 employing the fluid solids technique.

Other objects and advantages will appear hereinafter.

It has now been found that a relatively low degree of reduction of iron oxides to metallic iron is sufficient to activate the catalysts to a degree desirable for satisfactory operation while at the same time producing iron catalysts of substantially reduced carbonization and disintegration tendencies. Furthermore, it has been found that an optimum range of catalyst reduction exists within which catalysts exhibiting both highest activity and selectivity and lowest carbonization and disintegration tendencies may be produced.

More specifically, the present invention evaluates the surprising discovery that iron catalysts which are obtained from their oxides by reduction by an amount between 5% and 50% of that required for complete reduction have activities and selectivities equivalent to those of catalysts obtained by oxide reduction of more than 50% and up to 95% or even complete reduction, while the catalysts of lower degree of reduction form only about one-half, or less, of the carbon formed on the more thoroughly reduced catalyst. This effect of limited catalyst reduction applies to all conventional iron-type catalysts such as sintered and resintered iron pyrites ashes, various mill scales, ammonia synthesis catalyst obtained from a high purity fused magnetite promoted with alkali metal promoters and alumina, etc. While hydrogen is the preferred reducing agent, the invention is not limited to its use, but applies to all conventional fixed bed or fluid methods of iron oxide reduction, provided reduction is limited to the degree indicated.

In accordance with the present invention, the hydrocarbon synthesis, particularly the fluid type hydrocarbon synthesis, is carried out in the presence of iron-type catalysts obtained by the reduction of iron oxides by a degree within the range of 5%—50%, preferably 10%—25% of that required for complete reduction to the metal. These degrees of reduction correspond to oxygen contents of about 26 to 14%, preferably about 25 to 21% by weight of the total catalyst. The catalysts are promoted with between 0.5% and 5% of conventional alkali metal promoters such as the halides, oxides, carbonates, acetates, phosphates, of sodium or potassium the potassium compounds being particularly preferred. When applied in fluid operation the catalysts should have a particle size of about 20—200 microns, preferably about 30—100 microns.

It is believed that in the process of the present invention the oxygen removal from the catalyst is confined to the surface of each catalyst particle. The activity of this surface may be maintained by continuous or periodic suitable treatment of the catalyst with reducing gases such as H_2 in a manner known *per se*. Here again the catalyst treatment may be so controlled that the interior of the catalyst particle is not disrupted, the treatment being such that heavy product deposits are removed in order to recover a clean catalyst surface.

Catalyst suitable for the purposes of the present invention may be prepared as follows:—

EXAMPLE 1.

Pyrites ore, preferably of low silica (less than 1.5%) and low phosphorus (less than 0.01%), is roasted in air and sintered in a conventional type sintering machine at temperatures of 1800° to 2500° F. to produce a mixture of iron oxides containing less than 0.06% sulfur. The dry pyrites ash is ground to the desired particle size and then promoted by thoroughly mixing or mulling with 5 to 15% by weight of an aqueous solution containing the desired amount (0.5 to 3.0 wt. % based on dry iron oxides) of dissolved promoter (potassium carbonate). The composite is then dried in a steam-heated oven at temperatures below 400° F. Different batches of this material are reduced with 400 to 6000 V/V/hr. of H_2 at 850° to 930° F. for different times. For example, reduction to an oxygen content of about 20 to 25% requires a treatment lasting about 2 to 10 hours.

EXAMPLE 2.

Dry pyrites ash containing less than 0.06% sulfur, prepared as in Example 1 and having a particle size of $\frac{1}{8}$ to $\frac{1}{4}$ inches in diameter, is thoroughly mixed with the desired amount (0.5 to 3.0 wt. %) of potassium carbonate promotor dissolved in an aqueous solution so that the resulting moisture content is 4 to 8 wt. % based on the pyrites ash. Four to nine wt. % of coke based on pyrites ash is added and thoroughly mixed and the whole is passed through a conventional type sintering machine at temperatures of about 2200°

to 2500° F. The composite is then ground to the desired particle size. Different batches of this material are reduced to different iron oxygen contents, substantially as described in Example 1.

EXAMPLE 3.

