PATENT SPECIFICATION

649,464

Date of Application and filing Complete Specification: June 30, 1948.
Nos. 17509/48 and 17510/48.
Application made in United States of America on Oct. 1, 1947.
Application made in United States of America on Oct. 1, 1947.
Complete Specification Published: Jan. 24, 1951.

3511

Index at acceptance:—**Class 1(i),** F3b(1: 2x), F3c5.

COMPLETE SPECIFICATION

Hydrogenation Catalysts

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 relates to catalytic conversions and improved catalysts therefor. More particularly, the invention is concerned with improved catalysts for the catalytic hydrogenation of carbonaceous materials and it finds its most useful application in the catalytic synthesis of normally liquid hydrocarbons and oxygenated compounds from CO and H_2.

The catalysts most commonly used in the hydrogenation of carbonaceous materials such as hydrocarbons or carbon monoxide are the metals of Groups VI and VIII of the Periodic System and their oxides and sulfides. The former group of catalysts is more active in the hydrogenation of various types of hydrocarbon materials while the latter group is preferred in the synthesis of valuable products from carbon monoxide and hydrogen. The choice of the proper catalyst and the conditions at which it is applied depend mainly on the type of product desired.

For example, in the conversion of carbon monoxide with hydrogen, nickel catalysts may be used over a wide range of temperatures and pressures to produce predominantly normally gaseous hydrocarbons useful as fuel gases of high heating value and as starting materials for further synthetic processes such as polymerization, alkylation, oxidation, etc. Cobalt type catalysts when employed at relatively low temperatures of about 380°—450° F. and low pressures of about 1—10 atmospheres abs. yield predominantly saturated hydrocarbons useful as diesel oils, lubricants, paraffin wax, etc. For the synthesis of high grade motor fuels, on the other hand, iron type catalysts are more suitable particularly when used at relatively high temperatures of about 450°—800° F. and pressures of about 3—100 atmospheres abs. or higher, because a predominantly unsaturated product of high octane rating is formed at these conditions.

Catalytic hydrogenation reactions in general and particularly the synthesis of hydrocarbons from CO and H_2 are extremely temperature sensitive and subject to relatively rapid catalyst deactivation mainly resulting from the deposition on the catalyst of involatile carbonaceous deposits such as wax, coke, or the like. This situation has led, in recent years, to various attempts and proposals to employ the so-called fluid catalyst technique wherein the gasiform reactants are contacted with a dense turbulent bed of finely divided catalyst fluidized by the gasiform reactants and products. The fluid technique permits catalyst replacement without interruption of the process and greatly improved temperature control and thus constitutes a suitable means for solving the aforementioned problems. However, the adaptation of hydrogenation reactions and particularly of the hydrocarbon synthesis to the fluid catalyst technique has encountered serious difficulties, particularly when iron catalysts are used.

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able, for example, when iron-type synthesis catalysts are used that the catalyst be active in the temperature range above 600° F. and still be largely selective to C_4+ hydrocarbons, since under these conditions high octane motor fuels are obtained. None of the prior art catalysts complies satisfactorily with all of these requirements.

Synthesis catalysts are usually prepared by the reduction of various natural or synthetic metal oxides or by the decomposition of metal carbonyls, the catalytic activity being enhanced by the addition of such promoters as various compounds of alkali metals or the oxides of chromium, zinc, aluminum, magnesium, manganese, the rare earth metals and others in small amount of about 1—10%. While some of these catalysts exhibit excellent activity characteristics they are without exception deficient with respect to ease of fluidization, and/or attrition resistance particularly when used in commercial runs of several hundred hours duration. Even fluidized catalysts obtained from sintered iron, which have been found to exhibit excellent fluidization and attrition characteristics show signs of disintegration in long run operation.

