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(54) Fischer-Tropsch process with cobalt-promoted catalysts.

(57) Fe-Co spinels, containing low levels of cobalt, which are fully reduced/carburized ex situ, provide exceptionally high activity and selectivity in the conversion of CO/H_2 to C_2-C_{20} alpha olefins in both a fixed bed and slurry type process. These unsupported iron-cobalt catalysts maintain good activity and selectivity under low pressure reaction conditions.

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FISCHER-TROPSCH PROCESS WITH COBALT-PROMOTED CATALYSTS

FIELD OF THE INVENTION

The invention relates to a Fischer-Tropsch process for producing high amounts of C_2 to C_{20} olefins, particularly those in the C_2-C_4 range, using as a catalyst, an unsupported iron-cobalt single phase spinel, in which the atomic ratio of Fe:Co is 7:1 or above.

DISCLOSURE IN THE ART

Fischer-Tropsch processes have long been known to produce gaseous and liquid hydrocarbons containing olefins. Because of the importance of these olefins, particularly as feedstocks for the chemical industry, modifications of the Fischer-Tropsch process are constantly being pursued toward the goals of maximizing olefin selectivity with the particular objective of maintaining high catalyst activity and stability under the reaction conditions. The main thrust of the efforts in this area has been in the area of catalyst formulation.

Coprecipitated iron-based catalysts, including those containing cobalt, are known for producing olefins. High levels of cobalt in an iron-cobalt alloy are known to produce enhanced selectivity to olefinic products, as described in Stud. Surf. Sci. Catal. 7, Pt/A, pp. 432 (1981).

Other disclosures in the art directed to coprecipitated iron-cobalt catalysts and/or alloys include: U.S. Patent 2,850,515, U.S. Patent 2,686,195, U.S. Patent 2,662, 090, and U.S. Patent 2,735,862; AICHE 1981 Summer Nat'l Meeting Preprint No. 408, "The Synthesis of Light Hydrocarbons from CO and H_2 Mixtures over Selected Metal Catalysts" ACS 173rd Symposium, Fuel Division, New Orleans, March 1977; J. Catalysis 1981, No. 72(1), pp. 37-50; Adv. Chem. Ser. 1981, 194, 573-88; Physics Reports (Section C of Physics Letters) 12 No. 5 (1974) pp. 35-374; UK Patent Application No. 2050859A; J. Catalysis 72, 95-110 - (1981) ; Gmelins Handbuch der Anorganische Chemie 8, Auflage (1959), pp. 59; Hydrocarbon Processing, May 1983, pp. 88-96; and Chem. Ing. Tech. 49 (1977) No. 6, pp. 463-468.

There is further disclosed a method for producing high surface area metal oxides in the French article, "C. R. Acad. Sc. Paris", p. 268 (28 May 1969) by P. Courte and B. Delmon. The article describes a process for producing high surface area metal oxides by evaporating to dryness aqueous solutions of the corresponding glycolic acid, lactic acid, malic or tartaric acid metal salts. One oxide that was prepared by their described method was $CoFe_2O_4$.

However, the above references do not describe or suggest the use of single phase iron-cobalt spinels having an Fe:Co atomic ratio of 7:1 or above or suggest their applicability in conducting or carrying out Fischer-Tropsch processes for synthesizing olefins.

What is particularly desired in fixed bed Fischer-Tropsch processes are new catalysts for selectively producing high levels of olefins and low levels of methane under the desirable combined conditions of high catalyst activity and stability.

SUMMARY OF THE INVENTION

It has been found that an unsupported iron-cobalt single phase spinel which is isostructural with Fe_3O_4 as determined by X-ray diffractometry and possesses an initial BET surface area of about 0.1 m^2/g and greater and an iron:cobalt atomic ratio of 7:1 or greater provide desirable catalyst properties in Fischer-Tropsch processes. It has also been found that if a product predominating in C_2-C_6 olefins is desired, a smaller spinel surface area, such as for example, in the range of about 0.1 to 5 m^2/g, would be preferred while if a product predominating in C_2-C_{20} olefins is desired, a spinel surface area of greater than 5 m^2/g would be preferred.

Spinels can be conveniently prepared in a high temperature solid state sintering reaction in a temperature range of about 600 to 1100°C between stoichiometric amounts of mixtures of the component metal oxides and/ or metals, in an inert or vacuum atmosphere. The spinels prepared in this manner can then be treated, if desired, with promoter agents, such as Group IA or IIA metal salts, and particularly potassium carbonate. The resulting combined iron and cobalt/potassium atomic ratio is desirably in the range of about 20:1 to 200:1. The promoted catalyst is then reduced in a hydrogen containing gas and carbided before use in the Fischer-Tropsch process.

In accordance with the above-described procedure, there is provided a hydrocarbon synthesis catalyst composition comprising an unsupported iron-cobalt single phase spinel, said spinel having the initial empirical formula:

$$Fe_x\ Co_y\ O_4$$

wherein x and y are integer or decimal values, other than zero, with the proviso that the sum of x + y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 and said spinel having an initial BET surface area of up to about 5 m^2/g. If desired, the spinel can contain a promoter agent, such as Group IA or IIA metal salts.

Preferred embodiments of the composition include the substantially reduced and carbided form of the spinel, which is an active Fisher-Tropsch catalyst in processes for producing low molecular weight olefins.

Furthermore, the process for producing the subject spinel portion of the composition comprises, as mentioned above, the step of heating a mixture of cobalt and iron, as their oxides, free metals, or mixtures thereof, to produce the empirical composition: $Fe_xCo_yO_4$, where x and y are integers or decimal values, other than zero, and where the sum of x + y is 3, and the ratio of x/y is about 7:1, or above, for a time sufficient to produce said single phase spinel being isostructural with Fe_3O_4, and having a surface area of up to about 5 m^2/g.

There is further provided in accordance with the present invention, a process for synthesizing a hydrocarbon mixture containing C_2-C_6 olefins comprising the step of contacting a catalyst composition, comprised of an unsupported iron cobalt spinel, optionally promoted with Group IA or IIA metal salts, said spinel initially exhibiting a single spinel phase, being isostructural with Fe_3O_4, as determined by X-ray diffractometry, and possessing an initial BET nitrogen surface area of up to about 5 m^2/g, and an iron-cobalt atomic ratio of 7:1 or above, with a mixture of CO and hydrogen under process conditions of pressure, space velocity and elevated temperature for a time sufficient to produce said C_2-C_6 olefins.

Generally, it is preferred that the spinels have a surface area greater than 5 m^2/g and, it has been found that such high surface area, iron-cobalt catalysts can be prepared by the process of adding an alpha-hydroxy aliphatic carboxylic acid, e.g., glycolic acid, to an aqueous solution containing dissolved iron and cobalt salts and subsequently evaporating the solution to dryness to yield an amorphous mixed metal oxide, which on calcining at elevated temperature, exhibits a spinel crystal structure and possesses a high surface area.

These preferred unsupported high surface area Fe-Co spinels prepared in this manner, possess surface areas (BET) in the range of about 100-200 m^2/g (square meters per gram), which are significantly higher than corresponding Fe-Co spinels prepared by a process such as previously described.

After the optional addition of promoter agents, by surface deposition or impregnation, such as a Group IA or IIA metal salt, particularly an alkali carbonate, the high surface area spinels are then subjected to high temperature, e.g., 300-400°C, H_2 reduction to obtain a fully reduced alloy, followed by treatment with H_2/CO at 300-400°C to convert the alloy to a fully carburized state.

The resulting high surface are a reduced and carburized catalysts, provide unusually high activity, selectivity and activity maintenance in the direct conversion of CO/H_2 to alpha-olefins under reactor conditions. These catalysts are especially useful in low pressure slurry reactor systems where alpha-olefin residence times in the reaction zone can be minimized, and the physical properties of the catalyst bed are conducive to use of finely divided powdered catalyst.

In accordance with this last described procedure, there is provided a composition of matter comprising an unsupported, iron-cobalt spinel, optionally promoted with Group IA or IIA metal salts, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with FE_3O_4, and possessing a BET surface area greater than 5 m^2/g and an iron-cobalt atomic ratio of about 7 to 1 or above.

Further provided is a composition of matter comprising an iron-cobalt metallic alloy, being isostructural with metallic alpha-iron, as determined by X-ray diffractometry, and possessing a BET surface area greater than 5 m^2/g, said alloy being produced by contacting the above-described FE:Co spinel with a reducing atmosphere.

Also provided is a composition of matter comprising a reduced and carbided iron-cobalt alloy, said composition being substantially isostructural with Chi-Fe_5C_2 (Hagg carbide) , as determined by X-ray diffractometry, and possessing a BET surface area of about 0.1 m^2/g or greater, said composition produced by contacting the above-described iron-cobalt alloy with a carbiding atmosphere. A related composition is also provided being isostructural with Fe_3C (cementite) and having a BET surface greater than 5 m^2/g.

The process for producing the iron-cobalt spinel composition described above comprises the steps of: (a) evaporating a liquid solution comprising a mixture of iron and cobalt salts of at least one alpha-hydroxy aliphatic carboxylic acid, wherein the molar ratio of total moles of said acid to total moles

of said iron and cobalt, taken as the free metals, is about 1:1 or above, and wherein the atomic ratio of iron:cobalt, taken as the free metals in said mixture is greater than 2 to 1; yielding an amorphous residue; and (b) calcining said residue at elevated temperature for a time sufficient to yield an iron-cobalt spinel, exhibiting a single spinel phase, isostructural with Fe_3O_4, as determined by powder X-ray diffractometry.

The above-described iron-cobalt alloy composition of matter may be prepared by a process comprising contacting the above-described iron-cobalt spinel, with a reducing atmosphere under conditions of elevated temperature, pressure, space velocity for a time sufficient to substantially reduce the metal oxides of the spinel.

The above-described reduced and carbided spinel may be prepared by a process comprising the step of contacting the above-described iron-cobalt metal alloy, with a carbiding atmosphere under conditions of elevated temperature, pressure, space velocity, for a time sufficient to substantially carbide said alloy.

