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[54] **COBALT-PROMOTED FISCHER-TROPSCH CATALYSTS**

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[52] **U.S. Cl.** **518/717**; 502/524; 518/720; 518/721

[58] **Field of Search** 518/700, 717, 720, 721

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[57] **ABSTRACT**

Iron-cobalt spinels which contain low levels of cobalt, in an iron/cobalt atomic ratio of 7:1 to 35:1, are converted to Fischer-Tropsch catalysts upon reduction and carbiding that exhibit high activity and selectivity to C_2-C_6 olefins and low CH_4 production.

15 Claims, No Drawings

COBALT-PROMOTED FISCHER-TROPSCH CATALYSTS

FIELD OF THE INVENTION

This invention relates to a Fischer-Tropsch process for producing low molecular weight olefins, particularly those in the C_2–C_4 range, using as a catalyst, an unsupported alkali or alkaline earth metal salt promoted iron-cobalt single phase spinel, in which the atomic ratio of Fe:Co is 7:1 or above, and said spinel having a measured BET nitrogen surface area of up to about 5 m^2/g.

DISCLOSURES IN THE ART

Fischer-Tropsch processes have long been known to produce gaseous and liquid hydrocarbons containing C_2–C_4 olefins. Because of the importance of C_2–C_4 olefins, particularly as feedstocks for the chemical industry, modifications of the Fischer-Tropsch process are constantly being pursued toward the goals of maximizing C_2–C_4 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 C_2–C_4 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. Pat. Nos. 2,850,515, 2,686,195, 2,662,090, and 2,735,862; AICHE 1981 Summer Nat'l Meeting Preprint No. 408, "The Synthesis of Light Hydrocrobons 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. 335–374; 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 C_2–C_4 olefins.

What is particularly desired in fixed bed Fischer-Tropsch processes are new catalysts for selectively producing high levels of C_2–C_4 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 unsupported alkali or alkaline earth metal salt promoted iron-cobalt single phase spinels containing low levels of cobalt, i.e. iron:cobalt atomic ratios of 7:1–35:1 and higher provide desirable catalyst properties in fixed bed Fischer-Tropsch processes. The initial spinels are single phase and isostructural with Fe_3O_4 as shown by X-ray diffractometry and possess measured BET nitrogen surface areas of up to 5 m^2/g (square meters per gram).

The spinels are 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 are then treated with promoter agents, alkali metal and alkaline earth 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 Fisher-Tropsch process.

In accordance with this invention there is provided, a hydrocarbon synthesis catalyst composition comprising an unsupported, Group IA or IIA metal salt promoted iron-cobalt single phase spinel, 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 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.

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

Furthermore, there is provided a process for producing the subject spinel portion of the composition comprising 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 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 Group IA or IIA metal salt promoted 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 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.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The subject iron-cobalt spinels are new 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 $\frac{1}{8}$th of the available tetrahedral interstices and $\frac{2}{3}$ 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 Spinel 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 up to about 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 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 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.

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 is also used in the composition and is used to particularly promote olefin formation in the process. Representative examples of classes of suitable promoter agents include alkali metal and alklaine earth metal salts including carbonates, bicarbonates, organic acid salts, inorganic acid salts, i.e. acetates, 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 graom-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, pourous 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 fixed bed Fisher-Tropsch process for making C_2–C_4 olefins from CO/hydrogen.

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

The subject spinel is 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.

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 350° 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.

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.

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.

Also a subject of the instant invention is a Fischer-Tropsch fixed bed process for producing C_2–C_6 olefins by utilizing the reduced and carbided iron-cobalt spinel, described hereinabove.

Although a fixed bed Fischer-Tropsch process is one desired mode for utilizing the claimed catalysts described herein, a slurry type process wherein the catalyst is suspended in a liquid hydrocarbon can also be utilized, as described in copending application, Ser. No. 561,192, filed Dec. 14, 1983 (C-1629), hereby incorporated by reference for that purpose.