This general lack of mechanical resistance or steady decrease of mechanical strength during operation is particularly characteristic for iron type catalysts. It has been found to be closely connected to a high rate of carbon deposition on the catalyst, encountered at the conditions required by the synthesis using iron catalysts. The catalyst disintegration which accompanies excessive carbon deposition is believed to be the result of a migration of carbon into the iron lattice by the mechanism of interstitial carbide formation followed by decomposition of the carbide to free carbon. This process may continue until the catalyst mass contains about 99% of carbon.

It will be appreciated from the above that catalysts of satisfactory activity, selectivity to useful products, and catalyst life which may be used in commercial operation without substantial catalyst disintegration and carbon deposition is a need strongly felt particularly in the synthesis art. This drawback, for example, has been the major obstacle in all attempts to apply the fluid catalyst technique to the iron-catalyzed hydrocarbon synthesis. The present invention overcomes this obstacle and affords various other advantages.

It is, therefore, the principal object of the present invention to provide improved catalysts for the hydrogenation of carbonaceous materials and more particularly for the catalytic conversion of CO with H_2.

A further object of the invention is to provide improved hydrogenation processes and more particularly an improved hydrocarbon synthesis process, employing fluidized catalysts, which are not subject to excessive disintegration and carbon formation.

A more specific object of the invention is to provide improved iron catalysts of highest disintegration resistance when used in the synthesis of hydrocarbons from CO and H_2 employing the fluid catalyst technique.

Other and further objects and advantages of the invention will appear hereinafter.

In accordance with the present invention, carbon deposition on hydrogenation and iron type synthesis catalysts is substantially reduced and catalyst disintegration correspondingly suppressed while activity, selectivity and catalyst life are maintained at highest levels, by supporting the active metal obtained by the decomposition of its carbonyl, e.g. $Fe(CO)_5$, on a dense turbulent fluidised mass of a substantially inactive non-metallic carrier material of high attrition and disintegration resistance. The support for the carbonyl iron is preferably adsorptive and capable of promoting the selectivity of the final catalyst to liquid products. The carrier material itself may act as a promoter or it may contain small amounts of a conventional promoter such as K_2CO_3, $NaSiO_3$, KOH, KF, NaF, KBF_4, Na_2CO_3 or the like.

Carbonyl compounds of other metals having hydrogenating activity, particularly of Groups VI and VIII of the Periodic System may be used.

While a fairly wide variety of inactive supports is available for the purposes of this invention, superior results have been consistently obtained when using synthetic spinels such as $ZnO.Al_2O_3$, $Cr_2O_3.Al_2O_3$, $CaO.Al_2O_3$. Other suitable supports are stable carbonates, for example those of Group II of the Periodic System, particularly barium, calcium or zinc carbonate in which case an extraneous promoter is not usually required. Other supports which may be used include active carbons, for example the carbon formed in the synthesis reaction, ordinary soft glass having a composition such as $R_2O.CaO.6SiO_3$; in which R is an alkali metal; alumina-containing cracking catalysts such as silica-alumina composites which may contain about 87.5% Al_2O_3 and 12.5% SiO_2; silica-magnesia composites which may contain about 87.5% MgO and 12.5 SiO_2; etc. Mixtures of these supports may be used if desired.

Specific examples, are silica-alumina and silica-magnesia composites of varying composition, bauxite, fuller's earth, various clays, natural or artificial spinels such as compounds of alumina with zinc oxide, copper oxide, etc. These materials may be subjected to various heat treatments, particularly calcination, preceding their use as carrier materials and the calcination may be so controlled as to effect mild dehydration or to result in partial or substantially complete sintering or fusion. Various powdered metals or alloys may also be used as carrier materials. Materials containing Zn, Cu, Cr, Mo, W, Fe, etc. are especially useful.

The relative proportions of the constituents of the catalysts of the present invention may vary within wide limits. It has been found, however that catalysts of excellent activity, selectivity, carbonization, mechanical strength and fluidization characteristics may be obtained by combining as little as 0.2% by weight of carbonyl metal in the supports of the invention, particularly the synthetic spinels listed above. The metal concentration may, therefore, be advantageously held within the most economical limits of preferably about 0.2%—10% without detrimentally affecting the catalytic performance of the catalyst. The amount of promoter added may vary between about 0.5 and 10%, preferably about 1—5%, depending on the character of the promoter and of the support.

