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COMPLETE SPECIFICATION

An Improved Catalyst and Method of Producing same

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised 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 is directed to an improved catalyst and to a method for the preparation thereof. The present invention is further directed to an improved method for effecting the synthesizing of hydrocarbons and oxygenated compounds from carbon monoxide and hydrogen.

It is well known to the art to synthesize hydrocarbons and oxygenated derivatives of hydrocarbons by passing a mixture of carbon monoxide and hydrogen over a suitable catalyst at elevated temperatures and pressures. This reaction is commonly designated as the Fischer-Tropsch synthesis and is usually carried out at temperatures in the range of about 450° to 675° F. and pressures in the range of 100 to 500 pounds per square inch. Such reactions have customarily been carried out in the presence of catalysts comprising the oxides of metals in Group VIII of the Periodic Table such as the oxides of iron, cobalt, and nickel. It is also known to use such oxides as catalyst either alone or supported on an inert material such as alumina, kieselguhr, and other such supporting agents. It has also been known to add to the active catalytic material in the catalyst composition a substance usually designated as a promoter which exerts a specific effect on the catalyst activity selectivity of the reactants to useful products, and on the active life of the catalyst. Catalysts containing promoters in substantially small quantities often permit consistently high conversion of the reactants to desired products over much longer periods of operation than is possible when using an unpromoted catalyst.

It is also known to the art that the products obtained by reacting carbon monoxide and hydrogen in the presence of a catalyst vary in type, configuration and molecular weight depending upon the type of catalyst employed. Paraffinic and olefinic hydrocarbons are the usual products obtained in a reaction of this type while the by-products consist chiefly of water, oxygenated compounds and carbon monoxide. Experience has shown that the oxygenated compounds are predominantly alcoholic in nature and that small amounts of esters, organic acids, ketones and aldehydes are usually also formed.

It is an object of the present invention to provide a mass suitable for use as a catalyst for conducting chemical reactions. It is another object of the present invention to provide methods for preparing said improved catalyst composition. It is still another object of the present invention to provide an improved method for reacting a mixture of hydrogen and carbon monoxide in the presence of a catalyst to produce hydrocarbons and oxygenated compounds.

The improved catalyst of the present invention comprises a solid mass prepared by mixing a major proportion of iron or an iron oxide with a minor proportion of an alkali metal ferrate and subsequently contacting the mixture with a reducing atmosphere at a superatmospheric temperature. Prior to the reduction step, the

[*Price* 2/-]

mixture is also desirably heated at a superatmospheric temperature in the presence of an oxidizing gas. The incorporation of the alkali metal ferrate serves to increase the catalytic activity of the iron oxide so that at the temperatures of the reduction operation customarily employed in the Fischer-Tropsch synthesis the synthesis of hydrocarbons and oxygenated material is promoted. As the iron oxide constituent, a major portion of an iron oxide such as ferroferric iron oxide or alpha or gamma Fe_2O_3 may be used, and as the alkali metal ferrate potassium ferrate, K_2FeO_4, or sodium ferrate are eminently suitable. It is preferred to employ the alkali metal ferrate in the improved catalyst composition in an amount between 0.2 and 20%, based on the weight of the iron oxide present in the mixture prior to reduction.

One of the methods of the present invention may be described briefly as involving the preparation of a catalyst which method comprises the steps of forming an alkali metal ferrate by adding to a mixture of $Fe(OH)_3$ and an alkali metal hydroxide an oxidizing agent such as bromine, adding the thus formed alkali metal ferrate to the iron or iron oxide catalyst, intimately mixing the two, drying and pilling the mixture, and heating the mixture at an elevated temperature in the presence of air and subsequently in the presence of a reducing atmosphere to obtain the finished catalyst.

Another method of the present invention may be described briefly as involving the preparation of a catalyst comprising a major portion of iron or iron oxide and a minor portion of alkali metal ferrate as the promoting material with the method of preparing the catalyst comprising metal nitrate, such as potassium nitrate, igniting the mixture and after ignition washing the mixture with alcohol, drying and adding selected amounts of the reaction product to iron or iron oxide and ball milling the mixture in the presence of alcohol. After milling, the mixture is dried, pilled, and heated in a free-oxygen containing atmosphere at an elevated temperature. Prior to employing the oxidized material as a catalyst it should be subjected to a reducing atmosphere at an elevated temperature.

