



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 21/08, C07C 27/00		A1	(11) International Publication Number: WO 00/10705
			(43) International Publication Date: 2 March 2000 (02.03.00)
(21) International Application Number: PCT/US99/18962 (22) International Filing Date: 19 August 1999 (19.08.99) (30) Priority Data: 60/097,192 20 August 1998 (20.08.98) US 60/097,193 20 August 1998 (20.08.98) US 60/097,194 20 August 1998 (20.08.98) US 09/377,007 18 August 1999 (18.08.99) US 09/377,008 18 August 1999 (18.08.99) US 09/376,873 18 August 1999 (18.08.99) US (71) Applicant: CONOCO INC. [US/US]; McLean Building, Suite 2084, 600 North Dairy Ashford, Houston, TX 77210-4783 (US). (72) Inventors: MANZER, Leo, E.; 714 Burnley Road, Wilmington, DE 19803 (US). KOURTAKIS, Konstantinos; 241 Lafayette Drive, Swedesboro, NJ 08085 (US). (74) Agent: PAYNE, JoAnna; 1000 South Pine, P.O. Box 1267, Ponca City, OK 77252-1267 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: FISCHER-TROPSCH PROCESSES USING XEROGEL AND AEROGEL CATALYSTS			
(57) Abstract			
<p>A process is disclosed for producing hydrocarbons. The process involves contacting a feed stream comprising hydrogen and carbon monoxide with a catalyst in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising hydrocarbons. In accordance with this invention, the catalyst used in the process is prepared by a method including at least (1) forming a catalyst gel by mixing (a) at least one dissolved compound of a catalytic metal for Fischer-Tropsch reactions (e.g., iron, cobalt, nickel and/or ruthenium compound(s) dissolved in water and/or ethanol); (b) (i) at least one dissolved alkoxide of titanium, zirconium and/or tantalum, and optionally (ii) at least one dissolved aluminum compound (the alkoxide and aluminum components (i) and (ii) being dissolved in a non-aqueous solvent; and at least when necessary to hydrolyze the alkoxide component (i) and aluminum compound component (ii), (c) water supplement; and (2) drying the gel.</p>			

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FISCHER-TROPSCH PROCESSES USING XEROGEL AND AEROGEL CATALYSTS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. provisional patent application Serial Number 60/097,192, filed August 20, 1998, U.S. provisional patent application Serial Number 60/097,193, filed August 20, 1998, and U.S. provisional patent application Serial Number 60/097,194, filed August 20, 1998, all of which are incorporated herein by reference in their entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

FIELD OF THE INVENTION

The present invention relates to a process for the preparation of hydrocarbons from synthesis gas, (i.e., a mixture of carbon monoxide and hydrogen), typically labeled the Fischer-Tropsch process. Particularly, this invention relates to catalysts containing a xerogel or aerogel matrix, containing titanium oxide, zirconium oxide or tantalum oxide, for the Fischer-Tropsch process.

BACKGROUND OF THE INVENTION

Large quantities of methane, the main component of natural gas, are available in many areas of the world. Methane can be used as a starting material for the production of hydrocarbons. The conversion of methane to hydrocarbons is typically carried out in two steps. In the first step methane is reformed with water or partially oxidized with oxygen to produce carbon monoxide and hydrogen (i.e., synthesis gas or syngas). In a second step, the syngas is converted to hydrocarbons.

The preparation of hydrocarbons from synthesis gas is well known in the art and is usually referred to as Fischer-Tropsch synthesis, the Fischer-Tropsch process, or Fischer-Tropsch reaction(s). Catalysts for use in such synthesis usually contain a catalytically active Group VIII (CAS) metal. In particular, iron, cobalt, nickel, and ruthenium have been abundantly used as the catalytically active metals. Cobalt and ruthenium have been found to be most suitable for catalyzing a process in which synthesis gas is converted to primarily hydrocarbons having five or more carbon atoms (i.e., where the C_5^+ selectivity of the catalyst is high). Additionally, the catalysts often contain one or more promoters and a support or carrier material. Rhenium is a widely used promoter.

The Fischer-Tropsch reaction involves the catalytic hydrogenation of carbon monoxide to produce a variety of products ranging from methane to higher aliphatic alcohols. The methanation reaction was first described in the early 1900's, and the later work by Fischer and Tropsch dealing with higher hydrocarbon synthesis was described in the 1920's.

The Fischer-Tropsch synthesis reactions are highly exothermic and reaction vessels must be designed for adequate heat exchange capacity. Because the feed streams to Fischer-Tropsch reaction vessels are gases while the product streams include liquids, the reaction vessels must have the ability

to continuously produce and remove the desired range of liquid hydrocarbon products. The process has been considered for the conversion of carbonaceous feedstock, e.g., coal or natural gas, to higher value liquid fuel or petrochemicals. The first major commercial use of the Fischer-Tropsch process was in Germany during the 1930's. More than 10,000 B/D (barrels per day) of products were manufactured with a cobalt based catalyst in a fixed-bed reactor. This work has been described by Fischer and Pichler in Ger. Pat. No. 731,295 issued Aug. 2, 1936.

Motivated by production of high-grade gasoline from natural gas, research on the possible use of the fluidized bed for Fischer-Tropsch synthesis was conducted in the United States in the mid-1940s. Based on laboratory results, Hydrocarbon Research, Inc. constructed a dense-phase fluidized bed reactor, the Hydrocol unit, at Carthage, Texas, using powdered iron as the catalyst. Due to disappointing levels of conversion, scale-up problems, and rising natural gas prices, operations at this plant were suspended in 1957. Research has continued, however, on developing Fischer-Tropsch reactors such as slurry-bubble columns, as disclosed in U.S. Patent No. 5,348,982 issued September 20, 1994.

Commercial practice of the Fischer-Tropsch process has continued from 1954 to the present day in South Africa in the SASOL plants. These plants use iron-based catalysts, and produce gasoline in relatively high-temperature fluid-bed reactors and wax in relatively low-temperature fixed-bed reactors.

Research is likewise continuing on the development of more efficient Fischer-Tropsch catalyst systems and reaction systems that increase the selectivity for high-value hydrocarbons in the Fischer-Tropsch product stream. In particular, a number of studies describe the behavior of iron, cobalt or ruthenium based catalysts in various reactor types, together with the development of catalyst compositions and preparations.

There are significant differences in the molecular weight distributions of the hydrocarbon products from Fischer-Tropsch reaction systems. Product distribution or product selectivity depends heavily on the type and structure of the catalysts and on the reactor type and operating conditions. Accordingly, it is highly desirable to maximize the selectivity of the Fischer-Tropsch synthesis to the production of high-value liquid hydrocarbons, such as hydrocarbons with five or more carbon atoms per hydrocarbon chain.

U.S. Pat. No. 4,659,681 issued on Apr. 21, 1987, describes the laser synthesis of iron based catalyst particles in the 1-100 micron particle size range for use in a slurry reactor for Fischer-Tropsch synthesis.

U.S. Pat. No. 4,619,910 issued on Oct. 28, 1986, U.S. Pat. No. 4,670,472 issued on Jun. 2, 1987, and U.S. Pat. No. 4,681,867 issued on Jul. 21, 1987, describe a series of catalysts for use in a slurry Fischer-Tropsch process in which synthesis gas is selectively converted to higher hydrocarbons of relatively narrow carbon number range. Reactions of the catalyst with air and water and

calcination are specifically avoided in the catalyst preparation procedure. The catalysts are activated in a fixed-bed reactor by reaction with $\text{CO} + \text{H}_2$ prior to slurrying in the oil phase in the absence of air.

Catalyst supports for catalysts used in Fischer-Tropsch synthesis of hydrocarbons have typically been oxides (e.g., silica, alumina, titania, zirconia or mixtures thereof, such as silica-alumina). It has been claimed that the Fischer-Tropsch synthesis reaction is only weakly dependent on the chemical identity of the metal oxide support (see E. Iglesia et al. 1993, In: "Computer-Aided Design of Catalysts," ed. E. R. Becker et al., p. 215, New York, Marcel Dekker, Inc.). The products prepared by using these catalysts usually have a very wide range of molecular weights.

U.S. Pat. No. 4,477,595 discloses ruthenium on titania as a hydrocarbon synthesis catalyst for the production of C_5 to C_{40} hydrocarbons, with a majority of paraffins in the C_5 to C_{20} range. U.S. Pat. No. 4,542,122 discloses a cobalt or cobalt-thoria on titania having a preferred ratio of rutile to anatase, as a hydrocarbon synthesis catalyst. U.S. Pat. No. 4,088,671 discloses a cobalt-ruthenium catalyst where the support can be titania but preferably is alumina for economic reasons. U.S. Pat. No. 4,413,064 discloses an alumina supported catalyst having cobalt, ruthenium and a Group IIIA or Group IVB metal oxide, e.g., thoria. European Patent No. 142,887 discloses a silica supported cobalt catalyst together with zirconium, titanium, ruthenium and/or chromium.

U.S. Pat. No. 4,801,573 discloses a promoted cobalt and rhenium catalyst, preferably supported on alumina that is characterized by low acidity, high surface area, and high purity, which properties are said to be necessary for high activity, low deactivation, and high molecular weight products. The amount of cobalt is most preferably about 10 to 40 wt % of the catalyst. The content of rhenium is most preferably about 2 to 20 wt % of the cobalt content. Related U.S. Pat. No. 4,857,559 discloses a catalyst most preferably having 10 to 45 wt % cobalt and a rhenium content of about 2 to 20 wt % of the cobalt content. In both of the above patents the method of depositing the active metals and promoter on the alumina support is described as not critical.