Materials suitable for the formation of the carbonyl compounds include a wide variety of metal-containing substances or compositions reducible to the metallic state such as oxides, carbonates, hydroxides, etc. Pure forms of the metals are not required since the volatilization of the carbonyl compound effects the separation of the desired constituents. For example, in the formation of iron carbonyl various types of powdered iron, reduced iron oxides, or a number of reduced iron ores are suitable.

The carbonyl compounds are formed by contacting the subdivided metal or metal-containing starting material with CO or a gas rich in CO under a suitable pressure at a temperature sufficiently high to promote the desired reaction but below the decomposition temperature of the carbonyl compound. For purpose of illustration the table below shows the atmospheric pressure decomposition temperatures of the most important metal carbonyls here involved as well as the temperature and pressure ranges preferred for their preparation.

Carbonyl	Temp. at which carbonyl begins to decompose, °F. (Atm. Press.)	Preferred Operating Conditions Temp. °F.	Press.lb/sq. in.
$Ni(CO)_4$	140	50—250	100—600
$Fe(CO)_5$	302	50—450	100—600
$Cr(CO)_6$	266	50—350	100—600
$Mo(CO)_6$	302	50—400	100—600
$W(CO)_5$	302	50—400	100—600
$[Co(CO)_4]_2$	127	50—225	100—600

The carbonyl vapors formed are then contacted with the subdivided carrier material at atmospheric to about 600 lbs/sq.in. pressure and at a temperature at which the carbonyl is rapidly decomposed, usually within the range of about 250° to 750° F. depending on the metal carbonyl used, so as to deposit the metal on the carrier material in the desired proportions. The decomposition of the carbonyl may take place in the hydrogenation or synthesis reactor itself. Particularly in this case it is not necessary that all of the carbonyl metal be deposited on the surface of the carrier material. good operation being obtained in this manner with mechanical mixtures of carbonyl metal and carrier material. If a promoter is required in the final catalyst it may be incorporated into the carrier material by suitable impregnation or mixing prior to the deposition of the carbonyl metal or it may be added continuously or intermittently as required by means of suitable solutions or as molten salts.

The preparation of the metal carbonyl may be carried out by passing the respective gasiform materials over the solids arranged as fixed beds in suitable reaction zones. However, in accordance with the preferred embodiment of the invention the fluid solids technique is employed for the preparation of the metal carbonyl as well as for its decomposition on the carrier material.

For this purpose, the metal-containing

starting material having a particle size of about 5—200 microns, preferably about 75—90% of 20—100 micron material is maintained in a reaction zone in the form of a dense turbulent mass of solids fluidized by the upwardly flowing CO-containing gas to assume an apparent density of about 30—150 lbs. per cu. ft. and a well defined upper level at the reaction conditions specified above. Superficial linear gas velocities of about 0.5—5 ft. per second are generally suitable mainly depending on the specific gravity and particle size of the solids used. This production of the metal carbonyl may be conducted in a fully continuous manner by supplying fresh metal-containing solids and withdrawing spent solids to and from the fluidized bed as a function of the rate of metal conversion.

The metal carbonyl vapors formed in the first stage of the process are then contacted with a dense turbulent carrier mass fluidized in a manner substantially analogous to that just described. The particle sizes of the carrier material may be generally somewhat larger than that specified for the metal-containing starting material and may fall within the approximate range of 20—500 microns preferably 20—200 microns and particularly 50—150 microns. If desired, the carbonyl vapors may be diluted with a non-oxidizing gas such as nitrogen or hydrogen to improve fluidization.

In accordance with the preferred embodiment of the invention, the active metal is added to the support by passing metal carbonyl vapors through or over the support at a suitable temperature which for iron catalysts is about 400°—1000° F., preferably about 600° F. The pressure may be in the range of from 1 to 50 atmospheres.