The present invention may further be described briefly as involving contacting a mixture of hydrogen and carbon monoxide with a catalyst which is obtained by subjecting to a reducing atmosphere at superatmospheric temperatures a major amount of iron oxide and a minor amount of alkali metal ferrate with the feed gases maintained under temperature and pressure conditions to cause the formation of substantial amounts of hydrocarbons and oxygenated 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.

In the preparation of the catalyst mass of the present invention, the alkali metal ferrate is introduced into intimate admixture with the iron oxide prior to the treatment of the catalyst with an oxidizing atmosphere and with a reducing atmosphere. As an example of the preparation of a suitable catalyst, iron oxide in the form of powdered ferroferric oxide is mixed with an alkali metal ferrate, such as potassium ferrate, an alcohol, such as ethyl alcohol, and the mixture thoroughly milled prior to drying at a temperature of 230° F. The dried catalyst composition is then pilled and heated at a superatmospheric temperature to obtain an active catalyst. The superatmospheric temperature to which the catalyst composition is heated in the presence of an oxygen - containing atmosphere is preferably of the order of 1000° F. Prior to use as a synthesis catalyst the improved catalyst composition is subsequently subjected to a reducing atmosphere such as dry hydrogen gas at a temperature preferably in the range between 700° and 1600° F. to obtain an active catalyst mass suitable for use in the Fischer-Tropsch synthesis.

While ferroferric oxide has been mentioned specifically as a component of the catalyst composition, it is intended that other forms of iron oxide, such as alpha or gamma iron oxide may be used in lieu of the ferroferric oxide. Similarly, finely divided metallic iron may be substituted for the oxide since on subsequent treatment with the free oxygen-containing atmosphere, the metallic iron will be converted to the oxide.

The alkali metal ferrates which may be employed in the composition of the present invention are preferably sodium and potassium ferrate with the latter being preferred. However, sodium ferrate may suitably be employed in the improved composition and although more expensive, lithium ferrate may also be used. As examples of the preferred composition, it may be mentioned that compositions comprising substantially 2 and 5% of potassium ferrate and substantially 98 and 95% ferroferric oxide have been found suitable in the synthesis of hydrocarbons from carbon monoxide and hydrogen over extended periods of time.

While the alkali metal ferrate is preferably employed in the purified form, it is not detrimental to the use of the composition if it contains minor proportions of relatively inactive contaminants. For example, the alkali metal ferrate may contain residual amounts of potassium bromide and potassium bromate formed during the preparation. A typical analysis of the alkali metal ferrate component of the improved composition is as follows:

K_2Fe_4	75%
KBr	20%
KBO_3	5%

The potassium ferrate prepared as described above is then employed in a catalyst composition comprising five parts by weight of potassium ferrate and 95 parts by weight of ferroferric oxide and after the mixture is oxidized and reduced as heretofore described, it is an active catalyst for synthesizing hydrocarbons.

Another mixture was formed in which an initial mixture comprising 37.5% potassium ferrate, K_2FeO_4, and 62.5% by weight of Fe_2O_3 with which was admixed ferroferric oxide to give a final mixture comprising 2% by weight of K_2FeO_4 and 98% by weight of iron oxide which after oxidation and reduction is an active catalyst for synthesizing hydrocarbons.

Another method of preparation which results in a catalyst comprising 100 parts ferroferric oxide to five parts by weight of the alkali metal ferrate includes the following steps.

A previously dried intimate mixture of one part by weight of fine iron fillings or iron powder and two parts by weight of potassium nitrate is placed on an iron plate such that the mixture is distributed as a continuous layer of about two centimeters in depth. To this layer is joined a small quantity of approximately equal parts by weight of fine iron filings or iron powder and potassium nitrate. The latter mixture is then ignited and the reaction is allowed to continue until completion. The formation of a dense, white cloud of volatile potassium requires suitable precautions for removal of the harmful fumes. The reaction product is a black melted hydroscopic mixture which is allowed to cool. On cooling sufficiently for handling it is transferred to a vessel containing absolute ethyl alcohol. The reaction mixture is washed with alcohol by decantation until it is substantially free of alkali, following which it is dried by evaporation in a vacuum. The dried material is then added to a given weight of iron oxide. The iron oxide employed may be ferroferric oxide or it may be alpha or gamma iron oxide.