U.S. Pat. No. 5,545,674 discloses a cobalt-based catalyst wherein the active metal is dispersed as a very thin film on the surface of a particulate support, preferably silica or titania or a titania-containing support. The catalyst may be prepared by spray techniques.

U.S. Pat. No. 5,028,634 discloses supported cobalt-based catalysts, preferably supported on high surface area aluminas. High surface area supports are said to be preferred because greater cobalt dispersion can be achieved as cobalt is added, with less tendency for one crystal of cobalt to fall on another crystal of cobalt. The cobalt loading on a titania support is preferably 10 to 25 wt %, while the preferred cobalt loading on an alumina support is 5 to 45 wt %.

International Publication Nos. WO 98/47618 and WO 98/47620 disclose the use of rhenium promoters and describe several functions served by the rhenium.

U.S. Pat. No. 5,248,701 discloses a copper promoted cobalt-manganese spinel that is said to be useful as a Fischer-Tropsch catalyst with selectivity for olefins and higher paraffins.

U.S. Pat. No. 5,302,622 discloses a supported cobalt and ruthenium based catalyst including other components and preferably prepared by a gelling procedure to incorporate the catalyst components in an alcogel formed from a hydrolyzable compound of silicon, and/or aluminum, and optional compounds. The cobalt content after calcination is preferably between 14 and 40 wt % of the catalyst.

UK Patent Application GB 2,258,414A, published February 10, 1993, discloses a supported catalyst containing cobalt, molybdenum and/or tungsten, and an additional element. The support is preferably one or more oxides of the elements Si, Al, Ti, Zr, Sn, Zn, Mg, and elements with atomic numbers from 57 to 71. After calcination, the preferred cobalt content is from 5 to 40 wt % of the catalyst. A preferred method of preparation of the catalyst includes the preparation of a gel containing the cobalt and other elements.

International Publication No. WO 96/19289 discloses active metal coated catalysts supported on an inorganic oxide, and notes that dispersion of the active metal on Fischer-Tropsch catalysts has essential effects on the activity of the catalyst and on the composition of the hydrocarbons obtained.

Despite the vast amount of research effort in this field, there is still a great need for new catalysts for Fischer-Tropsch synthesis, particularly catalysts that provide high C_5^+ hydrocarbon selectivities to maximize the value of the hydrocarbons produced and thus enhance the process economics.

SUMMARY OF THE INVENTION

This invention provides a process and catalyst for producing hydrocarbons, and a method for preparing the catalyst. The process comprises contacting a feed stream comprising hydrogen and carbon monoxide with a catalyst in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising hydrocarbons.

In accordance with this invention, the catalyst used in the process comprises an aerogel or xerogel matrix comprising a matrix metal selected from the group consisting of titanium, tantalum, zirconium, aluminum, and combinations thereof, and one or more catalytically active metals selected from the group consisting of iron, cobalt, nickel, and ruthenium dispersed in the matrix.

This invention also provides a catalyst comprising the dried reaction product of a first reagent comprising an alkoxide of a metal selected from the group consisting of titanium, tantalum, zirconium, and combinations thereof in a non-aqueous solvent, and a second reagent comprising a solution comprising one or more catalytically active metals selected from the group consisting of iron, cobalt, nickel, and ruthenium, wherein the product is an aerogel or xerogel.

This invention also provides a Fischer-Tropsch catalyst comprising an aerogel or xerogel formed from the hydrolysis and condensation reaction of a solution of a catalytically active metal selected from the group consisting of iron, cobalt, nickel, ruthenium, and combinations thereof and a matrix reagent comprising a non-aqueous solution of a metal selected from the group consisting of titanium, tantalum, zirconium, and combinations thereof.

This invention also includes a method for the preparation of a Fischer-Tropsch catalyst comprising mixing a non-aqueous solution of an alkoxide of a metal selected from the group consisting of titanium, tantalum, zirconium, and combinations thereof with one or more catalytically active metals selected from the group consisting of iron, cobalt, nickel, and ruthenium in a solvent, forming a gel, and drying the aged gel.

This invention provides a process for producing hydrocarbons, comprising contacting a feed stream comprising hydrogen and carbon monoxide with a catalyst in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising hydrocarbons, wherein the catalyst comprises a catalytically active metal selected from the group consisting of iron, cobalt, nickel, ruthenium, and combinations thereof dispersed in an aerogel or xerogel comprising a derivative of the hydrolysis and condensation of one or more alkoxides of a matrix metal selected from the group consisting of titanium, tantalum, zirconium, and combinations thereof and, optionally, aluminum.

This invention also provides a process characterized by using a catalyst prepared by a method comprising (1) forming a catalyst gel by mixing (a) at least one dissolved compound of a catalytic metal for Fischer-Tropsch reactions (e.g., at least one compound of a metal selected from the group consisting of iron, cobalt, nickel and ruthenium dissolved in water and/or ethanol); (b) (i) at least one dissolved alkoxide of a metal selected from the group consisting of titanium, zirconium and tantalum and optionally (ii) at least one dissolved aluminum compound, said alkoxide component (i) and said optional aluminum compound component (ii) being dissolved in a non-aqueous solvent (e.g., ethanol); and at least when necessary to hydrolyze the alkoxide component (i) and aluminum compound component (ii), (c) an aqueous supplement (e.g., water, aqueous acid or aqueous base); and (2) drying the gel.

DETAILED DESCRIPTION OF THE INVENTION

The feed gases charged to the process of the invention comprise hydrogen, or a hydrogen source, and carbon monoxide. H_2/CO mixtures suitable as a feedstock for conversion to hydrocarbons according to the process of this invention can be obtained from light hydrocarbons such as methane by means of steam reforming, partial oxidation, or other processes known in the art. The hydrogen is preferably provided by free hydrogen, although some Fischer-Tropsch catalysts have sufficient water gas shift activity to convert some water to hydrogen for use in the Fischer-Tropsch process. It is preferred that the molar ratio of hydrogen to carbon monoxide in the feed be greater

than 0.5:1 (e.g., from about 0.67 to 2.5). When cobalt, nickel, and/or ruthenium catalysts are used, the feed gas stream preferably contains hydrogen and carbon monoxide in a molar ratio of about 2:1. When iron catalysts are used, the feed gas stream preferably contains hydrogen and carbon monoxide in a molar ratio of about 0.67:1. The feed gas may also contain carbon dioxide. The feed gas stream should contain a low concentration of compounds or elements that have a deleterious effect on the catalyst, such as poisons. For example, the feed gas may need to be pre-treated to ensure that it contains low concentrations of sulfur or nitrogen compounds, such as hydrogen sulfide, ammonia and carbonyl sulfides.

The feed gas is contacted with the catalyst in a reaction zone. Mechanical arrangements of conventional design may be employed as the reaction zone including, for example, fixed bed, fluidized bed, slurry phase, slurry bubble column or ebullating bed reactors, among others, may be used. Accordingly, the size and physical form of the catalyst particles may vary depending on the reactor in which they are to be used.

A component of the catalysts used in this invention is the matrix material, which is essentially derived from solution (b) and which incorporates the active catalyst component, which is derived from dissolved component (a). A matrix is a skeletal framework of oxides and oxyhydroxides derived from the hydrolysis and condensation of alkoxides and other reagents. The framework typically comprises 30% or more, by weight, of the total catalyst composition. The matrix material comprises tantalum, titanium, or zirconium, and optionally aluminum oxide/hydroxide, xerogels or aerogels or mixtures thereof totaling from 99.9 to 30 mole %, preferably from 65 to 85 mole % of the catalyst composition. Various compounds can be used as precursors to the aluminum oxides/hydroxides, including by way of illustration and not limitation, aluminum: nitrates, acetates, alkoxides, acetylacetonates, and chlorides.

Combinations where the matrix metal is Ti, combinations where the matrix metal is a combination of Ti and Al, and combinations where the matrix metal is Zr are typical. Preferred combinations include combinations where the matrix metal is a combination of Ti and Al, where the atomic ratio Ti:Al is between about 1:9 and about 9:1. Also preferred are combinations including Al where the atomic ratio of Al to the total of Ta, Ti and Zr is about 1.01:1.

A gel may be described as a coherent, rigid three-dimensional polymeric network. The present gels are formed in a liquid medium, usually water, alcohol, or a mixture thereof. The term "alcogel" describes gels in which the pores are filled with predominantly alcohol. Gels whose pores are filled primarily with water may be referred to as aquagels or hydrogels.

A "xerogel" is a gel from which the liquid medium has been removed and replaced by a gas. In general, the structure is compressed and the porosity reduced significantly by the surface tension forces that occur as the liquid is removed. As soon as liquid begins to evaporate from a gel at temperatures below the critical temperature, surface tension creates concave menisci in the gel's

pores. As evaporation continues, the menisci retreat into the gel body, compressive forces build up around its perimeter, and the perimeter contracts, drawing the gel body inward. Eventually surface tension causes significant collapse of the gel body and a reduction of volume, often as much as two-thirds or more of the original volume. This shrinkage causes a significant reduction in the porosity, often as much as 90 to 95 percent depending on the system and pore sizes.

In contrast, an "aerogel" is a gel from which the liquid has been removed in such a way as to prevent significant collapse or change in the structure as liquid is removed. This is typically accomplished by heating the liquid-filled gel in an autoclave while maintaining the prevailing pressure above the vapor pressure of the liquid until the critical temperature of the liquid has been exceeded, and then gradually releasing the vapor, usually by gradually reducing the pressure either incrementally or continuously, while maintaining the temperature above the critical temperature. The critical temperature is the temperature above which it is impossible to liquefy a gas, regardless of how much pressure is applied. At temperatures above the critical temperature, the distinction between liquid and gas phases disappears and so do the physical manifestations of the gas/liquid interface. In the absence of an interface between liquid and gas phases, there is no surface tension and hence no surface tension forces to collapse the gel. Such a process may be termed "supercritical drying." Aerogels produced by supercritical drying typically have high porosities, on the order of from 50 to 99 percent by volume.