There is further provided by the present invention a process for synthesizing a hydrocarbon mixture containing C_2-C_{20} olefins comprising the step of contacting a catalyst composition, comprised of an unsupported iron cobalt spinel, said spinel initially exhibiting a single spinel phase being isostructural with Fe_3O_4, as determined by X-ray diffractometry, and possessing an initial BET surface area greater than 5 m^2/g and an Fe:Co atomic ratio of 7:1 or above, said contacting conducted with a mixture of CO and hydrogen under conditions of pressure, space velocity and elevated temperature for a time sufficient to produce said C_2-C_{20} olefins.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The subject iron-cobalt spinels useful in the subject process are as already noted compositions of matter which are isostructural with Fe_3O_4, as determined by x-ray diffractometry using copper K alpha radiation and exhibit a single spinel phase. By the term "spinel" is meant a crystal structure whose general stoichiometry corresponds to AB_2O_4, where A and B can be the same or different cations. Included within this definition is the commonly found spinel $MgAl_2O_4$. A and B can have the following cationic charge combinations: A = +2, B = +3, A = +4, B = +2, or A = +6, B = +1. Spinels are arranged of an approximately cubic close-packed arrangement of oxygen atoms with 1/8th of the available tetrahedral interstices and 1/2 of the octahedral interstices filled, and can exhibit hundreds of different phases. Further description of the spinel structure can be found in "Structural Inorganic Chemistry" by A. F. Wells, Third Edition, Oxford Press, and the article "Crystal Chemistry and Some Magnetic Properties of Mixed Metal Oxides With the Spinal Structure" by G. Blasse, Phillips Research Review Supplement, Volume 3, pp 1-30 (1964). By the term "isostructural" is meant crystallizing in the same general structure type in that the arrangement of the atoms remains very similar with only minor changes in unit cell constants, bond energies and angles. By the term "single phase spinel", as used herein, is meant one structural and compositional formula, corresponding to a single spinel material into which all of the metal components are incorporated, and exhibiting one characteristic X-ray diffraction pattern.

The subject iron-cobalt spinel possesses a BET surface area of about 0.1 m^2/g and greater, preferably greater than 5 m^2/g, as determined by the well-known nitrogen gas BET surface area measurement technique as described in the reference JACS 60, p. 309 (1938) by S. Brunauer, P. H. Emmett, and E. Teller. Generally, the spinel prepared by the above-described sintering of component oxides has a surface area of about 0.1 to 1 m^2/g. This range of surface area generally corresponds to a particle size range of about 1 to 10 microns. The spinel prepared by the above-described procedure of evaporating a liquid solution of a mixture of iron and cobalt salts of at least one alpha-hydroxy aliphatic carboxylic acid and calcining the residue at elevated temperatures has a surface area of greater than 5 m^2/g and generally in the range of about 50-300 m^2/g. This high surface area generally corresponds to a particle size range of about 0.01 to 0.002 microns.

The iron to cobalt atomic ratio of the metals in the spinel is about 7:1 or above and is preferably in the range of about 7:1 to 35:1 and particularly preferred in the range of 19 to 20:1.

The spinel can be represented by the formula: $Fe_xCo_yO_4$, wherein x and y are decimal or integer values, other than zero, and wherein the sum of x plus y is 3, and the ratio of x to y is 7:1 or above and preferably being about 7:1 to 35:1. Particularly preferred is where the iron to cobalt atomic ratio is about 19 to 20:1.

Representative examples of the various spinels corresponding to the formula are $Fe_{2.85}Co_{0.15}O_4$, $Fe_{2.625}Co_{0.375}O_4$, $Fe_{2.97}Co_{0.03}O_4$ and $Fe_{2.25}Co_{0.75}O_4$.

Physical properties in general of these subject spinels are similar to those of magnetite, Fe_3O_4, and include: melting point of above 1400°C, and color of brownish to blackish.

The iron-cobalt spinels are used in unsupported form in H_2/CO hydrocarbon synthesis.

A promoter agent can also be used in the composition and can be used to particularly promote olefin formation in the process. Representative examples of classes of suitable promoter agents include alkali metal and alkline earth metal salts including carbonates, bicarbonates, organic acid salts, i.e., acetates, inorganic acid salts, i.e. nitrates, halides, sulfates, and hydroxide salts of Group IA and IIA metals including lithium, sodium, potassium, cesium, rubidium, barium, strontium, magnesium, and the like. Preferably, the promoter agent is deposited or impregnated substantially on the surface of said spinel composition.

Representative examples of specific promoter agents are potassium carbonate, potassium sulfate, potassium bicarbonate, cesium chloride, rubidium nitrate, lithium acetate, potassium hydroxide, and the like. Preferred are the Group IA compounds and a particularly preferred promoter agent is potassium carbonate. The promoter, if used, is generally present in about a 0.1 to 10 gram-atom % as the metal ion of the total combined metal gram-atoms present. A preferred level of promoter agent is in the range of 1 to 2 gram-atom % of the total combined metal gram-atoms present. In the empirical formulas used herein, the amount of the promoter agent, e.g., potassium, is expressed in terms of gram atom percent based on the total gram-atoms of metals used. Thus, "1 gram-atom of potassium" signifies the presence of 1 gram-atom of potassium per 100 total gram atoms of combined gram atoms of Fe and Co. Thus, the symbol "1% K" as used herein indicates 1 gram-atom percent potassium based on each 100 gram atoms of the total combined gram atoms of iron and cobalt present.

A particularly preferred spinel composition of the subject invention is $Fe_{2.85}Co_{0.15}O_4$/1%K - (potassium taken as the carbonate).

The catalyst spinel in the subject process may also be used in conjunction and admixture with a diluent material; one which aids in heat transfer and removal from the catalyst bed. Suitable materials include powdered quartz, silicon carbide, powdered borosilicate glass, SiO_2, porous silica, kieselguhr, zeolites, talc, clays, Group II to VII metal oxides and rare earth oxides including TiO_2, SiO_2, Al_2O_3, MgO, La_2O_3, CeO_2, Cr_2O_3, MnO_2, and the like. Preferred is powdered quartz.

The diluent, if used, is generally used in a 1:4 to 9:1 diluent/spinel catalyst composition weight ratio. Preferred is a 1:1 weight ratio.

The utility of these spinels is their ability upon subsequent reduction and carbiding to form active catalysts in a Fisher-Tropsch process for making C_2-C_{20} olefins from CO/hydrogen.

The reduced and carbided forms of the above-described spinel are also subjects of this invention.

As hereinabove described, a low surface area spinel, i.e., up to about 5 m^2/g, can be prepared by a solid state high temperature reaction between (1) the component oxides, i.e. Fe_3O_4 and Co_3O_4, or (2) a mixture of iron metal, cobalt oxide and iron oxide, i.e. Fe metal, Co_3O_4 and Fe_2O_3, or (3) a mixture of cobalt metal, iron oxides and cobalt oxide, i.e. Co, Fe_3O_4, Fe_2O_3 and Co_3O_4 or (4) a mixture of iron and cobalt metals, iron oxide and cobalt oxide, i.e. Fe, Co, Fe_2O_3 and Co_3O_4, in the correct stoichiometric metals and oxygen ratio to result in the empirical formula for the composition as given above. Preferred is indicated reaction (1) between iron oxide and cobalt oxide. The reaction is conducted at temperatures in the range of about 600° to 1100°C and preferably from about 800 to 900°C, in an inert gas, oxygen-free atmosphere, or vacuum environment. Examples of useful inert gases are helium, nitrogen, argon, and the like. The solid state high temperature reaction "sintering" should be performed on thoroughly mixed samples of the metal oxides and/or metal and metal oxide mixtures. A method of forming the mixture is by intimate grinding and shaking. The sintering reaction should be conducted until a powder X-ray diffraction pattern indicates a single spinel phase is formed, being isostructural with Fe_3O_4, which generally requires about an 8 to 24 hour period and preferably about a 12 to 18 hour period. Generally, at the end of each reaction period the material is thoroughly ground and mixed and then resubjected to the high temperature conditions for an additional 1 to 5 cycles or until powder x-ray diffraction reveals the presence of a single spinel phase.

As hereinabove described, the preferred high surface area i.e. greater than about 5 m^2/g, spinel composition can be made by a process in which an aqueous solution of cobalt and iron salts of an alpha-hydroxy aliphatic carboxylic acid, is evaporated to dryness, leaving an amorphous residue, which is then heated at elevated temperature to substantially form the spinel, in a single spinel phase, being isostructural with Fe_3O_4 and possessing a surface area greater than 5 m^2/g, preferable above 50 m^2/g. The heating is conducted such that no significant loss in surface area of the final spinel is incurred.

The key to the synthesis of the subject spinels is in the use of an organic, saturated, aliphatic, alpha-hydroxy carboxylic acid to form a complex salt, which is soluble in the aforementioned aqueous medium, at a pH on the acidic side, i.e., pH of 5-7. The solubility of the iron and cobalt organic salts of the alpha-hydroxy carboxylic acid prevent crystallization from occurring, resulting in a crystalline product being obtained from the solution, which would possess a relatively low surface area.

The subject method utilizes an alpha-khydroxy aliphatic carboxylic acid which acts as a solubilizing agent for the iron and cobalt salts in the aqueous solution. Any saturated aliphatic alpha-hydroxy carboxylic acid, containing at least one alpha-hydroxy grouping, can be used to form the soluble iron and cobalt salts in the subject invention process in mildly basic aqueous solution, is deemed to be included within the scope of this invention. Representative examples of such acids which can be mono-hydroxy or di-hydroxy or mono-carboxylic or di-carboxylic are glycolic, malic, glyceric, mandelic, tartaric, lactic acids and mixtures thereof. A preferred carboxylic acid used in the process is glycolic acid.

The amount of acid used is at least the stoichiometric amount, i.e., 1 to 1 molar ratio for each metal present and preferably in about a 5-10% molar excess of the stoichiometric amount. Higher ratios can be used, if it is economical to do so. Lower amounts can also be used but would result in incomplete iron and cobalt acid salt formation.

The first step in the process comprises forming an aqueous solution by dissolving iron salts and cobalt salts, in a water-soluble salt form such as their nitrates, sulfates, chlorides, acetates, and the like, in water.

The concentration of the salts in the aqueous liquid is not critical to the extent that the salts are present in less than a saturated solution to avoid precipitation. For example, an 80-90% saturated solution, of combined dissolved metal molarities for avoiding precipitation in the process, can be effectively used.

The temperature of the aqueous solution is not critical and may be above room temperature to aid in the solubilizing process. However, room temperature is adequate and is the temperature generally used in the process. The pressure also is not critical in the process and atmospheric pressure is generally used.

The aqueous solution can also contain a small amount of organic solvent such as ethanol, acetone, and the like for aiding in the solubilizing of the iron and cobalt salts of the alpha-hydroxy carboxylic acid.

Following the dissolving of the iron and cobalt salts, the alpha-hydroxy carboxylic acid is added, together with a sufficient quantity of base, usually being ammonium hydroxide, sodium hydroxide, potassium hydroxide, and the like, preferably ammonium hydroxide, to solubilizing the resulting acid salts. The amount of base added is sufficient to keep the pH in the range of about 5 to 7.0.

It should be noted that the exact sequence of steps need not be adhered to as described above, with the proviso that the resulting aqueous solution contain dissolved iron and cobalt salts in stoichiometric amounts as iron and cobalt salts of alpha-hydroxy carboxylic acid in solution. If there are any insoluble materials present after addition of the base and organic acid, they should be filtered prior to the evaporation step.