Synthetic ammonia type catalysts are prepared by methods well known to the art. Purified natural magnetite is mixed with synthetic magnetite prepared by burning relatively pure iron in oxygen. Some relatively pure iron may be added to control the oxygen content during the subsequent fusion. The proportions in which the above constituents are added depend upon the impurities present in the individual constituents. Promotional amounts of potassium nitrate, equivalent to about 1.5 to 3.9% potassium oxide based on iron, and alumina (about 2.5 to 5.5% based on iron) are added and the whole is then fused in an electric resistance furnace. The melt is then cooled and the fused composites are broken up and ground to the desired particle size. Different batches of this material are reduced to different iron oxygen contents substantially as described in Example 1.

It has been found that the time to reduce iron catalysts is proportional to the diameter of the individual particle. The reduction of large particles requires considerably more time and expense as compared with smaller particles when being reduced with H_2. For example, when operating at 700° F. with throughput of about 50 cubic feet of fresh synthesis gas per pound of iron per hour and a pressure of about 400 pounds, the time for 95% reduction of a certain variety of iron oxide is shown in the following tabulation:—

Diameter	Time in Hours
30 microns	40
45 microns	63
90 microns	126

It may be seen from the above tabulation that considerably greater quantities of hydrogen must be used for the particles taking the longest time. Hence, in the manufacturing of catalyst, it may be desirable to grind the unreduced oxide to particles of about 30 microns or less and then reduce them with hydrogen. The finished particles may then be sintered at elevated temperatures in a mixture of reducing gases to form large particles of the desired size.

Another method of saving hydrogen involves separating particles of a variety of sizes (such as constitute a fluidizable catalyst (into size ranges and reduce the different sized particles in different vessels, the larger size requiring more holding time than the smaller ones. The separation may be accomplished within the reducing unit or prior to feeding into the unit. If it is accomplished within the unit, the cyclone separator installed in the different size vessels may be used to separate the finer particles which may then be fed into the vessel corresponding to the smaller particle size. Using this method of operation, the hydrogen rate may be adjusted so that the time for the reduction will be the same for all particle sizes, resulting in lower overall hydrogen requirements.

The beneficial effects of the process and catalysts of the present invention are demonstrated by experimental data summarized in the graphs of the accompanying drawing wherein:—

Figure 1 shows activity plotted as CO conversion, per cent. output, versus time on synthesis, in fixed-bed operation for a catalyst prepared substantially as described in Example 1, but reduced to various degrees, the essential synthesis conditions being indicated on the drawing, and

Figure 2 shows the amount of carbon on catalysts prepared in accordance with Examples 1 to 3, as a function of their oxygen content in a fluid, accelerated carbonization test under uniform conditions specified in the legend of the drawing.

The curve of Figure 1 shows that the catalyst which was reduced by only 18% had an initial activity equivalent to that of catalysts reduced by 65% or by 95%. Even the wholly unreduced catalyst, although exhibiting poor initial activity, showed increasing activity as the synthesis proceeded and approached the activity of the reduced catalysts after 150—200 hours of synthesis operation. While this induction period may be substantially cut down in fluid operation, a catalyst reduction of at least 5% is necessary for satisfactory initial operation.

A determination of the selectivities of the same catalysts resulted in the average values tabulated below.

Catalyst Reduction, % - - - - - - - - -	0	18	65	95
Selectivity, cc. C_4+/m^3 H_2+CO Consumed	170	173	179	161

These data show that the selectivities of the catalysts of low degree of reduction, in accordance with the present invention, were equivalent to those of the more thoroughly reduced catalysts.

The curve of Figure 2 demonstrates that carbon formation decreases as the oxygen content of the catalyst increases. The carbon formed on catalysts reduced by about 18% amounted to only about

40% of the carbon formed on catalysts reduced by about 95%, this reduction in carbon formation being largely independent of the composition of the iron-type catalysts used.

While the invention affords greatest advantages when applied to fluid synthesis operation, certain of its advantages are realized in fixed-bed operation and the scope of the present invention includes, therefore, both fluid and fixed-bed operation, although the former is the preferred embodiment of the invention.