In the practice of this invention one or more metal alkoxides (e.g., titanium n-butoxide) may be used as starting material for preparing the gels. The inorganic metal alkoxides used in this invention may include any alkoxide that contains from 1 to 20 carbon atoms and preferably contains 1 to 5 carbon atoms in the alkoxide group, and is preferably are soluble in the liquid reaction medium. C₁-C₄ alkoxides such as tantalum n-butoxide, titanium isopropoxide and zirconium isopropoxide are preferred.

Commercially available alkoxides can be used. However, inorganic alkoxides can be prepared by other routes. Examples include alkoxides prepared by the direct reaction of zero valent metals with alcohols in the presence of a catalyst. Many alkoxides can be formed by reaction of metal halides with alcohols. Alkoxy derivatives can be synthesized by the reaction of the alkoxide with alcohol in a ligand interchange reaction. Direct reactions of metal dialkylamides with alcohol also form alkoxide derivatives. Additional examples are disclosed in "Metal Alkoxides" by D.C. Bradley et al., Academic Press, (1978), which is incorporated herein by reference in its entirety.

The first step in the synthesis of the gels containing alcohol, or alcogels, consists of preparing non-aqueous solutions of the alkoxides and other reagents, and separate solutions containing protic solvents such as water. When the alkoxide solutions are mixed with the solutions containing the protic solvents, the alkoxides will react and polymerize to form a gel.

The medium utilized in the process generally is preferably a solvent for both the inorganic alkoxide or alkoxides that are used and the additional metal reagents and promoters that are added in the single step synthesis. Solubility of all of the components in their respective media (aqueous and non-aqueous) is preferred to produce highly dispersed materials. By employing soluble reagents in this manner, mixing and dispersion of the active metals and promoter reagents can be near atomic, mirroring their dispersion in their respective solutions. The gel thus produced by this process will therefore contain highly dispersed active metals and promoters. High dispersion results in catalyst metal particles in the nanometer size range, and highly efficient use of the catalytically active components.

Preferred embodiments include those wherein the catalytic metal of (a) is dissolved in a separate protic solvent (e.g., water) and this solution of catalytic metal compound(s) is mixed with the non-aqueous solution of (b). Also preferred, however, are embodiments wherein the catalytic metal is dissolved in the same non-aqueous solution as components (i) and (ii), and aqueous supplement (c) is used.

Typically, the concentration of the solvent used is linked to the alkoxide content. A molar ratio of 26.5:1 ethanol:total alkoxide can be used, although the molar ratio of ethanol:total alkoxide can be from about 5:1 to 53:1, or even greater. If a large excess of alcohol is used, gelation will not generally occur immediately; some solvent evaporation will be needed. At lower solvent concentrations, it is thought that a heavier gel will be formed, having less pore volume and surface area.

For this invention, water and any aqueous solutions are added in a dropwise fashion to the alcohol soluble alkoxide and other reagents to induce hydrolysis and condensation reaction. Depending on the alkoxide system, a discernible gel point can be reached in minutes or hours. The molar ratio of the total water added to the total Ti, Zr, Ta, and Al added (including water present in aqueous solutions) varies according to the specific inorganic alkoxide being reacted.

Generally, a molar ratio of water:alkoxide from about of 0.1:1 to 10:1 is used. For example, ratios close to 5:1 for tantalum(alkoxide)₅ and 4:1 for zirconium(alkoxide)₄ and titanium(alkoxides)₄ can be used. The amount of water utilized in the reaction is that calculated to hydrolyze the inorganic alkoxide in the reaction mixture. A ratio lower than that needed to hydrolyze the alkoxide species will result in a partially hydrolyzed material, which in most cases will reach a gel point at a much slower rate, depending on the aging procedure and the presence of atmospheric moisture.

The addition of acidic or basic reagents to the inorganic alkoxide medium can have an effect on the kinetics of the hydrolysis and condensation reactions, and the microstructure of the oxide/hydroxide matrices derived from the alkoxide precursor which entraps or incorporates the soluble metal and promoter reagents. Generally, a pH within the range of from 1 to 12 can be used, with a pH range of from 1 to 6 being preferred.

After reacting to form the alcogels of the present invention, it may be necessary to complete the gelation process with some aging of the gel. This aging can range from one minute to several days. In general, all alcogels are aged at room temperature in air for at least several hours.

Removal of solvent from the alcogels can be accomplished by several methods. Removal by vacuum drying or heating in air results in the formation of a xerogel. An aerogel of the material can typically be formed by charging in a pressurized system such as an autoclave. The solvent-containing gel that is formed in the practice of this invention is placed in an autoclave, where it can be contacted with a fluid above its critical temperature and pressure by allowing the supercritical fluid to flow through the gel material until the solvent is no longer being extracted by the supercritical fluid. In performing this extraction to produce an aerogel material, various supercritical fluids can be utilized at their critical temperature and pressure. For instance, fluorochlorocarbons typified by Freon[®] fluorochloromethanes (e.g., Freon[®] 11 (CCl_3F), 12 (CCl_2F_2) or 114 ($\text{CClF}_2\text{CClF}_2$), ammonia and carbon dioxide are all suitable for this process. Typically, the extraction fluids are gases at atmospheric conditions, so that pore collapse due to the capillary forces at the liquid/solid interface is avoided during drying. The resulting material will, in most cases, possess a higher surface area than the non-supercritically dried materials.

The xerogels and aerogels thus produced can be described as precursor salts dispersed in an oxide or oxyhydroxide matrix. The hydroxyl content is at this point undefined; a theoretical maximum corresponds to the valence of central metal atom. Hence, $\text{Ta}_2(\text{O}_{2-x}(\text{OH})_x)_5$ possesses a theoretical hydroxyl maximum when x is 2. The molar H_2O :alkoxide ratio can also impact the final xerogel stoichiometry; in this case, if H_2O :Ta is less than 5, there will be residual -OR groups in the unaged gel. However, reaction with atmospheric moisture will convert these to the corresponding -OH, and -O groups upon continued polymerization and dehydration. Aging, even under inert conditions, can also effect the condensation of the -OH, eliminating H_2O , through continuation of cross-linking and polymerization, i.e., gel formation.

Another component of the catalyst of the present invention is the catalytic metal. The catalytic metal is preferably selected from iron, cobalt, nickel and/or ruthenium. Normally, the catalytic metal component of the matrix is reduced to provide elemental metal (e.g., elemental iron, cobalt, nickel and/or ruthenium) before use. The catalyst must contain a catalytically effective amount of the metal component(s). The amount of catalytic metal present in the catalyst may vary widely. Typically, the catalyst comprises from about 0.1 to 50 mole % (as the metal) of total supported iron, cobalt, nickel and/or ruthenium per total moles of catalytic metal and matrix metal, and preferably from about 10 to 30 mole %.

Each of the catalytic metals can be used individually. Combinations, especially combinations of cobalt and ruthenium, can also be used. Preferred are catalysts comprising from about 2.5 to about

50 mole percent of a combination of cobalt and ruthenium where the ruthenium content is from about 0.001 to about 5 mole percent. Preferred matrix materials for these combinations include titanium and a combination of titanium and aluminum (e.g., a combination of titanium and aluminum having a Ti:Al atomic ratio between about 1:9 and about 9:1).

5 Optionally, the catalyst of the present invention may also comprise one or more additional promoters or modifiers known to those skilled in the art. When the catalytic metal is iron, cobalt, nickel and/or ruthenium, suitable promoters include at least one metal selected from the group consisting of Group IA (CAS) metals (i.e., Na, K, Rb, Cs), Group IIA metals (i.e., Mg, Ca, Sr, Ba), Group IB metals (i.e., Cu, Ag, and Au) Group IIIB metals (i.e., Sc, Y and La), Group IVB metals
10 (i.e., Ti, Zr and Hf), Group VB metals (i.e., V, Nb and Ta), and Rh, Pd, Os, Ir, PtMn, B, P, and Re. Preferably, any additional promoters for the cobalt and/or ruthenium are selected from Sc, Y, La, Ti, Zr, Hf, Rh, Pd, Os, Ir, Pt, Re, Nb, Cu, Ag, Mn, B, P, and Ta. Preferably, any additional promoters for the iron catalysts are selected from Na, K, Rb, Cs, Mg, Ca, Sr, and Ba. The amount of additional promoter, if present, is typically between 0.001 and 20 mole %, preferably from 2 to 5 mole %. More
15 preferred are catalysts comprising from about 10 to 25 mole percent of a combination of cobalt and rhenium where the rhenium content is from about 0.001 to 10 mole percent; and catalysts comprising from about 10 to 25 mole percent of cobalt and both rhenium and ruthenium where the rhenium and ruthenium together total about 0.001 to about 10 mole percent. Preferred matrix materials for these combinations include titanium and a combination of titanium and aluminum, for example, a
20 combination of titanium and aluminum having a Ti:Al atomic ratio between about 1:9 and about 9:1.

The most preferred method of preparation may vary among those skilled in the art, depending for example on the desired catalyst particle size. Those skilled in the art are able to select the most suitable method for a given set of requirements.