The amount of the reaction mixture added to the iron oxide may vary within rather wide limits, but it is contemplated that the amount of alkali metal ferrate will constitute between 0.2 and 20% by weight of the mixture. The mixture of iron oxide and the reaction product has added to it sufficient alcohol to permit adequate milling. It is then mixed thoroughly for about four hours by ball milling and then dried at approximately 110° C. and pilled. Then prior to the final reducing treatment, the pilled mixture is heated in a free oxygen containing atmosphere, such as air at a temperature of approximately 1000° F., for four and one half hours.

The presence of small amounts of iron filings or iron powder and/or potassium nitrates in the finished catalyst is not objectionable, since the calcining in the presence of a free oxygen containing atmosphere will oxidize the former to iron oxide and the latter will be decomposed to potassia.

In another method for preparing a catalyst in accordance with the present invention, a previously dried intimate mixture of one part by weight of fine iron powder and two parts by weight of potassium nitrate was placed on an iron plate and distributed as a layer of approximately 2 centimeters depth. A second layer of approximately equal parts by weight of iron powder and potassium nitrate was then placed adjacent to the second layer. The first layer was then ignited and the reaction allowed to go to completion. A dense white cloud of volatile potassium formed which was removed from the reaction zone. The reaction product was cooled sufficiently for handling and removed from the iron plate and heated in a free oxygen containing atmosphere at substantially 1000° F. for substantially 4 hours. After the foregoing calcining operation, the reaction product was ground into a fine powder and pilled into one-eighth inch pills. Subsequent to the pilling operation, the pills were placed in a reaction chamber and reduced in the presence of hydrogen for 24 hours at a temperature of 700° F. and at atmospheric pressure. The hydrogen was passed over the catalyst at a feed rate of hydrogen of 1000 volumes per volume of catalyst per hour.

The alkali metal ferrate promoter, for

example, potassium ferrate, to be added to the catalyst may be prepared in a number of ways. In the preferred procedure, $Fe(NO_3)_3.9H_2O$ is reacted with ammonium hydroxide to cause the precipitation of $Fe(OH)_3$ and the ferric hydroxide thus formed is filtered and then slurried with water. The water is admixed with solid KOH and to the mixture is added slowly liquid bromine and solid KOH until the mixture is saturated with respect to the latter. The reaction mixture should be kept at a temperature below approximately 140° F. The mixture is then heated carefully with stirring for substantially one-half hour at substantially 140° F., allowed to cool, and the top layer removed from the reaction mixture. The top layer is dried in a vacuum and then washed with alcohol until substantially free of alkali. The alcohol-washed material is also dried in a vacuum to produce a potassium ferrate substantially free from contaminating substances.

The purified potassium ferrate is then added to a powdered iron or to powdered oxide of iron such as ferroferric oxide or alpha and gamma ferric oxides. It is usually desired that sufficient potassium ferrate be added to the active catalytic material such that the finished catalyst will contain from 0.2 to 20 weight per cent. potassium ferrate based on the iron or iron oxide employed.

The mixture of potassium ferrate and iron or iron oxide is milled, preferably in the presence of a small amount of alcohol, dried at a temperature of substantially 230° F. and pilled. The pilled material is then heated at superatmospheric temperatures in the presence of air and subsequently with pressence of a reducing atmosphere to obtain an active catalyst containing promoting quantities of potassium ferrate.

The presence of both potassium bromide and potassium bromate in small amounts in the finished catalyst is not objectionable since both of these substances may have a tendency to promote the activity of the iron oxide catalyst in the hydrocarbon synthesis reaction.

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 practicing 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 12 which has been prepared by the reduction of a mixture of iron oxide and potassium ferrate. 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. Water 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 may be 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 directly to the reactor.

