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3460

COMPLETE SPECIFICATION.

Improvements in or relating to Catalysts for the Synthesis of 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 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 is directed to a method for preparing a composition adapted to be used as a catalyst. The invention is also directed to a composition adapted for use as a catalyst. The invention is further directed to an improved method for effecting the synthesis of hydrocarbons and oxygenated organic compounds from carbon monoxide and hydrogen.

It is known to the art to pass a mixture of carbon monoxide and hydrogen at elevated temperatures and pressures over a catalyst to obtain hydrocarbons and oxygenated derivatives of hydrocarbons as product. When carrying out such reactions it is preferred to employ a temperature in the range of 450° to 675° F. and a pressure in the range of 100 to 500 lbs./sq. in. Such a process of reacting hydrogen and carbon monoxide to obtain hydrocarbon product is usually designated as a Fischer-Tropsch synthesis. Heretofore when conducting such reactions it has been customary to employ oxides of such metals as iron, cobalt and nickel as a catalyst ; the oxides may be used alone but preferably are used as supported catalysts which are formed by impregnating aluminum, kieselguhr, or similar carriers with one or more of the desired oxides.

Among the specific catalysts which have been used before may be mentioned sintered iron promoted with an alkali metal compound and reduced in a hydrogen atmosphere, or prepared by contacting iron or metals of the iron group with mixtures of hydrogen and steam. The crystal structure of the several iron oxides is well known from the results of X-ray diffraction examination. The prior art workers have also employed as catalyst for the Fischer synthesis process reduced Fe_3O_4 or reduced alpha ferric oxide ; these catalysts have been prepared by reducing promoted Fe_3O_4 crystals directly or by reducing alpha Fe_2O_3.

It is an object of the present invention to provide a method for preparing a catalyst and, particularly, a catalyst adapted for use in the Fischer-Tropsch synthesis.

It is another object of the present invention to provide a mass suitable for use as a catalyst for conducting chemical reactions, and, more particularly, a mass which may be employed in the reaction of carbon monoxide and hydrogen at superatmospheric temperatures and pressures to obtain high yields of hydrocarbons and oxygenated organic compounds.

It is still another object of the present invention to provide an improved method for contacting a mixture of hydrogen and carbon monoxide with an iron oxide type catalyst under suitable temperatures and pressures to produce high yields of hydrocarbons as well as oxygenated organic compounds.

The method according to the invention for preparing the improved catalyst comprises the steps of preparing a mixture of a major proportion of iron oxide and a minor proportion of an alkali metal pyroantimoniate, heating said mixture at a superatmospheric temperature in the presence of a free oxygen-containing atmosphere, and subsequently contacting the mixture with a reducing atmosphere at a superatmospheric temperature. The heating step in the presence of the free-oxygen containing atmosphere is preferably conducted at a temperature of approximately 1000° F., e.g. for a period of approximately 4½ hours, the effect of which is to substantially oxidize the mass.

As indicated above the minor constituent of the catalyst of the invention is an alkali metal pyroantimoniate, such as sodium potassium or lithium, and this constituent serves as a stabilizing or promoting agent which enhances the activity of the iron component. The iron oxide used in the catalyst is desirably alpha or gamma iron oxide or ferro-ferric oxide.

The catalyst obtained by the method outlined above is particularly adapted for use in a Fischer-Tropsch synthesis operation and accordingly another aspect of the invention envisages a process which involves contacting a gaseous mixture containing carbon monoxide and hydrogen with said catalyst under conditions of temperature and pressure adapted to produce substantial amounts of hydrocarbons and oxygenated organic compounds.

It is preferred to contact the mixture of hydrogen and carbon monoxide with the catalyst at a temperature in the range of 450° to 675° F. and at a pressure within the range of 100 to 500 pounds per square inch gauge. It is also desirable for the hydrogen and carbon monoxide to be present in ratios within the range of 2 : 1 to 1 : 1 and to use feed rates within the range of 100 to 1500 volumes of feed per volume of catalyst per hour.

The alkali metal pyroantimoniate employed as a catalyst in the present invention is preferably potassium pyroantimoniate; however, the sodium or lithium pyroantimoniates may suitably be employed under some conditions. In preparing the catalyst employed in producing hydrocarbons from carbon monoxide and hydrogen, it is preferred to use the alkali metal pyroantimoniate in admixture with the iron oxide in an amount between 0.2 to 20% by weight of the catalyst mass and the iron oxide component in the amount between 80 and 99.8% by weight of the catalyst mass.