The latter method may be carried out to greatest advantage in a fluid system of the type illustrated semi-diagrammatically in the accompanying drawing, as will be hereinafter explained.

Referring now to Fig. 1 of the drawing, the system illustrated therein consists essentially of an elongated vertical fluid reactor (10), surrounded by a heating jacket (20). The upper portion of reactor (10) is expanded to form a separation zone (12) for the separation of suspended solids from gases.

In operation, reactor (10) may be supplied through line (1) with a finely divided selectivity-promoting support of the type specified above, having a fluidizable particle size of about 20—200 microns, preferably about 50—150 microns. A mixture of metal carbonyl vapors, say of iron carbonyl, with a non-oxidizing gas such as methane, nitrogen or hydrogen is introduced through line (3) and grid (5) into the lower portion of reactor (10) at a superficial velocity adapted to maintain the finely divided catalyst support in the form of a dense, turbulent, fluidized mass having a well defined upper level (L_{10}). Gas velocities of about 0.3—3 ft. per second are usually adequate at the particle sizes indicated to establish apparent densities of the fluidized solids mass of about 30—100 lbs. per cu. ft.

The mixture of $Fe(CO)_5$ vapors and non-oxidizing gas may be obtained by supplying its constituents in the proportion desired through lines (7) and (9), respectively, to line (3). However, the mixture may also be prepared by bubbling the non-oxidizing gas through a container of liquid iron carbonyl at room temperature and normal pressure.

Heating jacket (20) is supplied through tap (14) with a suitable heating fluid such as that sold under the Registered Trade Mark "Dowtherm" or superheated steam, so as to heat the fluidized solids mass in reactor (10) above the decomposition temperature of iron carbonyl, preferably to a temperature of about 600°—700° F. Spent heating fluid is withdrawn through tap (16). As a result of the excellent heat transfer and the perfect gas-solids distribution within the fluidized solids mass, the carbonyl iron formed is uniformly deposited throughout the fluidized mass to form a substantially uniform film of iron on the catalyst particles. The thickness of the iron film may be readily controlled to correspond to the concentration ranges specified above by a proper choice of the iron carbonyl concentration of the gas entering through line (3) and/or the contact time between gas and solids and/or the throughput of the gas-vapor mixture. Conditions suitable to establish an iron concentration of about 1—5% by weight include the decomposition of from about 4 to 20 pounds of iron carbonyl vapors on each 100 pound batch of catalyst support. The carbonyl vapors may be diluted with from about ½ to about 100 volumes of methane, nitrogen, or the like before passing it into the fluidizable catalyst support which is held at a temperature of about 600° F. A gas velocity of about 0.3—3 ft. per second and pressures up to about 400 psig, are employed. The preferred pressure range is about 5—10 psig.

The non-oxidizing gas and any excess iron carbonyl vapors are withdrawn overhead from (L_{10}) into separation zone (12) wherein most of the suspended solids settle out as a result of the decreased gas velocity. The gas is finally withdrawn through line (17) and may be recycled to the system, if desired, after further solids separation in conventional gas solids separators such as cyclones, precipitators, filters, etc. (not shown). Separated solids may be returned to reactor (10), passed to the synthesis reactor, or discarded.

The finished catalyst may either be withdrawn via overflow pipe (18) or via bottom drawoff line (22) to be directly supplied to a conventional fluid synthesis reactor. Instead of feeding the fresh support through line (1), it may be supplied through line (24) and suspended in the feed gases in line (3) in a manner known *per se* in the art of fluid catalyst operation. The system of the drawing may be operated continuously or batchwise as desired. A similar arrangement may be used for fixed bed activation of the catalyst support.

It will be understood that the system illustrated by the drawing may be used in a substantially analogous manner for the reactivation with a catalytic metal such as iron, of deactivated catalysts of the type here involved.