At this point, the resulting solution is evaporated, as for example, by air drying, or under reduced pressure, at elevated temperature, as practiced in a rotary evaporator, or in a vacuum drying oven.

The resulting material from the evaporation step is an amorphous residue, generally being a powder. This residue is heated at elevated temperature at 100 to 600°C for about 1 to 24 hours in generally air to result in a substantially single spinel phase which is isostructural with Fe_2O_4, as determined by X-ray diffractometry, as previously described herein. Preferred temperature range is 100-400°C, and particularly preferred is about 350°C for single phase spinel formation.

The details of the preparation of the high surface area spinel as well as reduced iron-cobalt alloys formed from the spinel by reduction and carbiding procedures are fully set out in U.S. Patent 4,518,707 and are not included in the present invention.

Prior to the hydrocarbon synthesis run, the iron-cobalt spinel is reduced in a reducing atmosphere at elevated temperature, generally in a temperature range of about 200 to 500°C and preferably 300 to 450°C. The reduction can be carried out with various reducing gases including hydrogen, CO, and mixtures thereof, and the like. Preferably, hydrogen gas, either by itself or in an inert carrier medium such as helium, neon, argon, or nitrogen, is preferably used. The pressure of the reducing gas in this procedure may be in the range of 1.5 to 1000 psig and preferably in the range of 15 to 150 psig. The reducing gas feed rate may be in the range of 1-10,000 V/V/hr and preferably in the range of 10-1000 V/V/hr. The reduction is carried out until the resulting Fe-Co alloy is substantially reduced and exhibits a powder X-ray diffraction pattern isostructural with alpha iron. This reduction usually requires about 2-20 hours.

In the reduction treatment of the low surface area spinel, the resulting reduced spinel generally has a BET surface area of up to 3 m^2/g and is useful in forming a carbided iron-cobalt catalyst useful in the subject Fischer-Tropsch process for making C_2 to C_6 olefins as described herein.

In the reduction of the high surface area spinel the resulting reduced spinel has a BET surface area of greater than 5 m^2/g, preferably in the range of about 5-10 m^2/g and particularly preferred in the range of about 6-8 m^2/g. These are useful in forming a carbided iron-cobalt catalyst useful in the embodiment of the subject Fischer-Tropsch process for making C_2-C_{20} olefins.

The iron-cobalt alloy can be prepared ex situ in a tube reactor or in situ in a Fischer-Tropsch slurry process. The in situ preparation is conducted in the slurry apparatus when the above-described spinel is reduced while suspended in the slurry liquid, in a reducing atmosphere being preferably a hydrogen atmosphere at elevated temperature being about 240°C, or above, preferably at 240-300°C, at a space velocity, pressure, and hydrogen concentration sufficient to cause substantial reduction of the spinel to the alloy. Substantial reduction is complete when the X-ray diffraction pattern shows a pattern substantially isostructural with alpha-iron.

The iron-cobalt catalyst which is believed to be the primary active catalyst in the process can be produced by carbiding the reduced iron-cobalt spinel, described hereinabove, generally having an X-ray diffraction pattern isostructural with chi Fe_5C_2 (Hagg carbide) , by heating at elevated temperature in a suitable carbiding atmosphere, containing CO, H_2/CO, and mixtures thereof. The spinel can also be reduced and carbided, concurrently, by contact with a CO/H_2 atmosphere under the hydrocarbon synthesis conditions described below.

Carbiding atmospheres which can be used include CO/hydrogen, aliphatic hydrocarbons, acetylene, aromatic hydrocarbons, and the like. A preferred carbiding atmosphere is CO/hydrogen. When using a CO/hydrogen carbiding atmosphere, mixtures of CO/hydrogen can be used in a 10:1 to 1:10 molar volume ratio. A preferred ratio used for carbiding purposes is 1:1 molar ratio.

The carbiding step is generally conducted at a temperature of 300 to 450°C and preferably 350 to 400°C. The pressure is generally about 0.30 psig, and a space velocity of about 200-1000 V/V/hr are chosen in order to completely carbide the reduced iron-cobalt spinel which can be subjected to X-ray diffractometry to determine when the material becomes isomorphous with chi-Fe_5C_2. At carbiding temperatures above about 450°C, the resulting Hagg type carbide, $Fe_{5-(5/3)y}Co_{(5/3)y}C_2$, becomes unstable and can rearrange crystallographically to the corresponding cementite type structure, $Fe_{3-y}Co_yC$. Also, in the ex situ carbiding step, a significant amount of carbon is also formed on the surface of the catalyst which tends to increase the surface area of the reduced, carbided catalyst.

A preferred method of carbiding the alloy is in situ in the slurry liquid to be used in a slurry Fischer-Tropsch process. A particularly preferred method is where the spinel is treated with a mixture of CO/hydrogen and reduced and carbided in situ in one step prior to hydrocarbon synthesis. The pressure is generally about 1 atmosphere, and a space velocity of about 20-20,000 V/V/hr is chosen in order to completely carbide the starting iron-cobalt oxide which can be determined by X-ray diffractometry when the material becomes isostructural with Haag carbide, Fe_5C_2. The Haag-type Fe-Co carbides produced in this process are of the general formula: $Fe_{5-(5/3)y}Co_{(5/3)y}C_2$, and also include surface carbon produced during the carbiding process. Carbiding temperatures above 500°C and preferably 500-700°C, lead to formation of a mixed Fe-Co carbide of the general formula $Fe_{3-y}Co_yC$, which is generally formed under ex situ procedures which allow the use of higher temperatures than possible in the in situ slurry process.

The above-described reduced spinel and carbided spinel, when prepared ex situ are generally pyrophoric and inconvenient to handle. In that case, the material is generally passivated by contact with 1 volume oxygen in 100 volumes of helium for a sufficient time to reduce or eliminate the pyrophoric nature. Generally, the oxygen used in the passivating process is used in an inert gas stream carrier such as helium for a sufficient time to cause passivation. Generally, this is conducted at room temperature and atmospheric pressure and space velocity which are convenient and easy to control and to result in an efficient process needed for complete passivation.

The Fischer-Tropsch process utilizing the catalysts described herein may be operated as a fixed bed process or as a slurry-type process wherein the catalyst is suspended in a liquid hydrocarbon and the CO/hydrogen mixture forced through the catalyst slurry allowing good contact between the CO/hydrogen and the catalyst to initiate and maintain the hydrocarbon synthesis process.

Advantages of a slurry process over that of a fixed bed process are that there is better control of the exothermic heat produced in the Fischer-Tropsch process during the reaction and that better control over catalyst activity maintenance by allowing continuous recycle, recovery, and rejuvenation procedures to be implemented. The slurry process can be operated in a batch or in a continuous cycle, and in the continuous cycle, the entire slurry can be circulated in the system allowing for better control of the primary products residence time in the reaction zone.

The slurry liquid used in the process is a liquid at the reaction temperature, must be chemically inert under the reaction conditions and must be a relatively good solvent for CO/hydrogen and possess good slurrying and dispersing properties for the finely divided catalyst. Representative classes of organic liquids which can be utilized are high boiling paraffins, aromatic hydrocarbons, ethers, amines, or mixtures thereof. The high boiling paraffins include C_{10}-C_{50} linear or branched paraffinic hydrocarbons; the aromatic hydrocarbons include C_7-C_{20} single ring and multi-and fused ring aromatic hydrocarbons; the ethers include aromatic ethers and substituted aromatic ethers where the ether oxygen is sterically hindered from being hydrogenated; the amines include long chain amines which can be primary, secondary, and tertiaryamines wherein primary amines preferably contain at least a C_{12} alkyl group in length, secondary amines preferably contain at least two alkyl groups being C_9 or greater in length, and tertiary amines preferably contain at least three alkyl groups being C_6 or higher in length. The slurry liquid can contain N and O in the molecular structure but not S, P, As or Sb, since these are poisons in the slurry process. Representative examples of specific liquid slurry solvents useful are dodecane, tetradecane, hexadecane, octadecane, cosane, tetracosane, octacosane, triacontane, dotriacontane, hexatriacontane, tetracontane, tetratetracontane, toluene, o-, m-, and p-xylene, mesitylene, C_1-C_{13} mono-and multialkyl substituted benzenes, dodecylbenzene, naphthalene, anthracene, biphenyl, diphenylether, dodecylamine, dinonylamine, trioctylamine, and the like. A preferred liquid hydrocarbon slurry solvent is octacosane.

The amount of catalyst used in the liquid hydrocarbon slurry solvent is generally about 10 to 60 g. of dry catalyst per 500 g. slurry liquid. Preferably about 30 to 50 g. dry catalyst per 500 g. slurry liquid slurry is utilized, being in about a respective 5:1 to 10:1 weight ratio.

The slurry system, comprised of the slurry liquid and finally divided catalyst, is generally stirred to promote good dispersion during the pretreatment process to avoid catalyst settling and to eliminate mass transport limitations between the gas and liquid phases. In a typical laboratory unit the rate of stirring is generally carried out in the range of about 600 to 1200 rpm and preferably 1000 to 1200 rpm.

Prior to the CO/hydrogen hydrocarbon synthesis run, the reduced and carbided iron-cobalt catalyst is generally conditioned in the slurry by purging with nitrogen to remove reactive oxygen-containing gases and then the temperature is increased while stirring to the reaction temperature range. Then the system is generally subjected to a hydrogen treatment for a sufficient time to insure complete removal of any surface metal oxide present which would interfere in hydrocarbon synthesis. The pressure and space velocity during the inert gas-hydrogen conditioning step are not critical and can be utilized in the range which is actually used during actual hydrocarbon synthesis.

Following the hydrogen reduction step, the CO/hydrogen feedstream is introduced into the slurry catalyst chamber and the pressure, space velocity, temperature, and hydrogen/CO molar ratio is then adjusted, as desired, for hydrocarbon synthesis conditions.

In the slurry process, the hydrogen and CO are used in a molar ratio in the gaseous feedstream in about a 10:1 to 1:10 molar ratio, preferably 3:1 to 0.5:1, and particularly preferred 1:1 to 2:1 molar ratio.

The temperature in the slurry process is generally in the range of about 200 to 300°C, preferably being 230 to 270°C, and particularly preferred of about 240-260°C. Higher temperature ranges can also be used but tend to lead to lighter products and more methane, lower temperature ranges can also be used but tend to lead to lower activity and wax formation.

The pressure useful in the slurry process is generally conducted in the range of about 50 to 400 psig and preferably about 70 to 225 psig. Higher pressures can also be used but tend to lead to waxy materials particularly in combination with lower temperature.