According to a preferred method of producing the catalyst mass of the invention, iron oxide in the form of ferro-ferric oxide is admixed with substantially pure potassium pyroantimoniate ($K_4Sb_2O_7$) and the admixture has added to it sufficient alcohol to permit mixing and to slurry it to a thick, smooth paste. The paste is then dried at substantially 225° F. to form a solid cake-like mass which is ground to pass a 30 mesh per linear inch screen, redried, and formed into pills. The pilled material is then heated in a free oxygen-containing atmosphere at 1000° F. for approximately 4½ hours and allowed to cool.

Before the catalyst prepared in the foregoing manner is suitable for employment in the synthesis of hydrocarbons and oxygenated organic compounds from carbon monoxide and hydrogen, it should be reduced by treatment with a reducing gas, such as hydrogen or carbon monoxide, at a temperature of approximately 500° to approximately 900° F. When hydrogen is the reducing gas, a temperature of approximately 700° F. and a hydrogen gas rate of approximately 1000 volumes per volume of catalyst per hour should be employed. When carbon monoxide is the reducing gas, a lower temperature of the order of 500° F. should be used.

The practice of the present invention may now be described by reference to the accompanying drawing which is a single figure in the form of a flow diagram showing a mode of practising one embodiment thereof.

Turning now specifically to the drawing, a mixture of carbon monoxide and hydrogen at the pressure desired for the synthesis reaction is passed through an inlet line represented by the numeral 11 into reactor 12. Within reactor 12 is arranged a catalyst mass 13 which has been prepared by the oxidation and reduction of a mixture of iron oxide and an alkali metal pyroantimoniate. Since the reaction of carbon monoxide and hydrogen is exothermic, tremendous amounts of heat are evolved during the reaction and must be removed from the catalyst bed 13. In order to maintain the temperature of the catalyst bed within the limits required for optimum conversion, a space is provided between reactor bed 13 and vessel 12 and a suitable fluid is passed into the space by inlet line 9 and withdrawn through outlet 10 for controlling the temperature of the catalyst bed.

The effluent from the catalyst bed 13 containing unreacted carbon monoxide and hydrogen, hydrocarbons and oxygenated compounds such as alcohols, carbon dioxide and water is removed through line 14 and passes through a cooling means 15 wherein the major portion of hydrocarbons and water are liquefied. The mixture is withdrawn from cooling means 15 and discharged into a settling means 16 where the total mixture is separated into a hydrocarbon phase and a water phase. The water layer is withdrawn continuously from settler 16 through line 17 and the hydrocarbon layer is withdrawn continuously through line 18. Non-condensible materials contained in the effluent are withdrawn from the top of settling means 16 through line 19; these exit gases may be conducted to a separation means, not shown, in order to recover unreacted carbon monoxide and hydrocarbon for recycling to the reactor 12 or may be recycled to the reactor directly.

The liquid hydrocarbon layer is passed through line 18 containing pump 20 and discharged into a distilling means 21, heat being supplied by heating coils 22 to heat the hydrocarbons therein. Hydrocarbon frac-

tions suitable for use as motor fuels, diesel fuel or components of lubricating oils are withdrawn from distilling means 21 through lines 23, 24, 25, 26 and 27. A heavy bottoms fraction is withdrawn through line 28 and may be employed as a lubricating oil or as a fuel oil.

It will be recognized by those skilled in the art that the hydrocarbons withdrawn from distillation unit 21 may be employed for many purposes. For example, light olefins, boiling in the range of C_4 and C_5 hydrocarbons may be alkylated with an isoparaffin, such as isobutane, in the presence of a suitable catalyst to produce a high octane motor fuel. The olefins are also especially valuable since they may form the feed stock for polymerization to polymers having molecular weight and viscosity characteristics suitable for use as lubricating oils. Also, the liquid fractions obtained in the synthesis process may be hydrogenated to improve the stability and octane characteristics thereof. It is to be pointed out that it may be desirable to recover oxygenated organic compounds from both the water and hydrocarbon phases removed from settler 16; the more water-soluble oxygenated hydrocarbons will be present in the water phase whereas the high molecular weight oxygenated compounds which are relatively insoluble in water will be present in the hydrocarbon phase.