Referring now to Fig. 2 of the drawing, the system illustrated therein consists essentially of two conventional fluid reactors 220 and 250 whose functions and cooperation will be forthwith explained using the preparation of an iron type catalyst for the synthesis of hydrocarbons from CO and H_2 as an example. It will be understood, however, that other catalysts of the type here involved may be prepared in a substantially analogous manner.

In operation, feed hopper (201) contains a finely divided mass of an iron-containing material such as reduced iron ore, or metallic iron having a particle size of about 20—100 microns. The iron material may flow by gravity from hopper (201) through lines (203) and (205) into reactor (220). Simultaneously, CO or a gas rich in CO such as producer gas, water gas, synthesis feed gas or the like is supplied through line (207) to the bottom of reactor (220) which it enters through distributing means such as a perforated grid (209. If desired, the iron-containing material may be passed through lines (203) and (211) to gas feed line (207) to form a dilute solids-in-gas suspension therein which enters reactor (220) through grid (209) in a manner known *per se* in the art of fluid solids handling. Particularly in the latter case, line (203) may have the form of a conventional standpipe aerated through taps (213) and high enough to create the pseudo-hydrostatic pressure required to force the suspension in line (207) into reactor (220) against the combined gas and pseudo-hydrostatic pressures of the reactor. The feed rate of gases and solids and the superficial gas velocity within reactor (220) are so controlled that a dense turbulent fluidized mass (M_{220}) is formed having a density of about 40—100 lbs. per cu. ft. and a well defined upper level (L_{220}). Gas velocities of about 0.5—1.5 ft. per second are suitable for this purpose at the particle sizes indicated.

Reactor (220) is provided with conventional temperature control means such as a heat transfer coil (215) which may be supplied with a suitable heat transfer medium such as that sold under the Registered Trade Mark Dowtherm, steam or the like to maintain mass (M_{220}) at the desired reaction temperature of about 50° to 450° F. The pressure within reactor (220) is preferably kept at about 100 to 600 lbs. per sq. in. for the purposes of the present example. At these conditions, CO reacts rapidly with the iron to form iron carbonyl. Spent solids may be withdrawn downwardly from mass (M_{220}) through a withdrawal well (217) and pipe (219), normally at about the same rate at which fresh solids are supplied through lines (205) and/or (211). However, the rates of solids supply and withdrawal may be varied to change the bed level (L_{220}) and with it the solids hold-up and contact time within reactor (220). Quite generally the dimensions and operating conditions of reactor (220) are so chosen that a slight excess of metal carbonyl is formed over that necessary to meet the metal requirements in the decomposition stage as carried out in vessel (250). Unconverted iron withdrawn through line (219) may be returned to hopper (201) to be re-treated in reactor (220).

The CO-concentration of the gases introduced through line (207) is preferably so chosen that the CO is substantially completely consumed on its path through reactor (220). In this manner the free CO-content of the vapors discharging from reactor (220) is at a minimum which aids the subsequent decomposition reaction of the iron-carbonyl in reactor (250). If required for proper fluidization, the gas in line (207) may be diluted with inert gases such as CO_2, N_2, H_2, etc. In operations employing reactor (250) as the synthesis vessel, it is not necessary to effect high CO conversions in reactor (220). In this type of operation unreacted CO may be either recycled or blended with the feed gas to the synthesis reaction.

The iron carbonyl vapors formed in mass (M_{220}) are withdrawn overhead from level (L_{220}) and enter an enlarged disengaging space (222) wherein most of the entrained solids settle out as as result of the reduced gas velocity. Solids fines which remain suspended may be separated from the vapors in a conventional gas-solids separating system (224) which may comprise filters, cyclones, precipitators, etc. Solids separated in system (224) may be returned through line (226) to mass (M_{220}). The carbonyl vapors leave through line (228) and are passed through line (230) to reactor (250) to be treated therein as will be forthwith described.