The space velocity, expressed as standard hourly space velocity (SHSV), used in the slurry process is generally about 100 to 4,000 volumes of gaseous feedstream/per volume of dry catalyst in the slurry/per hour and is preferably in the range of about 400 to 1,200 V/V/hr, and particularly preferred of 800-1,200 V/V/hr. Higher space velocities can also be used but tend to lead to lower % CO conversions, and lower space velocities can also be used but tend to lead to more paraffinic products.

Generally, after the pretreatment the CO/hydrogen feedstream is introduced to initiate and maintain hydrocarbon synthesis. By the use of the above-described catalysts in the system, the activity maintenance is very good and on a laboratory scale, e.g., 500 cc of slurry containing 50 g. of catalyst described herein, 30 days of continuous run have been observed without significant decline in percent CO conversion activity while maintaining good olefin synthesis activity.

The percent CO conversion obtainable in the subject process, while providing substantial quantities of olefins, ranges from about 30 to 80 percent or higher.

"Total hydrocarbons" produced in the process is related to the selectivity of percent CO conversion to hydrocarbons being hydrocarbons from C_1 to about C_{40} inclusive and is generally about 0 to 75 percent of the total CO converted, the remainder being converted to CO_2.

In that embodiment of the subject process utilizing a low surface area catalyst, the percent C_2-C_6 hydrocarbons of the total hydrocarbons produced including methane and above is about 10 to 30 wt.%. The percent of C_2-C_6 olefins produced, of the C_2-C_6 total hydrocarbons produced is about 80 to 90 wt.%. The olefins produced in the process are substantially alpha olefins. In the embodiment utilizing a high surface area catalyst, i.e., greater than 5 m^2/g, the percent of C_2-C_{20} hydrocarbons of the total hydrocarbons produced is about 60 to 90 wt.%. The percent of C_2-C_{20} olefins produced, of the C_2-C_{20} total hydrocarbons produced is about 60 to 70 wt.%. Again, the olefins produced are substantially alpha olefins.

The selectivity to methane based on the amount of CO conversion is about 1 to 10 weight percent of total hydrocarbons produced. Preferably about 5 percent, and lower, methane is produced in the process.

Preferably, the reaction process variables are adjusted to minimize CO_2 production, minimize methane production, maximize percent CO conversion, and maximize percent C_2-C_{20} and particularly C_2-C_4 olefin selectivity, while achieving activity maintenance in the catalyst system.

Generally, this format can be derived in a preferred mode of operating the process where the slurry liquid used is hexadecane, the catalyst used is reduced, carbided $Fe_{2.85}Co_{0.15}O_4$/1 % K as K_2Co_3, the catalyst liquid weight ratio is 40/500, the system is stirred at 600-1200 rpm, and the pretreatment procedure is conducted in situ in a single step using 9:1 H_2/N_2, at 220°C, atmospheric pressure, 1200 V/V/hr space velocity for a period of up to 5 hours, and the olefins synthesis process conducted at a hydrogen:CO molar ratio of 1:1, a temperature of about 245°C, a pressure of about 7-150 psig, and space velocity 1000-1200 V/V/hr. By carrying out the above process in the stated variable ranges efficient activity maintenance and production of C_2-C_{20} and particularly C_2-C_6 olefins can be achieved.

The effluent gases in the process exiting from the reactor may be recycled, if desired, to the reactor for further CO hydrocarbon synthesis.

As hereinbefore mentioned, the subject process may be carried out as a fixed bed process utilizing the claimed catalysts described herein.

Prior to the CO/hydrogen hydrocarbon synthesis fixed bed run, the iron-cobalt spinel is generally conditioned in the apparatus by purging with nitrogen to remove reactive gases and then the temperature is increased to the reaction temperature range. Then the system is generally subjected to the above-described hydrogen treatment for a sufficient time to insure complete reduction of metal oxides. However, the pressure, space velocity, and temperature during this reduction step are not critical and can be utilized in the range which is actually used during actual hydro-carbon synthesis.

Following the reduction step, the CO/hydrogen feedstream is introduced into the fixed bed apparatus catalyst chamber and the pressure, space velocity, temperature, and hydrogen/CO molar ratio are then adjusted as desired, for hydrocarbon synthesis conditions. Optionally, the reduction/carbiding can be carried out concurrently by contact with the CO/H_2 mixture at elevated temperature.

In the fixed bed process, the hydrogen and CO are used in a molar ratio in the gaseous feedstream of about a 10:1 to 1:10, preferably about a 3:1 to 0.5:1 molar H_2/CO ratio and more preferably 1:1 to 2:1 molar ratio. Higher and lower molar ratios may also be used.

The temperature in the fixed bed process is generally in the region of about 200 to 300°C and preferably being 250 to 280°C. Higher temperatures, such as in the range 300-350°C, tend to promote higher % CO conversion, lighter products, more methane and more CO_2, formed from the water-gas shift reaction.

The pressure useful in the fixed bed process is generally conducted in the range of about 50 to 1000 psig and preferably about 100 to 300 psig. Higher and lower pressures can also be used.

The space velocity, used in the fixed bed process is expressed as "standard" hourly space velocity (SHSV) and is generally about 200 to 4000 volumes of gaseous feedstream/per volume of dry catalyst (excluding diluent)/per hour and is preferably in the range of about 400 to 1200 V/V/hr. Higher and lower space velocities can also be used where higher space velocities tend to lead to increased olefin contents but decreased % CO conversion.

The percent CO conversion obtainable in the subject fixed bed process while providing substantial quantities of C_2-C_6 olefins, ranges from about 20 to 98% and preferably above about 30%. Higher and lower ratio percentages of CO conversion may also be utilized.

"Total hydrocarbons" produced in the fixed bed process is related to the selectivity of percent CO conversion to hydrocarbons, being hydrocarbons from C_1 to about C_{40} and above inclusive, and is generally about 0 to 50 percent, and higher, of the total CO converted and the remainder being substantially converted to Co_2.

The percent total C_2-C_6 hydrocarbons of the total hydrocarbons produced in the fixed bed process, including olefins and paraffins is generally about 20 to 80 wt. % and preferably about 50 to 80 wt. %. The percent of C_2-C_6 olefins produced of the C_2-C_6 total hydrocarbons produced is generally about 50 to 90 wt. % and preferably about 70 to 90 wt. % of the C_2-C_6 total hydrocarbons. The olefins produced in the process are substantially alpha olefins.

The selectivity to methane in the fixed bed process based on the amount of CO conversion is about 2 to 12 weight percent of total hydrocarbons produced. Preferably about 10 percent and lower methane is produced in the process.

As discussed above, the percent selectivity to CO_2 formation in the process is in the range of about 10 to 50 percent of CO converted, and generally about 30 to 50 percent.

The reaction process variables in the fixed bed process are preferably adjusted to minimize CO_2 production, minimize methane production, maximize percent CO conversion, and maximize percent C_2-C_6 olefin selectivity, while achieving activity maintenance in the catalyst system.

The catalyst in the process may become contaminated with high molecular weight hydrocarbons on exposure to carbon monoxide hydrogenation reaction conditions. As a result of this catalyst activity may be diminished. In the event that this is observed it may be possible to recover nearly full catalyst activity by exposing the catalyst to a solvent wash and/or hydrogen treatment at elevated temperatures. We have found that this procedure can in some cases restore the catalyst with its initial performance characteristics.

Generally, this format can be achieved in a preferred mode of operating the fixed bed process where the formula of the catalyst used is $Fe_{2.85}Co_{0.15}O_4$/1% K. The pretreatment procedure is conducted at 500°C in a 9:1 H_2/N_2 stream @ 680 v/v/hr. under 100 psig for 5-7 hours, and the hydrocarbon synthesis run is conducted at the CO/hydrogen molar ratio is 1:1 to 2:1, the temperature is conducted in the range 230-270°C, at a pressure of 150-300 psig, and space velocity 1000-1800 v/v/hr (SHSV). By carrying out the above process in the stated variable ranges efficient activity maintenance and production of C_2-C_6 olefins can be achieved.

The effluent gases in the process exiting from the reactor may be recycled if desired to the reactor for further CO/hydrocarbon synthesis.

Methods for collecting the products in the process are known in the art and include distillation, fractional distillation, and the like. Methods for analyzing the product liquid hydrocarbons and gaseous streams are also known in the art and generally include gas chromatography, liquid chromatography, high pressure liquid chromatography and the like.

Apparatus useful in the subject process can include any conventional fixed bed type reactor, being horizontal or vertical, moving bed, fluid bed, and the like or any conventional slurry-type reactor for carrying out the slurry-phase type of operation. The slurry-type reactors can be horizontal or vertical, stationary or cyclical. Other apparatus not specifically described herein will be obvious to one skilled in the art from a reading of this disclosure.

The following examples are illustration of the best mode of carrying out the claimed invention as contemplated by us and should not be construed as being limitations on the scope and spirit of the instant invention.

EXAMPLE 1

Solid solutions with the generic empirical formula: $Fe_{3-y}Co_yO_4$/1%K (1 gram-atom percent potassium as the carbonate) were prepared by the following procedure. Mixtures of Fe_2O_3, Fe metal and Co_3O_4 in the following molar ratios, (4/3 -4y/9) Fe_2O_3 + 1/3 (1-y/3) Fe + y/3 Co_3O_4,where the value of y independently was: 0, 0.03; 0.150; 0.375; and 0.750, corresponding respectively to the following weights in grams of Fe_2O_3, Fe metal, and Co_3O_4; 21.080, 1.8400, 0.00; 22.750, 1.9891, 0.2594; 21.797, 1.9054, 1.2974; 20.0163, 1.7502, 3.2338; 11.381, 0.9590, 4.2904. The materials - (reagent quality or better from Alfa Chemicals Co.) were well mixed, placed into a quartz tube, evacuated to 10^{-3} torr, sealed in the tube under vacuum and then heated to 800°C for 24 hours. The resulting solids were isolated after cooling and breaking the tube open, ground to a powder, and resubjected to the same high temperature sintering procedure, at 800° to 1000°C for an additional 24 hours. Powder X-ray diffraction analysis was then conducted to ensure that the sintered material was isostructural with pure standard sample of Fe_3O_4. The catalyst powder was then pelletized and sintered in a sealed tube as described above under vacuum at 1000°C for several hours. The sintered pellets were then crushed, seived and the resulting pellets impregnated with aqueous potassium carbonate to achieve the desired potassium loading,

being about 1 gram-atom percent potassium, and dried. The BET (nitrogen) surface areas measured were in the range from about 0.25 to 0.30 m^2/g. The results are listed below in Table I.

TABLE 1

Composition	$Fe_{3-y}Co_yO_4/1\%$ K	
	y	BET (m^2/g)
Control	0.00	0.27
A	0.0275	0.30
B	0.150	0.29
C	0.375	0.25
D	0.750	0.28

The powder x-ray diffraction spectrum of each of the obtained Fe-Co spinels showed that they were a single phase and isostructural with Fe_3O_4. They differed from one another in slight shifts of the 2 theta reflection values without altering the overall profile.