Typically, at least a portion of the metal(s) of the catalytic metal component (a) of the
25 catalysts of the present invention is present in a reduced state (i.e., in the metallic state). Therefore, it is normally advantageous to activate the catalyst prior to use by a reduction treatment, in the presence of hydrogen at an elevated temperature. Typically, the catalyst is treated with hydrogen at a temperature in the range of from about 75°C to about 500°C, for about 0.5 to about 24 hours at a pressure of about 1 to about 75 atm. Pure hydrogen may be used in the reduction treatment, as well
30 as a mixture of hydrogen and an inert gas such as nitrogen. The amount of hydrogen may range from about 1% to about 100% by volume.

The Fischer-Tropsch process is typically run in a continuous mode. In this mode, the gas hourly space velocity through the reaction zone typically may range from about 100 volumes/hour/volume catalyst (v/hr/v) to about 10,000 v/hr/v, preferably from about 300 v/hr/v
35 to about 2,000 v/hr/v. The reaction zone temperature is typically in the range from about 160°C to about 300°C. Preferably, the reaction zone is operated at conversion promoting conditions at

temperatures from about 190°C to about 260°C. The reaction zone pressure is typically in the range of about 80 psig (653 kPa) to about 1000 psig (6994 kPa), preferably, from 80 psig (653 kPa) to about 600 psig (4237 kPa), and still more preferably, from about 140 psig (1066 kPa) to about 400 psig (2858 kPa).

5 The products resulting from the process will have a great range of molecular weights. Typically, the carbon number range of the product hydrocarbons will start at methane and continue to the limits observable by modern analysis, about 50 to 100 carbons per molecule. The process is particularly useful for making hydrocarbons having five or more carbon atoms, especially when the above-referenced preferred space velocity, temperature and pressure ranges are employed.

10 The wide range of hydrocarbons produced in the reaction zone will typically afford liquid phase products at the reaction zone operating conditions. Therefore the effluent stream of the reaction zone will often be a mixed phase stream including liquid and vapor phase products. The effluent stream of the reaction zone may be cooled to effect the condensation of additional amounts of hydrocarbons and passed into a vapor-liquid separation zone separating the liquid and vapor phase
15 products. The vapor phase material may be passed into a second stage of cooling for recovery of additional hydrocarbons. The liquid phase material from the initial vapor-liquid separation zone, together with any liquid from a subsequent separation zone, may be fed into a fractionation column. Typically, a stripping column is employed first to remove light hydrocarbons such as propane and butane. The remaining hydrocarbons may be passed into a fractionation column where they are
20 separated by boiling point range into products such as naphtha, kerosene and fuel oils. Hydrocarbons recovered from the reaction zone and having a boiling point above that of the desired products may be passed into conventional processing equipment such as a hydrocracking zone in order to reduce their molecular weight. The gas phase recovered from the reactor zone effluent stream after hydrocarbon recovery may be partially recycled if it contains a sufficient quantity of hydrogen and/or
25 carbon monoxide.

Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following embodiments are to be construed as illustrative, and not as constraining the scope of the present invention in any way whatsoever.

30 EXAMPLES

General Procedure For Batch Tests

Each of the catalyst samples was treated with hydrogen prior to use in the Fischer-Tropsch reaction. The catalyst sample was placed in a small quartz crucible in a chamber and purged with 500 sccm ($8.3 \times 10^{-6} \text{ m}^3/\text{s}$) nitrogen at room temperature for 15 minutes. The sample was then
35 heated under 100 sccm ($1.7 \times 10^{-6} \text{ m}^3/\text{s}$) hydrogen at 1°C/minute to 100°C and held at 100°C for one

hour. The catalysts were then heated at 1°C/minute to 400°C and held at 400°C for four hours under 100 sccm ($1.7 \times 10^{-6} \text{ m}^3/\text{s}$) hydrogen. The samples were cooled in hydrogen and purged with nitrogen before use.

5 A 2 mL pressure vessel was heated at either 200°C or 225°C under 1000 psig (6994 kPa) of $\text{H}_2:\text{CO}$ (2:1) and maintained at that temperature and pressure for 1 hour when heated at 225°C or for 6 hours when heated at 200°C. In a typical run, roughly 50 mg of the hydrogen catalyst and 1 mL of n-octane was added to the vessel. After one hour, the reactor vessel was cooled in ice, vented, and an internal standard of di-n-butylether was added. The reaction product was analyzed on an HP6890 gas chromatograph. Hydrocarbons in the range of $\text{C}_{11}\text{-C}_{40}$ were analyzed relative to the internal
10 standard. The lower hydrocarbons were not analyzed since they are masked by the solvent and are also vented as the pressure is reduced.

A C_{11}^+ Productivity ($\text{g C}_{11}^+/\text{hour/kg catalyst}$) was calculated based on the integrated production of the $\text{C}_{11}\text{-C}_{40}$ hydrocarbons per kg of catalyst per hour. The logarithm of the weight fraction for each carbon number $\ln(W_n/n)$ was plotted as the ordinate vs. number of carbon atoms in
15 (W_n/n) as the abscissa. From the slope, a value of alpha was obtained. Some runs displayed a double alpha as shown in the tables. The results of runs over a variety of catalysts at 225°C are shown in Table 1 and at 200°C are shown in Table 2.

Catalyst Preparation

The catalyst compositions are given in atomic ratios except where otherwise noted.

20 EXAMPLE 1

A 0.1151 M ruthenium (III) chloride solution in ethanol (1.794 mL), a 60 volume % solution of titanium n-butoxide (20.008 mL) in ethanol, and ethanol (45.665 mL) were simultaneously added to a 150 mL petri dish with gentle agitation, under a nitrogen blanket. In a second step, a 1.0 M aqueous nickel (II) chloride solution (5.987 mL) was added to this mixture. A gel point was realized
25 within minutes; the material was brown. After aging for approximately 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel with a nominal composition of Ru (0.005)/Ni (0.145)/Ti (0.85).

EXAMPLE 2

The same procedure and solutions were used as described in Example 1, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 3.497 mL; titanium
30 n-butoxide solution, 19.508 mL; ethanol, 44.524 mL; and nickel (II) chloride solution, 5.636 mL. A brown alcogel formed within minutes of addition of the aqueous solution. The final xerogel had a nominal composition of Ru (0.01)/Ni (0.14)/Ti (0.85).

EXAMPLE 3

The same procedure and solutions were used as described in Example 1, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 8.134 mL; titanium n-butoxide solution, 18.148 mL; ethanol, 41.42 mL; and nickel (II) chloride solution, 4.681 mL. A dark alcogel formed within minutes of addition of the aqueous solution. The final xerogel had a nominal composition of Ru (0.025)/Ni (0.125)/Ti (0.85).

EXAMPLE 4

The same procedure and solutions were used as described in Example 1, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 14.575 mL; titanium n-butoxide solution, 16.259 mL; ethanol, 37.108 mL; and nickel (II) chloride solution, 3.355 mL. A dark alcogel formed within minutes of addition of the aqueous solution. The final xerogel had a nominal composition of Ru (0.05)/Ni (0.1)/Ti (0.85).

EXAMPLE 5

The same procedure and solutions were used as described in Example 1, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 1.794 mL; 1.0 M cobalt(II)chloride hexahydrate in ethanol, 2.993 mL; titanium n-butoxide solution, 20.008 mL; ethanol, 42.671 mL; and nickel (II) chloride solution, 2.993 mL. A dark-brown, glassy alcogel formed within minutes of addition of the aqueous solution. The final xerogel had a nominal composition of Ru (0.005)/Co (0.0725)/Ni (0.0725)/Ti (0.85).

EXAMPLE 6

The same procedure and solutions were used as described in Example 1, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 3.497 mL; 1.0 M cobalt(II)chloride hexahydrate in ethanol, 2.818 mL; titanium n-butoxide solution, 19.508 mL; ethanol, 41.706 mL; and nickel (II) chloride solution, 2.818 mL. A dark- brown glassy alcogel formed within minutes of addition of the aqueous solution. The final xerogel had a nominal composition of Ru (0.01)/Co (0.07)/Ni (0.07)/Ti (0.85).

EXAMPLE 7

Cobalt(II) chloride, 1.0 M in ethanol (4.28 mL), 60 volume % in ethanol of titanium n-butoxide (21.460 mL), and ethanol (37.86 mL) were simultaneously added to a 150 mL petri dish with gentle agitation. In a second step, a 0.3309 M aqueous ruthenium(III) chloride (6.692 mL) solution was added while gently agitating. A gel point was rapidly developed. The alcogel thus produced was clear, and dark blue in color. It was aged approximately 24 hours, and dried under vacuum for 5 hours at 110°C. The final xerogel had a nominal composition of Ru (0.05)/Co (0.1)/Ti (0.85).

EXAMPLE 8

The same procedure and solutions were used as described in Example 7, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 5.408 mL; 0.2871 M HAuCl₄ in ethanol, 6.225 mL; titanium n-butoxide solution, 18.34 mL; and ethanol, 36.458 mL. The alcogel was brown in color. The final xerogel had a nominal composition of Ru (0.05)/Au (0.05)/Ti (0.9).

EXAMPLE 9

The same procedure and solutions were used as described in Example 8, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 5.637 mL; 0.2871 M HAuCl₄ in ethanol, 3.249 mL; titanium n-butoxide solution, 19.674 mL; and ethanol, 39.265 mL. A brown alcogel formed. The final xerogel had a nominal composition of Ru (0.05)/Au (0.025)/Ti (0.925).

EXAMPLE 10

The same procedure and solutions were used as described in Example 7, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 7.737 mL; cobalt(II) chloride, 1.0 M in ethanol, 10.241 mL; titanium n-butoxide solution, 21.894 mL; and ethanol, 31.993 mL. A clear, red alcogel formed within minutes of the addition of aqueous solution. The same procedures were followed in subsequent processing steps, as described in Example 1. The final xerogel had a nominal composition of Ru (0.05)/Co (0.02)/Ti (0.75).