A finely divided substantially inactive carrier such as a zinc-alumina spinel, a silica-alumina composite containing about 88% of Al_2O_3 and 12% SiO_2, or 50% SiO_2 and 3% Al_2O_3, or a silica-magnesia composite containing about 88% MgO and 12% SiO_2, or similar composites, which may be impregnated with about 0.5—10%, preferably about 1—5% of a promoter such as a halide, oxide, or carbonate of potassium or sodium and which may have a particle size of about 100—200 microns is supplied from hopper (232) through standpipe (234) and lines (236) and/or (238) to reactor (250) substantially as outlined in connection with reactor (220). Standpipe (234) is provided with aeration taps (240).

The iron carbonyl vapors supplied from line (228) substantially at the temperature of reactor (220) enter reactor (250) through line (230) and grid (242), if desired together with finely divided carrier material fed through line (238). The fluidization conditions within reactor (220) are substantially the same as those outlined in connection with reactor (220) except that the bed density of mass (M_{250}) having level (L_{250}) may be somewhat lower, that is about 20—60 lbs. per cu. ft. at the particle sizes and gas velocities specified. If desired a non-oxidizing gas such as H_2, N_2, etc. may be added in any suitable proportion through line (245) to aid in the fluidization of mass (M_{250}).

Reactor (250) is provided with suitable heating means such as a coil (244) containing a heating fluid such as that sold under the Registered Trade Mark Dowtherm, superheated steam, etc. so as to heat the fluidized mass in reactor (250) above the decomposition temperature of iron carbonyl, preferably to a temperature of about 600°—700° F. As a result of the excellent heat transfer and the perfect gas-solids distribution within the fluidized solids mass the carbonyl iron formed is uniformly distributed throughout mass (M_{250}) to form a substantially uniform film of iron on the surface of the carrier particles. The thickness of this film may be readily controlled within the ranges of metal content specified above by a proper choice of the iron carbonyl concentration of the gas entering through line (230) and/or the contact time between gas and solids and/or the throughput of the gas-vapor mixture.

Excess gases and unconverted iron-carbonyl vapors are withdrawn overhead from level (L_{250}) into disengaging zone (252) and gas-solids separator (254) from which separated solids may be returned through pipe (256). Gases and vapors now substantially free of solids may be either vented through line (258) or recycled through lines (260) and (228) to gas feed line (230) or through lines (260) and (261) to gas feed line (207) of reactor (220) to effect reduction and/or formation of carbonyls in reactor (220). Finished catalyst of the desired composition may be withdrawn through withdrawal well (247) and pipe (249) to be passed to storage or directly to a separate synthesis reactor (not shown). at a rate adequate to control the desired holdup and contact time in reactor (250) as outlined in connection with reactor (220).

In accordance with a preferred embodiment of the invention, reactor (250) may be the synthesis reactor itself operated at a synthesis temperature of about 600°—750° F. and a pressure of about 200—400 lbs. per sq. in. In this case a synthesis gas containing H_2 and CO in the ratio of about 1—2:1 is supplied through line (245). Reactor (250) may be supplied from hopper (232) with an amount of carrier material sufficient to establish the desired holdup in reactor (250). No substantial further addition of carrier material is required. The iron-carbonyl vapors may be supplied continuously or intermittently through line (228) either alternately or together with the synthesis gas in proportions adequate to maintain the desired iron concentration on the catalyst. Although there is a continuous addition of metal as carbonyl, the desired proportion may be substantially maintained by a corresponding loss of iron-rich fines through separator (254). Any loss of carrier material may be made up by a controlled supply from hopper (232). Instead of feeding the carbonyl vapors directly to reactor (250) they may be absorbed in a cooled recycle stream (262) of the fluidized material withdrawn from the reactor (250), before its return to the reactor. In this manner a more uniform distribution of the highly active metal is accomplished. The iron-rich fines lost through separator (254) may be recovered by any suitable means, such as oil scrubbing, and returned to hopper (201), for reuse.

When reactor (250) is used as the synthesis reactor the following operating conditions may be employed to give yields of C_4+ hydrocarbons amounting to about 180—190 cc./m³ H_2+CO consumed: pressure, 400 lbs.; temperature, 650° F.; H_2/CO ratio, 2/1; recycle ratio, 2—3/1; and a fresh feed rate corresponding to about 75—100 cu. ft./hr. of H_2+CO/lb. of iron.