While the above discussion has described a method for carrying out the synthesis reaction in the presence of catalysts employing a fixed bed operation, it is to be pointed out that other methods for carrying out the aforesaid synthesis reaction may at times be desirable. For example, the catalyst may be employed in the form of a suspension in a gaseous stream and passed through the reaction zone. The technique for carrying out reactions in a suspension of catalyst, commonly designated as a fluidized catalyst, is well known, and, accordingly, the details of such an operation will not here be given. The catalyst employed in the process of this invention lends itself well to use either in the form of pellets or pills for the fixed bed type of operation or to use as a finely divided powder suspended in a gaseous stream in the fluid catalytic synthesis operation.

The invention will be further illustrated by the following examples:

Example I.

In this example, a method is described for preparing a catalyst mass suitable for employment in the synthesis of hydrocarbons in accordance with the present invention.

In describing the method for preparing the catalyst mass, reference is made to employment of potassium pyroantimoniate. It is to be understood that the description is given for illustrative purposes only. In preparing the potassium pyroantimoniate, 100 parts of potassium hydroxide were heated in a suitable container until the mass was fused. To the fused molten mass was added gradually 12.6 parts of Sb_2O_5, following which the mixture was heated for approximately 15 minutes and allowed to cool. The cooled reaction mixture had added to it approximately 200 parts of distilled water and was then thoroughly agitated and then filtered. The filtrate was set aside while the residue had added to it 100 parts of molten potassium hydroxide. Additional amounts of potassium hydroxide to the extent of 20 parts were then added and the total mixture heated for 15 minutes, cooled and washed with 200 parts of distilled water. Following the washing treatment, the reaction body was thoroughly stirred and refiltered. The second filtrate was then combined with the first filtrate, which was previously set aside, and the combined filtrates evaporated at a reduced pressure at a temperature of 122° F. until crystallization occurred. The crystals which separated were filtered free from the liquor and were substantially pure potassium pyroantimoniate ($K4Sb_2O_7$).

The crystalline material was further purified by washing with absolute alcohol until substantially free of alkali. The washed crystals were dried at 207° F. and then a selected amount was added to a weighed amount of iron oxide such as ferro-ferric oxide, preferably an amount of the purified pyroantimoniate sufficient to give a catalyst composition of 5% potassium pyroantimoniate and 95% iron oxide, and the resultant mixture, after the addition of sufficient alcohol to permit mixing, was slurried to a thick, smooth paste. This paste was then dried at 225° F. to form a solid cake-like mass which was ground to pass a 30 mesh per linear inch screen, redried and formed into pills. The pilled material was then heated in a free oxygen-containing atmosphere at 1000° F. for 4½ hours and allowed to cool to obtain the finished catalyst.

Example II.

The catalyst prepared in accordance with Example I was treated with a reducing gas including free hydrogen at a temperature of 700° F. and a hydrogen gas rate of 1000 volumes per volume of catalyst per hour for 24 hours following which it was employed to synthesize hydrocarbons and oxygenated compounds from a feed mixture including one part of hydrogen and one part of carbon monoxide at a temperature between 550° and 575° F., a pressure of 150 pounds per square inch, and a feed rate of 200 volumes of feed gas mixture per volume of catalyst

per hour. The run was conducted for an 816 hour period during which time substantial quantities of hydrocarbons, including oxygenated organic compounds, and water, also including oxygenated organic compounds, were produced; the data presented in the following table show the conditions employed in the run and the result of the inspections of the products. The data included in the following table present high and low figures over the run period given with respect to the operating conditions. The examination of the products represents the inspections of the product produced over the run period for which the conditions are given:

TABLE I.