EXAMPLE 2

Catalyst B, $Fe_{2.85}Co_{.15}O_4/1\%$ K, where y = 0.15, was prepared by the procedure described in Example 1. X-ray diffraction analysis showed this material to be isostructural with Fe_3O_4, although there was a slight change in the unit cell constant where the unit cell constant is about 0.01 to 0.02 Å smaller than that of Fe_3O_4. The sintered material was found to have a low surface area, less than 5 m^2/g. This material was crushed and sieved to 20-80 mesh before use in this example under F-T (Fischer-Tropsch) fixed bed reaction conditions. The reactor was charged with 8.8 cc of catalyst with a thermocouple placed at the center of the bed. The catalyst compositions of 20-80 mesh particle size, were pretreated with hydrogen gas in nitrogen - (90% hydrogen/nitrogen) at 500°C, 100 sccm (680 v/v/hr.) of hydrogen gas at 100 psig for 5 to 7 hours in a fixed bed tubular vertical reactor constructed of 316 stainless steel, and being 0.51" internal diameter and 15" long. The runs were conducted using a 1:1 H_2/CO mixture, at 570 v/v/hr., 300 psig, at the indicated temperatures, which are furnace temperatures in this and the remaining examples unless otherwise indicated as bed temperatures. In many of the cases, the bed temperature was 10-30°C higher than the indicated furnace temperature, due to primarily to the limited heat removal capabilities of the reactor system and the highly exothermic nature of the reaction. The overall collected products which were collected after catalyst pretreatment, and one hour on stream with CO/H_2, were analyzed by gas chromatography.

Representative results obtained with catalyst composition B, $Fe_{2.85}Co_{0.15}O_4/1\%K$, relative to the control (see Table I) are presented below in Table II.

TABLE II

Catalyst	Fe_3O_4/1%K[a]	$Fe_{2.85}Co_{0.15}O_4$/1%K[b]
Temp °C	305	270
% CO Conversion	79	98
% CO to CO_2	36	42
% CO to HC[c]	43	56
Wt. % Selectivity		
CH_4	8.5	9.1
C_2H_6	2.1	4.3
C_2H_4	6.5	9.8
C_3H_8	1.4	1.9
C_3H_6	10.6	20.3
C_4H_{10}	1.7	tr.
C_4H_8	9.5	9.3
C_5^+	59.7	45.2

[a]Control.

[b]Composition B.

[c]Hydrocarbons.

As is seen from the data, Catalyst B, derived from the cobalt-containing spinel, exhibited greater activity at lower temperatures and higher C_2-C_4 olefin selectivity than the all iron control catalyst.

It should be noted that unless stated differently herein, the catalysts used in each of the following examples were in powder form of 20-80 mesh, used as is, or diluted with crushed quartz powder, totalling a catalyst volume of about 8-8.8 cc.

Further, the apparatus used was the same as described in this Example 2 and the pretreatment procedure was substantially the same as described in Example 2.

Values for selectivity weight percentages of product hydrocarbons are reported on a CO_2-free basis unless otherwise stated.

EXAMPLE 3

Four (4) cc. of Catalyst B, described above in Example 2, was mixed with 20-80 mesh solid quartz powder (crushed quartz tubes) in 4.0 cc quantity, and the mixture was placed into the reactor described in Example 1, and pretreated by contacting with a 9:1 H_2/N_2 feedstream at 500°C, 750 v/v/hr., 100 psig, for 5.5 hours.

The mixed diluted catalyst was then contacted with 1:1 H_2/CO at 270°C, 300 psig, at 2000 v/v/hr. for 12 hours on stream. The product distribution was analyzed by gas chromatography, and the results are given below in Table III.

TABLE III

Catalyst	1:1 Catalyst B/quartz powder
% Conversion	62
% CO to CO_2	24
% CO to H.C.	38
Wt. % Selectivity	
CH_4	9.2
C_2^o-C_5^o	7.9
$C_2^=$-$C_5^=$	48.2
C_6^+	34.7

As is seen from the data, the catalyst derived from the iron-cobalt spinel provides good activity and high C_2-C_5 olefin selectivity with high H/CO feed rates.

EXAMPLE 4

Catalyst B, in a 1:1 admixture with crushed quartz, as described in Example 3, was run under a different set of F-T synthesis conditions as described below.

Following substantially the same pretreatment, described in Example 3, about 8 cc of the catalyst in the same described apparatus as above was contacted with 1:1 H_2/CO, at a bed temperature of 250° to 270°C, a standard hourly space velocity - (SHSV) of 1000 v/v/hr. at 300 psig, for 12 hours. The products were collected and the product distribution data were analyzed by gas chromatography. Results are given below in Table IV.

TABLE IV

% CO conversion	98
% CO to CO_2	43
% CO to HC	55
Wt. % Selectivity CH_4	7.2
$C_2^=/C_2^o$	2.6
C_2/C_1	2.1
% C_2-C_6	50.8
% Olefins (of C_2-C_6 total)	86
C_7^+	42

As is seen from the data, the Fe-Co Catalyst B generates a C_2-C_6 fraction which is olefin rich even at high conversion conditions.

EXAMPLE 5

Catalyst B and the control, prepared by the procedure described in Example 1, were pretreated by the procedure described in Example 3 in the apparatus described in Example 2.

Each catalyst in 8 cc volume, after pretreatment, was contacted with 1:1 H_2/CO at 300 psig pressure, 1000 v/v/hr. (SHSV) for 12 hour run times at the temperatures listed below in Table V, in same apparatus described in Example 2. Product samples were collected and analyzed after 12 hours onstream with CO/H_2.

TABLE V

	Catalyst B	Control	Control
% CO Conversion	98	67	87
% CO to CO_2	40	31	37
% CO to HC	58	36	50
Temp. °C	270	305	340
$C_2:C_1$	2.2	1.2	0.7
% C_2-C_6	62	41	53
% Olefin (of C_2-C_6 total)	89	88	70
Weight % Selectivity			
C_1	7.4	5.8	19.0
C_2^o	4.4	1.3	7.8
$C_2^=$	11.6	5.4	5.7
C_3^o	1.5	1.0	2.6
$C_3^=$	20.0	9.4	15.9
C_4^o	tr.	1.4	2.0
$C_4^=$	11.3	8.8	8.6
C_5^o	0.3	1.0	1.1
$C_5^=$	7.4	7.0	4.0
C_6^o	0.8	0.3	2.6
$C_6^=$	4.6	5.0	3.0
C_7^+	30.7	53.6	27.7

As is seen from the data, the catalyst derived from the cobalt containing spinel provided greater activity, i.e. 98% CO conversion, than the all-iron oxide control catalysts even though they were operated at 35°C and 70°C higher temperatures. The Fe-Co catalyst generated more C-C_6 olefins than either of the control catalysts and substantially less methane than the control catalyst at high conversion (about 87%) conditions.

EXAMPLE 6

Catalyst Preparation

Following the general procedure described in Example 1 the following catalysts were prepared having the empirical formula: $Fe_{3-y}Co_yO_4$/1%K: where y = 0.03, 0.15, 0.375 and 0.75, respectively. The surface areas of the obtained materials were in the range of 0.1 to 0.5 m^2g.

The above-prepared catalysts were pretreated by the procedure described in Example 2 and in the apparatus described in Example 4, and subjected to hydrocarbon synthesis under the following reaction conditions:

Temperature = 295 ± 10°C

Pressure = 300 psig

Space Velocity = 1000 v/v/hr.

H_2/CO ratio = 1:1

Run Time = 12 hours

Catalyst = 8 cc volume, 20-80 mesh size

Analysis of products were performed after 12 hours of run time. Results are shown in Table VI below.

TABLE VI

Performance of $Fe_{3-y}Co_yO_4$/1%K

y =	0.03	0.15	0.375	0.80
% CO Conversion	97	98	97	98
To CO_2	27	40	41	42
To HC's	70	58	56	56
Wt. % Selectivity				
CH_4	8.3	7.4	18.0	13.2
$C_2^=-C_6^=$	46.5	53.1	41.4	53.0
$C_2^o-C_6^o$	6.9	7.2	13.3	10.6
C_7^+	38.3	32.3	27.3	23.2

The results show the importance of maintaining the Fe:Co atomic ratio within the preferred range i.e. y = 0.03 to y = 0.40 at the specific conditions in this Example, excessive levels of CH_4 are generated at high cobalt levels, i.e., y = 0.375 where Fe:Co = 7:1.

EXAMPLE 7

This example shows the performance of Catalyst C, $Fe_{2.625}Co_{0.375}O_4$ in hydrocarbon synthesis at different temperatures.

The catalyst was pretreated according to the procedure described in Example 2 and in the same desscribed apparatus. The hydrocarbon synthesis runs were conducted at the indicated temperatures using 8 cc. volume of catalyst being undiluted with quartz and 20-80 mesh particle size at 1:1 H_2/CO, 1000 v/v/hr. (SHSV), 300 psig for 1-12 hours on-stream.

TABLE VII

Performance of $Fe_{2.625}Co_{.375}O_4$/1%K

Furnace Temp °C	225	240	260	270	280	290
Bed Temp °C	230	248	304	325	331	340
% CO Conversion	30	31	97	98	98	98
To CO_2	4	7	40	33	41	41
To HC's	26	24	57	55	57	57
Wt. % Selectivity - CO_2-free basis						
CH_4	8.1	8.2	19.1	16.7	18.3	19.1
$C_2^=-C_5^=$	42.3	55.3	37.1	31.9	37.8	24.8
$C_2^o-C_5^o$	14.4	22.0	17.7	10.6	13.2	14.8
C_6^+	35.2	34.5	26.1	40.8	30.7	41.3

As seen from the data, the change in CH_4 selectivity as a function of temperature-conversion indicates that catalysts which contain relatively high levels of cobalt, i.e. an iron/cobalt atomic ratio of 7.0, while useful should be operated at lower temperature-conversion conditions to achieve low CH_4 productivity. As further seen in the data, good C_2-C_6 olefin selectivity is achieved over the entire operating range. The system provided optimal performance in runs where the bed temperature was lower than 304°C.

EXAMPLE 8

This example shows the improved performance of Catalyst C, $Fe_{2.625}Co_{0.375}O_4$, at low (150 psig) pressure relative to (300 psig) high pressure conditions. The catalyst was prepared by the procedure outlined in Example 1, and subjected to the pretreatment and operating procedures substantially as described in Examples 2 and 4, respectively.

The results in Table VIII below show that even at relatively high cobalt levels, i.e. Fe:Co of 7.0, good olefin selectivity and high conversion can be achieved at lower pressures, i.e. 150 psig.