EXAMPLE 11

Under an inert nitrogen atmosphere, 0.09777 M ruthenium (III) chloride in ethanol (8.323 mL) was added together with 60 volume % in ethanol titanium n-butoxide (41.493 mL) into a 150 mL petri dish with gentle agitation. In a second step, H₂O (2.291 mL) was added to induce hydrolysis and polymerization. A gel point was rapidly realized; a clear, dark red alcogel formed. The final xerogel had a nominal composition of Ru (0.025)/Ti (0.975).

EXAMPLE 12

The same procedure and solutions were used as described in Example 11, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 15.183 mL; titanium n-butoxide solution, 16.08 mL; water, 2.037 mL; and ethanol, 36.7 mL. The alcogel formed within minutes; it was clear, and dark blue in color. The final xerogel had a nominal composition of Ru (0.05)/Ti (0.95).

EXAMPLE 13

The same procedure and solutions were used as described in Example 11, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 17.325 mL; titanium n-butoxide solution, 15.452 mL; 1.0 M cobalt (II) chloride hexahydrate in water, 5.082 mL; water,

1.957 mL; and ethanol, 30.184 mL. The alcogel formed within minutes; it was clear, and red-blue in color. The final xerogel had a nominal composition of Ru (0.05)/Co (0.15)/Ti (0.8).

EXAMPLE 14

5 The same procedure and solutions were used as described in Example 13, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 20.171 mL; titanium n-butoxide solution, 14.617 mL; 1.0 M cobalt (II) chloride hexahydrate in water, 11.833 mL; water, 1.851 mL; and ethanol, 21.528 mL. The alcogel formed within minutes, and was red-blue in color. The final xerogel had a nominal composition of Ru (0.05)/Co (0.3)/Ti (0.65).

EXAMPLE 15

10 The same procedure and solutions were used as described in Example 13, adjusting the volumetric addition for the desired stoichiometries: ruthenium (III) chloride, 24.136 mL; titanium n-butoxide solution, 13.454 mL; 1.0 M cobalt (II) chloride hexahydrate in water, 21.238 mL; water, 1.704 mL; and ethanol, 9.468 mL. The alcogel formed within minutes; it was clear, and blue in color. The final xerogel had a nominal composition of Ru (0.05)/Co (0.45)/Ti (0.50).

EXAMPLE 16

15 Ethanol (285.7 mL) was combined with titanium n-butoxide (25.44 g) in an inert atmosphere N₂ drybox. In a separate container, ruthenium trichloride (RuCl₃•0.2H₂O, 1.0153 g) and Re₂O₇ (2.527 g) were combined with water (47.69 mL) and additional ethanol (287 mL). Glacial acetic acid (0.6415 mL) and 70 wt. % nitric acid (0.5 mL) were added to the water mixture. The aqueous
20 solution containing the ruthenium chloride and rhenium (VII) oxide was added, in a dropwise fashion, to the titanium alkoxide solution. The apparatus was blanketed in nitrogen. A 1 L resin kettle, fitted with a three-neck flask, was used. A red-brown solution was obtained. The gel point was reached within 24 hours. A clear, very dark brown gel was formed.

25 The gel was aged at room temperature for twelve days prior to removal of solvent by supercritical CO₂. The material was placed in a stirred autoclave and extracted in CO₂ under supercritical conditions. CO₂ gas was purged over the catalyst for 7 hours at 40°C and 3500 psig(24.2 MPa). The material isolated was a free flowing powder. The final aerogel had a nominal composition of 5.7 wt. % Ru/23 wt. % Re/71.3 wt. % TiO₂.

EXAMPLE 17

30 Titanium n-butoxide (194.01 g) was added to ethanol (435.84 mL) in an inert atmosphere drybox. In a separate container, ruthenium (III) chloride (6.223 g) was combined with water (41.08 mL) along with 70% nitric acid (3.82 mL) and glacial acetic acid (4.892 mL). Ethanol (435.84 mL) was added to this water-based solution. The water-based solution was loaded into a dropping funnel. The titanium n-butoxide solution was added to a 1.5 L resin kettle inside of the
35 drybox. Under an inert nitrogen blanket, with gentle stirring, the water-based solution was added to

the alkoxide/alcohol solution. A gel point was reached within minutes. The material was dark brown in color. The material was aged for approximately 24 hours, and subsequently dried under vacuum at 110°C for 5 hours. The resultant xerogel was dark brown in color. The final catalyst had a nominal composition of 6.2 wt. % Ru/TiO₂.

5

EXAMPLE 18

Zirconium (IV) isopropoxide (186.709 g) was added to ethanol (435.84 mL) in an inert atmosphere drybox. In a separate container, ruthenium (III) chloride (6.223 g) was combined with water (41.08 mL) along with 70% nitric acid (3.82 mL) and glacial acetic acid (4.892 mL). Ethanol (435.84 mL) was added to this aqueous-based solution. The aqueous-based solution was loaded into a dropping funnel. The alkoxide solution was added to a 1.5 L resin kettle inside of the drybox. Under an inert nitrogen blanket, with gentle stirring, the aqueous solution was added to the alkoxide/alcohol solution. A gel point was reached within minutes. The material was dark brown in color. The material was aged for approximately 24 hours, and subsequently dried under vacuum at 110°C for 5 hours. The resultant xerogel was dark brown in color. The final catalyst had a nominal composition of 4.1 wt % Ru/ ZrO₂.

10

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EXAMPLE 19

Zirconium isopropoxide in propanol (6.527 mL, 2.231 M), titanium n-butoxide, 60 volume % in ethanol, (8.215 mL), and ethanol (36.386 mL) were added simultaneously to a 150 mL petri dish with gentle agitation. In a second step, 0.3309 M aqueous ruthenium (III) chloride (4.632 mL) solution was added while gently agitating. A gel point was rapidly developed. The alcogel thus produced was grayish-blue in color. It was aged approximately 24 hours, dried under vacuum for 5 hours at 110°C. The final xerogel had a nominal composition of Ru (0.05)/Ti (0.475)/Zr (0.475).

20

EXAMPLE 20

Zirconium isopropoxide, 2.231 M in propanol (5.255 mL), 60 volume % in ethanol titanium n-butoxide (6.614 mL) and ethanol (31.455 mL) were simultaneously added to a 150 mL petri dish with gentle agitation. In a second step, a 0.3309 M ruthenium (III) chloride (3.73 mL) aqueous solution was added while gently agitating. A gel point developed within seconds. The alcogel thus produced was grayish-blue. It was aged approximately 24 hours, dried under vacuum for 5 hours at 110°C. The final xerogel had a nominal composition of Ru (0.05)/Ti (0.475)/Zr (0.475).

25

30

EXAMPLE 21

The catalyst used was the same as that of Example 7.

EXAMPLE 22

Isobutyl alcohol (61.32 mL) was combined with tantalum ethoxide (40.491 g) in an inert atmosphere N₂ drybox. In a separate container, ruthenium trichloride (RuCl₃•0.2H₂O, 0.156 g) and rhenium trioxide (0.3884 g) were combined with water (8.978 g) and additional ethanol (61.32 mL).

35

Glacial acetic acid (0.8978 mL) and 70 wt. % nitric acid (0.835 mL) were added to the water mixture. The aqueous solution containing the ruthenium chloride and rhenium trioxide was added, in a dropwise fashion, to the tantalum alkoxide solution. The apparatus was blanketed in nitrogen. A 1 L resin kettle, fitted with a three-neck flask, was used. A clear solution was obtained. The gel point was reached within 15 minutes. A clear, dark red-amber gel, showing some haze, was formed.

The gel was aged at room temperature for twelve days prior to removal of solvent by supercritical CO₂. The material was placed in a stirred autoclave and extracted in CO₂ under supercritical conditions. CO₂ gas was purged over the catalyst for 7 hours at 40°C and 3500 psig (24.2 MPa). The material isolated was a free flowing powder. The final aerogel had a nominal composition of 0.33 wt.% Ru/1.33 wt.% Re/Ta₂O₅.

EXAMPLE 23

Cobalt (II) chloride (5.273 mL, 1.0 M in ethanol), titanium n-butoxide (10.898 mL, 60 volume % in ethanol), and ethanol (19.6 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step a solution containing ruthenium (III) chloride (1.992 mL, 0.3309 M aqueous solution) and platinum (IV) chloride (7.236 mL, 0.1822 M aqueous solution) was added to the alkoxide solution. A gel point was realized within minutes. After aging for about 24 hours at room temperatures, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.025)/Co (0.2)/Pt (0.05)/Ti (0.725).

EXAMPLE 24

A procedure similar to that described for Example 23 was used. Cobalt (II) chloride (6.292 mL, 1.0 M in ethanol), titanium n-butoxide (4.753 mL, 60 volume % in ethanol), and ethanol (8.035 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step a solution containing ruthenium (III) chloride (4.753 mL, 0.3309 M aqueous solution), platinum (IV) chloride (8.633 mL, 0.1822 M aqueous solution) and aluminum nitrate (Al(NO₃)₃•9H₂O, 11.01 mL, 1 M aqueous solution) was added to the alkoxide solution to induce gel formation. After aging for about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel catalyst. The final xerogel had a nominal composition of Ru (0.05)/Co (0.2)/Pt (0.05)/Ti (0.35)/ Al (0.35).

EXAMPLE 25

A procedure similar to that described for Example 23 was used. Titanium n-butoxide (8.009 mL, 60 volume % in ethanol) and ethanol (18.273 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step a solution containing ruthenium (III) chloride (4.516 mL, 0.3309 M aqueous solution) and aluminum nitrate nine hydrate (14.197 mL, 1 M aqueous solution) was added to the alkoxide solution to induce gel formation. After aging for

about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel catalyst. The final xerogel had a nominal composition of Ru (0.05)/ Ti (0.47)/ Al (0.475).