Conventional synthesis conditions may be employed in connection with the catalysts of the invention. Suitable conditions for fluid operation include temperatures of about 550°—750° F., pressures of about 200—800, preferably about 400—600, lbs. per sq. in., throughputs of about 5 to 40 standard cubic feet of fresh synthesis gas per pound of iron per hour, H_2:CO ratios in the fresh synthesis gas of about 0.5—3.0:1, gas recycle ratios of about 0.5:1, and superficial linear gas velocities of about 0.3—3 ft. per second at catalyst particle sizes of about 20—200 microns to establish apparent bed densities of about 40—150 lbs. per cu. ft.

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. An improved Fischer synthesis process which comprises contacting a gas containing CO and H_2 in synthesis proportions at synthesis conditions with an iron type catalyst comprising an iron oxide reduced by an amount between 5% and 50% of complete reduction and containing between 0.5% and 5% of an alkali metal promoter.

2. The process of claim 1 in which said catalyst is present in the form of a dense, turbulent mass of finely divided solids fluidized by an upwardly flowing gas.

3. The process of claim 1 or claim 2 in which the iron oxide is reduced by about 5—25% of complete reduction, preferably by between 10 and 25% of complete reduction.

4. The process of any of claims 1 to 3, in which said catalyst contains about 21 to 25% of oxygen by weight of total catalyst.

5. The process of any of claims 1 to 4 in which said catalyst is prepared by combining an iron oxide with a suitable amount of alkali metal promoter and subjecting the composite to an incomplete reduction with a gas rich in hydrogen.

6. The method of preparing iron-type catalysts for the synthesis of hydrocarbons and oxygenated compounds from CO and H_2 which comprises mixing an oxide of iron with a promotional amount of an alkali metal promoter and reducing the composite by an amount between 5% and 50% of complete reduction.

7. The method of claim 6 in which said oxide is reduced with a gas rich in hydrogen.

8. The method of claim 6 or claim 7, wherein said catalyst is ground to a fluidizable particle size.

9. The method of any of claims 6 to 8, wherein the oxide is 10—25% reduced.

10. The method of any of claims 6 to 9, wherein the promoter is present in an amount of 0.5—5% by weight and is a compound of sodium or potassium, preferably potassium.

11. Catalysts whenever prepared by the process of any of claims 6 to 10.

12. Catalysts as claimed in claim 11 having a particle size of 20—200 microns, preferably 30—100 microns.

13. Iron-type catalysts whenever prepared according to the methods or processes of manufacture hereinbefore particularly described and ascertained.

Dated this 24th day of January, 1949.
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FIG. 1.

Effect of Reduction with Electrolytic Hydrogen on Activity of Pyrites Ash Plus 2% K_2CO_3

2/1 H_2/CO, 250 PSIG., 650°F., 200 V/V/Hour, Fixed Bed

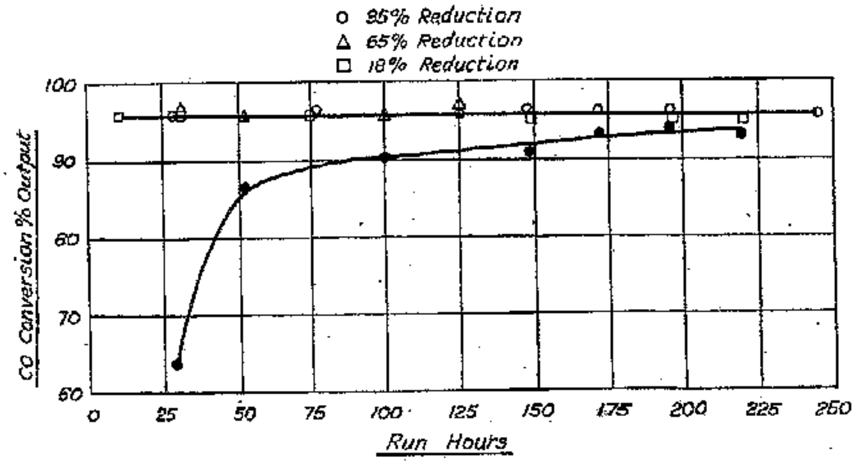

FIG. 2.

Atmospheric Pressure Fluid Carbonization Tests

Effect of Oxygen Content on Total Carbon

Temp: 700°F: Feed 2/1 H_2/CO Scrubbed; Linear Vel: 0.7-0.8 Ft/Sec.