TABLE VIII

Performance of $Fe_{2.625}Co_{.375}O_4$/1%K at 150 and 300 psig

Pressure (psig)	150	300
% CO Conversion	92	97
% To CO_2	38	41
% To HC	54	56
Wt. % Selectivity (CO_2-free basis)		
CH_4	7.2	17.9
$C_2^=-C_5^=$	53.4	38.1
$C_2^o-C_5^o$	4.5	12.7
C_6^+	34.9	31.3

EXAMPLE 9

This example shows the effect of H_2 treatment at 350°C to reduce CH_4 selectivity of an "aged catalyst", in this case Catalyst B, which had been onstream for 72 hours. It is believed that the treatment with H_2 at 350°C for 5 hrs. at 100 psig, 750 SHSV, removes a carbonaceous surface layer which develops on the catalyst during extended operating periods. The procedures described in Examples 1, 3 and 3 were used to respectively prepare, pretreat, and operate this catalyst under the hydrocarbon synthesis conditions of 270°C, 0.66:1 H_2/CO, 2000 v/v/hr. (SHSV), 300 psig, 50% catalyst dilution with quartz powder in 8 cc total volume, catalyst particle size of 20-80 mesh.

TABLE IX

H_2 Treatment Improves Time Dependent Performance of $Fe_{2.85}Co_{.15}O_4$/1%K

Hours on stream	72[a]	96[b]
% CO Conversion	48	62
% CO to CO_2	23	28
% CO to HC	25	34
Wt. % Selectivity (CO_2-free basis)		
CH_4	12.0	7.9
$C_2^=-C_5^=$	43.3	46.3
$C_2^o-C_5^o$	7.1	6.6
C_6^+	37.6	40.1

[a]Prior to hydrogen rejuvenation.

[b]After 72 hours onstream, H_2 treatment described above, then additional 24 hours onstream with CO/H_2.

EXAMPLE 10

This example demonstrates the performance of Catalyst B, $Fe_{2.85}Co_{0.15}O_4$, at various temperatures under hydrocarbon synthesis conditions. The catalyst was 50% diluted with quartz powder as described in the previous Example. The respective procedures outlined in Examples 1 and 3 were used to prepare, pretreat and operate this catalyst under the hydrocarbon synthesis conditions listed below in Table X.

TABLE X

$Fe_{2.85}Co_{.15}O_4$/1%K Performance

Run	1	2	3
Temp °C	230	250	270
Pressure (psig)	300	300	300
H_2/CO	1.0	1.0	1.0
SHSV	1800	1800	1800
% CO Conv.	36.4	97.5	98.4
HR on Stream	2	4	6
% CO to CO_2	14	44.0	43.0
% CO to HC	22.4	53.5	55.4
Wt. % Selectivity (CO_2-free basis)			
CO_2	37.9	45.0	43.8
CH_4	1.3 (2.1)	2.6 (4.7)	3.2 (5.7)
$C_2^=$	2.0 (3.22)	3.0 (5.5)	3.4 (6.0)
C_2^o	0.4 (0.6)	0.8 (1.5)	0.8 (1.4)
$C_3^=$	4.1 (6.6)	5.4 (9.8)	6.3 (11.2)
C_3^o	0.8 (1.3)	0.6 (1.1)	0.6 (1.1)
$C_4^=$	1.7 (2.7)	3.4 (6.2)	4.0 (7.1)
C_4^o	0.1 (0.2)	0.5 (0.9)	0.5 (0.9)
$C_5^=$	1.4 (2.3)	2.6 (4.7)	3.5 (6.2)
C_5^o	0.3 (0.5)	0.5 (0.9)	0.9 (1.6)
$C_6^=$	1.2 (1.9)	1.9 (3.5)	2.2 (3.9)
C_6^o	0.4 (0.6)	0.3 (0.5)	0.3 (0.5)
C_7^+	48.4 (78.0)	33.4 (60.7)	30.5 (54.4)

EXAMPLE 11

This example demonstrates the performance of Catalyst B, $Fe_{2.85}Co_{0.15}O_4$ at various temperatures in the form of undiluted catalyst. The catalyst was prepared by the procedure described in Example 1 and pretreated and operated as respectively described in Examples 2 and 4. The process conditions for each run are listed below in Table XI. In contrast to Run 4 shown below, bed dilution as employed in Example 10 allows the system to operate under more isothermal conditions thereby minimizing the extent of carbon and carbonaceous deposit formation.

TABLE XI

$Fe_{2.85}Co_{.15}O_4$/1%K Performance

Undiluted Bed

Run	1	2	3	4
SHSV:	1000	1000	570	570
Temp.	235	270	235	270
H_2:CO	1.0	1.0	1.0	1.0
Press	300	300	300	300
Time on stream hr.	8	10	16	18
% CO Conv.	29.4	98.0	49.1	98.0*
% CO to CO_2	8.0	42.0	22.0	40.0
% CO to HC	21.4	56.0	27.1	58.0
Wt. % Select. (CO_2-free basis)				
CO_2	26.2	42.5	43.5	40.2
CH_4	1.9	3.0	1.7	3.7
	(2.6)	(5.2)	(2.0)	(6.2)
$C_2^=$	4.3	4.5	2.5	4.0
	(5.8)	(7.8)	(4.4)	(6.7)
C_2^o	1.4	1.7	0.9	1.7
	(1.9)	(2.9)	(1.6)	(2.8)
$C_3^=$	6.4	7.8	6.6	8.3
	(8.7)	(13.4)	(11.6)	(13.8)
C_3^o	0.6	0.6	0.7	0.8
	(0.8)	(1.0)	(1.2)	(1.3)
$C_4^=$	1.4	4.4	2.5	3.8
	(1.9)	(7.6)	(4.4)	(6.3)
C_4^o	tr.	0.2	0.4	3.5
	(tr.)	(0.3)	(0.7)	(0.8)
$C_5^=$	0.9	2.8	1.7	2.7
	(1.2)	(4.8)	(2.9)	(4.5)
C_5^o	tr.	0.1	0.4	0.35
	(tr.)	(0.2)	(0.7)	(0.8)
C_6^+	56.9	32.4	39.1	34.2
	(76.8)	(55.9)	(68.6)	(57.0)

*Note: Bed plugging with wax and carbonaceous deposits limited continuous operating periods to ≤ 40-50 hrs.

EXAMPLE 12

Preparation of $Fe_{2.85}Co_{0.15}O_4$ Spinel

198.04 grams of ferric nitrate in 144 cc of water and 7.5 grams of cobalt nitrate in 8 cc of water were mixed together. To this solution was added a solution of 41.6 grams of 85% glycolic acid containing 45 cc of ammonium hydroxide such that the resulting pH of the ammonium glycolate solution was about 6.5. The ammonium glycolate solution constituted 0.51 moles of glycolic acid such that about a one to one molar ratio of total metals including iron and cobalt to glycolic acid resulted. The ammonium glycolate solution was added to the aqueous solution containing iron and cobalt salts and the contents stirred. The resulting solution was allowed to evaporate by air drying. Upon drying at room temperature the resulting solid was shown by X-ray diffraction to be an amorphous material because of lack of sharp discrete reflections. The solid was heated in air at 350°C for 2 hours. An X-ray diffraction pattern of the resulting material showed it to be a single phase cobalt-iron spinel isomorphous with Fe_3O_4. The X-ray diffraction peaks were broadened relative to a com-

positionally equivalent material obtained by a high temperature procedure. This indicated that the resulting obtained material was of very small particle size. The surface area of the resulting material was about 200 square meters per gram. Carbon analysis of the material indicated approximately 0.15% carbon percent. The resulting material was impregnated with one gram atomic percent of potassium using an aqueous solution of potassium carbonate and drying of the resulting impregnated sample at 125°C. The resulting solid had an empirical formula of $Fe_{2.85}Co_{0.15}O_4$/1% K.

Preparation of Alloy

The above obtained oxide was reduced at 400°C in a stream of 15 volume percent hydrogen/85% helium at 200 v/v/hr (SHSV) for 4 hours. One percent of oxygen in helium was introduced at room temperature for one hour to passivate the material. The X-ray of the resulting material was isostructural with alpha iron. The resulting BET nitrogen surface area was 8 m^2/g.

Preparation of Carbide

The above reduced material was treated at 400°C in a stream of 15 volume percent hydrogen/80% helium/5% CO at 200 v/v/hr. for four hours. Following this the sample was cooled to room temperature and 10% oxygen in helium was introduced for one hour to passivate the material. The X-ray diffraction pattern of the resulting material was isostructural with Fe_5C_2. The BET nitrogen surface area of the material was about 118 m^2/g. Analysis showed that about 60-70 weight percent of the material was carbon and thus the material was a composite of $Fe_{4.75}CO_{0.25}C_2$/1 gram-atom % K and surface carbon.

EXAMPLE 13

Into a slurry reactor, being a 300 cc Parr CSTR (continuous stirred tank reactor) was charged: 50 g of octacosane and 5.0 of the high surface area spinel, described above in Example 12. The system was purged with nitrogen and then H_2 while the temperature was increased from room temperature to 220°C, where the system was maintained under these conditions in a hydrogen atmosphere with stirring for a one-hr period at 600 rpm. The system was then placed under CO hydrogenation reaction conditions by adjusting the reaction temperature to 270°C, the H_2/CO volume ratio to 1:1, the space velocity to 1200 V gaseous feedstream/V dry catalyst/hr, the pressure to 70 psig, and the slurry stirrer speed to 600 rpm in the octacosane solvent. The effluent gas from the reactor was monitored by an HP-5840A Refinery Gas Analyzer to determine percent CO conversion and the nature of the hydrocarbon products. The results are listed below in Table XII under the high surface area spinels as "oxide".

Further runs were made based on the spinel which was (1) reduced ex situ, and (2) reduced/carbided ex situ, prior to being charged into the slurry liquid. The results are listed below in the Table as "reduced" and "reduced/carburized", respectively, together with the specific pretreatment conditions. The control, and the low surface area spinel also run under substantially the same conditions, are listed below.

The listed comparative sample, Fe_2O_3, was obtained from Alpha Chemicals and had a BET surface area of less than 10 m^2/g.

The listed comparative sample $Fe_{2.85}Co_{0.15}O_4$/1% K was made by sintering an intimate mixture of Fe_2O_3, Fe metal and CO_3O_4, in the appropriate molar ratio, at 800-1,000°C for 24 hours in an evacuated sealed tube. The solid was collected, crushed, pelletized and then the sintering procedure repeated. The obtained solid was crushed and then impregnated with aqueous potassium carbonate and then dried at 125°C for several hours in a drying oven. The surface area of the obtained solid was about 0.3 m^2/g.