The subject fixed bed process utilizes the above-described materials, as catalyst or catalyst precursors: the iron-cobalt spinel, or a mixture of iron-cobalt spinels, of different iron-cobalt atomic ratios, being in admixture with, isostructural with Fe_3O_4, and its reduced and carbided form. The reduced and carbided materials are generally made in situ in the apparatus, prior to, and during, the carrying out of the hydrocarbon synthesis process. A full discussion of the spinel and reduced form materials, their properties and their preparation are given hereinabove and need not be reiterated.

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 hydrocarbon synthesis.

Following the reduction step, the CO/hydrogen feedstream is introduced into the 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 process, the hydrogen and CO are used in a molar ratio in the gaseous feedstream of preferably about a 0.5 to 2.5 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 process is generally in the region of about 200° to 350° C. and preferably being 250° to 300° C. Higher temperatures 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 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 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 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 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, 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 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 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 process where the formula of the catalyst used is $Fe_{2.85}Co_{0.15}O_4$/1% K, having about 1 m^2/g BET surface area. 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 preferred process is any conventional fixed bed type reactor, being horizontal or vertical, moving bed, fluid bed, and the like. 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, $(4/3-4y/9)\ Fe_2O_3+\frac{1}{3}\ (1-y/3)\ Fe+y/3\ Co_3O_4$, 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

	$Fe_{3-y}Co_yO_4$/1% K	
Composition	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, $Fe_{2.85}Co_{0.15}O_4$/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

TABLE II-continued

Catalyst	Fe_3O_4/1% K[a]	$Fe_{2.85}Co_{0.15}O_4$/1% K[b]
% 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
$C_2°$–$C_5°$	7.9
$C_2^=$–$C_5^=$	48.2
C_6^+	34.7

As is seen from the data, the catalyst derived fom the iron-cobalt spinel provides good activity and high C_2–C_5 olefin selectivity with high H_2/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
$C_2^=/C_2°$	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 VI, in same apparatus described in Example 2. Product samples were collected and analyzed after 12 hours onstream with CO/H_2.

TABLE VI

	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
$C_2°$	4.4	1.3	7.8
$C_2^=$	11.6	5.4	5.7
$C_3°$	1.5	1.0	2.6
$C_3^=$	20.0	9.4	15.9
$C_4°$	tr.	1.4	2.0
$C_4^=$	11.3	8.8	8.6
$C_5°$	0.3	1.0	1.1
$C_5^=$	7.4	7.0	4.0
$C_6°$	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_2–C_6 olefins than either of the control catalysts and substantially less methane than the control catalyst at high conversion (about 87%) conditions.

EXAMPLE 7

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 VII below.

TABLE VII

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
$C_2^\circ-C_6^\circ$	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 8

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 described 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 onstream.

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
$C_2^\circ-C_5^\circ$	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 9

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
$C_2^\circ-C_5^\circ$	4.5	12.7
C_6+	34.9	31.3

EXAMPLE 10

This example shows the effect of H_2 treatment at 350° C. to reduce CH_4 selectivity of an "aged catalyst", in this 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
$C_2^\circ-C_5^\circ$	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 11

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

Run	$Fe_{2.85}Co_{.15}O_4$/1% K Performance 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°	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°	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°	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°	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°	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 12

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

Run	$Fe_{2.85}Co_{.15}O_4$/1% K Performance Undiluted Bed 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 (2.6)	3.0 (5.2)	1.7 (2.0)	3.7 (6.2)
$C_2^=$	4.3 (5.8)	4.5 (7.8)	2.5 (4.4)	4.0 (6.7)
C_2°	1.4 (1.9)	1.7 (2.9)	0.9 (1.6)	1.7 (2.8)
$C_3^=$	6.4 (8.7)	7.8 (13.4)	6.6 (11.6)	8.3 (13.8)
C_3°	0.6 (0.8)	0.6 (1.0)	0.7 (1.2)	0.8 (1.3)
$C_4^=$	1.4 (1.9)	4.4 (7.6)	2.5 (4.4)	3.8 (6.3)
C_4°	tr. (tr.)	0.2 (0.3)	0.4 (0.7)	3.5 (0.8)
$C_5^=$	0.9 (1.2)	2.8 (4.8)	1.7 (2.9)	2.7 (4.5)
C_5°	tr. (tr.)	0.1 (0.2)	0.4 (0.7)	0.35 (0.8)
C_6^+	56.9	32.4	39.1	34.2