It will be understood by those skilled in the art that standpipes (203) and (234) may be replaced by any suitable means for conveying finely divided solids such as screw conveyors, lock hoppers, etc.

The invention will be further illustrated by the following specific examples.

EXAMPLE I.

A zinc aluminate spinel ($ZnO.Al_2O_3$) was prepared by adding a $ZnSO_4$-solution to a solution of sodium aluminate, followed by filtering of the precipitate, drying and calcining at 1200° F. The product was impregnated with a K_2CO_3-solution, dried in an atmosphere of CO_2 and pilled. A portion of the catalyst now containing about 5% of K_2CO_3 was placed in a reactor and heated to about 625° F. A stream of nitrogen was bubbled through a vessel containing liquid iron carbonyl at room temperature and normal pressure and the gas partly saturated with $Fe(CO)_5$ was passed into the reactor containing about 50 cc. of the K_2CO_3 promoted zinc aluminate until about 1% by weight of carbonyl iron was deposited on the catalyst.

The untreated portion of the catalyst and that treated with iron carbonyl were employed as synthesis catalysts in a laboratory test unit at a temperature of about 625° F., a pressure of about 250 lbs. per sq. in., and an $H_2:CO$ feed ratio of 1:1.

The results of these runs are summarized below:

CATALYST	$ZnO.Al_2O_3+5\%\ K_2CO_3$	
	Untreated	Treated with $Fe(CO)_5$
Average Iron Content of Catalyst, wt. %	0.0	1.0
Hours on Stream	0.138	158—160
Synthesis Gas Feed Rate, v/v/hr.	400	260
CO-Conversion, %	5	98
Yield of C_4+, cc/cu.m. H_2+CO Cons.	Negligible	207
Average Carbon in Catalyst Bed, Excluding Wax, wt. %	Negligible	1.2

EXAMPLE II.

A Catalyst containing 46% carbonyl iron, 50% SiO_2, 3% Al_2O_3 and 1% K_2O was prepared substantially as described with reference to Fig. 2.

This material was tested in a fixed bed laboratory unit at the conditions and with the results listed below:

Temperature, °F.	600
Pressure, psig.	250
H_2/CO, Feed	1.17/1
V/V/Hr.	200
Run Hours	141—164
Material Balance, Wt. %	89
CO Conv., % Input	84
% Output	82
cc's Oil produced per cubic metre H_2+CO consumed	145
Distr. Ratio, C_4+C_1+	0.50
cc's and higher products produced per cubic metre H_2+CO consumed	215

The above data show that active and selective synthesis catalysts may be made by decomposing iron carbonyl on the fluidizable substantially inactive bases of the invention, such as synthetic spinels. Carbon formation was only a fraction of that of conventional iron catalysts of comparable activity and selectivity, indicating a superior resistance to disintegration. The catalyst of the invention thus combines highest activity and liquid product selectivity with low carbon forming tendencies and high resistance to attrition and disintegration, which makes it ideally suitable for fluid operation. An additional advantage resides in the fact that this improved performance may be accomplished with an iron concentration on the catalyst as low as about 0.2% by weight which may be readily maintained constant by continuous or intermittent reactivations with decomposing iron carbonyl.

While the above data were obtained in

fixed bed operation, it is noted that the catalysts of the invention compare just as favorably with conventional iron type catalysts in fluid operation, even though the higher gas throughputs, high recycle ratios and high catalyst turbulence typical for fluid operation quite generally cause a slight decrease of conversion and liquid product yields and an appreciable increase in carbon formation and catalyst disintegration. It follows that the catalysts of the present invention, as the result of the combination of characteristics demonstrated above, are particularly useful for fluid operation when prepared in fluidizable particle sizes substantially as outlined above. The conditions of fluid synthesis operation are well known in the art and need not be specified here in great detail for a proper understanding of the invention by those skilled in the art. Briefly, the conditions which are employed include temperatures of about 550°—750° F., pressures of about 200—650 lbs. per sq. in., catalyst particle sizes of about 50—150 microns, superficial gas velocities of about 0.3—3 ft. per second, bed densities of about 30—100 lbs. per cu. ft., H_2 : CO feed ratios of about 0.8—3 : 1, and recycle ratios of about 0.5—4.