TABLE XII

Slurried F-T Catalysts with 1:1 H_2:CO

Catalysts	%CO Conv.	$\%CO_2$	$\%CH_4$	$\%C_2-C_4$	%Olefin C_2-C_4
Fe_2O_3	<4.0	-	-	-	-
$Fe_{2.85}Co_{.15}O_4$/ 1% K	<4.0	-	-	-	-
Spinels (100+m^2/g) $Fe_{2.85}Co_{0.15}O_4$					
Oxide	78	48	3.1	7.3	92
Reduced[a]	55	62	2.2	10.9	88
Reduced/Carburized[b]	79	48	4.5	16.0	92

Conditions: 270°C, 1:1 H_2:CO, 1200 v/v/cat/hr. 70 psig, 600 rpm, octacosane solvent.

[a] H_2 at 350°C for 12 hours and 400°C for 24 hours.

[b] H_2/CO at 350°C for 12 hours and 400°C for 24 hours.

As is seen in this example, catalysts prepared from the high surface area spinel gave higher activity and C_2-C_4 olefin selectivity than conventional iron oxide catalysts.

EXAMPLE 14

The catalysts, apparatus, catalyst pretreatment and general CO hydrogenation procedures of Example 13 were used and repeated except that modified CO hydrogenations conditions were used at 250°C and 2:1 H_2:CO as listed in Table XIII.

TABLE XIII

Slurried F-T Catalysts with 2:1 H_2:CO

Catalysts	%CO Conv.	$\%CO_2$	$\%CH_4$	$\%C_2-C_4$	%Olefin C_2-C_4
Fe_2O_3	<5.0	20+	15+	14.0	60.0
*$Fe_{2.85}Co_{.15}O_4$/ 1%K	<4.0*	NA	NA	NA	NA
Spinels (100+m^2/g) $Fe_{2.85}$ $Co_{0.15}O_4$					
Oxide	31	62	4.1	18.2	90
Reduced[a]	54	63	2.4	11.1	89
Reduced/Carburized[b]	64	50	3.6	14.0	83

Conditions: 250°C, 2:1 H_2:CO, 1200 v/v/cat/hr. 70 psig, 600 rpm, octacosane solvent.

*Note: less than 5% conversion observed even at 270°C.

[a]H_2 at 350°C for 12 hours and 400°C for 24 hours.
[b]H_2/CO at 350°C for 12 hours and 400°C for 24 hours.

EXAMPLE 15

Utilizing the catalysts, apparatus, catalyst pretreatment and general CO/hydrogenation procedures described in Example 13, the following runs were made utilizing the specific process conditions listed in Table XIV below:

TABLE XIV

Comparative Study of Fe-Co Catalysts from High and Low Surface Spinel Precursors

	$Fe_{2.85}Co_{.15}O_4$/1% K	
Spinel Initial Surface Area	100+ m^2/g	<10 m^2/g
% CO Conversion	45	44
% CO to CO_2	-	-
% CO to HC	-	-
Wt% Selectivity		
CH_4	1.9	2.0
C_2-C_4	8.3	8.4
C_5+	32.3	23.6
CO_2	57.0	66.0
% Olefin in C_2-C_4	90	90

Conditions: 250°C, 1200 v/g CAT/hr, 1:1 H_2:CO, 70 psig, 600 RPM, octacosane solvent. Catalysts subjected to ex situ H_2 treatment at 300+°C followed by ex situ H_2/CO treatment 350+°C to affect complete reduction-carburization followed by oxygen passivation.

The results in Table XIV indicate that catalysts prepared from low and high surface area Fe-Co spinels provide comparable performance when they are both fully prereduced and carburized ex situ. The catalyst derived from the low surface area precursor generated more CO_2 and less C_5+ hydrocarbon than the catalyst generated from the high surface area precursor, under the stated reaction conditions.

EXAMPLE 16

Utilizing the catalysts, apparatus, pretreatment and general CO hydrogenation procedures described in Example 13, the following runs were made under the specific process conditions listed below in Table XV:

TABLE XV

Comparative Study of Carburized Catalysts from High Surface Area Spinel Precursors

Catalyst Precursor	A(a)	B(b)	Fe_3O_4/1% K(c)
% CO Conversion	64	42	65
% CO to CO_2	36	24	39
% CO to HC	28	18	26
Wt.% Selectivity			
CH_4	3.6	4.1	5.1
$C_2^=$	4.2	2.8	2.6
C_2^o	0.6	1.1	1.6
$C_3^=$	5.1	6.0	6.7
C_3^o	0.6	0.7	0.8
$C_4^=$	2.7	3.1	3.6
C_4^o	0.4	0.6	0.8
C_5^+	26.6	25.6	18.8
CO_2	56	56	60
% Olefin in C_2-C_4	88	83	80

(a) $Fe_{2.85}Co_{0.15}O_4$/1% K @ 100+ m^2/g.
(b) same as A but less than 1 m^2/g.
(c) surface area = 100 + m^2/g.

Conditions: 250°C, 1200 V/G CAT/hr, 2:1 H_2:CO, 70 psig, 600 RPM, octacosane, ex situ treated in H_2 at 300°+C and then H_2/CO at 350°C+.

As seen, catalysts generated from Fe-Co and Fe spinel precursors which are fully reduced and carbided ex situ, exhibited comparable activity under CO hydrogenation conditions. However, the Fe-Co based system generated less unwanted CH_4 and CO_2 and a C_2-C_4 fraction which is richer in alpha-olefins when compared to the Fe only analog.

Comparison of Fe-Co catalysts from high and low surface area spinel precursors, Runs A and B, indicates that the high surface precursor generated higher yields of alpha-olefins and lower methane than the low surface area precursor when both catalysts are prereduced/carbided ex situ. Similar results were noted in previous Example 15.

EXAMPLE 17

Utilizing the spinel catalysts, apparatus, and general CO hydrogenation conditions described in Example 13, the following runs were carried out utilizing the specific in situ pretreatment and hydrocarbon synthesis process conditions listed below in Table XVI:

TABLE XVI

Comparative Study of High Surface Area Oxide Catalysts

Catalyst	$Fe_{2.85}Co_{.15}O_4$/1% K	Fe_3O_4/1% K
Surface Area	100+ m^2/g	100+ m^2/g
% CO Conversion	60	8
% CO to CO_2	36	5.2
% CO to HC	24	2.8
Wt% Selectivity		
CH_4	1.8	4.0
C_2-C_4	8.0	15
C_5+	30.2	11
CO_2	60.0	65
% Olefin in C_2-C_4	88	80

Conditions: 250°C, 1200 V/G CAT/hr, 2:1 H_2:CO, 70 psig, 600 RPM octacosane. Catalyst charged to reactor as oxide, treated in situ with H_2 at 100 psig at 200°C for 1 hr before use.

As is seen, catalysts derived from high surface area spinels, with and without added cobalt, exhibited substantially different activities when employed and pretreated in situ directly under slurry reactor conditions. The Fe-Co catalyst is ca. 5-fold more active than the Fe only catalyst. The Fe-Co catalyst also generated less CH_4 and CO_2 than the Fe only catalyst and generates a C_2-C_4 fraction which is richer in alpha-olefins.

EXAMPLE 18

Utilizing the catalysts, apparatus, pretreatment and general CO hydrogenation procedures, described in Example 13, the following runs were made using the specific conditions listed below in Table XVII including comparative runs made at H_2/CO ratios of 1.0 and 2.0.

TABLE XVII

Performance of Fe and Fe-Co Alloy Catalysts

Precursor	Fe_3O_4/1%K(a)		$Fe_{2.85}Co_{.15}O_4$/1% K(b)	
% CO Con.	44	28	55	54
H_2/CO	1.0	2.0	1.0	2.0
% CO to CO_2	26	15	34	34
% CO to HC	18	13	21	20
Wt. % Sel.				
CH_4	1.8	1.0	2.2	2.4
C_2-C_4	11.1	5.0	10.9	11.1
C_5^+	28.1	41.0	24.8	23.5
CO_2	59	53	62	63
% Olefin in C_2-C_4	93	94	88	91

Conditions: 270°C, 1:1 H_2:CO, 1200 v/v Cat/hr., 70 psig, 600 rpm. Catalyst prereduced ex situ in H_2 at 350°C for 12 hours and 400°C for 24 hours.

(a) Initial spinel surface area - about 100 m^2/g.
(b) Initial spinel surface area - about 100 m^2/g.

EXAMPLE 19

Utilizing the pretreatment and general CO hydrogenation procedures described in Example 13, the following runs were made utilizing the specific catalyst and CO hydrogenation conditions described below.

The spinel described in Example 13, $Fe_{2.85}Co_{0.15}O_4$/1% K, was reduced and carbided ex situ similar to the procedure described in Example 13. A hydrogen/CO/helium feedstream in 1:1:7 molar ratio at 350°C and about 300 v/v/hr. for 24 hours was used. Powder x-ray diffraction analysis revealed the resulting material was isostructural with Hagg Carbide, Fe_5C_2. The elemental analysis of the material showed it to contain: Fe and Co in about a 19:1 atomic ratio and about 60-70 weight percent carbon. The surface area of the material was determined to be about 180-200 m^2/g.

The catalyst (40 cc. catalyst volume) was run under two different pressures in CO hydrogenation under the conditions listed below in Table XVIII.

The apparatus used was a 1 liter stirred tank reactor (316 S.S.) equipped with a Magnedrive™ head and an internal gas recycle.

Table XVIII

$Fe_{4.75}CO_{.25}C_2/1\%$ K

% CO Conversion	24	53
% CO to CO_2	11	23
% CO to HC	13	30
Pressure (psig)	75	150
Wt.% Selectivity		
CH_4	4.9	4.7
$C_2^=-C_{20}^=$	59.3	53.2
C_1-C_{10} Alcohols	7.8	11.5
$C_{20}^o-C_{20}^o$	26.2	20.6
$C_{21}+$	trace	10.6

Conditions: 240°C, 1:1 H_2/CO, 1,000 v/v/hr. 1,200 RPM, 100-150 hr. on stream.

EXAMPLE 20

Reduction of Spinel

The above obtained Spinel B of Example I was reduced at 400°C in a stream of 15 volume percent hydrogen/85% helium for 4 hours. One percent of oxygen in helium was introduced at room temperature for one hour to passivate the material. The X-ray of the resulting material was isostructural with alpha iron.

Preparation of Carbide

The above reduced Spinel B was treated at 400°C in a stream of 15 volume percent hydrogen/80% helium/5% CO at 200 v/v/hr. for four hours. Following this the sample was cooled to room temperature and 1.0% oxygen in helium was introduced for one hour to passivate the material. The X-ray diffraction pattern of the resulting material was isostructural with chi-Fe_5C_2. The measured BET nitrogen surface area of the material, including the carbide $Fe_{(5)-(5/3)y}Co_{(5/3)y}C_2$ and deposited carbon, was 173 m^2g.