EXAMPLE 26

5 A procedure similar to that described for Example 23 was used. Titanium n-butoxide (10.944 mL, 60 volume % in ethanol), and ethanol (24.979 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step a solution containing ruthenium (III) chloride (3.223 mL, 0.3309 M aqueous solution), platinum (IV) chloride (5.853 mL, 0.1822 M aqueous solution) was added to the alkoxide solution to induce gel formation. After aging
10 for about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.05)/Pt (0.05)/Ti (0.90).

EXAMPLE 27

15 A procedure similar to that described for Example 23 was used. Titanium n-butoxide (11.752 mL, 60 volume % in ethanol), and ethanol (26.823 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step a solution containing ruthenium (III) chloride (3.367 mL, 0.3309 M aqueous solution), platinum (IV) chloride (3.058 mL, 0.1822 M aqueous solution) was added to the alkoxide solution to induce gel formation. After aging for about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to
20 produce the final xerogel. The final xerogel had a nominal composition of Ru (0.05)/Pt (0.025)/Ti (0.925).

EXAMPLE 28

A procedure similar to that described for Example 23 was used. Titanium n-butoxide (10.944 mL, 60 volume % in ethanol), and ethanol (24.979 mL) were combined in a 150 mL petri
25 dish with gentle swirling, under a nitrogen atmosphere. In a second step a solution containing ruthenium (III) chloride (3.223 mL, 0.3309 M aqueous solution), platinum (IV) chloride (5.853 mL, 0.1822 M aqueous solution) was added to the alkoxide solution to induce gel formation. After aging for about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.05)/Pt (0.05)/Ti
30 (0.90).

EXAMPLE 29

A procedure similar to that described for Example 23 was used. Titanium n-butoxide (14.413 mL, 60 volume % in ethanol), and ethanol (28.766 mL) were combined in a 150 mL petri
35 dish with gentle swirling, under a nitrogen atmosphere. In a second step a solution containing ruthenium (III) chloride (4.130 mL, 0.3309 M aqueous solution), platinum (IV) chloride (3.750 mL, 0.1822 M aqueous solution) was added to the alkoxide solution to induce gel formation. After aging

for about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.05)/Pt (0.025)/Ti (0.925).

EXAMPLE 30

5 A procedure similar to that described for Example 23 was used. Ruthenium trichloride (8.515 mL, 0.09777 M in ethanol), titanium n-butoxide (18.036 mL, 60 volume % in ethanol), and ethanol (41.165 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step, palladium dichloride (4.428 mL, 0.188 M in water) was added to the alkoxide solution to induce formation of a red gel. After aging for about 24 hours at room
10 temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.025)/Pd (0.025)/Ti (0.95).

EXAMPLE 31

A procedure similar to that described for Example 23 was used. Ruthenium trichloride (15.503 mL, 0.09777 M in ethanol), titanium n-butoxide (15.986 mL, 60 volume % in ethanol), and
15 ethanol (36.486 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step, palladium dichloride (4.031 mL, 0.188 M in water) was added to the alkoxide solution to induce formation of a red gel. After aging for about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.05)/Pd (0.025)/Ti (0.925).

EXAMPLE 32

A procedure similar to that described for Example 23 was used. Ruthenium trichloride (17.743 mL, 0.09777 M in ethanol), titanium n-butoxide (15.329 mL, 60 volume % in ethanol), and ethanol (29.783 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step, an aqueous solution of cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$,
25 5.204 mL, 1 M aqueous) and palladium dichloride (4.614 mL, 0.188 M in water) was added to the alkoxide solution to induce gel formation. A dark red gel formed. After aging for about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.05)/Co (0.15)/Pd (0.025)/Ti (0.775).

EXAMPLE 33

30 A procedure similar to that described for Example 23 was used. Ruthenium trichloride (20.739 mL, 0.09777 M in ethanol), titanium n-butoxide (14.450 mL, 60 volume % in ethanol), and ethanol (20.814 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step, an aqueous solution of cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$,
12.166 mL, 1 M aqueous) and palladium dichloride (5.393 mL, 0.188 M in water) was added to the
35 alkoxide solution to induce gel formation. A dark red gel formed. After aging for about 24 hours at

room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.05)/Co (0.3)/Pd (0.05)/Ti (0.90).

EXAMPLE 34

A procedure similar to that described for Example 23 was used. Ruthenium trichloride (15.836 mL, 0.09777 M in ethanol), titanium n-butoxide (15.889 mL, 60 volume % in ethanol), and ethanol (36.263 mL) were combined in a 150 mL petri dish with gentle swirling, under a nitrogen atmosphere. In a second step, palladium dichloride (8.236 mL, 0.188 M in water) was added to the alkoxide solution to induce formation of a blue gel. After aging for about 24 hours at room temperature, the material was dried in a vacuum oven for five hours to produce the final xerogel. The final xerogel had a nominal composition of Ru (0.05)/ Pd (0.025)/Ti (0.625).

TABLE 1 (225°C)

Ex. No.	Catalyst	C ₁₁ ⁺ Productivity	Alpha
1	Ru (0.005)/Ni (0.145)/Ti (0.85)	5	0.76/0.89
2	Ru (0.01)/Ni (0.14)/Ti (0.85)	6	0.82
3	Ru (0.025)/Ni (0.125)/Ti (0.85)	7	0.75/0.86
4	Ru (0.05)/Ni (0.1)/Ti (0.85)	18	0.74/0.87
5	Ru (0.005)/Co (.0725)/Ni (0.0725)/Ti (0.85)	6	0.79
6	Ru (0.01)/Co (0.07)/Ni (0.07)/Ti (0.85)	11	0.79
7	Ru (0.05)/Co (0.1)/Ti (0.85)	277	0.83/0.92

TABLE 2 (200°C)

Ex. No.	Catalyst	C ₁₁ ⁺ Productivity	Alpha
8	Ru (0.05)/Au (0.02)/Ti (0.9)	7	0.87
9	Ru (0.05)/Au (0.025)/Ti (0.925)	32	0.89
10	Ru (0.05)/Co (0.2)/Ti (0.75)	14	0.88
11	Ru (0.025)/Ti (0.975)	26	0.87
12	Ru (0.05)/Ti (0.95)	28	0.87
13	Ru (0.05)/Co (0.15)/Ti (0.8)	31	0.86
14	Ru (0.05)/Co (0.3)/Ti (0.65)	40	0.86
15	Ru (0.05)/Co (0.45)/Ti (0.50)	63	0.88

16	5.7 wt.% Ru/23 wt.% Re/71.3 wt.% TiO ₂	7	0.9
17	6.2 wt. % Ru/TiO ₂	12	0.91
18	4.1 wt.% Ru/ ZrO ₂	5	0.92
19	Ru (0.05)/Ti (0.475)/Zr (0.475)	10	0.89
20	Ru (0.05)/Ti (0.475)/Zr (0.475)	9	0.88
21	Ru (0.05)/Co (0.1)/Ti (0.85)	42	0.88
22	0.33 wt.% Ru/1.33 wt.% Re/Ta ₂ O ₅	0.4	0.94
23	Ru (0.025)/Co (0.2)/Pt (0.05)/Ti (0.725)	11	0.89
24	Ru (0.05)/Co (0.2)/Pt (0.05)/Ti (0.35)/Al (0.35)	11	0.89
25	Ru (0.05)/Ti (0.470)/Al (0.475)	15	0.91
26	Ru (0.05)/Pt (0.05)/Ti (0.90)	3	0.91
27	Ru (0.05)/Pt (0.025)/Ti (0.925)	3	0.91
28	Ru (0.05)/Pt (0.05)/Ti (0.9)	7	0.8
29	Ru (0.05)/Pt (0.025)/Ti (0.925)	14	0.85
30	Ru (0.025)/Pd (0.025)/Ti (0.95)	14	0.91
31	Ru (0.05)/Pd (0.025)/Ti (0.925)	35	0.9
32	Ru (0.05)/Co (0.15)/Pd (0.025)/Ti (0.775)	19	0.87
33	Ru (0.05)/Co (0.30)/Pd (0.025)/Ti (0.625)	27	0.87
34	Ru (0.05)/Pd (0.05)/Ti (0.90)	16	0.9

General Procedure For Continuous Tests

5 The catalyst testing unit was composed of a syngas feed system, a tubular reactor, which had a set of wax and cold traps, back pressure regulators, and three gas chromatographs (one on-line and two off-line).

The carbon monoxide was purified before being fed to the reactor over a 22% lead oxide on alumina catalyst placed in a trap to remove any iron carbonyls present. The individual gases or mixtures of the gases were mixed in a 300 mL vessel filled with glass beads before entering the supply manifold feeding the reactor.

10 The reactor was made of 3/8 in. (0.95 cm) O.D. by 1/4 in. (0.63 cm) I.D. stainless steel tubing. The length of the reactor tubing was 14 in. (35.6 cm). The actual length of the catalyst bed was 10 in. (25.4 cm) with 2 in. (5.1 cm) of 25/30 mesh (0.71/0.59 mm) glass beads and glass wool at the inlet and outlet of the reactor.

15 The wax and cold traps were made of 75 mL pressure cylinders. The wax traps were set at 140°C while the cold traps were set at 0°C. The reactor had two wax traps in parallel followed by two cold traps in parallel. At any given time products from the reactor flowed through one wax and

one cold trap in series. Following a material balance period, the hot and cold traps used were switched to the other set in parallel, if needed. The wax traps collected a heavy hydrocarbon product distribution (usually between C₆ and above) while the cold traps collected a lighter hydrocarbon product distribution (usually between C₃ and C₂₀). Water, a major product of the Fischer-Tropsch process was collected in both the traps.