TABLE XI-continued

Run	$Fe_{2.85}Co_{.15}O_4$/1% K Performance Undiluted Bed 1	2	3	4
	(76.8)	(55.9)	(68.6)	(57.0)

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

What is claimed is:

1. A fixed bed process for synthesizing a hydrocarbon mixture containing C_2–C_6 olefins comprising the step of contacting a fixed bed of a catalyst composition comprised of an unsupported Group IA or IIA metal salt promoted iron-cobalt spinel: said spinel exhibiting a single spinel phase, being isostructural with Fe_3O_4 as determined by X-ray diffractometry and possessing a BET nitrogen surface area of up to 5 m^2/g, and an iron-cobalt atomic ratio of 7:1 or above; with a mixture of CO/hydrogen under process conditions of pressure, space velocity (SHSV) and elevated temperature for a time sufficient to produce said C_2–C_6 olefins.

2. The process of claim **1** wherein said hydrogen and CO are present in a molar ratio of about 0.5 to 2.5.

3. The process of claim **1** wherein said temperature is in a range of about 200° to 350° C.

4. The process of claim **1** wherein said pressure is in a range of about 50 to 1000 psig.

5. The process of claim **1** wherein said space velocity is in the range of about 200 to 4000 V/V/hr.

6. The process of claim **1** wherein said spinel is of the formula: $Fe_xCo_yO_4$, wherein x and y are integer or decimal values other than zero, the sum of x+y is 3 and the ratio of x/y is 7:1–35:1.

7. The process of claim **6** wherein the ratio x/y is 19–20:1.

8. The process of claim **6** wherein said spinel is of the formula: $Fe_{2.85}Co_{0.15}O_4$, $Fe_{2.625}Co_{0.375}O_4$, $Fe_{2.97}Co_{0.03}O_4$.

9. The process of claim **1** wherein said catalyst is further in admixture with a solid diluent which aids in heat transfer and removal from the catalyst bed.

10. The process of claim **1** wherein said Group IA or IIA metal promoter is present in about 0.1 to 10 gram-atom % as the metal ion of the total gram-atoms metal content.

11. The process of claim **10** wherein said promoter is selected from bicarbonates, carbonates, organic acid salts, inorganic acid salts, nitrates, sulfates, halides and hydroxides of Group IA and IIA metals.

12. The process of claim **11** wherein said promoter is potassium carbonate.

13. The process of claim **1** wherein said product hydrocarbon mixture contains about 20 wt. % and above C_2–C_6 hydrocarbons of the total weight of hydrocarbons produced.

14. The process of claim **13** wherein said C_2–C_6 hydrocarbons contain C_2–C_6 olefins as about 50 wt. % and above of said total C_2–C_6 hydrocarbons.

15. A fixed bed process for synthesizing a hydrocarbon mixture containing C_2–C_6 olefins comprising the step of contacting a fixed bed of a catalyst composition comprised of an unsupported iron-cobalt spinel of the formula: $Fe_{2.85}CO_{0.15}O_4$, containing about 1 gram-atom percent potassium as the carbonate, wherein said spinel exhibits a single spinel phase being isostructural with Fe_3O_4 as determined by X-ray diffractometry and initially possessing a surface area of about 1 m^2/g, with a 2:1 to 1:1 H_2/CO mixture, at about 150–300 psig, 1000–1800 v/v/hr (SHSV) and about 230°–270° C. for a time sufficient to produce said C_2–C_6 olefins.

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