Temperature....	550	550	550	575
Pressure, psig	150	150	150	150
Feed Rate, V/V. Hr.	200	200	200	200
H_2/CO Ratio	0.903–1.134C	0.903–1.000	0.881–0.9060	0.906–1.06
Hrs. on Stream	0–120	120–240	240–336	226–456
CO Conversion, Mol %	95.5–97.0	83.6–95.0	81.7–86.3	92.0–94.0
Output Yields, cc/M³ of H_2+CO Cons.:				
C_4+Hydrocarbon	158–214	153–192	203–212	170–264
Water	35–69	29–39	31–32	41–53
Hydrocarbon Layer Data: *				
Specific Gravity	0.7709	0.7786	0.7694	0.7668
Bromine Number	34.5	48.3	56.1	61.5
Alpha Olefin**	34.9			52.9
Beta Olefin**	20.7			30.6
Alpha/Beta Olefin Ratio	1.686			1.37
Alcohol, Wt. % $C_5H_{11}OH$	2.55			12.5
Carbonyl, Wt. % $(C_2H_5)_2CO$	2.55	3.92	4.63	5.96
Acid, Wt. % C_4H_9COOH	1.48	1.51	2.15	2.22
Water Layer Data:				
Alcohol, Wt. % C_2H_5OH	13.0	16.0	17.6	13.4
Carbonyl, Wt. % $(Ch_3)_2$ CO	1.61	1.28	2.61	2.94
Acids, Wt. % CH_3COOH	0.18	0.24	0.24	0.21

Temperature....	575	575	575
Pressure, psig.	150	150	150
Feed Rate, V/V. Hr.	200	200	200
H_2/CO Ratio	1.085		0.86–1.18
Hrs. on Stream	456–576	576–696	696–816
CO Conversion, Mol %	86.0		58.7–89.4
Output Yields, cc/M³ of H_2+CO Cons.:			
C_4+Hydrocarbon	189		176.214
Water	63		33–60
Hydrocarbon Layer Date: *			
Specific Gravity	0.7800	0.7848	0.7800
Bromine Number	63.6	63.0	53.0[1]
Alpha Olefin**			
Beta Olefin**			
Alpha/Beta Olefin Ratio			
Alcohol, Wt. % $C_5H_{11}OH$			
Carbonyl, Wt. % $(C_2H_5)_2CO$	6.33	5.57	4.05
Acid, Wt. % C_4H_9COOH	1.83	1.86	3.06
Water Layer Data:			
Alcohol, Wt. % C_2H_5OH	13.6	16.4	14.87
Carbonyl, Wt. % $(CH_3)_2CO$	1.86	1.63	0.78
Acids, Wt. % CH_3COOH	0.18	0.15	0.24

* Based on recovered liquid product.

** Calculated as bromine number based on olefin type determination by infra-red absorption, uncorrected for oxygenated compound interference.

It will be apparent from the data in the foregoing table and the inspection characteristics of the products obtained that very good yields of hydrocarbons and water were produced throughout the operating period. The amount of hydrocarbons produced ranged from 158 c.c. of C_4 and heavier hydrocarbons produced at the outset of the run to as high as 264 c.c. of C_4 and heavier hydrocarbons per cubic meter of feed gas charged. Similarly, substantial yields of water containing appreciable quantities of oxygenated organic compounds were also produced.

The examination of the products showed that the hydrocarbons produced contained appreciable quantities of alcohols calculated as amyl alcohol, and quantities of carbonyls and organic acids, which contribute to the commercial utility of the process.

Although specific examples illustrating the practice of the present invention have been given, these examples are for illustrative purposes only and are not intended to limit the scope of the invention. It is to be understood that the present invention is directed to a catalyst, to a method for preparing a catalyst, and to a method for obtaining hydrocarbons and oxygenated organic compounds involving contacting a mixture of CO and H_2 at suitable temperatures and pressures with a catalyst which before reduction comprises a major portion of iron oxide and a minor portion of an alkali metal pyroantimoniate as a promoter. It will be apparent to a worker skilled in the art that while specific examples of preferred temperature and pressure ranges for conducting the operation have been given, other conditions may at times be desirable and may be employed without departing from the scope of the invention.

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 preparing a Fischer-Tropsch synthesis catalyst which comprises the steps of preparing a mixture of a major proportion of iron oxide and a minor proportion of an alkali metal pyroantimoniate, heating said mixture at a superatmospheric temperature in the presence of a free oxygen-containing atmosphere, and subsequently contacting the mixture with a reducing atmosphere at a superatmospheric temperature.

2. A method according to Claim 1, wherein the alkali metal pyroantimoniate is potassium pyroantimoniate.

3. A method for producing a Fischer-Tropsch synthesis catalyst which comprises the steps of admixing iron oxide with potassium pyroantimoniate and alcohol to form a paste, drying the paste to form a solid cake-like mass, grinding the caked mass and forming it into pellets, subjecting said pellets to a free oxygen containing atmosphere at an elevated temperature and subsequently contacting said pellets with a reducing atmosphere at a superatmospheric temperature.