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 fractions suitable for use as motor fuels, diesel fuel or components of lubricating oils may be 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. Also, the liquid fractions obtained in the synthesis process may be hydrogenated to improve the stability and octance 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 practice of the present invention will be further illustrated by the following example:

To an aqueous solution containing 340 parts by weight of $Fe(NO_3)_3.9H_2O$ is added 90 parts by weight of NH_4OH. The precipitated $Fe(OH)_3$ is filtered dry and then slurried with substantially 50 parts by weight of distilled water. To the slurry is added 50 parts by weight of solid KOH and while the suspension is maintained at a temperature below 140° F., 50 parts by weight of liquid bromine and solid KOH are added. During this addition, the materials are added gradually with continual stirring. Sufficient solid KOH is added to the reaction mixture so that the latter is completely saturated with respect to the alkali. At this point, it is preferable to add an excess of solid KOH to the mixture, for example 20 parts by weight of excess alkali, before heating the mixture with stirring at a temperature of 140° F. for approximately one-half hour.

The heated mixture is allowed to cool and the top layer comprising potassium ferrate is decanted from the total mixture and dried under partial vacuum. Alkaline material remaining in the dried potassium ferrate may be removed by successive washings and decantations with alcohol. The potassium ferrate is then redried under vacuum and, as produced in this manner, is substantially free from alkaline contaminants and contains minor portions of potassium bromate and bromide as illustrated by the following analysis:

K_2FeO_4	75.0%
KBr	20.0%
$KBrO_3$	5.0%

To 100 parts by weight of ferroferric oxide in finely divided form is added sufficient of the above preparation to give a catalyst comprising 5 parts by weight of dried potassium ferrate and a small amount of alcohol to permit adequate milling. The mixture is then mixed thoroughly for substantially 4 hours by ball milling, dried at substantially 230° F. and pilled to a size desired for subsequent use in the synthesis process. The pilled material is then heated in free excess air at substantially 1000° F. for substantially 4 hours and allowed to cool.

The beneficial results to be obtained by using the above-prepared catalyst, containing 5 parts by weight of potassium ferrate per 100 parts by weight of ferroferric oxide, in the hydrogenation of carbon monoxide are exemplified by the following description and data:

The catalyst prepared in accordance with the above procedure is placed in a reaction chamber and reduced in the presence of hydrogen for 24 hours at a temperature of 700° F. and atmospheric pressure. The hydrogen is passed over the catalyst at a rate of 1000 volumes of hydrogen per volume of catalyst per hour. A synthesis gas mixture comprising one part of hydrogen per part of carbon monoxide is then passed over the catalyst at a pressure of 150 pounds per square inch gauge, a temperature of 575° F., and a rate of 200 volumes per volume of catalyst per hour.

The advantages of the practice of this invention will be illustrated by the following tabulated data obtained in the foregoing run which lasted for 1736 hours. In some of the columns in the following table a range of values are given and these respresent the maximum and minimum figures obtained for the period indicated.

TABLE I

Temperature, °F.	550	575——		575——		575	585
Pressure, p.s.i.g.	150	150——		150——		150——	
Feed Rate, V/V/Hr.	200	200——		200——		200——	
H_2/CO Ratio (Charge)	1.305	0.98—1.305	1.02—1.03	1.068—1.11	1.03—1.08	0.92—1.0	0.956—0.96
Hours on Stream	4—28	28—196	196—244	244—316	316—436	436—556	556—676
CO Conversion, Mol %	97.9	97.0—97.2	96.9—97.5	96.3—97.9	94.4—97.0	91.0—97.2	80.5—87.8
H_2+CO Conversion, Mol %	79.1	85.8—85.9	88.3—89.6	80.3—82.4	78.5—86.8	75.4—86.7	71.5—87.9
Output Yields, cc./M^3 of H_2+CO Consumed:							
C_4+Hydrocarbon	164	241—243	214—232	204—247	214—268	211—226	177—265
Water	54	44—47	12—35	46—50	23—59	39—48	33—36
Hydrocarbon Layer Data:*							
Specific Gravity	0.7484	0.7424—0.7580	0.7720	0.7720	0.7626	0.7727	0.8000
Bromine Number	53.8	54.5—90.6	63.0	63.0	69.7	66.6	64.4
Alpha Olefin**		51.1—61.6	50.2	50.2	57.5	55.9	45.8
Beta Olefine**		21.5—25.9	33	22.9	20.9	21.5	25.1
Alpha/Beta Olefin Ratio		2.3—2.85	2.47	2.47	2.75	2.60	1.82
Alcohol, Wt. % $C_5H_{11}OH$		3.4—7.4	1.65	1.65	1.21	1.54	6.44
Carbonyl Wt. % $(C_2H_5)_2C$	0.78	1.42—2.44	—	—	1.63	1.96	2.46
Acid, Wt. % C_4H_9COOH	0.66	0.97—1.74	—	—	1.36	1.00	1.57
Water Layer Data:							
Alcohol, Wt. % C_2H_5OH	13.5	9.6—11.5	—	—	—	—	13.1
Carbonyl, Wt. % $(CH_3)_2C$	0.50	0.64—1.08	—	—	—	—	1.53
Acids, Wt. % CH_3COOH	0.12	0.06—0.30	—	—	—	—	0.18