General Analytical Procedure

The uncondensed gaseous products from the reactors were analyzed using a common on-line HP Refinery Gas Analyzer. The Refinery Gas Analyzer was equipped with two thermal conductivity detectors and measured the concentrations of CO, H₂, N₂, CO₂, CH₄, C₂ to C₅ alkenes/alkanes/isomers and water in the uncondensed reactor products.

The products from each of the hot and cold traps were separated into an aqueous and an organic phase. The organic phase from the hot trap was usually solid at room temperature. A portion of this solid product was dissolved in carbon disulfide before analysis. The organic phase from the cold trap was usually liquid at room temperature and was analyzed as obtained. The aqueous phase from the two traps was combined and analyzed for alcohols and other oxygenates.

Two off-line gas chromatographs equipped with flame ionization detectors were used for the analysis of the organic and aqueous phases collected from the wax and cold traps.

Catalyst Testing Procedure

Catalyst (3 g) to be tested was mixed with 4 grams of 25/30 mesh (0.71/0.59 mm) and 4 grams of 2 mm glass beads. The 14 in. (35.6 cm) tubular reactor was first loaded with 25/30 mesh (0.71/0.59 mm) glass beads so as to occupy 2 in. (5.1 cm) length of the reactor. The catalyst/glass bead mixture was then loaded and occupied 10 in. (25.4 cm) of the reactor length. The remaining 2 in. (5.1 cm) of reactor length was once again filled with 25/30 mesh (0.71/0.59 mm) glass beads. Both ends of the reactor were plugged with glass wool.

Catalyst activation was subsequently carried out using the following procedure. The reactor was heated to 120°C under nitrogen flow (100 cc/min and 40 psig (377 kPa)) at a rate of 1.5°C/min. The reactor was maintained at 120°C under these conditions for two hours for drying of the catalyst. At the end of the drying period, the flow was switched from nitrogen to hydrogen. The reactor was heated under hydrogen flow (100 cc/min and 40 psig (377 kPa)) at a rate of 1.4°C/min. to 350°C. The reactor was maintained at 350°C under these conditions for sixteen hours for catalyst reduction. At the end of the reduction period, the flow was switched back to nitrogen and the reactor cooled to reaction temperature (usually 220°C).

The reactor was pressurized to the desired reaction pressure and cooled to the desired reaction temperature. Syngas, with a 2:1 H₂/CO ratio was then fed to the reactor when reaction conditions were reached.

The first material balance period started at about four hours after the start of the reaction. A material balance period lasted for between 16 to 24 hours. During the material balance period, data were collected for feed syngas and exit uncondensed gas flow rates and compositions, weights and compositions of aqueous and organic phases collected in the wax and cold traps, and reaction conditions such as temperature and pressure. The information collected was then analyzed to get a total as well as individual carbon, hydrogen and oxygen material balances. From this information, CO Conversion (%), Selectivity/Alpha plot for all (C₁ to C₄₀) of the hydrocarbon products, C₅+ Productivity (g/hr/kg cat), weight percent CH₄ in hydrocarbon products (%) and other desired reactor outputs were calculated.

The results obtained from the continuous-flow Fischer-Tropsch catalyst testing unit are shown in Table 3.

Table 3 lists the catalyst composition, CO Conversion (%), Alpha value from the Anderson-Shultz-Flory plot of the hydrocarbon product distribution, C₅+ Productivity (g C₅+ /hour/kg catalyst) and weight percent methane in the total hydrocarbon product (%).

The temperature was 220°C, the pressure was from 340 psig (2445 kPa) to 362 (2597 kPa) and the space velocity was 2 NL/hour/g-catalyst for all the examples in Table 3.

Catalyst Preparation

EXAMPLE 35

Ethanol (141.72 mL) was combined with titanium n-butoxide (31.5412 g) in an inert atmosphere N₂ drybox. In a separate container, ruthenium trichloride (1.5196 g) was combined with water (6.678 g) and additional ethanol (141.72 mL). Glacial acetic acid (0.795 mL) and nitric acid (0.621 mL, 70 wt. %) were added to the water mixture. The aqueous acidic solution containing the ruthenium chloride was added, in a dropwise fashion, to the titanium alkoxide solution. The apparatus was blanketed in nitrogen. A 1 L resin kettle, fitted with a three-neck flask, was used. A clear solution was obtained. A dark, clear gel formed. The material was aged several hours and was dried at 120°C under vacuum for 5 hours. The final xerogel had a nominal composition of 9 wt. % Ru/91 wt. % TiO₂.

EXAMPLE 36

In an inert atmosphere drybox Ti-n-butoxide (118.044 mL) was combined with ethanol (78.696 mL) and loaded into a 1 L kettle. Additional ethanol was added to this solution. In a separate container, RuCl₃ (4.205 g) was combined with water (56.35 mL) and loaded into a dropping funnel, along with ethanol (196.1325 mL). Under a nitrogen purge, the aqueous solutions were slowly added to the alkoxide solution. A gel point was rapidly realized. The material was aged for 3 days before drying at 120°C under vacuum for 5 hours. The final xerogel had a nominal composition of Ru (0.05)/Ti (0.925).

EXAMPLE 37

The procedure was the same as that used for Example 24, except that 32.49 mL of a 0.26871 M HAuCl_4 solution in water was added to the aqueous RuCl_3 solution. The final xerogel had a nominal composition of Ru (0.05)/Au (0.025)/Ti (0.925).

EXAMPLE 38

In an inert atmosphere drybox Ti-n-butoxide (125.2 mL of 60 volume %, in ethanol) was loaded into a 1 L resin kettle along with ethanol (129.96 mL). In a separate container, RuCl_3 (2.912 g) was combined with water (39.04 mL). An additional ethanol (129.96 mL) was added to this mixture. Under a nitrogen purge, the aqueous solutions were slowly added to the alkoxide solution. A gel point was rapidly realized. The dark brown material was aged for 3 days before drying at 120°C under vacuum for 5 hours. The final xerogel had a nominal composition of Ru (0.05)/Ti (0.85).

EXAMPLE 39

In an inert atmosphere drybox, titanium n-butoxide (115.72 g) was added to ethanol (240 mL) along with a 1 M CoCl_2 (39.806 mL) in ethanol solution. This mixture was loaded into a 1 L resin kettle. In a dropping funnel, H_2O (25.50 mL) was combined with ruthenium trichloride (4.508 g) and ethanol (240 mL). This aqueous solution was slowly added to the alkoxide solution. The entire assembly was under nitrogen purge during this addition. A gel point was rapidly realized. The material was dark brown in color, was aged for 3 days and dried under vacuum at 120°C for 5 hours. The final xerogel had a nominal composition of Co (0.1)/Ru (0.05)/Ti (0.85).

TABLE 3

Example No.	Catalyst	% Conv.	alpha	C_5^+	% C_1
35	9 wt.% Ru/Titania	54.7	0.78	427	9.2
36	Ru (0.05)/Ti (0.925)	79.4	0.83	244	14.9
37	Ru (0.05)/Au (0.025)/Ti (0.925)	64.9	0.80	306	12.7
38	Ru (0.05)/Ti (0.85)	36.8	0.84	88	22.2
39	Co (0.1)/Ru (0.05)/Ti (0.85)	88.1	0.81	401	10.4

While a preferred embodiment of the present invention has been shown and described, it will be understood that variations can be made to the preferred embodiment without departing from the scope of, and which are equivalent to, the present invention. For example, the structure and composition of the catalyst can be modified and the process steps can be varied.

The complete disclosures of all patents, patent documents, and publications cited herein are incorporated by reference in their entirety. U.S. Patent Application Ser. No. _____ entitled Fischer-Tropsch Processes Using Catalysts on Mesoporous Supports, filed concurrently herewith on August 18, 1999, and U.S. Patent Application No. _____, entitled Fischer-Tropsch Processes Using Xerogel and Aerogel Catalysts By Destabilizing Aqueous Colloids, filed concurrently herewith on August 18, 1999, are hereby incorporated herein by reference in their entirety.

U.S. Patent Application No. 09/314,921, entitled Fischer-Tropsch Processes and Catalysts Using Fluorided Supports, filed May 19, 1999, U.S. Patent Application No. 09/314,920, entitled Fischer-Tropsch Processes and Catalysts Using Fluorided Alumina Supports, filed May 19, 1999, and U.S. Patent Application No. 09/314,811, entitled Fischer-Tropsch Processes and Catalysts With Promoters, filed May 19, 1999, are hereby incorporated herein by reference in their entirety.

The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention by the claims.