4. A method according to any one of Claims 1—3, wherein said mixture is heated to a temperature of approximately 1000° F. in the presence of the free oxygen-containing atmosphere and to a temperature in the approximate range of 500 to 700° F. in the reducing atmosphere.

5. A method according to any one of Claims 1—4, wherein the iron oxide is alpha or gamma iron oxide or ferro-ferric oxide.

6. A method according to any one of Claims 1—5, wherein the iron oxide and alkali metal pyroantimoniate are used in quantities within the ranges of 80 to 99.8% by weight and 0.2 to 20% by weight respectively.

7. A method according to Claim 6, wherein the iron oxide and alkali metal pyroantimoniate are used in quantities of approximately 95% and 5% respectively.

8. A synthesis catalyst whenever prepared by a method according to any one of the preceding claims.

9. A process for the synthesis of hydrocarbons and oxygenated compounds which comprises contacting a gaseous mixture containing carbon monoxide and hydrogen at a superatmospheric temperature and pressure with a catalyst as defined by Claim 8, removing product from contact with the catalyst and recovering hydrocarbons and oxygenated hydrocarbons therefrom.

10. A process according to Claim 9, wherein said synthesis temperature and pressure lie within the range of 450° to 675° F. and 100 to 500 pounds per square inch gauge respectively.

Dated this 19th day of September, 1947.

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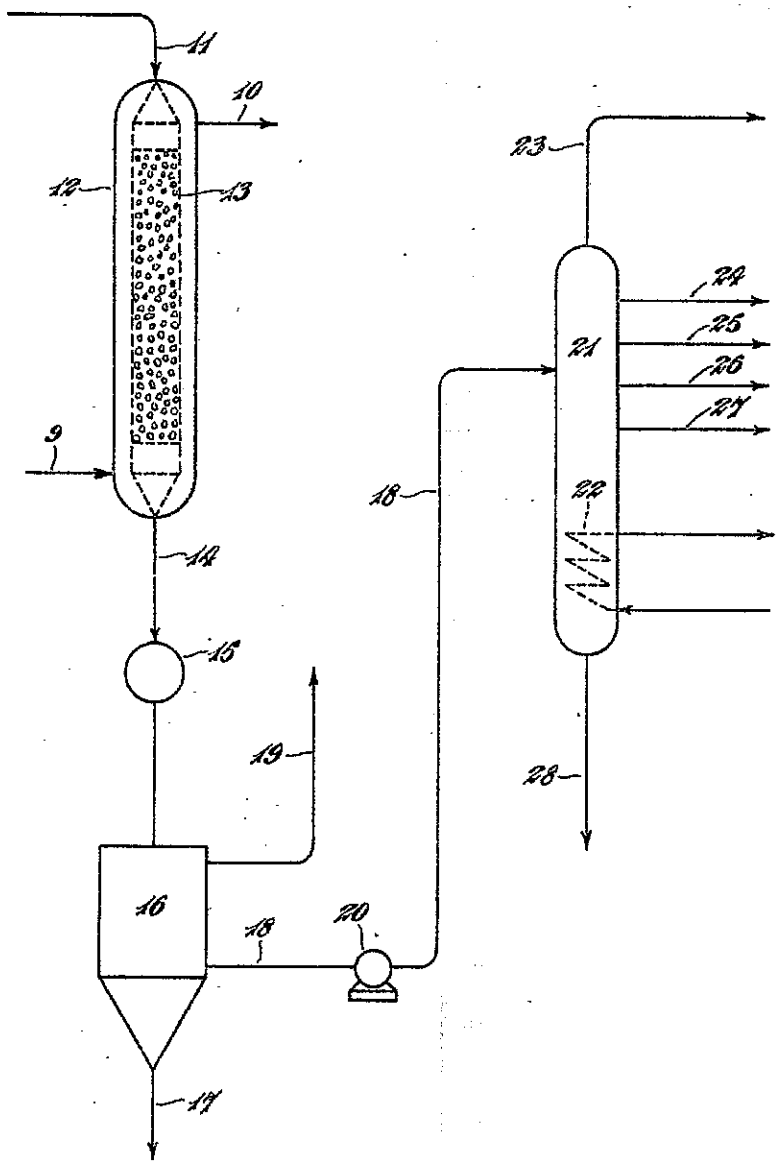

[This Drawing is a reproduction of the Original on a reduced scale.]

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