* Based on recovered liquid product.

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

TABLE I (Continued)

Temperature, °F.	585	600		600			
Pressure, p.s.i.g.	150			150			
Feed Rate, V/V/Hr.	200			200			
H_2/CO Ratio (Charge)	0.94	0.94	0.923—1.03	0.96	0.771—0.99	—	
Hours on Stream	676-700	700-806	806—902	902—926	926—1070	1070—1088	Reduced with H_2 at 700°F. for 24 Hours at 1000 V/V/Hr. and O p.s.i.g.
CO Conversion, Mol %	79.5	82.5	83.5—90.2	75.7	82.5—91.9	—	
H_2+CO.Conversion, Mol %	71.8	73.2	83.5—90.2	62.8	70.6—81.9	—	
Output Yields, cc./M^3 of H_2+CO Consumed:							
C_4+Hydrocarbon	195	223	191—231	288	188—223	—	
Water	107	28	29—37	37	27—50	—	
Hydrocarbon Layer Data:*							
Specific Gravity	0.7870		0.7711	0.7711	0.7719	—	
Bromine Number	58.1		62.8	62.8	70.2	—	
Alpha Olefin**	47.0		50.9	50.9	—	—	
Beta Olefine**	27.4		26.1	26.1	—	—	
Alpha/Beta Olefin Ratio	1.71		1.94	1.94	—	—	
Alcohol, Wt. % $C_5H_{11}OH$	7.48		4.84	4.84	—	—	
Carbonyl, Wt.%$(C_2H_5)_2C$	2.69		2.11	2.11	3.43	—	
Acid, Wt. % C_4H_9COOH	1.34		2.28	2.28	2.32	—	
Water Layer Data:							
Alcohol,Wt.%C_2H_5OH	13.3		11.4		10.5	—	
Carbonyl,Wt.%$(CH_2)_3CO$	0.76		1.2		0.88	—	
Acids, Wt. % CH_3COOH	0.30		0.2		0.30	—	

* Based on recovered liquid product.

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

TABLE I (Continued)

Temperature, °F.	600					600	
Pressure, p.s.i.g.	150					150	
Feed Rate, V/V/Hr.	200					200	
H_2/CO Ratio (Charge)	1.053	1.068—1.11	0.673	—	0.861—1.163	—	
Hours on Stream	1088—1112	1112—1232	1232—1280	1280—1352	1352—1472	1472—1520	Reduced with H_2 at 700°F. for 24 hours at 1000 V/V/Hr. and O p.s.i.g.
CO Conversion, Mol %	99.4	95.2—97.4	94.0	—	89.8—90.1	—	
H_2+CO Conversion, Mol %	86.9	78.7—87.9	88.8	—	73.1—79.9	—	
Output Yields, cc./M³ of H_2+CO Consumed:							
C_4+Hydrocarbon	124	198—222	203	—	171—205	—	
Water	53	59—81	13	—	30—60	—	
Hydrocarbon Layer Data:*							
Specific Gravity	0.8375	0.8002	0.7630	0.7630	0.7680	—	
Bromine Number	—	51.6	73.0	73.0	66	—	
Alpha Olefin**	—	—	—	—	—	—	
Beta Olefine**	—	—	—	—	—	—	
Alpha/Beta Olefin Ratio	—	—	—	—	—	—	
Alcohol, Wt. % $C_5H_{11}OH$	—	—	—	—	—	—	
Carbonyl, Wt. % $(C_2H_5)_2CO$	—	2.09	2.65	2.65	2.7	—	
Acid, Wt. % C_4H_9COOH	—	0.89	0.89	0.89	1.2	—	
Water Layer Data:							
Alcohol, Wt. % C_2H_5OH	—	5.3	8.1	8.1	11.5	—	
Carbonyl, Wt. % $(CH_3)_2CO$	—	1.6	0.70	0.70	0.80	—	
Acids, Wt. % CH_3COOH	—	0.1	0.09	0.09	0.30	—	

* Based on recovered liquid product.