CLAIMS

1. A process for producing hydrocarbons, comprising contacting a feed stream comprising hydrogen and carbon monoxide with a catalyst in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising hydrocarbons,
5 wherein the catalyst comprises a catalytically active metal selected from the group consisting of iron, cobalt, nickel, ruthenium, and combinations thereof dispersed in an aerogel or xerogel comprising a derivative of the hydrolysis and condensation of one or more alkoxides of a matrix metal selected from the group consisting of titanium, tantalum, zirconium, and combinations thereof.
2. The process of claim 1 wherein the catalyst further comprises aluminum.
- 10 3. The process of claim 2 wherein the atomic ratio of aluminum to the matrix metal is about 1.01:1.
4. The process of claim 2 wherein the matrix metal is titanium and the atomic ratio of titanium to aluminum is from about 1:9 to about 9:1.
5. The process of claim 1 wherein the catalytically active metal comprises from about
15 0.1 to 50 mole percent of the matrix metal and catalyst metal combined.
6. The process of claim 5 wherein the catalytically active metal comprises from about 10 to 30 mole percent of the matrix metal and catalyst metal combined.
7. The process of claim 6 wherein the catalytically active metal comprises cobalt and ruthenium and wherein the content of the catalytically active metal comprises from about 2.5 to about
20 50 mole percent of the matrix metal and catalyst metal combined.
8. The process of claim 7 wherein the ruthenium content is from about 0.001 to about 5 mole percent of the matrix metal and catalyst metal combined.
9. The process of claim 1 wherein the catalyst comprises one or more promoters selected from the group consisting of Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, Ag, Au, Sc, Y, La, Ti, Zr,
25 Hf, V, Nb, Ta, Rh, Pd, Os, Ir, Pt, Mn, B, P, and Re.
10. The process of claim 9 wherein the promoter comprises from about 0.001 to 20 mole percent of the total metal content.
11. The process of claim 10 wherein the promoter comprises from about 2 to 5 mole percent of the total metal content.
- 30 12. The process of claim 1 wherein the catalytically active metal is selected from the group consisting of cobalt, ruthenium, and combinations thereof, and the promoter is selected from the group consisting of Sc, Y, La, Ti, Zr, Hf, Rh, Pd, Os, Ir, Pt, Re, Nb, Cu, Ag, Mn, B, P, and Ta.
13. The process of claim 12 wherein the promoter is rhenium, the content of cobalt is from about 10 to about 25 mole percent, and the combined content of rhenium and ruthenium is from
35 about 0.001 to 10 mole percent.

14. The process of claim 12 wherein the catalytically active metal is cobalt, the cobalt content is from about 10 to about 25 mole percent, the promoter is rhenium, and the rhenium content is from about 0.001 to 5 mole percent.

15. A Fischer-Tropsch catalyst comprising an aerogel or xerogel matrix comprising a matrix metal selected from the group consisting of titanium, tantalum, zirconium, aluminum, and combinations thereof, and one or more catalytically active metals selected from the group consisting of iron, cobalt, nickel, and ruthenium dispersed in the matrix.

16. The catalyst of claim 15 wherein the catalytically active metal comprises from about 0.1 to 50 mole percent of the matrix metal and catalyst metal combined.

17. The catalyst of claim 16 wherein the catalytically active metal comprises from about 10 to 30 mole percent of the matrix metal and catalyst metal combined.

18. The catalyst of claim 17 wherein the catalytically active metal comprises cobalt and ruthenium and wherein the content of the catalytically active metal comprises from about 10 to 25 mole percent of the matrix metal and catalyst metal combined.

19. The catalyst of claim 18 wherein the ruthenium content is from about 0.001 to about 5 mole percent of the matrix metal and catalyst metal combined.

20. The catalyst of claim 15 wherein the catalyst further included one or more promoters selected from the group consisting of Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, Ag, Au, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Rh, Pd, Os, Ir, Pt, Mn, B, P, and Re.

21. The catalyst of claim 20 wherein the promoter comprises from about 2 to 5 mole percent of the total metal content.

22. The catalyst of claim 21 wherein the catalytically active metal is selected from the group consisting of cobalt, ruthenium, and combinations thereof, and the promoter is selected from the group consisting of Sc, Y, La, Ti, Zr, Hf, Rh, Pd, Os, Ir, Pt, Re, Nb, Cu, Ag, Mn, B, P, and Ta.

23. The catalyst of claim 22 wherein the promoter is rhenium, the content of cobalt is from about 10 to about 25 mole percent, and the combined content of rhenium and ruthenium is from about 0.001 to about 10 mole percent.

24. The catalyst of claim 22 wherein the catalytically active metal is cobalt, the cobalt content is from about 10 to about 25 mole percent, the promoter is rhenium, and the rhenium content is from about 0.001 to about 10 mole percent.

25. A Fischer-Tropsch catalyst comprising the dried reaction product of a first reagent comprising an alkoxide of a metal selected from the group consisting of titanium, tantalum, zirconium, and combinations thereof in a non-aqueous solvent, and a second reagent comprising a solution comprising one or more catalytically active metals selected from the group consisting of iron, cobalt, nickel, and ruthenium, wherein the product is an aerogel or xerogel.

26. The catalyst of claim 25 wherein the catalyst comprises the dried reaction product of the first reagent, second reagent, and a third reagent selected from the group consisting of aluminum nitrates, aluminum acetates, aluminum alkoxides, aluminum acetylacetonates, aluminum chlorides, and combinations thereof.

27. The catalyst of claim 26 wherein the third reagent is dissolved in a non-aqueous solvent.

28. The catalyst of claim 27 wherein the third reagent is dissolved in ethanol.

29. The catalyst of claim 28 wherein the catalytically active metal comprises from about 10 to 30 mole percent of the total metal content of the catalyst.

30. The catalyst of claim 29 wherein the catalyst comprises one or more promoters selected from the group consisting of Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, Ag, Au, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Rh, Pd, Os, Ir, Pt, Mn, B, P, and Re.

31. The catalyst of claim 30 wherein the promoter comprises from about 2 to 5 mole percent of the total metal content.

32. A Fischer-Tropsch catalyst comprising an aerogel or xerogel formed from the hydrolysis and condensation reaction of a solution of a catalytically active metal selected from the group consisting of iron, cobalt, nickel, ruthenium, and combinations thereof and a matrix reagent comprising a non-aqueous solution of a metal selected from the group consisting of titanium, tantalum, zirconium, and combinations thereof.

33. The catalyst of claim 32 further comprising aluminum.

34. The catalyst of claim 33 further comprising a reagent comprising one or more aqueous supplements selected from the group consisting of water, aqueous acid, aqueous base.

35. The catalyst of claim 34 wherein the catalytically active metal comprises from about 10 to 30 mole percent of the total metal content of the catalyst.

36. The catalyst of claim 35 wherein the catalyst further comprises one or more promoters selected from the group consisting of Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, Ag, Au, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Rh, Pd, Os, Ir, Pt, Mn, B, P, and Re.

37. The catalyst of claim 36 wherein the promoter comprises from about 2 to 5 mole percent of the total metal content of the catalyst.

38. A method for preparing a Fischer-Tropsch catalyst comprising mixing a non-aqueous solution of an alkoxide of a metal selected from the group consisting of titanium, tantalum, zirconium, and combinations thereof with one or more catalytically active metals selected from the group consisting of iron, cobalt, nickel, and ruthenium in a solvent, forming a gel, and drying the aged gel.

39. The method of claim 38 further including aging the gel.

40. The method of claim 39 further including aging the gel at room temperature in air.

41. The method of claim 40 further including reducing the catalyst.
42. The method of claim 41 further including reducing the catalyst in a hydrogen-containing stream.
43. The method of claim 38 wherein the catalytically active metal is dissolved in a non-
5 aqueous solvent.
44. The method of claim 43 comprising adding an aqueous supplement selected from the group consisting of water, aqueous acid, and aqueous base.
45. The method of claim 39 comprising vacuum drying the aged gel.
46. The method of claim 38 comprising supercritical extraction of solvent.
- 10 47. The method of claim 45 wherein supercritical extraction comprises the use of one or more extraction fluids selected from the group consisting of CCl_3F , CCl_2F_2 , $\text{CClF}_2\text{CClF}_2$, ammonia, and carbon dioxide.
48. The method of claim 46 comprising reducing the catalyst in a hydrogen-containing stream.
- 15 49. A process for producing hydrocarbons by contacting a feed stream comprising hydrogen and carbon monoxide with a catalyst in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising said hydrocarbons, characterized by using a catalyst prepared by a method comprising (1) forming a catalyst gel by mixing (a) at least one dissolved compound of a catalytic metal for Fischer-Tropsch reactions; (b) (i) at least one dissolved
20 alkoxide of a metal selected from the group consisting of titanium, zirconium and tantalum, and optionally (ii) at least one dissolved aluminum compound, said alkoxide component (i) and said optional aluminum compound component (ii) being dissolved in a non-aqueous solvent; and at least when necessary to hydrolyze the alkoxide component (i) and aluminum compound component (ii), (c) water supplement; and (2) drying the gel.
- 25 50. The process of Claim 49 wherein the catalytic metal of (a) is dissolved in water and this solution of catalytic metal is mixed with the non-aqueous solution of (b).
51. The process of Claim 49 wherein the catalytic metal is a combination of cobalt and ruthenium.
52. The process of Claim 49 wherein the drying (2) is accomplished by vacuum drying or
30 heating in air.
53. The process of Claim 49 wherein the drying (2) is accomplished by allowing supercritical fluid to flow through the gel material.
54. The process of Claim 49 wherein the catalyst preparation further comprises reduction treatment of the dried gel from (2).

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/18962

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 21/08; C07C 27/00

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/233, 238, 239, 241, 257, 258, 259, 260

518/700, 715

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, E	US 5,958,363 A (CORONADO) 28 September 1999(28/9/99), see entire document.	1-54
A	US 5,395,805 A (DROEGE et al) 07 March 1995(7/3/95), see entire document.	1-54
A	US 4,717,708 A (CHENG et al) 05 January 1988(5/1/88), see entire document.	1-54
A	US 4,469,814 A (ROBINSON et al) 04 September 1984(4/9/84), see entire document.	1-54
A	US 3,977,993 A (LYNCH) 31 August 1976(31/8/76), see entire document.	1-54



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

07 OCTOBER 1999

Date of mailing of the international search report

03 DEC 1999

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/18962

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

502/233, 238, 239, 241, 257, 258, 259, 260

518/700, 715