EXAMPLE 21

A slurry reactor, being a 300 cc Parr CSTR - (continuous stirred tank reactor) was charged with 50 g of octacosane and 5.0 g. of the resulting reduced, carbided, Spinel B, described above. The system was purged with nitrogen and then H_2 while the temperature was increased from room temperature to 220°C, where the system was maintained under these conditions with stirring for a one-hr period at 600 rpm to insure reduction. The system was then placed under CO hydrogenation reaction conditions by adjusting the reaction temperature to 270°C, the H_2/CO volume ratio to 1:1, the space velocity to 1200 V gaseous feedstream/V dry catalyst/hr, the pressure to 70 psig, and the slurry stirrer speed to 600 rpm in the octacosane solvent. The effluent gas from the reactor was monitored by an HP-5840A Refinery Gas Analyzer to determine percent CO conversion and the nature of the hydrocarbon products. The selectivity weight percentages of product hydrocarbons exclude CO_2 as a product.

A second run was conducted using a reduced, carbided spinel of the same empirical formula, $Fe_{2.85}Co_{0.15}O_4/1\%K$, and reduced and carbided by the same above-described procedure, but having an initial spinel BET surface area of above 100 m^2/g as prepared in accordance with the procedure of Example 12.

The results are listed below in Table XIX.

TABLE XIX

Comparative Study of Fe-Co Catalysts from High and Low Surface Spinel Precursors

Spinel (Surface Area)	$Fe_{2.85}Co_{.15}O_4$/1% K Precursor 100+ m^2/g	B
% CO Conversion	45	44
% CO to CO_2	26	29
% CO to HC	19	15
Wt% Selectivity		
CH_4	4.4	5.9
C_2-C_4	19.3	25
C_5^+	76.3	69.1
% Olefin in C_2-C_4	90	90

Conditions: 250°C, 1200 v/g CAT/hr, 1:1 H_2:CO, 70 psig, 600 RPM, octacosane solvent. Catalysts subjected to ex situ H_2 treatment at 300+°C followed by ex situ H_2/CO treatment 350+°C to affect complete reduction-carburization.

The results in Table XIX indicate that catalysts prepared from low and high surface area Fe-Co spinels provide comparable performance when they are fully ex situ prereduced and carburized.

As is seen, the catalyst derived from the low surface area precursor generated more CO_2, less C_5^+ hydrocarbons, but more C_2-C_4 olefins than the catalyst generated from the high surface area precursor, under the stated reaction conditions.

EXAMPLE 22

Utilizing the catalysts, apparatus, pretreatment and general CO hydrogenation conditions described in Example 21, the following runs were carried out utilizing the specific process conditions listed below in Table XX. The conversion for Catalyst B under the stated conditions was too low for accurate determination of products (NA = not available).

TABLE XX

Comparative Study of High Surface Area Oxide Catalysts

Catalyst	$Fe_{2.85}Co_{.15}O_4$/1% K	Fe_3O_4/1% K	B
Surface Area	100+ m^2/g	100+ m^2/g	0.29 m^2/g
% CO Conversion	60.0	8.0	4.0
Wt.% Selectivity			
CH_4	1.8	4.0	NA
C_2-C_4	8.0	15	NA
C_5^+	30.2	11	NA
CO_2	60.0	65	NA
% Olefin in C_2-C_4	8.8	80	NA

Conditions: 250°C, 1200 V/G CAT/hr, 2:1 H_2:CO, 70 psig, 600 RPM octacosane. Catalyst charged to reactor as oxide, treated in situ with H_2 at 100 psig at 200°C for 1 hr before use.

As is seen, the catalysts derived from low surface area spinels, with added cobalt, gave low activity when employed directly under the conditions described. By contrast, catalysts derived from the high surface area Fe-Co spinels exhibited high activity when employed under the above conditions. However, the enhanced activity effect is not due to the high surface area alone, but primarily to the presence of cobalt, since the high surface area cobalt-free catalyst also exhibited low activity.

At least some of the features comprising the present invention may be summarized as follows:

1. A process for synthesizing a hydrocarbon mixture containing C-C_{20} olefins characterized by comprising the contacting of a carbided and reduced, unsupported iron-cobalt single phase spinel catalyst, said spinel having the initial empirical formula:

$Fe_xCo_yO_4$

wherein x and y are integer or decimal values, other than zero, with the provisos that the sum of x + y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a single phase X-ray diffraction pattern substantially isostructural with that of Fe_3O_4 and said spinel having a measured BET surface area of about 0.1 m^2/g or greater with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said C_2-C_{20} olefins.

2. A process according to feature 1 further characterized in that said catalyst further comprises a promoter agent present in about 0.1 to 10 gram-atom percent of total gram-atoms of metal content.

3. A process according to feature 2 further characterized in that the said promoter agent is selected from bicarbonates, carbonates, organic acid salts, inorganic acid salts, nitrates, sulfates, halides and hydroxides of Group IA and IIA metals.

4. A process according to feature 3 further characterized in that the said promoter agent is potassium carbonate.

5. A process according to any one of features 1-4 further characterized in that the said spinel is of the formula: $Fe_{2.85}Co_{0.15}O_4$, $Fe_{2.625}Co_{0.375}O_4$, $Fe_{2.97}Co_{0.03}O_4$, $Fe_{2.25}Co_{0.75}O_4$.

6. A process according to any one of features 2-5 further characterized in that said catalyst comprises an unsupported iron-cobalt spinel composition of the formula: $Fe_{2.85}Co_{0.15}O_4$/1%K.

7. A process according to any one of features 1-6 further characterized in that the said hydrogen and CO are present in a H_2/CO molar ratio of about 1:10 to 10:1.

8. A process according to any one of features 1-7 further characterized in that the said elevated temperature is in a range of about 200°C to 300°C.

9. A process according to any one of features 1-8 further characterized in that the said contacting of said catalyst and said CO and hydrogen is carried out in a fixed bed reactor system.

10. A process according to feature 9 further characterized in that the said catalyst is admixed with a solid diluent.

11. A process according to feature 9 or feature 10 further characterized in that said contacting is carried at a pressure in the range of about 50 to 1000 psig.

12. A process according to any one of features 9-11 further characterized in that said contacting is carried out at a space velocity in the range of about 200 to 4000 v/v/hr.

13. A process according to any one of features 1-8 further characterized in that the said contacting of said catalyst and said CO and hydrogen is carried out in a slurry phase reactor system.

14. A process according to feature 13 further characterized in that said slurry phase system is comprised of an admixture of said catalyst with a slurry liquid selected from high boiling liquid paraffins, aromatic hydrocarbons, ethers, amines, or mixtures thereof.

15. A process according to feature 13 or feature 14 further characterized in that the said high boiling liquid paraffins are C_{12}-C_{60} linear or branched saturated aliphatic hydrocarbons.

16. A process according to any one of features 13-15 further characterized in that the weight ratio of slurry liquid: catalyst taken as the dry basis, is the range of about 10:1 to 5:1.

17. A process according to any one of features 13-16 further characterized in that the said spinel has an initial BET surface area greater than 5 m^2/g and the product hydrocarbon mixture contains about 60 wt.% or more of C_2-C_{20} olefins.

18. A process according to any one of features 9-16 further characterized in that the said spinel has an initial BET surface area of up to about 5 m^2/g and the product hydrocarbon mixture contains about 25 wt.% to 80 wt.% of C_2-C_6 hydrocarbons of the total weight of hydrocarbons produced.

Claims

1. A process for synthesizing a hydrocarbon mixture containing C_2-C_{20} olefins characterized by comprising the contacting of a carbided and reduced, unsupported iron-cobalt single phase spinel catalyst, said spinel having the initial empirical formula:

$Fe_xCo_yO_4$

wherein x and y are integer or decimal values, other than zero, with the provisos that the sum of x + y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a single phase X-ray diffraction pattern substantially isostructural with that of Fe_3O_4 and said spinel having a measured BET surface area of about 0.1 m^2/g or greater, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said C_2-C_{20} olefins.

2. A process according to claim 1 further characterized in that said catalyst further comprises a promoter agent present in about 0.1 to 10 gram-atom percent of total gram-atoms of metal content.

3. A process according to claim 2 further characterized in that the said promoter agent is selected from bicarbonates, carbonates, organic acid salts, inorganic acid salts, nitrates, sulfates, halides and hydroxides of Group IA and IIA metals (e.g. potassium carbonate).

4. A process according to any one of claims 1 to 3 further characterized in that the said spinel is of the formula: $Fe_{2.85}Co_{0.15}O_4$, $Fe_{2.625}Co_{0.375}O_4$, $Fe_{2.97}Co_{0.03}O_4$, $Fe_{2.25}Co_{0.75}O_4$, or comprises an unsupported iron-cobalt spinel composition of the formula: $Fe_{2.85}Co_{0.15}O_4$/1%K.

5. A process according to any one of claims 1 to 4 further characterized in that the said contacting of said catalyst and said CO and hydrogen is carried out in either a fixed bed reactor system or a slurry phase reactor system.

6. A process according to claim 5 performed in a fixed bed reactor system and in which the said catalyst is admixed with a solid diluent.

7. A process according to claim 5 further characterized in that said slurry phase system is comprised of an admixture of said catalyst with a slurry liquid selected from high boiling liquid paraffins, aromatic hydrocarbons, ethers, amines, or mixtures thereof.

8. A process according to claim 7 further characterized in that the said high boiling liquid paraffins are C_{12}-C_{60} linear or branched saturated aliphatic hydrocarbons.

9. A process according to any one of claims 5 to 8 in which in the slurry phase reactor system, the weight ratio of slurry liquid:catalyst taken as the dry basis, is the range of about 10:1 to 5:1.

10. A process according to any one of claims 5 to 9 in which in the slurry phase reactor system, the said spinel has an initial BET surface area greater than 5 m^2/g and the product hydrocarbon mixture contains about 60 wt.% or more of C_2-C_{20} olefins.

11. A process according to any one of claims 5 to 10 in which the said spinel has an initial BET surface area of up to about 5m^2/g and the product hydrocarbon mixture contains about 25 wt.% to 80 wt.% of C_2-C_6 hydrocarbons of the total weight of hydrocarbons produced.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 85 30 6917

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X,D	US-A-4 518 707 (S.L. SOLED et al.) * claims 1-13 *	1-6	C 07 C 1/04 B 01 J 23/00 B 01 J 23/74 B 01 J 23/78
A	DE-A-2 919 921 (W. VIELSTICH et al.) * claims 1, 9, 10 * & GB - A - 2 050 859 (Cat. D)	1	
A	US-A-4 228 138 (P.A. SERMON) * claim 1; column 1, lines 9-16 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

B 01 J 23/00
B 01 J 23/74
B 01 J 23/78
C 07 C 1/04

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	06-06-1986	KNAACK M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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