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

TABLE I (Continued)

Temperature, °F.	600—	575—	600—	625—
Pressure, p.s.i.g.	150—	150—	150—	
Feed Rate, V/V/Hr.	200—	200—	200—	
H_2/CO Ratio (Charge)	0.878	0.904—0.957	0.951	
Hours on Stream	1520—1544	1544—1640	1640—1712	1712—1736
CO Conversion, Mol %	84.3	47.9—74.4	47.7	—
H_2+CO Conversion, Mol %	70.8	41.0—63.8	39.7	—
Output Yields, cc./M^3 of H_2+CO Consumed:				
C_4+Hydrocarbon	191	130—205	163	—
Water	49	18—37	36	—
Hydrocarbon Layer Data:*				
Specific Gravity	—	—	—	—
Bromine Number	—	—	—	—
Alpha Olefin**	—	—	—	—
Beta Olefine**	—	—	—	—
Alpha/Beta Olefin Ratio	—	—	—	—
Alcohol, Wt. % $C_5H_{11}OH$	—	—	—	—
Carbonyl, Wt. % $(C_2H_5)_2CO$	—	—	—	—
Acid, Wt. % C_4H_9COOH	—	—	—	—
Water Layer Data:				
Alcohol, Wt. % C_2H_5OH	—	—	—	—
Carbonyl, Wt. % $(CH_3)_2CO$	—	—	—	—
Acids, Wt. % CH_3COOH	—	—	—	—

* Based on recovered liquid product.

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

It will be apparent from the foregoing data that the present invention allowed operation for an appreciable length of time while producing substantial quantities of hydrocarbons having a high content of alpha olefins and water containing oxygenated hydrocarbons which was rich in valuable oxygenated material.

It is important that a high content of alpha olefins be produced in the synthesis operation since these olefinic hydrocarbons lend themselves to polymerization for production of polymers having valuable lubricating qualities. The beta olefins on polymerization give polymers much less valuable as lubricants. In fact the polymers produced from beta olefins have characteristics which make them unsuitable for use as lubricating oils.

In another example 340 parts of $Fe(NO_3)_3.9H_2O$ was dissolved in distilled H_2O. A dilute solution of NH_4OH was added to the solution to precipitate $Fe(OH)_3$. This was filtered and to the filtrate a solution of 50 parts of solid KOH dissolved in distilled water was added. The mixture was stirred to a smooth paste while controlling the temperature. To the cooled material 50 parts of bromine was added below the surface of the solution while stirring vigorously. Solid KOH was then added in small quantities until saturation was obtained with the KOH being added to excess. During the addition of the KOH the temperature was maintained no higher than 41° C. and at approximately 25° C. The solution was then carefully heated to 60° C. for one-half hour, heat removed and the solution cooled. After approximately 24 hours, the upper half of the material, hereafter referred to as the upper layer, was removed. The upper layer and the bottom half, referred to as the lower layer, were then separately evaporated under vacuum at a temperature of 47° C. for two weeks. After this period both the upper layer and lower layer were removed from the heat treating operation and washed free of KOH by repeated separate washings with 95% ethyl alcohol. The washed samples were filtered and dried under a vacuum. The upper layer was analyzed as follows:

Fe_2O_3	62.5%
K_2FeO_4	37.5%

A weighed amount of material having the above composition was then suspended in 95% ethyl alcohol to which was added a weighed amount of ferroferric oxide which was thoroughly mixed by stirring to form a smooth slurry. The slurry was dried in an oven at 95° C. with air circulating freely for a period of 48 hours. The temperature was then raised to substantially 110° C. and maintained with the exception of a 12 hour period when the temperature rose to substantially 160° C., for three weeks. The dried material was pilled into ⅛ inch pills which were calcined for 4½ hours in the presence of an oxygen-containing atmosphere at 1000° F. following which the material was allowed to cool in air to atmospheric temperature. The catalyst prepared in the foregoing manner comprised 2% by weight K_2FeO_4 and 98% iron oxide and was then employed for the synthesis of hydrocarbons from carbon monoxide and hydrogen after being reduced in the presence of hydrogen for 24 hours at a temperature of 700° F. and at atmospheric pressure. During the reduction treatment the hydrogen was passed over the catalyst at the rate of 1000 volumes of hydrogen per volume of catalyst per hour. A synthesis gas mixture comprising one part of hydrogen per part of carbon monoxide was employed as the feed stock, the conditions of operation being 150 pounds pressure, a temperature of 575° F., and a feed rate of 200 volumes of feed per volume of catalyst per hour.

In synthesizing hydrocarbons in the foregoing manner using the catalyst, it was found that effective yields of C_4 and heavier hydrocarbons could be obtained, with the improved method of obtaining the catalyst, for over 600 hours. During certain periods of the operation as much as 307 cc. of C_4 and heavier hydrocarbons per cubic meter of feed consumed were obtained. During longer periods, C_4 and heavier hydrocarbon yields ranging from approximately 150 cc. to 237 cc. per cubic meter of feed stock consumed were obtained.

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 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.

The invention has been illustrated by specific examples wherein the catalyst mass comprises iron oxide and potassium ferrate. It is within the spirit and scope of the invention that the ferrates of other alkali metals besides potassium may be employed; specifically, sodium ferrate may be used as one component of the catalyst and, also, lithium ferrate may be employed. The latter may be less desirable to use than the sodium and potassium ferrates in view of its more expensive nature. It will usually be desirable, therefore, that potassium or sodium ferrate will be the minor component of the catalyst and iron oxide the major component.

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 of preparing a catalyst adapted for use in a Fischer-Tropsch synthesis comprising the steps of preparing a mixture of a major proportion of iron or an iron oxide and a minor proportion of an alkali metal ferrate and subsequently contacting the mixture with a reducing atmosphere at a superatmospheric temperature.

2. A method according to Claim 1, wherein said mixture is heated at a superatmospheric temperature in the presence of an oxidizing gas, prior to being contacted with the reducing atmosphere.

3. A method according to Claim 1 or 2, wherein the mixture contacted with the reducing atmosphere contains the alkali metal ferrate in an amount within the range of 0.2 to 20 per cent. by weight based on the iron oxide.

4. A method according to any one of Claims 1—13, wherein the alkali metal ferrate is substantially free from contaminating materials.

5. A method according to Claim 3 or 4, wherein the mixture contacted with the reducing atmosphere comprises substantially 95% iron oxide and substantially 5% potassium ferrate.

6. A method according to any one of Claims 1—4, wherein the alkali metal ferrate is potassium ferrate.

7. A method according to any one of the preceding claims, wherein iron oxide is ferroferric oxide, alpha ferric oxide, or gamma ferric oxide.

8. A method according to any one of the preceding claims, wherein the mixture is reduced at a temperature within the range of 700° to 1600° F.

9. A method according to any one of the preceding claims, wherein the alkali metal ferrate is prepared by igniting a mixture of finely divided iron and alkali metal nitrate.

10. A method according to Claim 9, wherein the alkali metal nitrate is potassium nitrate.

11. A method according to Claim 9, wherein the alkali metal ferrate is prepared by forming a first mixture of one part of finely divided iron and two parts of alkali metal nitrate, forming a second mixture of equal parts of finely divided iron and metal nitrate adjacent the first mixture, igniting the second mixture, allowing the reaction to proceed to the first mixture, completing the reaction of the first and second mixture and recovering the desired alkali metal ferrate.

12. A catalyst whenever prepared by a method according to any one of Claims 1—11.

13. A process for the synthesis of hydrocarbons and oxygenated organic compounds from a gaseous mixture containing carbon monoxide and hydrogen by contacting said gaseous mixture at a superatmospheric temperature and pressure with a catalyst according to Claim 12.

14. A process according to Claim 13, wherein said synthesis is carried out at a temperature within the range of 450° to 675° F. and a pressure in the range of 100 to 500 pounds per square inch gauge.

Dated this 2nd day of September, 1947.

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