Fluid operation of either or both the catalyst preparation and the hydrocarbon synthesis in the presence of the catalyst of the invention has the outstanding advantage over fixed bed operation that the iron concentration throughout the catalyst bed may be maintained substantially uniform as a result of the high turbulence of the fluidized bed. In fixed bed operation, on the other hand, the carbonyl iron is deposited preferentially on the first carrier layers contacted by the carbonyl during the preparation of the catalyst, which leads to serious disturbances in the operation of the process. This is illustrated by the fact that it was found that the first 10% of a carbonyl iron catalyst bed prepared in fixed bed operation contained about 8.4% of iron while the subsequent 90% of the bed contained only 0.19% of iron.

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. The method of preparing hydrogenation catalysts by contacting a vaporous carbonyl compound of a metal having hydrogenating activity with a dense turbulent fluidised mass of a substantially inactive non-metallic carrier material having a high resistance to disintegration under conditions such that the metal carbonyl is decomposed and a minor proportion of the metal is deposited onto the carrier material.

2. The method of claim 1 wherein the metal is selected from the carbonyl forming metals of Groups VI and VIII of the Periodic System.

3. The method of claims 1 or 2 wherein the metal is iron.

4. The method of any of claims 1 to 3 wherein the metal carbonyl is formed by contacting the metal in the form of a dense turbulent fluidised mass with carbon monoxide under suitable conditions of temperature and pressure.

5. The method as claimed in claim 4 wherein the metal carbonyl is formed in a first zone and decomposed to deposit the metal on the carrier in a second zone the exit gases from this second zone being recycled to the first zone.

6. The method as claimed in claim 5 wherein the said second zone is a conversion zone for the hydrogenation of carbon monoxide with hydrogen to form normally liquid hydrocarbons.

7. The method as claimed in any of claims 1 to 6 wherein the amount of metal deposited on the carrier material is from 0.2 to 10% by weight of the total catalyst.

8. The method as claimed in any of the above claims wherein the carrier material is a synthetic spinel preferably a zinc oxide-alumina spinel.

9. The method as claimed in any of claims 1 to 7 wherein the carrier matreial is a carbonate of a Group II metal.

10. The method as claimed in any of claims 1 to 7 wherein the carrier material has particle sizes between 20 and 200 microns preferably between 50 and 150 microns.

11. The method as claimed in any of the above claims wherein the catalyst is promoted with a small amount, preferably from 0.5 to 10% by weight of catalyst, of an alkali metal promoter, preferably potassium carbonate.

12. Hydrogenation catalysts whenever prepared according to any of claims 1 to 11.

13. An improved process for the catalytic hydrogenation of carbonaceous materials wherein there is used a hydrogenation catalyst as claimed in claim 12.

14. Improved hydrogenation catalysts and methods of preparing them as hereinbefore described with particular reference to the accompanying drawings.

Dated this 29th day of June, 1948.

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Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1951.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
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[This Drawing is a reproduction of the Original on a reduced scale.]

FIG. 1.

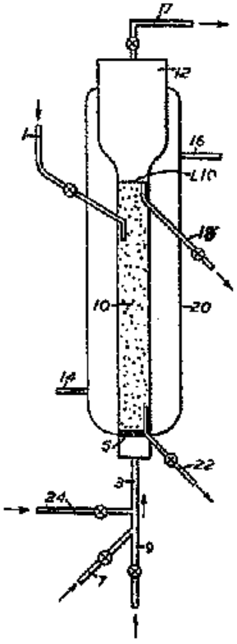

FIG. 2.